levels if the water meets the other specifications. Water used for processing food or beverages must also meet drinking-water standards.

It is technically possible to treat any water to give it a composition suitable for special uses. If the water requires extensive treatment, however, especially if large amounts of water are involved, it may not be economically feasible to use some supply sources. Industrial plants having large water requirements are commonly located with reference to availability of water.

Although water temperature is not a chemical property and has not received much consideration here, the temperature of a supply and the seasonal fluctuation of that temperature are major considerations in the use of water for cooling by industry. In some areas, ground water is used extensively for this purpose because its temperature is uniform and is below air temperatures during warm weather. Some industries have recharged ground-water aquifers with cold water from surface streams each winter and have withdrawn the cool stored water in the summer when the regularly used surface supply is too warm for efficient cooling. In the past there were instances of industrial plants located along the same stream using and reusing the water for cooling until the temperature of the water for many miles of river was far above normal levels. Excessively high temperatures deplete dissolved oxygen and interfere with normal stream ecology, an effect sometimes called thermal pollution. In recent years these practices have been regulated to prevent undesirable ecologic stress.

Industrial expansion has contributed greatly to increasing per capita use of water in the United States. Much of the industrial use, however, is nonconsumptive. That is, the water is not evaporated or incorporated into the finished product, but is released after use without significant change in quantity, possibly with an increased load of dissolved or suspended material or perhaps with very little change from its original composition. As water supplies have become more fully used, however, many industries have found it necessary to conserve and reuse water that in former years would have been allowed to flow down a sewer or back to a surface stream. In some places, reclaimed sewage has been used for certain noncritical industrial purposes.

Recirculation of water that is depleted by evaporation, as in a cooling tower, introduces concentration factors, and intensified reuse can be expected to raise the average solute concentration in effluents.

Recreational and Esthetic Uses

Considerable attention is now being paid to recreational uses of rivers and lakes for such purposes as swimming, fishing, and boating and for simple esthetic enjoyment. The cost of restoring water bodies that have lost their value for such purposes because of pollution may be substantial, but there is strong public support in many places for the aim of creating or protecting waters for these purposes.

Water for swimming and other sports in which water is in contact with the skin obviously must conform to sanitary requirements. Fish that are sought by anglers require clean water and a good supply of dissolved oxygen. Certain metal ions may be lethal to fish and other aquatic life forms when present at levels near or below the limits given for public water supplies. Copper, zinc, and aluminum, which are not among the metals for which limits are prescribed for public water supplies, are toxic to fish and many other species of aquatic life. The absence of fish from low-pH lakes in Europe and North America is believed to be the result of aluminum brought into solution by precipitation having a low pH ("acid rain") (Cronan and Schofield, 1979).

One of the important factors in the assimilation of dissolved metal ions by aquatic biota is the tendency for increasing concentrations in species higher in the food chain. One of the more insidious effects of mercury-containing waste that enters rivers and lakes is an increase in mercury content of fish to the extent that they become dangerous to eat. Some species of fish are more sensitive than others to ions and organic solutes, and certain combinations of ions may exert synergistic effects. McKee and Wolf (1963) compiled many references on the effects of dissolved material on fish. Water-quality requirements for fish have been summarized by NAS–NAE (1972).

Although highly impure water is attractive in appearance when viewed from a distance, it is obvious that even the lowest standards of pollution control must aim to produce a product reasonably pleasing to the senses of the viewer from close at hand, while walking along the shore or riding over the water in a boat. The surroundings of the water body are an important part of this esthetic impression.

WATER-MANAGEMENT CONCEPTS AND PROBLEMS

The term "water-quality management" is frequently used in recent literature. Sometimes it is used as a synonym for "pollution control." Most of the time, however, it implies the use and development of water resources in a way that maintains water quality at the optimum level. This may involve many administrative and engineering activities concerned with decreasing the pollution loads contributed to streams through better and more complete sewage treatment, cleaning up existing pollution by dredging and other means, and designing and building storage facilities to increase low flows of streams and thus to decrease quality fluctuations, or any of a number of related activities. The use of the term also implies that enough is known about the natural-water circulation systems so that quality indeed can be effectively managed.

"Clean water" legislation in the United States, and the accompanying emphasis on pollution abatement, resulted in large expenditures during the 1960's and 1970's aimed at decreasing "point sources" of contaminants. These point sources were taken to be sewage outfalls and industrial waste streams. It is generally agreed that substantial improvement in the quality of stream water resulted in many places. However, it has become evident that "nonpoint sources" have a major impact and that control of these sources poses a much more difficult problem. Some aspects of this topic have been discussed in this book in different contexts. The effects of agricultural practices—fertilization, use of pesticides, and cultivation techniques, for example—may have profound influences on water quality both in surface streams and underground.

Pollution, as the term was defined in the preceding section, entails a level of contamination that is harmful, and pollution control, therefore, would have as a goal keeping the concentrations of contaminating substances at relatively low levels, though not necessarily eliminating them altogether. A different goal has often been advocated—the elimination of pollution altogether, thereby restoring waters to a pristine state. For various reasons, such a goal is unrealistic, not to mention unattainable. One of the best ways of controlling pollution is through conservation of resources, reuse of processed materials, and increased vigilance at all levels to prevent loss by leaks and spills. Perfection in this effort cannot be expected. Moreover, for some uses of processed material, recovery of the material is impracticable. For example, the recovery of lead after leaded gasoline had been burned or after paint had been spread, if not impossible, would require prohibitively large expenditures of energy.

The maintenance of a healthy industrial economy appears to require a large and probably increasing per capita energy use. The rapid increase in energy cost that occurred during the 1970's made it evident that there may be an economic limit to energy use as well as a limit

Table 29. Water-quality requirements

[Concentrations, which represent upper limits for water at point of use before addition of internal conditioners, are in milligrams per liter except as indicated (U.S.

Constituent	Boiler feedwater pressure (pounds per square inch gauge)				Textiles (scouring, bleaching, and dyeing)
	0–150	150–700	700–1,500	1,500–5,000	
Silica (SiO_2)	30	10	0.7	0.01	
Aluminum (Al)	5	.1	.01	.01	
Iron (Fe)	1	.3	.05	.01	.1
Manganese (Mn)	.3	.1	.01		.01
Calcium (Ca)		0	0		
Magnesium (Mg)		0	0		
Ammonium (NH_4)	.1	.1	.1	.7	
Copper (Cu)	.5	.05	.05	.01	.01
Zinc (Zn)		0	0		
Bicarbonate (HCO_3)	170	120	48		
Sulfate (SO_4)					
Chloride (Cl)					
Fluoride (F)					
Nitrate (NO_3)					
Hardness as $CaCO_3$	20	0	0	0	25
Alkalinity as $CaCO_3$	140	100	40	0	
Acidity as $CaCO_3$	0	0	0	0	
pH	8.0–10.0	8.2–10.0	8.2–9.0	8.8–9.2	([3])
Dissolved solids	700	500	200	.5	100
Color (units)					5
Organics:					
CCl_4 extract	1	1	.5	0	
Methylene-blue active substances	1	1	.5	0	
Chemical oxygen demand	5	5	.5	0	
Dissolved oxygen	2.5	.007	.007	.007	
Temperature (°F)					
Suspended solids	10	5	0	0	5

[1]Not to exceed U.S. Public Health Service drinking-water standards

[2]Limit for noncarbonate hardness, 70 mg/L as $CaCO_3$.

[3]Ranges from 2.5 to 10.5, depending on process and product.

related to the finite availability of fossil fuel. There may be an environmental limit as well—a point at which the environmental damage from high energy use becomes too great to be tolerated.

The concept of water-quality management is related in a general way to broader concepts of management of water resources for full and efficient use by humans. This kind of water use may involve extensive storage and transport facilities to make water available when and where it is needed. Sometimes a considerable degree of chemical control is required to make the quality of the water satisfactory, as in the treatment of public water supplies.

As the intensiveness of development of water supplies increases, the interweaving of chemical effects with the various physical processes in the circulation of water becomes more and more evident and of greater and greater practical importance. Some of the chemical effects of water storage in reservoirs have already been mentioned. There are some undesirable chemical effects in many impoundments; perhaps most significant is the tendency for water to become stratified at times and for previously accumulated sediments to contribute undesirable impurities to the water near the reservoir bottom. In arid climates, however, a more visible and generally objectionable feature of large open-storage reservoirs is the loss of water by evaporation. Evaporation losses from Lake Mead on the Colorado River average 849,000 acre-ft per year (Meyers, 1962, p. 94), equivalent to a depth of more than 6 ft over the surface of the lake.

A means of storage that avoids some of the disadvantages and inefficiencies of surface reservoirs would have considerable appeal. The method most frequently suggested, and one that is generally believed to have the greatest promise, is the injection of surface water into the ground-water body for later removal by pumping. The integration of surface-water and ground-water systems that would result if this technique were adopted on a large scale has a very logical appeal to the water-resources planner.

for selected industries and processes

Federal Water Pollution Control Administration, 1968)]

Chemical pulp and paper		Wood chemicals	Synthetic rubber	Petroleum products	Canned, dried, and frozen fruits and vegetables	Soft-drinks bottling	Leather tanning (general finishing processes)	Hydraulic cement manufacture
Unbleached	Bleached							
50	50	50			50			35
1.0	.1	.3	.1	1	.2	.3	.3	25
.5	.05	.2	.1		.2	.05	.2	.5
20	20	100	80	75		100		
12	12	50	36	30				
		250						
		100			250	500	250	250
200	200	500		300	250	500	250	250
					1	([1])		
		5			10			
100	100	900	350	[2]350	250		soft	
		200	150		250	85		400
					0			0
6–10	6–10	6.5–8.0	6.2–8.3	6.0–9.0	6.5–8.5		6.0–8.0	6.5–8.5
		1,000		1,000	500			600
30	10	20	20		5	10	5	
					.2	([4])	([5])	1
	95							
10	10	30	5	10	10			500

[4]Carbon chloroform extract limit, 0.2 mg/L; also specified to be free of taste and odor

[5]Carbon chloroform extract limit, 0.2 mg/L.

It should be evident from the descriptions of chemical systems and influences in surface streams and in ground-water bodies that the two environments are very different. Conversion of a surface water to a ground water in large quantity at a rapid rate and with a minimum of effort and expense is necessary in successful artificial recharge of ground-water reservoirs. Chemical factors that appear subtle and unimportant to the casual observer may create great difficulties in the recharging process.

Recharging techniques most commonly used include spreading water on the land surface and allowing it to percolate to the water table and injecting water directly through wells, in a reversal of the usual pumping process. Some success has, of course, been attained in both ways, partly inadvertently. For example, most irrigation projects have brought about extensive ground-water recharge by infiltration from irrigated fields as well as from unlined ditches and canals. "Water flooding" as a means of recovering petroleum is practiced extensively, and highly unfavorable chemical conditions have been overcome as brines are pumped back down wells in these operations.

Extensive withdrawals of ground water have resulted in some areas in the subsidence of the land surface (Poland and Green, 1962; Holzer and others, 1979). Poland (1981) showed that the land-subsidence problem is substantial. In 17 affected areas of the United States the measured subsidence ranged from 0.3 to 9.0 m. Areas affected included 16,000 km^2 in California, 12,000 km^2 in Texas, and 2,700 km^2 in Arizona.

Subsidence of the city of Venice, Italy, related to ground-water withdrawals in an adjacent industrial area has been studied extensively. Gambolati and others (1974) concluded that subsidence between 1930 and 1973 has been 15 cm. Water from surface sources was substituted for some of the industrial wells during the 1970's. Apparently subsidence had stopped by 1979 (Volpi and others, 1979). Even a small amount of subsidence can add significantly to flood hazards in Venice. The aquifer storage space lost by subsidence probably cannot be regained. However, a more conservative management policy under which water pumped out is replaced periodically can at least prevent or minimize future subsidence.

The subsidence effects noted above have generally been attributed to compaction of sediments when they were dewatered. The finer grained material in some ground-water systems might contain water differing in chemical composition from the bulk solution present in the coarser material. The normal pattern of water movement in such systems concentrates flow through the coarser fraction. It seems possible that the composition of ground water pumped from wells where subsidence is occurring might be affected as the fine-grained material that usually does not yield much water is "squeezed dry." Such effects do not seem to have been documented, but might be discernible if they were looked for.

Whether recharge is accomplished by spreading or by injection, some consideration of chemical and biological factors is required to enable recharging to continue over extended periods. From descriptions in the literature, it is evident that most attempts at injection through wells have encountered difficulties. Often, insufficient thought has been given to the effects on water compositions of injecting the water into a new environment or to reactions that might occur between native and introduced solutes. Changes in Eh and in pH might occur, altering the solubility of solutes such as calcium and iron and causing precipitates that might clog openings around the injection well. Or the new solution might dissolve objectionable amounts of impurities from solids that were stable in the previous environment, or create environments promoting or sustaining biological growths in and near the injection well.

There is an extensive literature on the nonchemical aspects of artificial recharge. An introduction to earlier literature can be obtained from the bibliography by Todd (1959). More recent papers describing recharging experiments in which some consideration was given to chemistry include one by Reed and others (1966) on work done at Kalamazoo, Mich., and two reports on experiences in Oregon and Washington by Price and others (1965) and by Foxworthy and Bryant (1967). Artificial-recharge experiments in the Grand Prairie region of Arkansas included some chemical considerations described by Sniegocki (1963). More recently, U.S. Geological Survey studies of recharging techniques and effects, both chemical and physical, were made in the Ogallala aquifer of western Texas (Wood and Signor, 1975; Brown and others, 1978; Wood, 1978) and at Bay Park, Long Island, N.Y. (Vecchioli and Ku, 1972; Ragone, 1977). Microbiologic factors were also studied (Ehrlich and others, 1979) at Bay Park.

Wise management of water resources could be said to have the following goals: providing sufficient quantities of water of acceptable quality for all beneficial uses, using fair methods of allocation when total supplies are temporarily inadequate, and, insofar as possible, developing resources in such a way as to avoid overcommitments so that in the long term there will be no continuous shortages or significant continuous water-quality impairment.

Sources of freshwater are renewable but are finite in quantity, and their availability is variable both in time and from place to place. Obviously, the goals of management mentioned above cannot be fully attained, and, indeed, in some ways the goals are incompatible. Metropolitan areas require large supplies of water. Commonly, these supplies have been obtained from surface- or ground-water sources in the surrounding area; in some instances, water has been imported from drainage basins or ground-water systems hundreds of kilometers distant.

Water-development projects for other purposes, notably for the irrigation of agricultural land in arid or semiarid regions, may involve much larger quantities of water. All such developments have costs as well as benefits. The benefits are generally self-evident, but many of the costs are intangible, including environmental effects both in the areas of water use and in areas from which water is taken.

A part of the environmental cost is the deterioration of water quality resulting from water use and waste disposal in the impacted areas. The kinds of effects that might be anticipated and their time frame generally have not been well understood. An improved ability to predict water-quality changes related to water-resource development is one goal toward which research in chemistry of natural aqueous systems must be directed. Although utopia will never be reached, a more complete grasp of the water-quality-related costs of water-resource development will certainly help in making wiser decisions.

A few decades ago, public opinion seemed willing to support development of water resources on a broad scale and there were various far-reaching proposals for transferring large amounts of water from one region to another. Proposals for supplementing water supplies in water-short regions of the Southwestern United States where population was increasing were among the more seriously considered. During the 1960's, the State of California began to implement a plan to transfer water from streams in the northern part of the State south to parts of the San Joaquin Valley and over the Tehachapi Mountains into water-short areas farther south. Water deliveries to the Los Angeles area began in the mid-1970's.

Economic and political factors play important roles in water-transfer plans of this type, and the future of such plans in the field of water-resources management is difficult to predict. The Colorado River basin in the Southwestern United States is an example of an area in which water use has been increasing. A brief review of management efforts and water-quality factors affecting the Colorado River is indicative of the present limited ability to cope with large-scale water-distribution problems.

Hydrologic studies of the Colorado River have been carried on by the U.S. Geological Survey since the bureau was formed in 1879. Water-quality data, much of it based on daily sampling, have been obtained at some points in the lower part of the basin (downstream from Lees Ferry, Ariz., which is near the Arizona–Utah border) continuously since 1925. A review of these records up to 1965 was made by Irelan (1971). His observations and those of contemporaries offer some insight into the changes in water quality that the development of water resources in the basin have brought about. They also provide some indications of the factors that affect the usefulness of records of this kind for predicting trends.

Prior to the completion of Hoover Dam on the Colorado River near Las Vegas, Nev., the riverflow was essentially uncontrolled. As noted by Irelan (1971, p. E4), dissolved solids at points downstream from the Grand Canyon reached 1,500 mg/L during the fall and winter low-flow periods in most years, and in some years the maximum was near 1,800 mg/L. Hoover Dam was completed in 1935 and, subsequently, two additional dams, Davis and Parker, were constructed downstream. The construction of Glen Canyon Dam forming Lake Powell just upstream from Lees Ferry was completed in 1963. Reservoir storage capacity in the four impoundments is equivalent to several years of average river discharge.

The storage reservoirs mix high- and low-flow water and damp out the annual fluctuation of solute concentrations. Some calcium carbonate is precipitated out in the reservoirs, as noted earlier, and evaporation tends to increase solute concentrations. Also, some solutes are added by dissolution of soluble rock strata in the reservoirs. Irelan's (1971, p. E10) compilation showed that water released from Lake Mead, the reservoir formed by Hoover Dam, from 1937 to 1964 ranged in dissolved solids from near 600 to a little over 800 mg/L (annual discharge-weighted averages). Water diverted into the Colorado River Aqueduct at Parker Dam, for use by the Metropolitan Water District of Southern California, had about the same composition. From 1941 to 1965, the annual weighted average hardness of this water ranged from 286 to 388 mg/L as $CaCO_3$ (Irelan, 1971, p. E11).

It has long been recognized that the Colorado River water is higher in dissolved-solids concentration than would be considered fully satisfactory for a public supply in other parts of the United States, and that successful use of the water for irrigation requires good drainage to avoid solute accumulation in the soil (Howard, 1930, p. 6). The Metropolitan Water District of Southern California (MWD) has successfully used the water after treatment to decrease its hardness. Other sources available to MWD provide water of substantially lower solute concentration. Other large-scale users in the lower part of the basin have no such alternatives, however.

As noted by Irelan (1971, p. E31), saline drainage water pumped from wells in the Wellton-Mohawk area east of Yuma, Ariz., brought about deterioration in the quality of the river water crossing the International Boundary in 1961. Remedial measures of various kinds have been required since then to maintain the quality of water delivered to Mexico at acceptable levels.

Other water-development projects in the Colorado River basin, both above and below Lees Ferry, have been planned or are under construction. They can be expected to bring about some further increases in solute concentrations in the water available from the river in the lower part of the basin, but there is no agreement as to probable timing or magnitude of such increases. Irelan (1971, p.

E39) concluded that some increases probably would occur after projects proposed but not in operation in 1969 were completed. Hill (1965) predicted that the hardness of water diverted from the river for use by the MWD might reach 435 mg/L (as $CaCO_3$) by 1990. A later prediction by Valantine (1974) called for dissolved-solids concentrations at the Parker Dam (Lake Havasu) diversion point to average 800 mg/L by 1990, and 980 mg/L by the year 2000.

Irelan's (1971, p. E39) short-term prediction was that mineral concentrations in the water of the lower river would be stabilized temporarily at concentrations less than those of 1965. The filling of Lake Powell, behind Glen Canyon Dam, decreased downstream flow in that year. Records published in the series "Water Resources Data for Arizona" for the years 1971–82 and 1966–70, in the U.S. Geological Survey Water-Supply Paper series, show that this prediction was accurate. The dissolved-solids concentration in Lake Havasu averaged 811 mg/L in 1965. In 1968, the dissolved-solids concentrations generally were a little less than 700 mg/L and subsequently, through 1982, ranged from near or a little less than 700 to about 750 mg/L. Hardness concentrations during the 1969–83 period were generally lower than in 1965 and were below 350 mg/L most of the time.

Data of the type available for the Colorado River permit relatively accurate computation of annual solute loads transported past sampling points. Evaluation techniques used by Irelan (1971) included many such calculations. One approach is the cumulative mass diagram in which the cumulative solute load is plotted on the ordinate against time on the abscissa. A change in slope of this line may indicate a perturbation in the stream regimen. It is evident that differences in total flow produced by wet and dry years have a substantial influence and that other factors tend to be obscured by such differences. The Colorado, at least in its lower reaches, is definitely a managed stream in many respects. Still, the effects of management actions on water quality are difficult to discern closely without careful studies.

The Colorado River system is large in terms of area, flow, and solute load. The relative importance of different factors that influence the system is difficult to determine, and because of the system's size the results of perturbations may be slow to appear. The effects on water composition caused by seasonal and year-to-year variations in precipitation and runoff, as noted in preceding discussions of river-water chemistry, tend to be decreased in streams controlled by storage reservoirs. An example given in the section "Frequency Distributions" demonstrated that the seasonal changes in dissolved-solids concentration that were characteristic of the lower Colorado River before the construction of storage reservoirs no longer occur. The total storage capacity of Lakes Powell, Mead, Mohave, and Havasu is more than 54 million acre-feet. Hely (1969) reported that annual discharge of the river at Lees Ferry ranged from a maximum of 22 million to a minimum of 4.4 million acre-feet during the period 1896–1962. The mean annual discharge was about 13.4 million acre-feet during that period. Thus, the storage capacity is sufficient to hold about 4 years of average runoff, and effects of single abnormally wet or dry years on the composition of water in the lower river should be rather small, although some of the inflow to the larger reservoirs in wet years may pass through them without completely mixing with previously stored water. A succession of wet years, however, could cause major changes, especially if they followed a dry period in which stored water had been depleted extensively.

Predictions of dissolved-solids values to be expected in future years cannot take into account the effects of major long-term fluctuations in annual discharge, as such events cannot be foreseen accurately. The Lake Havasu predictions cited earlier in this discussion assumed a continuation of discharges near the recent average. As Hely (1969) and other investigators have noted, the average annual Colorado River discharge for the first 30 years of the 20th century was more than 4 million acre-feet greater than the average for the second 30 years, possibly indicating some long-term cyclic effect.

During 1983 and 1984 the flow of the Colorado River above Lake Powell was very much above normal, and as a result large volumes of stored water were spilled from all the reservoirs. By late 1984 the diluting effect of high flows had become distinctly noticeable in the lowermost reservoir, Lake Havasu. Dissolved-solids concentration of stored water in the lake in the early part of 1985 was substantially below 600 mg/L (U.S. Geological Survey, unpub. data, 1985). This dilution effect can be expected to influence the composition of water in the lower part of the Colorado River for several years.

Owing to the unpredictable nature of large fluctuations in flow, long-term predictions of stored-water quality have a large element of uncertainty. Water users dependent on the lower Colorado River would obviously welcome a return to more abundant supplies if, indeed, the apparent dry cycle is coming to an end. Development based on overly optimistic estimates, however, would seem from the historical record to be very unwise.

The long record of hydrologic data available for the Colorado River offers many opportunities for studying the effects of natural and human-induced processes. One of the purposes of this book is to provide the background as well as encouragement for such studies. The value of long-term records cannot by fully realized without a concurrent emphasis on interpretation.

Smaller scale studies of natural-water chemistry may offer greater opportunity for evaluating and understanding the effects of some of the processes and chemically activated controls on the occurrence and behavior of individual elements. Applications of theoretical chemistry that have been described here and further research in these areas remain a challenge for present and future students of natural-water chemistry.

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