11.9 Salinization and Saline Environments

A Vengosh, Duke University, Durham, NC, USA

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Glossary

Additive agricultural chemicals chemicals added to

irrigation water (e.g., nitrogen fertilizers, gypsum, dolomite, boron compounds).

Afforestation an establishment of a forest or plantation in an area where there were no trees.

Arsenate the oxic form (species) of arsenic in water; occurs in oxidizing water.

Arsenite the reduced form (species) of arsenic in water; occurs in reduced water.

Artificial recharge man-made recharge of aquifers through artificial basins or reverse pumping wells that replenish the aquifer as a compensation for overexploitation.

Base-exchange reactions chemical reactions that involve exchange of dissolved and adsorbed cations (e.g., Ca²⁺, Mg²⁺, Na⁺) from adsorption sites on clay minerals and/or oxides.

Boron species boron in aquatic solutions occurs as uncharged boric acid $(B(OH)_3^0)$ and borate ion $(B(OH)_4^-)$ forms.

Boron isotopes the stable isotope ratio of boron, ¹¹B/¹⁰B, is defined in delta notation: $\delta^{11}B = \{[^{11}B/^{10}B]_{sample}/[^{11}B/^{10}B]_{STD} - 1\} \times 1000$, where STD is a standard. **Ca-chloride water composition** the definition of water with a high proportion of calcium over the sum of

sulfate and bicarbonate; $Ca/(SO_4 + HCO_3) > 1$ in equivalent units.

Chlorine radioactive isotope ratio the activity of the radioactive ³⁶Cl isotope is normalized to the total chloride content, ³⁶Cl/Cl.

Conservative mixing mixing of two or more water bodies that involves nonreactive mixing of dissolved salts in the water; the concentrations of the dissolved water reflect the relative mixing proportions of the water bodies.

Criterion continuous concentration an estimate of the highest concentration of a material in surface freshwater to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect.

Cross-formational flow flow of groundwater from one aquifer, typically confined, to an overlying aquifer. **Denitrification** reduction of nitrate molecule (NO_3^-) under reduced conditions to nitrogen gas.

Disinfection byproducts formation of hazardous byproducts during chlorine disinfection of drinking water, typically with high organic matter; generation of trihalomethanes (THMs), and specifically brominated trihalomethanes (e.g., bromodichloromethane; BDCM) during the disinfection process.

Dissociation of boric acid to borate ion an increase in the pH will convert boric acid to the borate ion species. The

dissociation constant is defined at the pH at which the fraction of boric acid is equal to that of borate ion. **Dissolved inorganic carbon** the sum of dissolved inorganic carbon (DIC) species in a solution that is composed of carbon dioxide, carbonic acid, bicarbonate anion, and carbonate anion. The relative proportions of these species vary with pH.

Dolomitization a chemical reaction of Mg-rich water with calcium carbonate (e.g., limestone) rocks that involves Mg^{2+} and Ca^{2+} exchange, resulting in Ca-rich residual solution.

Efflorescent salt crusts salts that are generated in soil or shallow unsaturated zones that were formed by evaporation of saline soil solution that have reached the saturation level of different soluble minerals (e.g., gypsum, halite).

Electrical conductivity a field measure of the salinity of water, known also as specific conductance, that measures a solution's ability to conduct an electric current. The SI unit is siemens per centimeter (S cm^{-1}). A reciprocal quantity is electrical resistivity.

Endorheic rivers rivers that flow to inland basins and never reach the ocean.

Ethylene dibromide (EDB) type of soil fumigant enriched in bromide.

Evapotranspiration the combined evaporation and plant transpiration from soil surface; evaporation involves transport of water to the air from the soil solution, surface water, while transpiration accounts for water transport through a plant. The combined effect results in water loss and accumulation of salt residue.

Exchangeable adsorption sites one of the adsorption reaction processes involves exchange of cations (e.g., Ca^{2+} , Mg^{2+} , Na^+) from adsorption sites on clay minerals and/or oxides and water. The capacity of exchangeable adsorption sites varies among the mineral types and will determine the magnitude of the exchange reaction process.

Fossil water known also as nonrenewable groundwater, includes water that was recharged to an aquifer during historical/geological time and is not originated from the modern hydrological cycle. Fossil water is typically identified by radioactive age-dating isotopes (e.g., ¹⁴C, tritium) and stable oxygen and hydrogen isotopes that are different from those of modern precipitation.

Freshening fresh groundwater flow and displacement of saline groundwater.

Imported water water that is used from external sources outside a region or an aquifer; typically, water is imported from areas of high abundance to areas where natural water resources are not sufficient to accommodate water demands. **Incongruent silicate mineral reactions** a weathering chemical reaction that involves reaction of silicate minerals (e.g., aluminosilicates) in rocks and soils with carbon dioxide that generates clay minerals (e.g., kaolinite) and residual water enriched in bicarbonate. While in *congruent* dissolution the mineral is completely dissolved into solution, *incongruent* dissolution involves formation of a new mineral from the ions that were dissolved from mineral weathering. **Inner-sphere complex** a chemical bond that is typically covalent between oxyanions and the electron-donating oxygen ion on a mineral surface without the presence of water molecules.

Ionic strength a measure of the salinity of a solution that is expressed as the square root of the sum of the individual ion concentrations (in molality unit; mol kg⁻¹ {H₂O}) multiplied by the charge number of that ion. Generally, multivalent ions contribute strongly to the ionic strength of a solution relative to monovalent ions.

Isotopic fractionation preferential and/or selective incorporation of specific isotopes into different phases (dissolved, solid, vapor) that results in enrichment and/or depletion of the isotopes and changing of their ratios in the reaction products.

Meteoric water line the linear correlation between δ^2 H and δ^{18} O values in precipitation that reflects the local temperature and relative humidity; typically, the linear correlation has a slope ~8 and an intercept value that increases with aridity (lower relative humidity), known as deuterium excess.

Mineral saturation the concentration level of ions from which different minerals will begin to precipitate into a solid state.

Mobilization leaching of ions and trace elements from a solid phase (e.g., mineral surface) to the dissolved phase in water.

Nitrogen isotopes the 'delta' notation, defined as $\delta^{15}N_{NO_3} = [(^{15}N)^{14}N)_{sample}/(^{15}N)^{14}N)_{AIR} - 1] \times 10^3$.

Osteosarcoma bone cancer associated with long-term exposure to radioactive nuclides that are bioaccumulated in bone tissue.

Outer-sphere complex a chemical bond that is typically an ion pair in which oxyanions and surface functional groups on a mineral surface are separated by one or more water molecules.

Overexploitation of an aquifer water pumping rates of an aquifer beyond the natural replenishment rates.

Oxyanions speciation of trace elements such as arsenic, selenium, and boron into anionic forms.

Sodium adsorption ratio (SAR) the relative activity of sodium ions in exchange reactions with soil.

Selenate, Se(VI) the oxidized form of selenium in oxidizing water.

Selenite, **Se(IV)** the reduced form of selenium in reducing water.

Sinkholes a natural depression or hole in land surface caused by subsurface dissolution of rocks.

Sodic subsoil a dense clay soil zone with high capacity for sodium adsorption, which reduces the hydraulic conductivity of the soil.

Softener backwash saline water saline effluents that are generated during the regeneration process of softener in which a brine is flushed through the ion-exchange column to remove calcium to provide available exchangeable sites for calcium removal process of softeners.

Stable oxygen and hydrogen isotopes in water $\delta^{18}O_{H_2O}$ (=[(¹⁸O/¹⁶O)_{sample}/(¹⁸O/¹⁶O)_{STD} -1] x10³) and $\delta^{2}H_{H_2O}$ $(=[(^{2} H/^{1} H) sample/(^{2} H/^{1} H)_{STD} -1] x10^{3})$, where STD is standard mean ocean water (SMOW).

Strontium isotopes the ratio of radiogenic ⁸⁷Sr to stable ⁸⁶Sr isotopes, ⁸⁷Sr/⁸⁶Sr.

Sulfur isotope in sulfate $\delta^{34}S_{SO_4}$ (=[(³⁴ S/³⁶ S)_{sample}/(³⁴ S/³⁶ S)_{STD} -1] x10³).

Total dissolved solids a measure of water salinity; the sum of dissolved salts in water.

11.9.1 Introduction

One of the most conspicuous phenomena of water-quality degradation, particularly in arid and semiarid zones, is salinization of water resources. Rates of salinization vary widely: in some cases, it is a long-term phenomenon associated with geologic processes; in others, it is induced by human activities and thus very recent. The net result is that during the last century, many aquifers and river basins worldwide have become unsuitable for human consumption owing to high levels of salinization (Ranjan et al., 2006; Sowers et al., 2011; Vengosh and Rosenthal, 1994; Vengosh et al., 2001). Likewise, each year, large areas of soil become salinized and unusable for agriculture production (Dregne, 2002; Rengasamy, 2006).

Salinization is a global environmental phenomenon that affects diverse aspects of our lives: changing the chemical composition of natural water resources; degrading the quality of water supplied to domestic and agriculture sectors; affecting ecological systems by loss of biodiversity and taxonomic replacement by halotolerant species; contributing to loss of fertile soil; resulting in collapse of agricultural and fishery industries; changing local climatic conditions; and creating severe health problems (Dregne, 2002; Jackson et al., 2001; Postel, 1999; Rengasamy, 2006; Shiklomanov, 1997; Williams, 2001a,b; Williams et al., 2002). The damage due to salinity in the Colorado River Basin alone, for example, has been estimated to be between \$500 and \$750 million per year and could exceed \$1 billion per year if the salinity in the Imperial Dam increased from 700 to 900 mg l^{-1} (US Department of the Interior, 2003). In Australia, accelerating soil salinization has become a profound environmental and economic disaster (Gordon et al., 2003; Rengasamy, 2006; Scanlon et al., 2005; Timms, 2005; Williams et al., 2002); Western Australia is "losing an area equal to one football oval an hour" due to spreading salinity (Murphy, 1999). In the early 2000s, the annual cost of dryland salinization in Australia was estimated at AU\$700 million for lost land and AU\$130 million for lost production (Williams et al., 2002). In short, salinization processes have become pervasive.

Salinity in water is usually defined as the sum of the dissolved constituents (total dissolved solids – TDS, in milligrams per liter) and occasionally also by one of the dissolved salt ions, typically the chloride content, although chloride comprises only a fraction of the total dissolved salts in water. The chloride to total dissolved solids (Cl/TDS) ratio varies from 0.1 in nonmarine saline waters to ~0.5 in marine saline waters. **Total organic carbon (TOC)** The concentration of carbon bound in organic compounds in water; can be used as a measure of water quality.

Uranium decay chains a group of radioactive nuclides that are generated from the parent ²³⁸U, ²³⁵U, and ²³²Th isotopes through cascades of radiogenic and radioactive nuclides of different half-lives, ending with the stable lead isotopes.

Water salinity is also defined by electrical conductivity (in microsiemens per centimeter), which is typically measured in the field during sampling. The typical instrument calibration by KCl solution may result, however, in different absolute 'salinity' values for different chemical compositions. In soil studies, the electrical conductivity and the ratio of $Na/\sqrt{(Ca+Mg)}$ (sodium adsorption ratio – SAR, in equivalent units) are often used as indirect measures of soil salinity.

In addition to chloride, high levels of other dissolved constituents may limit the use of water for domestic, agriculture, or industrial applications. In parts of China, eastern Africa, and India, for example, high fluoride content is associated with brackish to saline groundwater and causes severe dental and skeletal fluorosis (Ayenew et al., 2008; D'Alessandro et al., 2008; Misra and Mishra, 2007; Rango et al., 2009, 2010a,b,c; Shiklomanov, 1997). Hence, the 'salinity' problem is only the 'tip of the iceberg,' as high levels of sodium and chloride can be associated with high concentrations of other inorganic contaminants such as sulfate, boron, fluoride, and bioaccumulated elements such as selenium and arsenic (see Chapter 11.2). The salinization process may also enhance the mobilization of toxic trace elements in soils due to competition of ions for adsorption sitesand formation of metal-chloride complexes (Backstrom et al., 2003, 2004) and oxyanion complexes (Amrhein et al., 1998; Goldberg et al., 2008). Thus, the chemical evolution of the major dissolved constituents in a solution will determine the reactivity of trace elements with the host aquifer/streambed solids, and consequently their concentrations in water resources. For example, high concentrations of bicarbonate in groundwater can significantly enhance arsenic desorption from hydrous ferric oxide that could result in high As concentrations in HCO₃⁻-rich groundwater (Appelo et al., 2002; Czerniczyniec et al., 2007; Di Natale et al., 2008; Yu et al., 2006).

Salinity can also affect the radioactivity level of groundwater. Most naturally occurring radionuclides are highly retained to the aquifer matrix and are not soluble in associated groundwater. Radium is an exception since the ratio between adsorbed and dissolved radium depends on the salinity among other factors, and thus the concentration (activity) of dissolved radium typically increases with salinity (Herczeg et al., 1988; Krishnaswami et al., 1991; Miller and Sutcliffe, 1985; Moise et al., 2000; Sturchio et al., 2001; Tomita et al., 2010; Vinson, 2011; Vinson et al., 2009).

The World Health Organization (WHO) recommends that the chloride concentration of the water supply for human consumption should not exceed 250 mg l^{-1} . Yet, many countries have adopted higher national drinking water standards for

salinity, which can also vary for different regions within a country. For example, the US Environmental Protection Agency (EPA) has secondary (nonenforceable) standards of 250 mg l⁻¹ for chloride and 500 mg l⁻¹ for TDS (US Environmental Protection Agency, 2011b), yet each state in the United States has different enforceable standards (e.g., Florida – TDS of 500 mg l⁻¹, Utah – TDS of 2000 mg l⁻¹, California – TDS of 1000 mg l⁻¹). In Israel, the enforceable drinking water standard for chloride is much higher, at 600 mg l⁻¹.

Agriculture applications also depend upon the salinity level of irrigation water. Many crops, such as citrus, avocado, and mango, are sensitive to salt concentrations in irrigation water (Grieve and Poss, 2000; Kudo et al., 2010; Rengasamy, 2010; Scott et al., 2000; Wang et al., 2003). In addition, long-term irrigation with sodium-rich water results in a significant reduction of the hydraulic conductivity and hence the fertility of the irrigated soil. Similarly, various industrial sector applications require water of low salinity. The high-tech industry, for example, requires large amounts of water with low levels of dissolved salts. Hence, the salinity level of groundwater is one of the limiting factors that determine the suitability of water for various applications.

The salinity problem is a global phenomenon but it is more severe in water-scarce areas, such as arid and semiarid zones (Figure 1). Increasing demands for water have created tremendous pressures on water resources that have resulted in the lowering of ground and surface water levels and consequently increasing salinization. In the Middle East, for example, salinity is the main factor that limits water utilization, and future prospects for water use in Israel, the West Bank, the Gaza Strip, and Jordan are complicated by increasing salinization (Salameh, 1996; Vengosh and Rosenthal, 1994). The salinity problem thus has numerous grave economic, social, and political consequences (Sowers et al., 2011), particularly in cross-boundary basins that are shared by different communities (e.g., the Salinas Valley in California; Vengosh et al., 2002), friendly states (e.g., the Colorado River along the Mexico–US border; Stanton et al., 2001), and hostile states such as the Euphrates and Tigris rivers (Beaumont, 1996; Odemis et al., 2010), the Jordan River (Farber et al., 2004, 2005, 2007; Vengosh et al., 2001), the Gaza Strip (Ai-Yaqubi et al., 2007; Vengosh et al., 2005; Weinthal et al., 2005), the Aral Basin (Weinthal, 2002), and the Nile River (Elewa and El Nahry, 2009; Ohlsson, 1995).

Salinization of water resources also affects agricultural management. The composition of irrigation water will determine the salinity and fertility of the soil, and with time, the quality of the underlying water resource. The use of treated wastewater or other marginal waters (e.g., brackish water) with high contents of chloride, sodium, and boron is suitable only for salt-tolerant crops and requires special amending treatment of the soil. In addition, high boron in irrigation water and consequently in soil is also of concern in agriculture (Grieve and Poss, 2000; Koc, 2007), as boron is an essential micronutrient for plants but becomes toxic at high levels (typically >0.75 mg l^{-1} in irrigation water).

Finally, salinization processes are directly linked to global factors such as population growth and climate change. Increasing population leads to greater demands for food, which further increases the rate of freshwater withdrawal beyond the rate of natural replenishment (Figure 2), triggering salinization of aquifers. Furthermore, climate change models predict a reduction in precipitation in many arid and semiarid regions (Figure 1). A decrease in river discharge and aquifer replenishment coupled with an increase in temperature, and thus evaporation rates, would further worsen and accelerate salinization rates in the already salinized water resources of these regions.

This chapter provides an overview of global salinization phenomena and investigates the different mechanisms and geochemical processes that are associated with salinization. The overview includes salinization of rivers, lakes, and groundwater from different parts of the world. Special emphasis is given to the distinction between natural processes and anthropogenic forcing that generates salinity, such as wastewater



Figure 1 Map of arid and semiarid regions of the world.



Figure 2 Global distribution of annual renewable water resources (billion cubic meters per year). Data from AQUASTAT database; Information System on Water and Agriculture, Food and Agriculture Organization, United Nation, http://www.fao.org/nr/water/aquastat/dbase/index.stm.

contamination and agricultural runoff. As such, two anthropogenic salinization cycles are introduced – the agricultural and domestic cycles. The role of the unsaturated zone in shaping the chemical composition of dryland salinization is also discussed. An overview of the effects of salinity on the occurrence of health-related contaminants such as fluoride, oxyanions (arsenic, selenium, boron), radionuclides, trihalomethanes, and fish-kill algae is presented. Some useful geochemical and isotopic fingerprinting tracers are introduced for elucidating the salinity sources. Finally, the chemical and isotopic compositions of man-made 'new water' that is produced from desalination are analyzed with implications for predicting the chemical and isotopic compositions of future water resources in the Anthropocene Era.

11.9.2 River Salinization

More than one-half of the world's major rivers (Figure 3) are being seriously depleted and polluted, which causes degradation of the surrounding ecosystems and threatens the health and livelihood of people who depend upon these rivers for drinking water and irrigation (Meybeck, 2003). Rivers are being depleted and contaminated because the global demand for water is rising sharply. The problem will be further exacerbated by the need to supply food and drinking and irrigation water for an additional estimated 2 billion people by 2025 (Serageldin, 2000). The World Commission on Water for the twenty-first century has developed a list of 'stressed rivers,' which includes the Yellow River in China, the Amu Darya and Syr Darya in Central Asia, the Colorado River in the western United States, the Nile River in Egypt, the Volga River in Russia, the Ganges River in India, and the Jordan River in the Middle East (Figure 3) (Serageldin, 2000).

Salinization of surface water can occur through either natural or anthropogenic processes or a combination of the two. In the natural setting, particularly in a dryland environment, salts are deposited and stored in the unsaturated zone and are eventually transported to shallow groundwater that discharges into adjacent rivers. Some rivers flow through arid regions although their source lies in wetter parts of upper basins (Colorado, Rio Grande, Orange, Nile, Euphrates, Tigris, Jordan, Indus, Murray; Figure 3). About 50% of arid land is located in 'endorheic' regions in which there is no flow to the ocean. In these regions, rivers flow into lakes such as the Caspian, Aral, Chad, Great Salt, Eyre, Dead Sea, and Titicaca, all without outlets.

Salinization of rivers also occurs due to human intervention, such as diversion of upstream natural flow or dam construction, and consequently significant reduction of natural flow discharge. The Amu Darya and Syr Darya in Central Asia, for example, were almost desiccated due to the diversion of water for cotton irrigation in the former Soviet Union (Weinthal, 2002). While historical annual flow in these two rivers is estimated at 122 billion cubic meters per year, by the mid-1980s, the Amu Darya and Syr Darya no longer flowed to the Aral Sea (Micklin, 1988, 1992).



Figure 3 Map of major rivers of the world.

A.F. Pillsbury, in his classic 1981 paper, described how recycling of salts via irrigation and agricultural return flow controls the salinity of the downstream river in arid zones (Pillsbury, 1981). Once the natural salt balance is disturbed and salts begin to accumulate, either in the unsaturated zone or in drainage waters, the salinity in the downstream discharge water will increase. The salinity of the Colorado River is derived from a century of activity that includes upstream diversion of freshwater, massive irrigation, evapotranspiration and salt accumulation in the soil, and return of saline drainage flow back to the river (Pillsbury, 1981). Natural brines from Paradox Valley, for example, discharge to the Dolores River in Colorado, which is a tributary of the Colorado River. This brine discharge, with TDS of 250000 mg l^{-1} , annually contributes about 2×10^8 kg of dissolved salts to the Colorado River system (Kharaka et al., 1997).

The Colorado River Basin encompasses about 630 000 km² in seven states in western United States and northern Mexico (Figure 4). The river serves 33 million people and provides the basis for the regional economy in agriculture, livestock grazing, mining, forestry, manufacturing, oil and gas production, hydropower production, recreation, and tourism. During 1906–1998, the unregulated flow rate of the Colorado River varied widely from 6.1 to 30.2 billion cubic meters per year, with an average annual natural flow of approximately 18.6 billion cubic meters per year at Lee's Ferry, about 15 km south of the Utah–Arizona border (Colorado River Board of California, 2011). The 1992 Colorado River Compact allocated 9.2 billion cubic meters per year for each of the Upper and Lower Basin states, with the right of the Lower Basin to increase its use by 1.2 billion cubic meters

per year. The construction of reservoirs along the river (Figure 4) increases useable capacity of the Colorado river to about 74 billion cubic meters per year, from which Lake Powell (behind Glen Canyon Dam) and Lake Mead (behind Hoover Dam) have a combined capacity of approximately 62.8 billion cubic meters per year (Colorado River Board of California, 2011).

One of the major issues of concern for adequate management is the relatively high salinity of the Colorado River, with an estimated 9 million tons of salts passing the Hoover Dam annually (Colorado River Basin Salinity Control Forum, 2008). The salinity of the river increases as it flows downstream (Figure 5), but no systematic increase with time has been observed as salinity has fluctuated and overall decreased during the last four decades (Figure 6). These annual salinity variations have been shown to correlate inversely with the river flow (Butler and von Guerard, 1996). It has been estimated that about half of the salinity load in the Colorado River Basin is derived from natural saline discharge, 37% directly from irrigation, and the remaining 16% from reservoir-storage effects and municipal and industrial practices (US Bureau of Reclamation, 2003). The elevated salinity level of the Colorado River causes economic damage estimated at \$600 million per year, mainly to the agriculture sector in which irrigation with saline water reduces crop yields and adds labor costs for irrigation management and drainage requirements. Urban utilization of the saline Colorado River adds further additional costs due to more frequent replacement of plumbing and water-using appliances, use of water softeners, and the purchase of bottled water (Colorado River Board of California, 2011).



Figure 4 Map of the Upper and Lower basins of the Colorado River.

Similarly, the rise of salinity in the Nile delta in Egypt has been attributed to a disturbance of the natural salt balance after the construction of the Aswan dam (Lake Nassar) and the reduction of natural outflow of water from the Nile River to the Mediterranean Sea. About 50 billion cubic meters per year of the Nile water is used for irrigation. The recycling of drainage water has increased the salinity of the northern part of the Nile close to the outlets to the Mediterranean Sea (Elewa and El Nahry, 2009; Kotb et al., 2000).

Reduction of the natural river flow and increasing discharge of saline drainage water are also the primary sources of increasing salinity in the Euphrates and Tigris rivers in Iraq (Fattah and Baki, 1980; Odemis et al., 2010; Robson et al., 1984). In addition, the water quality has deteriorated due to sewage pollution (Al-Muhandis, 1977; Mutlak et al., 1980). Upstream, in Turkey, the government has embarked since the mid-1960s on a large-scale program for the development of southeastern Turkey (Beaumont, 1996). The Southeastern Anatolia Project (GAP) with the Ataturk Dam is one of the largest water projects in the world, annually diverting for irrigation more than 13 billion cubic meters from the Euphrates and Tigris rivers. Consequently, the annual flow of the downstream Euphrates River has been reduced by 30–50%, out of an annual natural discharge of ~30 billion cubic meters per year (Beaumont, 1996). Massive irrigation in downstream Syria and Iraq has resulted in the formation of saline agricultural return flows that together with local shallow groundwater are discharged to the downstream sections of the river. As a result, the salinity of the Euphrates River, close to its confluence into the Persian Gulf, has risen to 3000 mg l⁻¹ (Fattah and Baki, 1980; Robson et al., 1984).

In the dryland river environment, river salinization is also exacerbated by land clearing of deep-rooted natural vegetation, which accelerates recharge rates and causes groundwater tables to rise and dissolve salts in the unsaturated zone. In the Murray–Darling Basin in South Australia, soluble aerosols derived from the ocean are deposited in the drainage basin, concentrated by evapotranspiration, and discharged to the



Figure 5 Variations in the salinity $(mg l^{-1})$ of the Colorado River with flow distance along the southern Colorado Basin as measured in October 2003. Distance along river (in km) is initiated from Hoover Dam (see locations in **Figure 4**). Data from unpublished results, Duke University.

Murray River (Herczeg et al., 1993; White et al., 2009). Largescale cleaning of natural vegetation and its replacement by annual crops and pastures have increased the amount of water leaking through the unsaturated zone. Excess irrigation has also increased groundwater levels (Williams et al., 2002 and references therein). The rise of saline groundwater and mobilization of salts stored in the unsaturated zone have formed saline seepages that discharge to streams and the soil surface, which affects runoff salinity. Consequently, in the Murray River (Table 1) water salinity has gradually increased during the last 50 years such that Na⁺ and Cl⁻ and overall major ion compositions are now similar to that of seawater (Herczeg et al., 1993). In the Sandspruit River, a tributary of the Berg River in the semiarid Western Cape Province of South Africa, salinization of the river (TDS range from 4500 to 9000 mg l^{-1}) was also attributed to accumulation and leaching of salts from the soil. Elemental mass-balance calculations suggest that the salts are derived from both recycling of meteoric aerosols and soil leaching (Flügel, 1995).

The Lower Jordan River along the border between Israel and Jordan (Figure 7) represents a different type of river salinization in the dryland environment. A tenfold reduction of surface water flow in the Jordan River (50-200 million cubic meters per year during the last 50 years relative to \sim 1400 million cubic meters per year in historic times) and intensification of shallow groundwater discharge resulted in salinization of the Jordan River (Farber et al., 2004, 2005; Holtzman et al., 2005; Shavit et al., 2002). During August 2001, the salinity of the southern end of the Jordan River, just before its confluence into the Dead Sea, reached 11 g l^{-1} , a quarter of the Mediterranean seawater salinity (Figure 8). Based on ion ratios (Na/Cl, Br/Cl) and strontium, boron, oxygen, and oxygen isotope variations, the rise of salinity in the southern section of the Jordan River (Table 1; Figure 8) was attributed to the discharge of saline groundwater (Farber et al., 2004, 2005; Vengosh et al., 2001). It was suggested that the shallow saline groundwater originated



Figure 6 Time series of the salinity variations (mg l⁻¹) of the Colorado River at Imperial Dam since 1970. Data from Colorado River Basin Salinity Control Forum (2008).

from both leaching of local saline marl sediments and upflow of underlying hypersaline brines (Farber et al., 2007).

Likewise, the salinity of the Rio Grande River increases to about 2000 mg l⁻¹ along 1200 km flow distance. The parallel decrease of the Br/Cl ratio of the salinized river implies discharge of saline groundwater that interacted with halite deposits (Eastoe et al., 2010; Moore et al., 2008b; Phillips et al., 2003). Additional geochemical tools such as boron, strontium, and sulfur isotopes were used to suggest that the salinization of the Rio Grande River along the border of the United States and Mexico is derived from upwelling basin saline groundwater rather than anthropogenic (e.g., wastewater) sources (Moore et al., 2008b). The impact of evaporite dissolution was demonstrated also in the Ebro River Basin in Spain as long-term monitoring of the salinity (large variations, TDS up to 1000 mg l^{-1}) has shown that the TDS is mostly controlled by variations of SO_4^{2-} , Na^+ , and Ca^{2+} ions, reflecting preferential dissolution of gypsum and carbonate minerals as part of surficial chemical weathering (Negrel et al., 2007).

Salinization of rivers can also occur in temperate climate zones due to direct anthropogenic contamination. For example, the Rhine River has suffered from discharge of potash mine drainage brines since the opening of potash mines more than 100 years ago. Chloride levels and salt fluxes have increased by a factor of 15–20. The rise of the annual chloride load at the Rhine River mouth (recorded since 1880) reflects an increase from a natural load of less than 5 kg s⁻¹ to more than 300 kg s⁻¹ in the 1960s (Meybeck and Helmer, 1989). Another example is the Arno River in northern Tuscany, Italy. Pollution by wastewater resulted in a downstream increase in Na⁺, Cl⁻, and SO₄^{2–} ions with a distinctive sulfur isotopic composition (Cortecci et al., 2002, 2007).

To summarize, there are five major sources of soluble salts in river basins: (1) meteoric salts, (2) salts derived from waterrock interaction (e.g., dissolution of evaporitic rocks), (3) salts

| Site | Source | TDS | Ca | Mg | Na | К | CI | <i>S0</i> ₄ | HCO3 | NO ₃ | Br | B (ppb) | Na/CI | SO₄/CI | Br/Cl | B/Cl (×10 ⁻³) |
|--|------------------------------------|---------|-------|-------|--------|------|--------|------------------------|------|-----------------|------|---------|-------|--------|-------|------------------------------|
| Seawater (Red Sea) Freshwater rivers | | 41 390 | 418 | 1442 | 12396 | 516 | 23290 | 3077 | 161 | _ | 75.6 | 5.3 | 0.86 | 0.05 | 1.5 | 0.8 |
| Amazon River | Berner and Berner (2012) | 39 | 5.2 | 1 | 1.5 | 0.8 | 1.1 | 1.7 | 20 | - | - | 6 | 2.1 | 0.6 | - | 18.2 |
| Orinoco River | Berner and Berner (2012) | 35 | 3.3 | 1 | 1.5 | 0.7 | 2.9 | 3.4 | 11 | - | - | 2 | 0.8 | 0.4 | - | 27.1 |
| Mississippi (1905) | Berner and Berner (2012) | 216 | 34 | 8.9 | 11 | 2.8 | 10.3 | 25.5 | 116 | - | - | - | 1.7 | 0.9 | - | - |
| Mackenzie | Berner and Berner (2012) | 211 | 33 | 10.4 | 7 | 1.1 | 8.9 | 36.1 | 111 | - | - | 12 | 1.2 | 1.5 | - | 4.4 |
| Danube | Berner and Berner (2012) | 307 | 49 | 9 | 9 | 1 | 19.5 | 24 | 190 | - | - | - | 0.7 | 0.5 | - | - |
| Congo | Berner and Berner (2012) | 34 | 2.4 | 1.4 | 2 | 1.4 | 1.4 | 1.2 | 13.4 | - | - | 3 | 2.2 | 0.3 | - | 7.2 |
| Zambeze | Berner and Berner (2012) | 58 | 9.7 | 2.2 | 4 | 1.2 | 1 | 3 | 25 | - | - | - | 6.7 | 1.1 | - | - |
| Saline rivers | | | | | | | | | | | | | | | | |
| Murray River, South Australia | Herczeg et al. (1993) | 448 | 21 | 17 | 101 | 6 | 171 | 38 | 94 | - | 0.4 | - | 0.91 | 0.08 | 1.1 | - |
| Jordan River (south end) | Vengosh et al. (2001) | 1109 | 545 | 705 | 2300 | 170 | 5370 | 1650 | 254 | 20 | 81 | 2800 | 0.66 | 0.11 | 6.7 | 1.7 |
| Tigris River (Baghdad, 1977) | Mutlak et al. (1980) | 521 | 64 | 21.7 | 47.7 | - | 82.6 | 66.5 | 238 | 10 | - | 200 | 0.89 | 0.3 | - | 8.7 |
| Saline lakes | | | | | | | | | | | | | | | | |
| Salton Sea (1989) | Schroeder and Rivera (1993) | 40700 | 950 | 1300 | 11 000 | 220 | 17 000 | 10 000 | 185 | - | 13 | 12 000 | 1 | 0.22 | 0.3 | 2.3 |
| Aral Sea (1991) | Linnikov and Podbereznyi (1996) | 59120 | 1020 | 3600 | 14 600 | 640 | 22 650 | 16 180 | 430 | - | - | - | 0.99 | 0.26 | - | - |
| Caspian Sea | Peeters et al. (2000) | 12385 | 340 | 700 | 3016 | 88 | 5233 | 3008 | _ | _ | _ | _ | 0.89 | 0.2 | _ | _ |
| Dead Sea Rift Valley Seawater intrusion | Starinsky (1974) | 337 800 | 17600 | 42120 | 41 300 | 7600 | 224200 | 280 | 200 | - | 4500 | 54 690 | 0.28 | 0.005 | 10 | 0.8 |

Table 1 Chemical composition of saline water from various sources

(Continued)

| Site | Source | TDS | Ca | Mg | Na | K | CI | <i>S0</i> ₄ | HCO₃ | NO3 | Br | B (ppb) | Na/Cl | SO₄/CI | Br/Cl | B/Cl (×10 ⁻³) |
|---|--|----------------|-------------|------------|--------------|------------|---------------|------------------------|-----------|--------|-------------|------------|--------------|--------------|------------|------------------------------|
| Coastal aquifer, Israel Salinas Valley, California Saline plumes and uncoming of brines | Vengosh et al. (1994) Vengosh et al. (2002) | | 980 410 | 245 126 | 2830 450 | 22 12 | 6304 1670 | 470 212 | 206 62 | _ | 21.3 5.4 | 950 245 | 0.69 0.42 | 0.03 0.05 | 1.5 1.5 | 5 4.8 |
| Coastal aquifer, Israel (Beer Tovivva) | Vengosh et al. (1999a b) | 2560 | 176 | 97 | 545 | 3.9 | 1125 | 143 | 370 | 98 | 3.5 | 508 | 0.75 | 0.05 | 1.4 | 1.5 |
| Ogallala aquifer, Texas Dammam aquifer, Kuwait | Mehta et al. (2000a,b) Al-Ruwaih (1995) | 67 530 4062 | 1460 470 | 388 138 | 23850 635 | 32 15.2 | 36120 1241 | 5610 1189 | 41 77 | _ 8 | 6.2 - | _ 1500 | 1 0.77 | 0.06 0.35 | 0.07 - | _ 3.9 |
| Jordan Valley, Jericho, Cenomanian aquifer | Marie and Vengosh (2001) | 8270 | 490 | 580 | 1700 | 110 | 4950 | 105 | 275 | 62 | 83 | - | 0.52 | 0.02 | 7.4 | - |
| Pleistocene aquifer Groundwater associated | Marie and Vengosh (2001) | 3100 | 156 | 208 | 590 | 84 | 1372 | 295 | 363 | 29 | 10 | - | 0.66 | 0.16 | 3.3 | - |
| with freezing process | | | | | | | | | | | | | | | | |
| Sweden | Bein and Arad (1992) | 18200 | 3690 | 31 | 2850 | 12 | 11100 | 522 | 7 | - | 79 | - | 0.39 | 0.02 | 3.1 | - |
| Finland <i>Agricultural drainage</i> | Bein and Arad (1992) | 14400 | 3900 | 13 | 1500 | 7 | 8900 | 1 | 21 | - | 77 | - | 0.25 | <0.01 | 3.8 | - |
| San Joaquin Valley, California | Mitchell et al. (2000) | 4580 | 192 | 242 | 952 | - | 499 | 2650 | - | 44 | - | 5940 | 2.9 | 1.9 | - | 3.9 |
| Mendota, San Joaquin Valley, California | Kharaka et al. (1996) | 14280 | 438 | 285 | 3720 | 3.1 | 1210 | 8350 | 250 | 25 | 3.4 | - | 4.7 | 2.5 | 1.2 | - |
| Imperial Valley, California | Schroeder and Rivera (1993) | 6715 | 310 | 330 | 1420 | 19 | 1200 | 3000 | 383 | 53 | - | - | 1.9 | 0.9 | | |
| Imperial Valley, California Wastewaters | Schroeder and Rivera (1993) | 8250 | 560 | 320 | 1700 | 24 | 2600 | 2700 | 342 | 5 | 2.3 | 1700 | 1 | 0.4 | 0.4 | 2 |
| Dan Reclamation Project, Israel (1993) | Vengosh and Keren (1996) | 1300 | 80 | 30 | 264 | 34.2 | 361 | 112.5 | 420 | - | 0.4 | 500 | 1.1 | 0.11 | 0.5 | 6 |
| Orleans, Cape Cod, Massachusetts | DeSimone et al. (1997) | 1700 | 440 | 0.3 | 100 | 30 | 950 | 19 | 134 | 30 | - | 200 | 0.16 | 0.007 | - | 0.7 |

The ion concentrations are reported in mg l^{-1} (unless otherwise stated) whereas the ionic ratios are molar.

Table 1

(Continued)



Figure 7 Map of the Jordan River between the Sea of Galilee (Lake Tiberias) and the Dead Sea along the border of Israel and Jordan.



Figure 8 Variation of chloride content of the Jordan River with flow distance. Distance (km) refers to the beginning of the Jordan River flow (Alumot dam) downstream from the Sea of Galilee. Data from Farber et al. (2004).

derived from remnants of formation water entrapped in the basin, (4) geothermal waters, and (5) anthropogenic salts (e.g., wastewater effluent; Farber et al., 2004; Moore et al., 2008b; Vengosh et al., 2001; Williams, 2001a). Meteoric salts are concentrated via in-stream net evaporation and evapotranspiration along the river flow. In addition, meteoric salts can be recycled through irrigation in the watershed and development of saline agricultural drainage water that flows to the river.

Overall, rivers are one of the most sensitive hydrological systems to global and climatic changes. In addition to the reduction in precipitation and increased aridity that are projected for arid and semiarid regions as a result of global warming, population growth and increasing pressure on shallow aguifer systems combined with river contamination will cause a significant increase in river salinity. One example of these processes is the ongoing changes in the water quality of the Ganges River Basin, which supports approximately 500 million people, about 40% of the total population in India (Misra, 2011). The growing population and urbanization in the Ganges Basin has led to increased utilization of shallow groundwater, lowering the water table, and a reduction in surface and subsurface discharge to the Ganges River. At the same time, enormous solid waste production and disposal has filled small natural channels and changed flow patterns; this, coupled with accelerated disposal of domestic wastewater, has led to severe degradation of water quality. Compounding these ongoing changes, climate change models predict that a temperature rise may reduce precipitation by up to 16%, which could reduce the groundwater recharge by 50% (Misra, 2011). Thus, in spite of the enormous discharge of surface water in the Ganges Basin (annual surface water potential of 525 billion cubic meters; Misra, 2011), even the mighty Ganges River is not immune to significant salinization.

11.9.3 Lake Salinization

Naturally occurring salt lakes typically reflect a hydrological equilibrium that has been developed over geological time (see Chapter 7.12). The wide range of the chemical compositions of natural salt lakes represents their different sources; salts that are derived from the evolution of freshwater inflows (e.g., the Great Salt Lake, Utah; Jones et al., 2009; Spencer et al., 1985), hydrothermal fluids (Qaidam Basin, China; Vengosh et al., 1995), remnants of evaporated seawater (Dead Sea, Israel; Katz and Starinsky, 2009; Starinsky, 1974; Stein et al., 1997; Torfstein et al., 2005; Waldmann et al., 2007), and long-term accumulation of marine aerosols (Lake Eyre, Australia; Chivas et al., 1991; Vengosh et al., 1991a).

The term lake salinization as used in this chapter, however, applies to direct anthropogenic activity and the ongoing transformation of freshwater lakes into salt lakes. In principle, the diversion of freshwater from one basin to another, or the diversion of natural lake inflows, are the principal processes that could result in lake salinization. The consequences may be devastating; for example, the diversion of almost all of the water from the Amu Darya and Syr Darya in central Asia to grow cotton and other crops (Weinthal, 2002) led to major desiccation of the Aral Sea (Micklin, 1988, 1992). From discharge rates of about 55 billion cubic meters per year during the 1960s, the river inflow to the Aral Sea decreased to 22 billion cubic meters per year in the 1970s, a range of 6-15 billion cubic meters per year during the 1980s and 1990s, and 2-10 billion cubic meters per year between 2000 and 2010 (Micklin, 2010). Water levels dropped by 30 m (55 m above sea level in 1950 to 25 m in 2010) and the water volume reduced from 1089 km³ in 1960 (whole lake) to two separate small basins (the Western Basin with a volume of 56 km³ and the Eastern Basin with a volume of 0.64 km³) in 2009 (Micklin, 2010). The salinity rose exponentially from 10 g l^{-1} in the 1960s to over 100 g l^{-1} in the Western Basin and over 200 g l^{-1} in the Eastern Basin in 2008 (Figure 9; Zavialov et al., 2009). The rise of the salinity has led to the destruction of the once-thriving fisheries industry and has produced severe health problems in the region associated with resuspension of contaminated sediments from the desiccated lake to the atmosphere (Micklin, 1988, 1992, 2010).

Lake Chad in the Sahel region in Africa has shrunk by 75% in the last three decades because of both periodic droughts and massive diversions of water for irrigation. The rich fisheries that used to support the local population have collapsed entirely (Abramovitz, 1996; Roche, 1975). The salinity of the alkaline (pH 9.8) Mono Lake (90 g l⁻¹), situated in an arid basin in eastern California, has increased nearly twofold over the past 50–60 years as a consequence of watershed runoff diversions to the city of Los Angeles (Blum et al., 1998). Draining saline agricultural return flow from the Imperial Valley in southern California during the twentieth century into the lake of the Salton Sea resulted in salt accumulation and the creation of a salt lake with a salinity that rose from almost zero to 46 g l⁻¹ in 2005 (Figure 10; Amrhein et al., 2001; Cohen, 2009; Cohen



Figure 9 Time series of the salinity variations $(mg l^{-1})$ of the Aral Sea since 1960. Note that the desiccation of the lake generated in the late 1980s two separated lakes, the Eastern and Western basins. Data integrated from Linnikov and Podbereznyi (1996), Micklin (2010), and Zavialov et al. (2009).



Figure 10 Historical salinization of the Salton Sea (California, USA) during the twentieth century. Data integrated from Amrhein et al. (2001), Cohen (2009), Cohen and Hyun (2006), Schroeder and Rivera (1993), and Schroeder et al. (1991).

and Hyun, 2006; Hely et al., 1966; Schroeder and Rivera, 1993; Schroeder et al., 1991, 2002; Wardlaw and Valentine, 2005).

The desiccation of the Dead Sea due to a significant reduction of freshwater discharge from the Jordan River (Farber et al., 2004; Holtzman et al., 2005; Shavit et al., 2002) and other tributaries, combined with potash salt production by Israel and Jordan, has resulted in a dramatic reduction of the water level (Figure 11), at a rate of about 1 m per year (Oren et al., 2010; Salameh and Wl-Naser, 1999; Yechieli et al., 1998). Since the early 1980s, the Dead Sea desiccation has been associated with increasing rates of formation of sinkholes along the lakeshores that have resulted in increasing damage to infrastructure (Closson and Abou Karaki, 2009; Closson et al., 2010; Ezersky et al., 2009; Shalev et al., 2006; Yechieli et al., 2006). A detailed



Figure 11 Historical variations of the Dead Sea (Israel) water level since 1975. Note the continued drop in lake level at a rate of about a meter per year. Data were kindly provided by Dr Irena Pankratov, Israel Water Authority.

investigation revealed that more than a thousand sinkholes have developed along the western coast of the Dead Sea since the early 1980s, with the rate of formation accelerating (up to 150-200 sinkholes per year) with time. The sinkholes occur along a narrow strip 60 km long and <1 km wide and spread parallel to the general direction of the fault system associated with the Dead Sea Transform (Shalev et al., 2006; Yechieli et al., 2006). The desiccation of the Dead Sea caused the retreat of the saline water-freshwater-groundwater interface and the advance of freshwater into salt deposits along the Dead Sea shore, leading to salt dissolution and formation of the sinkholes. Data from groundwater associated with sinkholes show Na/Cl ratios (0.5-0.6) that are higher than that of typical Dead Sea brine (0.25), which confirm that halite dissolution is the major factor in generating sinkholes (Yechieli et al., 2006).

In general, the salinity and water chemistry of a lake is determined by (1) the imbalance between evaporation and water inflows, typically due to the diversion of freshwater discharge, climate change, and a reduction in precipitation that could induce water deficit and rise in salinity (Tweed et al., 2009); (2) the salinity and chemical composition of the inflow waters; and (3) precipitation of minerals within the lake once the concentrations of dissolved salts reach the saturation levels of these minerals (see Chapter 7.12). The effect of inflow water is demonstrated by the low (marine ratio of $<1.5 \times 10^{-3}$) Br/Cl ratios of the Salton Sea, which preserve the composition of the drainage and agriculture inflows from the Imperial Valley, originated from the Colorado River with low Br/Cl ratios (Figure 12).

Lake salinization can also occur by subsurface discharge of saline groundwater. The balance between the freshwater (typically surface water) and the saline subsurface inflows will determine the salinity of the lake. The Sea of Galilee (Lake Kinneret) in Israel is an example of subsurface discharge of saline



Figure 12 Bromide versus chloride concentrations (in mmol I^{-1}) of agricultural drainage waters in Imperial Valley (open circles) and Salton Sea (closed circles) in southern California, USA. Note the identical Br/Cl ratios measured in both the agricultural drainage waters and the saline lake, implying that the lake originated from the agricultural drainage inflows. The Br/Cl ratios are lower than the marine ratio, indicating that salinity originated from dissolution of halite mineral. Data were integrated from Amrhein et al. (2001), Schroeder et al. (1991), and Schroeder and Rivera (1993).

groundwater to a freshwater lake. The chemical composition of the lake mimics the chemical composition of the saline groundwater, as shown by the relatively high Br/Cl ratio (Bergelson et al., 1999; Kolodny et al., 1999; Nishri et al., 1999) and ²²⁶Ra activity (Raanan et al., 2009) of the Sea of Galilee. Variations of the lake levels and salinity during the last 60 years (Figure 13) reflect the balance between the surface freshwater inflows, groundwater discharge, evaporation, pumping to Israel National Water Carrier, and diversion of the surface saline inflows from the lake (Kolodny et al., 1999; Nishri et al., 1999). The large fluctuations and low lake levels during the last decade reflect the reduction of precipitation and consecutive drought that have affected this and other water resources in the Middle East during this time (Sowers et al., 2011).

During the early stages of lake salinization, the chemical composition of the saline lake water mimics the composition of the freshwater inflow. This was demonstrated in the case of the Aral Sea (Table 1) where the chemical composition of the brackish lake water during its early stages of salinization (salinity of 14 g l^{-1} in 1971) was identical to that of evaporated lake water during 1991 (salinity of 56 g l^{-1} ; Figure 14) (Linnikov and Podbereznyi, 1996). Yet, as the Aral Sea continued to desiccate and the salinity continued to increase (Figure 9), the calcium and bicarbonate contents of the brines sampled from the East (TDS = 121.6 g l^{-1}) and West (97.7 g l^{-1}) basins during 2005–2006 were lower (Figure 14, data from Linnikov and Podbereznyi, 1996; Zavialov et al., 2009), indicating secondary precipitation of carbonate and perhaps gypsum in the shrinking lake. The Na/Cl ratio of the evolved saline lake was identical to the ratios measured during early stages of evolution (Figure 14), indicating that the lake



Figure 13 (a) Historical variations of the Sea of Galilee (Israel) water level since 1950. Note the sharp variations in the lake level particularly during the last 20 years. Data were kindly provided by Dr Irena Pankratov, Israel Water Authority; (b) Salinity variations of the Sea of Galilee (Israel) since 1950. Note the large variations in salinity that reflect (1) phase of a closed basin in which evaporation increased the lake salinity; (2) initiating pumping of the lake water to Israel National Water Carrier and diversion of the surface saline springs that flow to the lake; and (3) major drought episodes associated with a significant drop in the lake level. Data were kindly provided by Dr Irena Pankratov, Israel Water Authority.

water did not reach the halite saturation stage. Likewise, the rise of salinity of the Salton Sea (Figure 10) resulted in calcite and gypsum precipitation in the lake bottom sediments and temporal variations in the concentrations of Ca^{2+} , HCO_3^{-} , and SO_4^{2-} relative to Cl^- , in water from the Salton Sea (Schroeder et al., 2002). Similarly, brines from Australian ephemeral salt lakes have high Br/Cl ratios due to precipitation of halite crust, while brines from ephemeral salt lakes that lack halite crusts have Br/Cl ratios identical to inflow surface water and groundwater (Cartwright et al., 2009).

Saturation of the saline water and precipitation of minerals (Hardie and Eugster, 1970) have two important negative

feedbacks that limit salt accumulation in salt lakes. In this respect, the saturation level of calcite, gypsum, and halite in brines will determine the salinity and composition of the residual brines. In the Salton Sea, the lake water had a total salinity of 46 g l^{-1} , and was oversaturated with respect to calcite, which controls the Ca²⁺ and HCO₃⁻ levels of the lake. Combined biologic activity, sulfate reduction processes, and baseexchange reactions (Na⁺ removal) added additional dissolved Ca^{2+} , which enhanced calcite precipitation (Amrhein et al., 2001). At higher salinity levels, such as the Dead Sea (Table 1; Katz and Starinsky, 2009) with a salinity of 340 g l^{-1} , the low water activity and thus the low vapor pressure of the hypersaline brines impose low evaporation rates. Yechieli et al. (1998) predicted that despite a significant reduction in freshwater inflows to the Dead Sea, the Dead Sea will not totally desiccate but will reach a new equilibrium given the low water activity. The geometry of the lake basin and the size of the surface area are also important factors that control the amount of evaporation water (Yechieli et al., 1998). In sum, while the rate of salinization is rapid during the early stages of salinization, it decreases at later stages due to salt precipitation and low water activity of the brines. While the absolute salinity continues to increase, the rate of salinization is expected to decrease.

Global warming and reduction of precipitation in semiarid and arid climatic zones are expected to intensify the salinization of many salt lakes. In the Salton Sea in California, it has been predicted that salinity will rise from $46 \text{ g} \text{ l}^{-1}$ (Figure 10) to about 300 g l^{-1} by the end of the twenty-first century, with a rapid increase to about 200 g l^{-1} within the next 20–30 years (Cohen, 2009; Cohen and Hyun, 2006). The Australian salt lakes demonstrate perhaps the best example of further salinization of salt lakes due to climatic change. The salt lakes in Australia (Timms, 2005) were formed by long-term deposition of meteoric salts with seawater-like composition (Chivas et al., 1991; Vengosh et al., 1991a). Yet, a study of the Corangamite area in southeast Australia has revealed that a severe multiyear drought (11 years of below-average rainfall between 1997 and 2008) resulted in a 60% reduction in lake areas, an 80% decrease in volume, and a significant rise in salinity; conductivity rose from less than 50 mS cm^{-1} prior to 1997 to 200 mS cm^{-1} in 2006 in Lake Corangamite (Tweed et al., 2009). It is predicted that by 2025 most natural salt lakes will show adverse changes; many permanent salt lakes will decrease in size and increase in salinity, and many nonnatural saline lakes will be formed. In certain regions, such as in southern Australia, many seasonally filled salt lakes are likely to become drier for longer periods (Williams, 2002). Restoration plans for handling the ongoing salinity crisis of salt lakes such as the Salton Sea (Cohen, 2009; Cohen and Hyun, 2006) and the Aral Sea (Micklin, 2010) will have to deal with the challenges of further aridification that are associated with global warming and the inevitable intensification of salt lake salinization.

11.9.4 Groundwater Salinization

11.9.4.1 Seawater Intrusion and Saltwater Displacement in Coastal Aquifers

Saltwater intrusion is one of the most widespread and important processes that degrade water quality to levels exceeding



Figure 14 Concentrations of sodium, calcium, sulfate, and bicarbonate versus chloride contents $(mmol l^{-1})$ of the Aral Sea during different stages of lake desiccation and salinization, marked by the year of sampling. Note that the rise in salinity that was recorded in the lake since 1970 (see **Figure 9**) was associated with an apparent conservative increase of sodium and sulfate, while calcium and bicarbonate contents in the lately evolved lake were depleted relative to the expected conservative evaporation represented by chloride contents. These depletions suggest precipitation of secondary minerals such as calcium carbonate. Data were integrated from Linnikov and Podbereznyi (1996) and Zavialov et al. (2009).

acceptable drinking and irrigation water standards, and endanger future water exploitation in coastal aquifers. This problem is intensified due to population growth, and the fact that about 70% of the world's population occupies the coastal plain zones (Jones et al., 1999; Meybeck, 2003). Human activities (e.g., urbanization, agricultural development, tourism) in coastal areas increase the rate of groundwater salinization (Jones et al., 1999). In the United Sates, saltwater intrusion into coastal aquifers has been identified in the eastern Atlantic (Andreasen and Fleck, 1997; Lin et al., 2009; Meisler et al., 1985; Stringfield and LeGrand, 1969; Wicks and Herman, 1996; Wicks et al., 1995), and the southern (Langman and Ellis, 2010) and western Pacific (Izbicki, 1991, 1996; Todd, 1989; Vengosh et al., 2002) coasts. In Europe, seawater intrusion has been documented within many of the coastal aquifers, particularly along the Mediterranean Sea and its eastern part in the archipelagos in the Aegean Sea (Alcalá and Custodio, 2008; Custodio, 2010; de Montety et al., 2008). Along the eastern Mediterranean, seawater intrusion has been reported to significantly intrude the coastal aquifer of Israel (Russak and Sivan, 2010; Sivan et al., 2005; Vengosh et al., 2005; Yechieli and Sivan, 2011; Yechieli et al., 2009).

Seawater intrusion may occur in areas of high precipitation, such as the Jeju volcanic island in South Korea, where the annual average rainfall is about 1870 mm and the estimated groundwater recharge is 1.4×10^9 m³ year⁻¹. Although the groundwater withdrawal in the volcanic island is only 5% of the estimated replenishment, Br/Cl and δ^{18} O data indicate that

seawater has intruded 2.5 km inland due to the high conductivity and heterogeneity of the basaltic aquifers (Kim et al., 2003; Koh et al., 2009; Park et al., 2005). The Jeju island salinization case demonstrates that the predicted rise of sea level could lead to seawater intrusion in similar volcanic islands in the Pacific and further salinization of their groundwater.

In many coastal aquifers around the world, modern seawater intrusion typically occurs due to extensive freshwater withdrawals. Average ocean water has a TDS of $35 \text{ g} \text{ l}^{-1}$ while internal seas may have higher (e.g., Mediterranean Sea, Red Sea; TDS \sim 40 g l⁻¹) or lower salinities. Nevertheless, seawater has a uniform chemistry due to the long residence time of its major constituents, with the following features: predominance of Cl⁻ and Na⁺ with a molar ratio of 0.86, an excess of Cl⁻ over the alkali ions (Na+K), and Mg²⁺ greatly in excess over Ca^{2+} (Mg/Ca=4.5-5.2; Table 1). Seawater also has uniform Br/Cl (1.5×10^{-3}) , $\delta^{18}O_{H_2O}$ (0–1‰), $\delta^{34}S_{SO_4}$ (21‰), $\delta^{11}B$ (39‰), and ⁸⁷Sr/⁸⁶Sr (0.7092) values. In contrast, fresh groundwaters are characterized by highly variable chemical compositions, although the typical fresh groundwater is dominated by Ca-Mg-HCO₃ ions. In most cases, Ca²⁺ predominates over Mg^{2+} content. The variations of conservative constituents in a mixed groundwater (Cl⁻, $\delta^{18}O_{H_2O}$, $\delta^2H_{H_2O}$ Br/Cl) reflect the relative mixing proportions of fresh groundwater and seawater. For stable oxygen and hydrogen isotopes, the slope of a mixing curve between seawater ($\delta^{18}O_{H_2O} \sim \delta^2 H_{H_2O} \sim 0\%$) and freshwater in the coordination of $\delta^2 H_{H_2O}$ versus $\delta^{18}O_{H_2O}$ will always be lower than the Meteoric Water Line (i.e., <8) (Gat, 1974).

Yet, the most striking phenomenon that characterizes seawater intrusion into coastal aquifers is the difference between the chemical composition of the saline water associated with saltwater intrusion and the theoretical mixture between seawater and groundwater (Jones et al., 1999). In many cases, the saline water has a Ca–chloride composition (i.e., the ratio of Ca/(SO₄+HCO₃) > 1) with low ratios of Na⁺, SO₄^{2–}, K⁺, and boron to chloride relative to modern ocean water (Table 1).

This geochemical modification during seawater intrusion has been attributed to base-exchange reactions with the aquifer rocks (Appelo, 1994; Appelo and Geirnart, 1991; Appelo and Postma, 2005; Appelo and Willemsen, 1987; Jones et al., 1999; Sayles and Mangelsdorf, 1977). Typically cation exchangers in aquifers are clay minerals, organic matter, oxyhydroxides, and fine-grained rock materials, which have mostly Ca²⁺ adsorbed on their surfaces due to the predominance of Ca²⁺ in freshwater. When seawater intrudes into a coastal aquifer saturated with Ca-rich groundwater, Na⁺ replaces part of the Ca²⁺ on the solid surface. As a result, Na⁺ is retained by the solid phase while Ca^{2+} is released to the water. Consequently, the solute composition changes from an Mg-chloride into a Ca-chloride, the Na/Cl ratio decreases, and the (Ca + Mg)/Cl ratio increases (Appelo, 1994; Appelo and Geirnart, 1991; Appelo and Postma, 2005; Appelo and Willemsen, 1987; Custodio, 1987a, 1997; Jones et al., 1999). Under such conditions, the relative enrichments in calcium and magnesium as normalized to chloride concentrations should be balanced by the relative depletion of sodium (i.e., $\Delta Ca + Mg = -\Delta Na$; where Δ is the difference between a conservative mixing value and actual concentration in salinized groundwater; Vengosh et al., 2002). Together with Ca²⁺, exchangeable Sr²⁺ is released



Figure 15 ⁸⁷Sr/⁸⁶Sr ratio versus calcium content of saline groundwater associated with seawater intrusion into the coastal aquifer of Salinas Valley, California, USA. The increase of ⁸⁷Sr/⁸⁶Sr with calcium concentration suggests that base-exchange reactions occur at an early stage of seawater intrusion and that strontium in exchange sites that is mobilized to the salinized water has a high ⁸⁷Sr/⁸⁶Sr ratio. Data from Vengosh et al. (2002).

to the dissolved phase (Johnson and DePaolo, 1994). The 87 Sr/ 86 Sr ratio of adsorbed strontium can therefore affect the Sr isotopic composition of the saline groundwater. In the Salinas Valley of central California, the 87 Sr/ 86 Sr ratio of salinized coastal groundwater increases with Ca²⁺ content (Figure 15), indicating the contribution of a high 87 Sr/ 86 Sr ratio source from the clays. Due to the accumulation of 87 Rb in potassium-rich clay minerals, it has been proposed that base-exchange reactions are associated with radiogenic 87 Sr/ 86 Sr input to saline water (Vengosh et al., 2002), while in dolomitization processes, Sr from old marine carbonate is characterized by a lower 87 Sr/ 86 Sr composition (e.g., the Dead Sea brines; Stein et al., 1997).

In addition to base-exchange reactions, boron and potassium are typically adsorbed during seawater intrusion (Jones et al., 1999). The adsorption of boron is accompanied by an isotopic fractionation in which the light isotope, ¹⁰B, is preferentially retained into the adsorbed phase, resulting in an enrichment of ¹¹B in the residual salinized groundwater. Consequently, saline groundwater associated with seawater intrusion is characterized by low B/Cl ratios ($< 8 \times 10^{-4}$) and high δ^{11} B values (>39‰) relative to those of seawater (Figure 16; Vengosh, 1998; Vengosh et al., 1994, 1999a,b). The intrusion of seawater into coastal aquifers is also associated with redox conditions along the saltwater-freshwater interface. Consequently, fractionation of sulfur isotopes during sulfate reduction processes results in high $\delta^{34}S_{SO_4}$ values in the residual sulfate, and thus saline groundwater associated with seawater intrusion is characterized by low SO₄/Cl ratios (<0.05) and high δ^{34} S_{SO₄} values (>20%; Krouse and Mayer, 2000).

Climate change and fluctuations of sea levels during the Quaternary resulted in numerous cycles of seawater



Figure 16 δ^{11} B values versus boron to chloride ratios (molar unit) in saline groundwater from the Mediterranean coastal aquifer associated with saltwater intrusion (Vengosh et al., 1994) and the North Carolina coastal aquifer associated with refreshing processes and reverse base-exchange reactions (Vinson et al., 2011). The comparison shows that seawater intrusion is associated with boron retention and ¹¹B enrichment while seawater displacement mobilizes boron from the aquifer rocks with lower δ^{11} B values.

encroachment but also fresh groundwater flow cycles into coastal aquifer saturated with saline groundwater and seaward displacement of intruded seawater. Fresh groundwater flow and displacement of saline groundwater (freshening) cause an opposite, defined as 'reverse,' base-exchange reaction. Ca^{2+} and Mg^{2+} , which are abundant in fresh groundwater, replace Na⁺ on the exchange sites of clay minerals with concomitant release of Na⁺ to the water. The flushing of the saline groundwater therefore generates Na-HCO3-type saline groundwater with Na/Cl ratio>1 and low concentrations of Ca²⁺ and Mg²⁺ (Appelo, 1994; Appelo and Geirnart, 1991; Appelo and Postma 2005; Appelo and Willemsen, 1987; Chapelle and Knobel, 1983; Jones et al., 1999). The conspicuous difference in the chemical composition between saline groundwater originating from seawater intrusion and seawater displacement is critical in evaluating the sources and mechanisms of groundwater salinization in coastal aquifers (Russak and Sivan, 2010; Yechieli et al., 2009). The variations of Ca²⁺, Sr²⁺, Mg²⁺, and K⁺ and ratios to chloride can be used to distinguish saline water originating from freshening processes (Russak and Sivan, 2010).

Another mechanism for the formation of Na–HCO₃ saline groundwater in coastal aquifers is oxidation of organic carbon that generates dissolved inorganic carbon (DIC), coupled with base-exchange reactions. Much study has been conducted in the Black Creek aquifer of South Carolina where the DIC concentration in groundwater near the Atlantic coast was 10 fold higher than that in groundwater from recharge areas (Chapelle and Knobel, 1983; Chapelle and McMahon, 1991; Knobel et al., 1998; McMahon and Chapelle, 1991). Thus, the bicarbonate content in the saline groundwater cannot be attributed only to fresh groundwater contribution but rather additional DIC must be generated within confined aquifers in order to account for the high HCO_3 concentrations in the saline groundwater. Generation of CO_2 from microbial respiration could produce carbonate mineral dissolution and thus Ca^{2+} mobilization, which would be exchanged by Na⁺, resulting in the observed Na-HCO₃ composition (Vinson, 2011).

Saline Na-HCO3 water is often associated with high boron contents and B/Cl ratios (i.e., greater than seawater) as demonstrated in southern Mediterranean coastal aquifers (Vengosh et al., 2005), the Saloum delta aquifer of Senegal (Faye et al., 2005), sandstone and shale aquifers in Michigan (Ravenscroft and McArthur, 2004), the delta aquifer of the Bengal Basin in southern Bangladesh (Halim et al., 2010; Ravenscroft and McArthur, 2004), and the coastal aquifer of North Carolina (Vinson et al., 2011). The relative enrichment of boron relative to the expected conservative mixing between seawater and freshwater suggests that boron is mobilized from the adsorption sites. One possible explanation for the relative boron enrichment is that the equilibrium between adsorbed and dissolved boron is reequilibrated during freshening processes resulting in desorption of boron. The strong correlation between Na/Cl and B/Cl ratios that characterize many of the saline Na-HCO3-type groundwaters suggests that the arrival of low-saline, calcium-rich, and boron-poor water to the saline-saturated aquifer triggers the reverse-base-exchange reactions and boron mobilization to the water.

Since boron adsorption is associated with isotopic fractionation in which ${}^{10}B(OH)_4^-$ is retained onto adsorbed sites in clay minerals, the $\delta^{11}B$ value of adsorbed boron is typically lower than that of seawater. Spivack et al. (1987) showed that desorbed boron from marine sediments has a $\delta^{11}B$ value of about +15%. During desorption of boron, all of the boron is mobilized without any isotopic discrimination (Spivack et al., 1987). Therefore, the $\delta^{11}B$ of a solution that originated from boron desorption is expected to be lower than that of seawater. This is demonstrated in Na–HCO₃ saline groundwater in the coastal aquifer of North Carolina that has both high B/Cl ratios and low $\delta^{11}B$ values relative to seawater (Vinson et al., 2011; Figure 16).

The ability to distinguish direct seawater intrusion from mixing of saline groundwater originating from displacement of seawater and freshening could be important for predicting salinization processes. Direct seawater intrusion would result in accelerated salinization rates, while mixing with saline groundwater that originated from diluted seawater could induce much lower salinization rates. This was demonstrated in the coastal aquifer of North Carolina (Figure 16) where the chemical and boron isotopic compositions of the saline groundwater indicate that it originated from diluted, apparently fossil seawater, which was consistent with a slow (2.5-fold in 20 years) rate of salinization (Vinson et al., 2011). Likewise, some areas of the Saloum delta aquifer of Senegal show evidence of seawater intrusion (low Na/Cl and B/Cl ratios) while others show evidence of freshening (high Na/Cl and B/Cl ratios; Faye et al., 2005).

Intrusion of modern seawater is not the only salinization process occurring in coastal aquifers, as salinization can also result from mixing with fossil seawater. Fossil seawater represents past invasions of seawater into coastal aquifers accompanying rises in sea levels. Direct measurements and estimated residence times of seawater in coastal aquifers have been reported by using ¹⁴C and tritium age-dating techniques in Germany (Hahn, 1991), India (Sukhija, 1996), coastal aquifers along the Gulf of Guinea in Togo (Akouvi et al., 2008), Japan (Yamanaka and Kumagai, 2006), the coastal plain of Suriname (Groen et al., 2000), and the Mediterranean coastal aquifer of Israel (Sivan et al., 2005; Yechieli and Sivan, 2011; Yechieli et al., 2000, 2009). It was shown, for example, that modern seawater intruded the upper and unconfined subaquifers of the coastal aquifer in Israel, whereas saline groundwater that occupies the underlying and confined subaquifers has an apparent age range of 10000–15000 years (Yechieli and Sivan, 2011).

11.9.4.2 Mixing with External Saline Waters in Noncoastal Areas

Many studies of regional aquifer systems have shown a general sequence of major ion evolution from low-saline Ca-Mg-HCO₃ water type to saline Na-SO₄-Cl groundwater along a hydraulic gradient (Hendry and Schwartz, 1988; Herczeg and Edmunds, 2000; Herczeg et al., 1991, 2001; Mazor, 1997). In addition to the increasing salinity, the ratio of Na⁺ and Cl⁻ ions relative to the other dissolved salts (i.e., Na+Cl/TDS) increases with flow, as demonstrated in the saline groundwater from the Murray aquifer in South Australia (Herczeg et al., 2001) and the Cretaceous sandstone aquifer of the Milk River Formation, Alberta, western Canada (Hendry and Schwartz, 1988; Herczeg and Edmunds, 2000). The gradual increase of salinity and the chemical modification toward predominance of chloride and sodium ions is a result of several possible processes: (1) advection and diffusion of saline fluids entrapped in impermeable zones in the aquifer and/or outside the aquifer that are connected to an active permeable zone in the aquifer; and (2) dissolution of soluble salts such as gypsum and halite minerals within the aquifer. For example, several models have been postulated to explain the increase of salinity along flow paths in the Cretaceous sandstone aquifer of Milk River Formation. Hendry and Schwartz (1988) hypothesized that the salinity increase is due to diffusion of solute from the underlying aquitard. The entrapment of saline fluids in geological units of low hydraulic conductivity that are connected to active aquifers may result in diffusion of solutes and a gradual increase in the salinity of the aquifer (Herczeg and Edmunds, 2000).

Likewise, salinization of many aquifers is induced by flow of saline groundwater from adjacent or underlying aquifers (e.g., Bouchaou et al., 2009; Hsissou et al., 1999; Kloppmann et al., 2001; Magaritz et al., 1984; Maslia and Prowell, 1990; Sánchez-Martos and Pulido-Bosch, 1999; Sánchez-Martos et al., 2002; Vengosh and Benzvi, 1994; Vengosh et al., 1999a,b, 2002, 2005). For example, in the Upper Floridian aquifer in Georgia, USA, faults breach the nearly impermeable units of the underlying confined aquifer and allow upward leaking of saline groundwater (Maslia and Prowell, 1990). Similarly, extensive saline plumes in the Ogallala aquifer in the Southern High Plains, Texas, USA, are attributed to crossformational flow from underlying evaporite units (Mehta et al., 2000a,b). The aquifer permeability will determine the flow paths of the underlying, typically pressurized, saline groundwater. This was demonstrated in deep reclaimed lake areas (polders) in the western Netherlands where saline groundwater from an underlying aquifer flows through paleochannel areas in the aquifer (de Louw et al., 2010). In the shallow (up to 150 m) Devonian formations of the Michigan Basin of southwestern Ontario, saline groundwater with geochemical characteristics similar to deep brines (e.g., high $\delta^2 H_{H_2O'}$ $\delta^{18}O_{H_2O'}$ Br/Cl and low N/Cl and SO₄/Cl ratios) indicate that the high-salinity fluids migrated into discrete areas of the Devonian and Pleistocene formations. The crossformational fluid flow from depth probably occurred along discrete fractures that were formed during or following deglaciation (Weaver et al., 1995). Finally, evidence for the migration of the Middle Devonian Marcellus brines to shallow aquifers in the Appalachian basin (northeastern Pennsylvania) was shown by saline groundwater with distinctive Br/Cl, ⁸⁷Sr/⁸⁶Sr, and Ba/Sr fingerprints (Warner et al. 2012).

Saline plumes formed by uprising of saline groundwater are also a major source of salinity in the Mediterranean coastal aquifer of Israel (Table 1; Figure 17) (Vengosh et al., 1994, 1999b). Likewise, groundwater in the Gaza Strip is salinized by lateral flow of saline groundwater from the eastern part of the aquifer. The flow rate and thus the rate of salinization have been accelerated due to overexploitation and reduction of groundwater levels within the Gaza Strip to levels exceeding drinking water standards (Vengosh et al., 2005). This salinization phenomenon is one of the fundamental water-quality problems in the Gaza Strip where the salinity level of groundwater exceeds international drinking water standards. Diversion of the external saline flow via pumping and desalinization has been proposed to mitigate the highly salinized aquifer that is the only source of drinking and irrigation water for the rapidly growing population in the Gaza Strip (Weinthal et al., 2005).

Several models have been suggested to explain the origin of saline groundwater in nonmarine settings. These include brines originated from residual evaporated seawater entrapped as formation water, saline water originated from seawater freezing, and saline water generated by evaporite dissolution. Residual evaporated seawaters that were modified by waterrock interactions such as dolomitization are typically characterized by a Ca-chloride composition $(Ca/(SO_4 + HCO_3) > 1)$ with an Na/Cl ratio below seawater ratio value (Figure 18), Br/Cl \geq seawater ratio (1.5 \times 10⁻³), relative depletion of sulfate (SO₄/Cl < 0.05), δ^{34} S_{SO₄} \geq 20‰, and δ^{11} B \geq 39‰ (Carpenter et al., 1974; McCaffrey et al., 1987; Raab and Spiro, 1991; Starinsky, 1974; Stein et al., 1997; Vengosh et al., 1992; Wilson and Long, 1993). Upon hydrological contact and mixing of brines with fresh groundwater, the chemical composition of the hypersaline brine dominates the composition of the mixture owing to the extreme difference in salinity between the brines and the freshwater. Consequently, dilution or flushing of entrapped brines by low-saline groundwater has only a minor effect on the chemical and isotopic compositions of saline groundwater derived from brine intrusion.

In the Dead Sea Rift Valley, deep pressurized brines that are the residue of evaporated seawater (greater than 10-fold evaporation; Starinsky, 1974) are in hydrological contact with overlying fresh groundwater (Farber et al., 2007; Marie and Vengosh, 2001). Once the natural hydrological balance is disturbed due to exploitation of the overlying fresh groundwater,



Figure 17 Chloride (in mg l^{-1}) distribution in groundwater from the central and southern part of the Mediterranean coastal aquifer of Israel. Note the saline plumes in the central and eastern parts of the aquifer.

the salinization process starts or accelerates. In the Jericho area in the southern Jordan Valley, rapid rates of salinization due to the upconing of underlying brines are found in wells located near the major Rift faults (Farber et al., 2004, 2005, 2007; Marie and Vengosh, 2001). Due to the high salinity of the apparent original brines (>100 g l⁻¹), mixture with only a small fraction of brine leads to devastating salinization phenomena in overlying freshwater resources.

An additional source of salinity in polar areas is residual brines derived from the freezing of seawater (Bottomley et al., 1999; Herut et al., 1990; Marion et al., 1999; Nelson and Thompson, 1954; Richardson, 1976; Stotler et al., 2009; Wang et al., 2000). Bein and Arad (1992) suggested that deep saline groundwater from Sweden and Finland, which is characterized by low Na/Cl and high Br/Cl ratios, is the remnant of frozen seawater formed during the last glaciations, followed by dilution with meteoric water (Bein and Arad, 1992).

Dissolution of evaporite minerals in sedimentary basins is also a common feature of salinization. This type of salinization process has been reported for groundwater in the Ogallala Formation in the Southern High Plains, Texas, USA (Mehta et al.,

2000a,b), the Dammam aquifer in Kuwait (Al-Ruwaih, 1995), the Nubian Sandstone aquifer in the Sinai and Negev deserts (Rosenthal et al., 1998; Vengosh et al., 2007), the Great Artesian Basin in Australia (Herczeg et al., 1991; Love et al., 2000), and the Hammamet-Nabeul shallow aquifer in northeastern Tunisia (Moussa et al., 2011). In the case of halite dissolution, the saline water is dominated by Na⁺ and Cl⁻ ions, Na/Cl ratio \sim 1, and Br/Cl < seawater ratio (e.g., the Ogallala Formation; Table 1; Mehta et al., 2000a,b). Salinization can also be derived from dissolution of marine Ca-sulfate (e.g., gypsum) as evidenced in Pinawa, Canada (Nesbitt and Cramer, 1993), the Salinas Valley in California (Vengosh et al., 2002), and the Nubian Sandstone aguifer in the Negev, Israel (Vengosh et al., 2007). Typically, gypsum dissolution would produce saline water with Ca/SO₄ ratio~1. However, the dissolution of gypsum can also be associated with Ca²⁺ uptake onto the exchange substrate, displacing Na⁺ to the solution. The residual water would be enriched in Na-SO₄ (Nesbitt and Cramer, 1993). Dissolution of gypsum would affect the sulfur isotopic composition of the salinized water. The $\delta^{34}S_{SO_4}$ values of marine sulfate varied over geological time, with a maximum



Figure 18 Variation of Na/Cl, Br/Cl, A/Cl, and δ^{11} B values during evaporation of seawater. Degree of evaporation is defined as the ratio of Br⁻ content in the solution at different stages of evaporation to the initial Br⁻ concentration in seawater. Data were integrated from McCaffrey et al. (1987), Raab and Spiro (1991), and Vengosh et al. (1992).

near +35‰ in the Cambrian and less than +10‰ in the Permian. In contrast, oxidation of sedimentary sulfides, which are significantly depleted in ³⁴S relative to oceanic sulfate, will result in low $\delta^{34}S_{SO_4}$ values with typical ranges of -30% to +5% (Krouse and Mayer, 2000). Likewise, the ⁸⁷Sr/⁸⁶Sr ratio of marine sulfate minerals will mimic the Sr isotopic composition of co-genetic seawater, and thus salinization resulting from gypsum dissolution will carry the isotopic imprint of the 87Sr/86Sr of ocean water at the time of the mineral deposition. This was demonstrated in the Nubian Sandstone aquifer of the Negev, Israel, where sulfaterich groundwater flows from the underlying Jurassic aquifer to the overlying Nubian Sandstone aquifer. The chemical and isotopic compositions of the Jurassic groundwater $(\delta^{34}S_{SO_4} \sim +14\%; {}^{87}Sr/{}^{86}Sr \sim 0.70764)$ was interpreted as reflecting dissolution of Late Triassic marine gypsum deposits as these isotopic signatures are consistent with the $\delta^{34}S_{SO}$ and ⁸⁷Sr/⁸⁶Sr values of the Jurassic seawater (Vengosh et al., 2007). Finally, the Sr isotope compositions of sulfate-rich saline waters from the High Atlas (Warner et al., 2010) and Anti-Atlas (Ettayfi et al., 2012) mountains in Morocco are consistent with the Lower Cretaceous and Early Cambrian secular seawater Sr isotope ratios, respectively, reflecting interaction of groundwater with carbonate and sulfate aquifer rocks.

11.9.4.3 Salinization of Shallow Groundwater in River Basins

In many river basins in arid and semiarid zones, groundwater substitutes for surface water as the major water resource for domestic and agricultural applications. In arid regions, such as the Jordan Valley (Farber et al., 2007), the Lower Mesopotamian Plain of the Euphrates River, Iraq (Barica, 1972), the Hueco Bolson Basin of Texas and Chihuahua of the US-Mexico border (Eastoe et al., 2008, 2010), the alluvial aquifer system in arid Alice Springs in central Australia (Vanderzalm et al., 2011), the arid region of Namibia (Shanyengana et al., 2004), and the sub-Saharan Draa and Ziz basins in southern Morocco (Warner et al., 2010), the local populations are entirely dependent on agriculture and are concentrated near the river channels and/or associated oases. One of the factors affecting agricultural productivity is the salinity of the irrigation water; salinity is thus a key limiting factor in sustainable agricultural development and the overall livelihood of the local populations in these regions.

In some of the arid basins, surface water is imported from areas of higher precipitation and is stored in dammed reservoirs before being discharged for downstream irrigation. As discussed earlier in the chapter, salinization of surface water resulting from evaporation (either in the reservoirs or during irrigation), leads to saline agriculture return flows that are recharged into local aquifers. In addition, salinization of the shallow groundwater may result from dissolution of salts in the unsaturated zone and/or by lateral flow of adjacent saline groundwater, particularly due to reverse hydrological gradients in the inner parts of the alluvial aquifers evolved from differential pumping in the basin valley (Figure 19). In an attempt to delineate the sources and mechanisms of groundwater salinization in a managed arid watershed, one can define three types of geochemical tracers (R_1, R_2, R_3) that are capable of delineating the three principal saline sources (Figure 20):

- (1) R₁ type Tracers are used to identify *evaporation* (process 1 in **Figure 20**) and *mixing* with external groundwater (process 3), but do not identify salt dissolution. These tracers include water isotopes (δ^{18} O, δ^{2} H) and ion concentrations.
- (2) R₂ type Tracers are used to identify *dissolution of salts* (process 2 in Figure 20) and *mixing* with external groundwater (process 3), but not evaporation (process 1). These tracers include several ion ratios, particularly the ratios of conservative elements such as Br/Cl and B/Cl.
- (3) R₃ type Tracers that are sensitive to *mixing* with external groundwater (process 3), but not to evaporation and salt



Figure 19 Schematic illustration of possible salinization mechanisms of surface water and shallow groundwater in alluvial aquifers where imported water is stored in dammed reservoirs and used for irrigation. The possible salinization includes (1) inflow of fresh and saline water to dammed reservoir; (2) evaporation from the reservoir; (3) evaporation during irrigation of the imported water; (4) dissolution of salts from the unsaturated zone during irrigation; (5) lateral flow of low-saline water to the alluvial aquifers; and (6) lateral flow of saline water to the alluvial aquifers.

dissolution (processes 1 and 2). These tracers include the isotopic compositions of dissolved constituents in the water such as strontium (87 Sr/ 86 Sr), sulfur (${\delta}^{34}$ S_{SO4}), and boron (${\delta}^{11}$ B) isotopes.

In the sub-Saharan Draa Basin of southern Morocco, winter snowmelt from the Atlas Mountains is captured in a reservoir, stored, and discharged downstream for irrigation in six oases. Shallow groundwater from the oases shows a large salinity range, with TDS up to 12 000 mg l⁻¹. The Br/Cl and B/Cl ratios of the shallow groundwater decrease with increasing salinity, which suggests that the major mechanism of salinization of the shallow groundwater in the Draa Basin is dissolution of salts stored in the unsaturated zone and salinization of the underlying shallow groundwater (Warner et al., 2010; 2013).

11.9.4.4 Salinization of Nonrenewable Groundwater

The impact of salinization is more conspicuous in an aquifer where the freshwater is not renewable (i.e., fossil; see Chapter 7.14). Numerous studies have shown that groundwater resources across the Sahara and the Sahel regions in northern Africa and in the arid zones of the Middle East are fossil and



Figure 20 Schematic illustration of possible variations of three types of geochemical tracers (R_1 , R_2 , R_3) that are capable of delineating the three principal saline mechanisms of shallow groundwater in alluvial aquifers; see text for detailed explanation.

reflect paleorecharge during periods of higher rainfall in the late Pleistocene (Cook and Herczeg, 2000; Edmunds and Droubi, 1998; Edmunds and Gaye, 1994; Edmunds et al., 1999, 2002; Gave and Edmunds, 1996; Phillips, 1994; Vengosh et al., 2007). Typically, fresh paleowaters overlie saline dense water bodies. With geological time, a fragile hydraulic equilibrium is generated between the two water bodies. Well construction and groundwater extraction can affect this delicate hydrological equilibrium. Exploitation of paleowaters, without modern replenishment, may lead to rapid salinization of groundwater resources. In the Middle East and northern Africa, salinization of fossil groundwater has had devastating effects since in some cases they are the only sources of potable water (Bouchaou et al., 2008, 2009; Salameh, 1996; Sowers et al., 2011; Vengosh and Rosenthal, 1994; Vengosh et al., 2007). In the Damman carbonate aquifer in Bahrain, for example, overexploitation has resulted in a drop of the piezometric surface by 4 m and an increase in the salinity by over 3 g l^{-1} , owing to a combination of leakage from a deeper aquifer, marine intrusion, sabkha water migration, and agricultural drainage. More than half of the area of the Damman aquifer has become saline as a result of overexploitation (Edmunds and Droubi, 1998). In southern Israel, the extraction of brackish paleowater from the Lower Cretaceous Nubian Sandstone aquifer in areas along the Rift Dead Sea Valley has resulted in mixing with Ca-chloride brine and the salinization of the associated groundwater (Yechieli et al., 1992). Another example is the Sakakah Aquifer in the northeastern part of Saudi Arabia where mixing relationships between fossil fresh and saline (TDS up to 3000 mg l^{-1}) groundwater have degraded water quality (Al-Bassam, 1998).

In the Souss-Massa Basin in southwest Morocco, stable isotopes, tritium, and ¹⁴C data for local groundwater indicate two types of groundwater: (1) fresh and young groundwater originating from recharge from the High Atlas Mountains, particularly in the eastern part of the basin; and (2) more saline and old (several thousands of years) groundwater in the western part of the basin, where most groundwater exploitation has taken place. The exploitation of fossil rather than the renewable groundwater in the aquifer has led to high salinization rates in the western part of the aquifer (Bouchaou et al., 2008).

11.9.5 Salinization of Dryland Environment

Salinity of water and soil in the dryland environment is a natural phenomenon resulting from a long-term accumulation of salts on the ground and lack of their adequate flushing in the unsaturated zone. Salt accumulation and formation of efflorescent crusts have been documented in the upper unsaturated zone (Cartwright et al., 2004, 2006, 2007b; Gee and Hillel, 1988; Jackson et al., 2009; Leaney et al., 2003; Nativ et al., 1997; Ng et al., 2009; Scanlon et al., 2009a,b; Stonestrom et al., 2009) and fracture surfaces (Kamai et al., 2009; Weisbrod et al., 2000) in many arid areas. The accumulation of soluble salts in soil occurs when evaporation exceeds precipitation and salts are not leached but remain in the upper soil layers in low-lying areas. Natural soil salinization, referred to as 'primary salinization,' occurs in arid and semiarid climatic zones. 'Secondary salinization' is the term used to describe soil salinized as a consequence of direct human activities (Dehaan and Taylor, 2002; Fitzpatrick et al., 2000; Shimojimaa et al., 1996). Excessive salinity in soil results in toxicity for crops, reduction in soil fertility, reduction of availability of water to plants by reducing the osmotic potential of the soil solution, and a significant change in the hydraulic properties of soil (Bresler et al., 1982; Frenkel et al., 1978; Hillel, 1980).

Most of the salts that have accumulated in the unsaturated zone in arid environments of the southwestern United States and in the Murray Basin, Australia, originated from long-term atmospheric deposition of chloride and sulfate salts (Scanlon et al., 2009a,b). The salt accumulation has been attributed to surface evaporation (Allison and Barnes, 1985; Allison et al., 1990), wetting and drying cycles (Chambers et al., 1996; Drever and Smith, 1978; Keren and Gast, 1981), soil capillarity, and capillarity transport of water and salts from bulk rock matrix toward the fracture surface (Weisbrod et al., 2000).

In the western United States, recharge typically occurs within surrounding highlands, and groundwater flows toward the basin centers. Along the flow path, the salinity of the groundwater increases by several orders of magnitude by both salt dissolution and evaporation (Richter and Kreitler, 1986, 1993). The chemistry of the residual saline groundwater is primarily controlled by the initial freshwater composition and the subsequent saturation of typical minerals (calcite, gypsum, spiolite, halite; Eugster and Jones, 1979; Hardie and Eugster, 1970). It has been demonstrated, for example, that evaporation and mineral precipitation control the salinity of groundwater that flows to Deep Spring Lake (Jones, 1965), Death Valley (Hunt et al., 1996), and the Sierra Nevada Basin (Garrels and MacKenzie, 1967).

While the source of the salts is natural, the process of salinization in the dryland environment refers to human intervention. The most widespread phenomenon of dryland salinization is the response to changes in land use, such as land clearing and replacing natural vegetation with annual crops and pastures. The natural vegetation in arid and semiarid zones uses any available water, and thus the amount of water that percolates below the root zone is minimal, estimated at between 1 and 5 mm year⁻¹ in the case of South Australia (Allison and Barnes, 1985). Over thousands of years, salts have accumulated in the unsaturated zone and their mobilization and leaching to the underlying saturated zone was constrained by the slow recharge flux. Large-scale replacement of the natural vegetation with annual crops and pastures with short roots significantly increased the amount of water percolating below the root zone, increasing the recharge rate and consequently the rate that salts leached into the underlying groundwater (Scanlon et al., 2009a; Williams, 2002). Thus, the salts that historically were stored in the root zone began to flush through the unsaturated to the saturated zone, causing salinization of the underlying groundwater. Leaney et al. (2003) predicted that salt flux from the unsaturated zone in the Murray-Darling Basin of southeastern Australia (with soil salinity up to 15000 mg l^{-1}) will increase the salinity of the shallow groundwater ($\sim 1000 \text{ mg l}^{-1}$) by a factor of 2–6. Indeed, a systematic survey of salts in borehole samples collected beneath natural ecosystems, nonirrigated ('rain-fed') croplands, and irrigated croplands in the southwestern United States and in the Murray-Darling Basin in Australia showed increased mobilization of chloride and sulfate following land use changes (Scanlon et al., 2009a). Similar cases of soil and shallow groundwater salinization induced by land use changes were reported in Argentina (Lavado and Taboada, 1987), India (Choudhari and Sharma, 1984), and South Africa (Flügel, 1995).

Another type of anthropogenic-induced salinization in dryland environments is afforestation. Since deep tree roots can efficiently draw water from the underlying shallow groundwater, afforestation of grasslands may reverse the downward flux of groundwater from the soil to the saturated zone. As a result, transpiration of water by deep roots may leave its salt load in the unsaturated zone. Consequently, afforestation reduces natural groundwater recharge and causes salinization of the soil and shallow groundwater (Jackson et al., 2009; Jobbagy and Jackson, 2004; Nosetto et al., 2009). Evidence of soil and groundwater salinization due to tree establishment on grasslands has been shown in the northern Caspian region (Sapanov, 2000), Australia (Heuperman, 1999), and the Argentine Pampas (Berthrong et al., 2009; Jobbagy and Jackson, 2004; Nosetto et al., 2009). A systematic chemical survey of the upper 30 cm of soil in 153 plantation sites worldwide showed that afforestation is associated with a significant decrease in nutrient cations (Ca^{2+} , Mg^{2+} , K^+) and increase in sodium due to selective uptake of the cations by the plants (Berthrong et al., 2009; Jobbagy and Jackson, 2004).

One of the most dramatic large-scale salinization phenomena occurs in Australia (Allison and Barnes, 1985; Allison et al., 1990; Cartwright et al., 2004, 2006, 2007b; Fitzpatrick et al., 2000; Herczeg et al., 1993, 2001; Leaney et al., 2003; Peck and Hatton, 2003; Scanlon et al., 2009a;



Figure 21 The dryland salinization cycle (the Australian model): (1) salt accumulation and precipitation of minerals; (2) selective dissolution and transport of soluble salts in the vadoze zone; (3) storage of salts influenced by soil permeability; (4) leaching and salinization of groundwater; (5) rise of saline groundwater; (6) capillarity evaporation of rising groundwater; (7) soil salinization; and (8) lateral solute transport and salinization of streams and rivers. Modified from Fitzpatrick RW, Merry R, Cox J (2000) What are saline soils and what happens when they are drained? *Journal of Australian Association of Natural Resource Management* 6: 26–30.

Williams et al., 2002). The Australian case is used here to describe the chemical evolution of solutes in the dryland environment. The dryland salinization cycle (Figure 21) is a complex process that begins with salt accumulation on the surface and soil, precipitation and dissolution of nonsoluble (carbonate) and soluble (gypsum and halite) minerals, and incongruent silicate mineral reactions (Eugster and Jones, 1979; Hardie and Eugster, 1970). The salts that accumulate in the soil are flushed into the vadose zone. Two factors control the rate of flushing: mineral solubility and soil physical properties such as permeability. The different solubility of different minerals leads to chemical separation of minerals within the unsaturated zone; the higher the solubility of the mineral, the longer will the ions derived from its dissolution travel in the unsaturated zone. This process is also known as wetting and drying and involves complete precipitation of dissolved salts during dry conditions and subsequent dissolution of soluble salts during wet periods (Drever and Smith, 1978). This results in an uneven distribution of ions along the unsaturated zone: Ca²⁺, Mg²⁺, and HCO₃⁻ tend to accumulate at relatively shallow depths, SO₄²⁻ at intermediate depths, and Na⁺ and Cl⁻ are highly mobilized to greater depths of the unsaturated zone. The Na/Ca ratio fractionates along the travel of solute in the vadose zone; Ca²⁺ is removed by precipitation of carbonate minerals whereas Na⁺ remains in solution, or even increases due to dissolution of halite. In addition, the mobilization of Na⁺ triggers base-exchange reactions; Na⁺ is adsorbed on clay and oxides, but the Ca²⁺ that is released from the adsorbed sites is taken up by precipitation of soil carbonate.

The overall chemical composition of the solutes that are generated in the dryland environment depends on the initial fluid and soil compositions. In Australia, the solutes are derived from marine aerosols and deposited on the soil (Herczeg et al., 2001; Scanlon et al., 2009a). ¹⁴C ages of soil solutions

reveal that most of the recharge occurred during wet climatic periods more than 20000 years ago (Leaney et al., 2003). Likewise, decreases in ³H and ¹⁴C activities with groundwater depth from the Shepparton Formation in the southeast Murray Basin and northern Victoria, Australia, suggest dominantly preland clearing vertical recharge (Cartwright et al., 2006, 2007b). Consequently, with thousands of years of salt accumulation and numerous wet and dry cycles through the unsaturated zone, the saline groundwater in the dryland environment has become 'marine-like' with a predominance of Na⁺ and Cl⁻ ions and Na/Cl and Br/Cl ratios identical to those of seawater (Herczeg et al., 1993, 2001; Mazor and George, 1992). In addition, the Australian salts lakes, which represent groundwater discharge zones, are characterized by marine chemical and isotopic (sulfur and boron) compositions modified by internal lake processes (Chivas et al., 1991; Vengosh et al., 1991a).

In addition to atmospheric deposition, water-rock interactions, triggered by generation of acids from CO₂ accumulation and oxidation of organic matter in the soil, can modify the original chemistry of the meteoric deposition. The 'nonmarine' signature of the saline groundwater and salt lakes in the western United States reflects the role of water-rock interactions in shaping the chemical composition of both initial and evolved groundwater in the arid zone in this region (Eugster and Jones, 1979; Hardie and Eugster, 1970). Numerous drying and wetting cycles may also result in precipitation of halite minerals in the saturated zone that change the chemistry of the recharge solutions. Variations in Br/Cl ratios in water from the Honeysuckle Creek area in the southeast Murray-Darling Basin in Australia indicate that the transformed salts are derived from a combination of both halite dissolution and a residual evaporated solution (Cartwright et al., 2004).

The second factor that controls salinization of dry land environments is the physical characteristics (e.g., permeability) of the soil. In the arid zone of Australia, rainfall was not always sufficient to leach the salts, and the clay layers in deep sodic subsoil prevents downward movement of water and salts, leading to a saline zone (Fitzpatrick et al., 2000). Differential residence time and salinity due to aquifer permeability was documented in groundwater from the Shepparton Formation in the southeast Murray Basin. Recharge in highly permeable paleovalleys produced relatively lower saline groundwater (TDS~3000 mg l^{-1}) with a 'bomb pulse' ³⁶Cl signature, suggesting relatively young recharge. In contrast, recharge in areas of low permeability generated much higher salinity (TDS up to 60000 mg l⁻¹) with low Br/Cl and low ³⁶Cl activities. The correlation between Br/Cl and R³⁶Cl values suggests old halite dissolution and slow transport through the impermeable unsaturated zone (Cartwright et al., 2006).

In addition to the natural accumulation of salts in soil due to the decrease of soil permeability (also called 'subsoil transient salinity'; Fitzpatrick et al., 2000), anthropogenic salinization due to the rise of saline groundwater has also been described in South Australia (Allison and Barnes, 1985; Allison et al., 1990; Cox et al., 2002; Herczeg et al., 1993). The selective leaching process in the unsaturated zone generates two types of saline groundwater (1) Na–Cl groundwater; and (2) sulfaterich water. The rising of Na–Cl groundwater creates halitedominant soils, where chloride is the dominant anion. The rising of sulfate-enriched groundwater creates three types of soils: (1) gypsic soil – under aerobic conditions and saturation of calcium sulfate; (2) sulfidic soil – under anaerobic conditions and sufficient organic carbon, bacteria uses the oxygen associated with sulfate and produces pyrite; (3) sulfunic soil – exposure of pyrite to oxygen in the air causes oxidation of pyrite and formation of sulfuric acid, which consequently reduces the soil pH and enhances leaching of basic cations, anions, and trace elements into the soil solution (Cox et al., 2002; Fitzpatrick et al., 2000).

The differentiation of soil permeability due to clay content, sodium uptake by clays, and mineral precipitation also prevents salts from flushing downward through the unsaturated zone, and causes lateral flow of saline soil solutions and shallow groundwater toward low-lying areas. The final stage of the dryland cycle is salinization of adjacent streams and rivers that occupy low-lying areas. The chemical composition of the salinized river in the dryland environment reflects the net results of salt recycling between soil, subsoil, groundwater, secondary soil, soil solution, and surface water (Figure 21).

11.9.6 Anthropogenic Salinization

11.9.6.1 Urban Environment and Wastewater Salinization

The salinity of domestic wastewater is a function of the combined salinity of the source water supplied to a municipality and the salts added directly by humans (Figure 22). The 'manmade' salts include detergents, washing powders, and salts generated in daily household operations such as salts used for dishwashers and for refreshing ion-exchange columns typically used in softeners. In Israel, for example, the average net human contribution of chloride, sodium, and boron to domestic wastewater were 125, 120, and 0.6 mg, respectively, for 1 l of wastewater in the early 1990s (Hoffman, 1993; Vengosh et al., 1994). Common treatment for sewage purification will reduce the turbidity, the concentrations of organic constituents, and the nutrient loads but will not remove the dissolved inorganic salts unless sewage is treated through tertiary treatment such as desalination (see Section 11.9.9). Consequently, in many arid and semiarid countries, treated sewage is commonly saline. In Israel, the chloride content of domestic sewage effluent from the Dan metropolitan area was between 300 and 400 mg l⁻¹ during the early 1990s (Harussi et al., 2001; Vengosh et al., 1994).

Wastewater has become a valuable resource in many waterdeficient countries and reusing treated wastewater for agriculture has substituted for natural water sources in some places in Europe (Bixio et al., 2006, 2008), the United States (Crook and Surampalli, 2005), and many Mediterranean (Maton et al., 2010) and Middle East countries. In Israel, treated sewage effluents have been increasingly used for agriculture (Friedler, 2001); from a total of 530×10^6 m³ of sewage produced in 2010, 355×10^6 m³ (about 75%) was treated and used for irrigation (Israel Water Authority, 2011). Likewise, Jordan has been increasingly using wastewater for the agricultural sector (Al-Khashman, 2009; Carr et al., 2011; Hadadin et al., 2010). Yet, the salinity and the presence of other inorganic constituents in wastewater pose a significant risk for soil and consequently for aquifer salinization following decades of irrigation (Banin and Fish, 1995; Beltrán, 1999; Fernandez-Cirelli et al., 2009; Klay et al., 2010; Tarchouna et al., 2010). Soil and groundwater salinization due to long-term application of treated wastewater have been reported, for example, in Israel (Gavrieli et al., 2001; Kass et al., 2005; Rebhun, 2004; Ronen et al., 1987; Vengosh and Keren, 1996), Cape Cod, Massachusetts, USA (DeSimone et al., 1997), Texas, USA (Duan et al., 2011), Tunisia (Klay et al., 2010), southern France (Tarchouna et al., 2010), Portugal (Stigter et al., 1998), and Senegal (Re et al., 2011). It is therefore crucial to reduce the salinity of wastewater if this resource is to become a sustainable alternative water source for agriculture. Possible solutions for salt reduction were outlined by Weber et al. (1996) and include



Figure 22 The domestic wastewater salinization cycle: (1) supply water to a municipality; (2) salts added within the urban environment; (3) sewage generation; (4) sewage treatment; (5) reuse of treated sewage for irrigation; (6) contamination of water resources.

separation of saline effluents from major treated sewage streams that are diverted from the sewage treatment plants; substitution of sodium by potassium salts in ion-exchangers; construction of centralized systems for the supply of soft water in industrial areas that would eliminate the need for softeners and thus reduce the impact of softener backwash saline water; precipitation of Ca^{2+} and Mg^{2+} in the effluents from ion-exchangers and recycling of the NaCI solution; a reduction of the discharge of salts by the meat-processing (koshering) process; and establishing new membrane technology for salt removal in treated wastewater effluents (Weber et al., 1996).

Boron is commonly high in domestic wastewater due to the use of synthetic Na-borate additives derived from natural Na-borate minerals that are used as bleaching agents (Nishikoori et al., 2011; Raymond and Butterwick, 1992; Vengosh et al., 1994; Waggott, 1969). Given that high concentrations of boron in irrigation water (>1 mg l^{-1} for most crops) could be toxic for many plants (Bastias et al., 2010; Davis et al., 2002; Karabal et al., 2003; Kaya et al., 2009; Lehto et al., 2010; Papadakis et al., 2004; Reid, 2010; Scialli et al., 2010; Smith et al., 2010; Sotiropoulos et al., 1999; Thompson et al., 1976), some countries have set regulations for reducing boron additives in detergents and washing powders. This has been implemented in Israel; in 1999, the Israeli Ministry of Environment established a new regulation to reduce the boron content in detergents from 8.4 g kg⁻¹ (old standard) to 0.5 g kg⁻¹ (2008 standard; Weber and Juanicó, 2004). The result was a reduction in the boron concentration in sewage from the Dan Region Sewage Reclamation Project near Tel Aviv (the Shafdan) from about 0.9 mg l^{-1} before the regulation during the early 1990s (Vengosh et al., 1994) to about 0.2 mg l^{-1} in 2006 (Kloppmann et al., 2009).

The typical chemical composition of saline domestic sewage is presented in **Table 1**. The use of household NaCl salt and Na-rich and B-rich detergents results in typical ionic ratios of Na/Cl>1, a low Br/Cl ratio (i.e., Br/Cl<seawater ratio due to halite dissolution; Vengosh and Pankratov, 1998), and a high B/Cl ratio (greater than seawater ratio of 8×10^{-4} ; Kloppmann et al., 2008a; Leenhouts et al., 1998; Vengosh et al., 1994, 1999a; Widory et al., 2004). Since Na-borate additives are derived from natural borate deposits (mainly from the western United States, Turkey, and China), the boron isotopic composition of wastewater is similar to the mineral borate isotopic ratios, with a typical δ^{11} B range of 0–10‰ (Eisenhut et al., 1995; Vengosh et al., 1994). This isotopic composition is different from those of other salinity sources (e.g., seawater intrusion with $\delta^{11}B > 39\%$; Figure 23) and thus several studies have utilized this method for tracing wastewater contamination in water resources (Bassett et al., 1995; Eisenhut et al., 1995; Hogan and Blum, 2003; Kloppmann et al., 2008a; Leenhouts et al., 1998; Vengosh et al., 1994, 1999a; Widory et al., 2004). The anthropogenic sulfate in wastewater also has a distinctive isotopic ratio (Houhou et al., 2010; Torssander et al., 2006). This tracer was used to detect pollution of the Arno River in northern Tuscany with a distinctive sulfur isotopic ratio ($\delta^{34}S_{SO_4} = 6-8\%$; Cortecci et al., 2007), urban groundwater contamination in Metro Manila, Philippines (Hosono et al., 2010), shallow groundwater of the Taipei urban area (Hosono et al., 2011), and groundwater from Shuicheng Basin, southwestern China (Li et al., 2010).

One of the major sources of salts that affect the salinity of domestic wastewater is the discharge of softener backwash effluent. In suburban and rural areas, where the local groundwater supply is hard (high Ca^{2+} and Mg^{2+} concentrations), softener backwash may be an important salinity source for the local watershed and groundwater. In the Greater Phoenix Metropolitan Area, Arizona, a population of 12 million people annually generated 45500 tons of salts to wastewater from water softeners, which constitutes ~39% of the city's salt contribution (Daugherty et al., 2010). Kelly et al. (2008) estimated that an average of 125 kg year⁻¹ of salts are used for softening per house in rural communities in southeastern New York. Similarly, residential development in the Detroit metropolitan



Figure 23 Schematic illustration of the expected boron isotope variations upon salinization by (1) seawater intrusion; (2) dissolution of marine evaporites; and (3) contamination from sewage effluents. Note the enrichment in ¹¹B that is associated with boron adsorption process. Data from Vengosh et al. (1994).

area resulted in increasing salinity in local streams (Thomas, 2000). During regeneration (refreshing) of softeners, an NaCl solution is passed through a resin and releases, by ionexchange reactions, the adsorbed Ca^{2+} and Mg^{2+} ions that are retained from the supply water in order to increase the reactivity of the softener for the next load of Ca- and Mg-rich supply water. The chloride and sodium contents in backwash brine can reach to 10000 and 6000 mg l^{-1} , respectively (Gross and Bounds, 2007). While sodium may be retained during the regeneration process due to the release Ca²⁺ and Mg²⁺ ions, excess utilization of NaCl solution for regeneration masks this differential uptake of sodium, resulting in Na/Cl ratios close to unity in backwash effluents. In addition to the large potential salinization of softener backwash effluents, introducing these brines into septic tanks, which are common in many private homes in rural areas in the United Sates, inhibits anaerobic digestion and thus reduces the efficiency of biological remediation such as nitrifying microorganisms. Consequently, nitrogen removal in septic tanks could be inhibited in systems receiving water softener backwash brine (Gross and Bounds, 2007).

11.9.6.2 Deicing and Salinization

Another significant source of anthropogenic salinization is the use of road deicing salts. Salt has been used for road deicing for several decades, particularly in the eastern and northeastern states of the United States and Canada. The use of road salt has improved fuel efficiency and reduced accidents, yet at the same time has caused salinization of associated watersheds and groundwater. The use of rock salt for road deicing in the United States has dramatically increased in the last 75 years (Jackson and Jobbagy, 2005; Richter and Kreitler, 1993). Contamination of water resources can occur from leaking of brine generated in storage piles of salt (Wilmoth, 1972) and from the dissolution of salts applied onto the roads (Howard and Beck, 1993; Williams et al., 2000). Deicing salts were found to be the major salinity source of the North Branch of the Chicago River through direct runoff flow and wastewater effluent discharge in the large metropolitan area of Chicago (Jackson et al., 2008). In cases where salt is applied as a powder, salt particles may become airborne and be transported considerable distances downwind (Jones and Hutchon, 1983; Richter and Kreitler, 1993). Kaushal et al. (2005) showed that widespread increases in suburban and urban development in the northeastern United States are associated with a continuous increase in chloride concentrations in local streams: from less than 10 mg l^{-1} during the late 1960s to 100 mg l^{-1} during the late 1990s. During winter, some streams in Maryland, New York, and New Hampshire have exceedingly high chloride concentrations (>4600 mg l^{-1}), up to 100 times greater than unimpacted forest streams during summer (Kaushal et al., 2005). Kelly et al. (2008) showed that between 1986 and 2005 chloride and sodium concentrations in a rural stream in southeastern New York increased by rates of 1.5 and 0.9 mg l^{-1} per year, respectively. The average chloride concentration increased from $\sim 15 \text{ mg l}^{-1}$ in 1986 to about 50 mg l⁻¹ in 2005 (Kelly et al., 2008). If the chloride rise is extrapolated into the next century, it seems that many rural streams in the northeast of the United States will have baseline chloride contents

exceeding the drinking water threshold of 250 mg l^{-1} (Jackson and Jobbagy, 2005). Hence, increases in roadways and deicer use are causing salinization of freshwaters, degrading habitat for aquatic organisms, and impacting large supplies of drinking water for humans throughout the region. Likewise, a survey of 23 springs in the Greater Toronto Area of southern Ontario in Canada recorded high chloride levels (up to 1200 mg l⁻¹), resulting from the winter application of road deicing salts (Williams et al., 2000).

The most common road deicing practice is to apply pure sodium chloride to main urban roads and highways. Calcium chloride salt is also used but not as frequently since it is more expensive and known to make road surfaces more slippery when wet (Richter and Kreitler, 1993). Hence, the predominant geochemical signal of road deicing is Na–Cl composition with a Na/Cl ratio close to unity (Table 1; Howard and Beck, 1993). In contrast, the use of calcium chloride salt would result in saline water with a Ca–chloride composition and Na/Cl $\ll 1$.

11.9.6.3 Agricultural Drainage and the Unsaturated Zone

The salinity of agriculture return flow is controlled by (1) the composition of the parent irrigation water; (2) the composition and source of additive commercial chemicals (e.g., nitrogen fertilizers, gypsum, dolomite, boron compounds), pesticides, and herbicides; and (3) the nature of the soil through which the irrigation water flows (Beltrán, 1999; Böhlke, 2002; Böhlke and Horan, 2000; Causape et al., 2004a,b; Corwin et al., 2007; Garcia-Garizabal and Causape, 2010; Gates et al., 2002; Johnson et al., 1999; Milnes and Renard, 2004; Suarez, 1989; Tanji and Valoppi, 1989; Tedeschi et al., 2001; Westcot, 1988). In the western United States, for example, saline drainage waters from the Imperial Valley in southern California are characterized by high sodium (Na/Cl>1), sulfate, and boron and typically low Br/Cl ratios (Table 1; data from Schroeder and Rivera, 1993). The conspicuously low Br/Cl $((3-4) \times 10^{-4})$ in the drainage water is one order of magnitude lower than seawater (1.5×10^{-3}) or atmospheric $(>1.5 \times 10^{-3})$ ratios (Figure 12; Davis et al., 1998). While this composition could be related to the chemistry of the Colorado River, which is the major water source for irrigation in this area, the high concentration of selenium in the drainage water is attributed to mobilization from oxidized alkaline soils derived predominantly from natural seleniferous marine sediments (Hern and Feltz, 1998; Grieve et al., 2001; Rhoades et al., 1989; Schroeder and Rivera, 1993; see Chapter 11.2). As a result, agricultural practices have caused significant changes in groundwater geochemistry due to mobilization of natural contaminants and intensification of water-rock interactions that further enhance water mineralization (Böhlke and Irwin, 1992).

The salinity of agricultural return flow also depends on the balance between the amount of salt entering the soil and the amount of salt that is removed (Westcot, 1988). A change from natural vegetation to agricultural crops and the application of irrigation water may add salts to the system. The amount of salt is further increased, as evaporation and transpiration exceed recharge. Approximately 60% of the supplied irrigation water will be transpired through growing crops but the majority of salts remain in the residual solution. Consequently,



Figure 24 The agriculture salinization cycle: (1) supply water for irrigation; (2) salts added with fertilizers and amendment treatment; (3) generation of irrigation water; (4) soil salinization; (5) formation of agricultural return flow; (6) possible contamination of water resources.

adequate drainage is one of the key factors that control soil salinization; nevertheless, the nonreactivity of some of the soluble salts (i.e., conservative ions) makes them a long-term hazard.

The salinity of agricultural return flow is also a function of the salinity of the soil. In arid and semiarid areas, the natural salinity of the soil is high and thus flushing with irrigation water enhances salt dissolution in the soil. In some cases, the occurrence of contaminants in the protolith lead to high concentrations in agricultural effluents. A survey of the quality of drainage water in the western United States shows that the drainage waters are typically saline with elevated concentrations of sodium, selenium, boron, arsenic, and mercury (Hern and Feltz, 1998). In San Joaquin Valley, Salinas Valley, and Imperial Valley in California, drainage waters are highly saline and contaminate the associated ground- and surface waters (Amrhein et al., 2001; Glenn et al., 1999; Kharaka et al., 1996; Rhoades et al., 1989; Schroeder and Rivera, 1993). For example, the agricultural drainage salt generation during irrigation of crops in San Joaquin Valley in California annually exceeds 600 000 tons, which accumulates at a rapid rate, causing serious concern for the environment and the local agricultural industry (Jung and Sun, 2001). The soil reactivity is also enhanced by the composition of the irrigation water and added fertilizers. As high salinity is typically associated with high sodium content, exchangeable sodium replaces exchangeable calcium. As a result, the soil becomes impermeable. The 'sodium hazard' is expressed as the 'sodium adsorption ratio,' which represents the relative activity of sodium ions in exchange reactions with soil. Typically, irrigation waters with SAR values higher than 10 are considered to be sodium hazards (e.g., San Joaquin Valley; Mitchell et al., 2000). In cases of high SAR soil, gypsum or calcium carbonate can be applied to reverse the sodium exchange and improve soil physical properties (Agassi et al., 2003; Keren, 1991; Keren and Ben-Hur, 2003; Keren and Klein, 1995; Keren and Singer, 1988; Li and Keren, 2008, 2009; Nadler et al., 1996; Tarchitzky et al., 1999).

The chemical composition of agricultural drainage (Figure 24) is influenced by the quality of the water source that is used for irrigation. In many water-scarce areas, the only available water for irrigation is treated domestic sewage. Hence, the end product of urban wastewater (Figure 22) can be the initial water for agriculture (Figure 24). Other types of marginal waters (e.g., brackish waters) may also affect the salinity of agricultural return flows.

The second factor that determines the chemistry of the agriculture cycle is fertilizers and other types of additives that are directly added to the irrigation water. Nitrate is the predominant ion contributed by fertilizers (McMahon et al., 2008). Böhlke (2002) showed that artificial fertilizer is the largest nonpoint source of nitrogen in rural areas, consistent with the global increase in the use of nitrogen fertilizer since the middle of the twentieth century. Nitrate derived from fertilizers is characterized by relatively low $\delta^{15}N_{NO_3}$ values (-4% to +3%; Kendall and Aravena, 2000, and references therein). ($\delta^{15}N_{NO_3}$ =[($^{15}N/^{14}N$)_{sample}/($^{15}N/^{14}N$)_{AIR}-1] × 10³. AIR refers to N₂ in air (Coplen et al., 2002).) Other major forms of nitrogen applied to crops are urea, (CO(NH₂)₂), ammonia (NH₃), ammonium nitrate (NH₄NO₃), and animal manure (Böhlke, 2002; Kendall and Aravena, 2000).

In addition to nitrogen application, other types of ammandates are added to the irrigation water. These include dolomite to provide calcium and magnesium for plant growth and to neutralize acid soils (Böhlke, 2002), and gypsum, which is used in soil with irrigation water having high SAR values in order to neutralize the exchangeable Na⁺ in the soil (e.g., Salinas Valley, California; Vengosh et al., 2002). In addition, application of KCl salts as fertilizers results in chloride contamination, and use of Na–borate or Ca–borate fertilizers in boron-depleted soil contributes boron (Komor, 1997). The use of soil fumigants like ethylene dibromide (EDB) (Böhlke, 2002; Doty et al., 2003; Redeker et al., 2000) can lead to degradation and release of bromide to groundwater, as evidenced by conspicuously high Br/Cl ratios in shallow groundwater underlying strawberry cultivation in the Salinas Valley (Vengosh et al., 2002).

Another source of salinity that is associated with agricultural activity is animal waste, including cattle (Gooddy et al., 2002; Hao and Chang, 2003; Harter et al., 2002; Hudak, 1999, 2000a,b, 2003; Hudak and Blanchard, 1997) and swine manure (Krapac et al., 2002). It has been demonstrated that the salinity of soil and underlying groundwater increases significantly following long-term manure applications (Hao and Chang, 2003; Hudak, 1999, 2000a,b, 2003; Hudak and Blanchard, 1997; Krapac et al., 2002). Manure often has high concentrations of chloride (1700 mg l^{-1} in swine manure), sodium (840 mg l^{-1}), potassium (3960 mg l^{-1}), and ammonium with $\delta^{15}N_{NO_2}$ values > 9‰ (Krapac et al., 2002). Animal waste is also characterized by high Br/Cl ratios; cattle, horse, and goat wastes with Br/Cl ranging from 2.6×10^{-3} to 127×10^{-3} (Hudak, 2003) were shown to affect groundwater in Spain and Portugal (Alcalá and Custodio, 2008). In general, saline groundwater with high nitrate (with high $\delta^{15}N_{NO_2}$) combined with high Br/Cl and K/Cl ratios suggests contamination from animal wastes.

The third stage in the agriculture cycle (Figure 24) is transport and reactivity with the unsaturated zone. The unsaturated zone acts as a buffer and modifies the original chemical composition of the irrigation water (or any other recharge water). Microbial oxidation of ammonium releases protons (H⁺) that generate acidity along with nitrate production in soils (Böhlke, 2002) that may induce dissolution of calcium carbonate minerals (Curtin et al., 1998; De Boer and Kowalchuk, 2001; Furrer et al., 1990; Murkved et al., 2007; Rudebeck and Persson, 1998; Vance and David, 1991). Consequently, nitrate-rich waters in carbonate aquifers are associated with high calcium derived from dissolution of the aquifer matrix. For example, in the mid-Atlantic coastal plain in the United States, groundwater recharged beneath fertilized fields has a unique Ca-Mg-NO3 composition with positive correlations between nitrate and other inorganic constituents such as Mg²⁺, Ca²⁺, Sr²⁺, Ba²⁺, K⁺, and Cl⁻ (Hamilton and Helsel, 1995; Hamilton et al., 1993). In the Gaza Strip, which is part of the Mediterranean coastal aquifer, dissolution of the Pleistocene carbonate aquifer matrix is reflected in high ⁸⁷Sr/⁸⁶Sr ratios in nitrate-rich groundwater, relative to groundwaters with lower nitrate concentrations that are associated with lower ⁸⁷Sr/⁸⁶Sr ratios (Vengosh et al., 2005).

Using irrigation water that is enriched in sodium with high SAR values triggers ion-exchange reactions (Agassi et al., 2003; Keren, 1991; Keren and Ben-Hur, 2003; Keren and Klein, 1995; Keren and Singer, 1988; Li and Keren, 2008, 2009; Nadler et al., 1996; Stigter et al., 1998; Tarchitzky et al., 1999). The capacity of ion exchange on clay minerals is limited, however, and depends on various lithological (e.g., clay content) and environmental (e.g., pH, solute composition) factors. Nonethe uptake of Na^+ and release of Ca^{2+} (and Mg^{2+}) is a major geochemical modifier that is associated with transport of irrigation water in the unsaturated zone. The Na/Cl ratio is a good indicator of the efficiency of the base-exchange reactions; low Na/Cl ratios (i.e., below the original value of the irrigation water) reflect continuation of exchange reactions whereas the increase of the Na/Cl ratio toward the original Na/Cl value of the irrigation water suggests exhaustion of the exchangeable sites and reduction in the clay capacity for exchange

reactions (Vengosh and Keren, 1996). Kass et al. (2005) showed that irrigation with Ca-rich water causes an opposite reaction where Na⁺ is released and the residual groundwater has an Na/Cl that is higher than that of the irrigation water. Similarly, the ability of clay minerals to adsorb reactive elements (e.g., boron, potassium) is limited, and after long-term recharge or irrigation, the capacity of adsorption decreases (DeSimone et al., 1997; Stigter et al., 1998; Vengosh and Keren, 1996). In most cases, the potassium level in groundwater is low and the K/Cl ratios in groundwater associated with agricultural recharge are typically low due to adsorption of potassium onto clay minerals (Böhlke, 2002).

The amount of organic load associated with anthropogenic contamination and redox conditions also controls the reactivity of the unsaturated zone and consequently the salinity of associated water. In aerobic conditions, the degradation of organic matter will enhance acidity and result in accumulation of HCO₃⁻ and Ca²⁺ due to dissolution of the carbonate matrix of the host aquifer. In addition, the contents of sulfate and nitrate are expected to vary conservatively under oxic conditions in the unsaturated zone. Thus, high sulfate and nitrate contents, which are common in many irrigation waters, would also be preserved in underlying groundwater. In contrast, in anaerobic conditions, sulfate and nitrate reduction will enhance calcium carbonate precipitation, and hence sulfate (by sulfate reduction), nitrate (denitrification), and calcium (precipitation) will be removed during flux to the unsaturated zone (Böhlke, 2002; Böhlke and Horan, 2000; Gooddy et al., 2002). Under anaerobic conditions, the original chemical signature of the agricultural return flow would therefore be modified and the residual underlying groundwater would become relatively depleted in sulfate and nitrate concentrations, with high $\delta^{34}S_{SO_4}$ and $\delta^{15}N_{NO_2}$ values relative to the irrigation water.

11.9.7 Salinity and the Occurrence of Health-Related Contaminants

Salinization of water resources is often associated with an increase in the concentrations of *associated* contaminants, including inorganic constituents (e.g., fluoride, arsenic, boron, and radium), organic compounds such as toxic disinfection byproducts, and biological contaminants such as toxic saltwater algae. The occurrence of these contaminants in water resources has important implications for possible bioaccumulation in plants and the food chain, toxicity of the water, and direct effects on human health.

As shown in this section, numerous studies have shown that the concentrations of trace elements in water resources are typically correlated with the overall water salinity. In surface water, this positive correlation is directly linked to evaporation and the apparent conservative behavior of trace elements in the water. In groundwater, this correlation may be derived from surface evaporation of recharged water during the replenishment process, water–rock interactions that mobilize both major and trace elements, or the net salinity impacts on the solubility and/or reactivity of inorganic trace metals, resulting in progressively higher contents of trace elements with increasing salinity.

11.9.7.1 Fluoride and Salinity

Many water resources in China, eastern Africa, and India are characterized by high fluoride contents that are associated with elevated salinity and cause widespread dental and skeletal fluorosis (Ayenew et al., 2008; D'Alessandro et al., 2008; Misra and Mishra, 2007; Mor et al., 2009; Rango et al., 2009, 2010a,b,c; Shiklomanov, 1997; Viero et al., 2009). An example of fluoride contamination in lakes and groundwater is the Central Rift Valley of Ethiopia (Rango et al., 2009, 2010a,b,c, 2013), where fluoride concentrations linearly increase with salinity in both groundwater and alkaline (pH 10) lakes (Figure 25). While the linear relationships in groundwater reflect mobilization of fluoride together with major elements such as Na⁺ and HCO_3^- (Figure 25) due to weathering of amorphous glass in the young basalts of the Rift Valley (Rango et al., 2010b), in alkaline lakes these correlations are due to surface evaporation and the associated concentration of ions. The salinization of groundwater and lakes in the Ethiopian Rift Valley has therefore direct implications for the levels of health-related contaminants such as fluoride. Since the local rural population in the East African Rift Valley consumes groundwater primarily as drinking water, the high fluoride levels in groundwater result in a high frequency of fluorosis (Rango et al., 2009, 2010a,b,c, 2012). In addition to fluoride, the extensive weathering of the basaltic rocks leads to mobilization of other health-related trace element contaminants to the groundwater such as arsenic, boron, and vanadium (Rango et al., 2010a).

11.9.7.2 Oxyanions and Salinity

The relationship between salinity and oxyanions, particularly arsenic, selenium, and boron, depends on two key factors: (1) the speciation of the oxyanions as a function of environmental conditions such as pH, redox state, temperature,

pressure, and salinity; and (2) the type of bond that the oxvanion species makes with surface functional groups in oxides and clay minerals; an oxyanion may form an inner-sphere com*plex* (i.e., a chemical bond that is typically covalent between the oxyanion and the electron-donating oxygen ion without the presence of water molecules) or an outer-sphere complex (i.e., an ion pair in which the oxyanion and the surface functional groups are separated by one or more water molecules; McBride, 1977; Sposito, 1984; Stumm and Morgan, 1995). While ionic strength has no effect on the degree of adsorption through inner-sphere complex formation, high salinity will reduce the adsorption of outer-sphere-forming ions because adsorption is suppressed by the competition of other anions (McBride, 1977). The affinity of oxyanion species to form surface complexes (inner- or outer-sphere complexes) depends on the valence of the adsorbed species. Increasing salinity will therefore reduce the adsorption capacity of some oxyanions species and increase their concentrations in the residual saline water.

11.9.7.2.1 Arsenic

The extent to which arsenic mobilization is affected by salinity depends on its valence state. As shown in Chapter 11.2 at near-neutral pH, oxidized As(V) (arsenate) occurs as anionic $H_2AsO_4^-$ or $HAsO_4^{2-}$, subject to pH-sensitive adsorption onto metal oxides. Under reducing conditions, arsenic aquatic species are composed of arsenite (As(III)) in which the uncharged $H_3AsO_3^0$ is dissociated to $H_2AsO_3^-$ (p K_a =9.3). Consequently, at pH < 9 the uncharged $H_3AsO_3^0$ is less effectively adsorbed than the anionic As(V) form. Given the differential reactivity of arsenic species, the relationship of arsenic with salinity depends primarily on the redox conditions, arsenate ($H_2AsO_4^-$ and $HAsO_4^{2-}$ are the predominant species at neutral pH) adsorption onto Fe and Al amorphous oxides is



Figure 25 Fluoride and bicarbonate concentrations versus TDS (mg I^{-1}) in groundwater (red circles) and lakes (blue squares) from the Central Rift Valley in Ethiopia. While groundwater mineralization induces fluoride mobilization, evaporation processes further increase fluoride contents in alkaline (pH 10) lakes. Data from unpublished results, Duke University.

through an inner-sphere complex, which is not associated with the ionic strength of the solution (Goldberg and Johnston, 2001; Liu et al., 2008). In contrast, under reduced conditions, arsenite adsorption on amorphous Al oxides reaches an adsorption maximum at around pH 8 but decreases with increasing ionic strength (i.e., outer-sphere complex mechanism; Goldberg and Johnston, 2001). Thus, salinization under reduced conditions and neutral pH results in high As contents in the salinized water.

In addition to the possible *direct* effect of ionic strength on As adsorption, salinization of surface water could indirectly affect As distribution. One possible scenario is salinity-induced stratification of lake water that would generate reducing conditions in the bottom water, produce arsenite species, and, consequently, decrease the reactivity of the overall arsenic with oxides in sediments. For example, As contents were found to be linearly correlated with chloride contents in evaporation ponds from the San Joaquin Valley of California, in conjunction with the increase of the arsenite fraction of the total arsenic and organic arsenic. This trend was associated with increasing reducing conditions (high dissolved organic matter, low dissolved oxygen, and elevated sulfide concentrations) in the evaporation ponds (Gao et al., 2007). Although some removal of As to sediments in the pond was monitored (Gao et al., 2007), the reduced noncharged arsenic species was less reactive, resulting in the apparent conservative behavior of arsenic in the ponds. Likewise, saltwater intrusion into coastal and delta aquifers typically generates anoxic conditions, which will favor formation of uncharged arsenite species and will decrease arsenic removal. This was demonstrated in the reduced and high-salinity groundwater from the Red River Delta in Vietnam (Jessen et al., 2008). Another example of the high correlation between As and salinity under reduced conditions is oil field brines, as petroleum reservoir waters from sedimentary basins in southeastern Mexico show maximum As concentrations of 2000 μ g l⁻¹ and a linear correlation with chloride content (Birkle et al., 2010).

Changes in salinity could also affect the environmental conditions that control the resilience of anaerobic bacteria, which grow by dissimilatory reduction of As(V) to As(III) (Blum et al., 1998). As demonstrated in the hypersaline alkaline Mono and Searles lakes in California, lake salinity can control the rate of microbial activity, such as arsenate reduction and arsenite oxidation, as well as the microbial population that triggers different biogeochemical reactions (e.g., denitrification and arsenate reduction; Blum et al., 1998; Kulp et al., 2007).

In oxic groundwater, where arsenate (As(V)) is the dominant species, salinity should not, in principle, affect As mobilization. Nonetheless, correlations between As and salinity have been observed in oxic groundwater from the Southern High Plains aquifer in Texas (Scanlon et al., 2009b) and the Sali River alluvial basin in northwest Argentina (Nicolli et al., 2010). While in Texas this correlation has been attributed to mixing of low saline groundwater with As-rich saline groundwater from the underlying Triassic Dockum aquifer (Scanlon et al., 2009b), in the shallow oxic aquifer in Argentina, the correlation results from evaporation combined with the high pH and Na—HCO₃ composition of the water that apparently reduces As adsorption (Nicolli et al., 2010). Likewise, in oxic groundwater from the Rift Valley of Ethiopia in which sodium and bicarbonate are the major components of the dissolved constituents (Figure 25), a positive correlation is observed between As and TDS, suggesting that As is derived from weathering of the volcanic glass (Rango et al., 2010b).

11.9.7.2.2 Selenium

Selenium is both a micronutrient essential for animal nutrition and a potentially toxic trace element for ecological systems. The US EPA has set a limiting factor of 5 µg l^{-1} for *criterion* continuous concentration, which is an estimate of the highest concentration of a material in surface freshwater to which an aquatic community can be exposed indefinitely without resulting in an unacceptable effect (US Environmental Protection Agency, 2011a). As shown in Chapter 11.2, the dominant inorganic Se species are selenite, Se(IV), and selenate, Se(VI). While selenate is thermodynamically stable under oxidizing conditions, the transformation rates of Se(IV) to Se(VI) are sufficiently slow that both species can coexist in water in oxic environments (Masscheleyn et al., 1990). The reduced form, selenite, is strongly adsorbed by oxides while selenate adsorbs weakly and is readily leached to water (Dzombak and Morel, 1990). While the strong adsorption of selenite (SeO_3^{2-} species) is through inner-sphere surface complexes, the weak adsorption of selenate is through outer-sphere complexes and therefore is salinity-dependent (Hayes et al., 1988). This was demonstrated in experimental column studies, which showed that selenate is more mobile than other conservative anions such as sulfate and chloride (Goldhamer et al., 1986).

High correlations between selenium and salinity were reported in shallow groundwater from the San Joaquin Valley in California (Deverel and Fujii, 1987; Deverel and Gallanthine, 2007; Presser and Swain, 1990; Schoups et al., 2005; Tanji and Valoppi, 1989), brines of the Salton Sea in California (Schroeder et al., 2002), saline seeps associated with cultivated drylands of the Great Plains region of North America (Miller et al., 1981), and stream discharge to the Ashley Creek, part of the Upper Colorado River Basin in Utah (Naftz et al., 2008).

11.9.7.2.3 Boron

Boron is an essential element for plant growth but can be toxic at higher levels in irrigation water or soil solutions (Bastias et al., 2010; Davis et al., 2002; Karabal et al., 2003; Kaya et al., 2009; Lehto et al., 2010; Papadakis et al., 2004; Reid, 2010; Scialli et al., 2010; Smith et al., 2010; Sotiropoulos et al., 1999; Thompson et al., 1976). Numerous studies have shown that boron concentrations in water are highly correlated with salinity. Yet, boron can be reactive with clay minerals and oxides. Boron in aquatic solutions occurs as uncharged boric acid $(B(OH)_3^0)$ and borate ion $(B(OH)_4^-)$ species. The distribution of boron species in solution is controlled by pH and the dissociation of boric acid to borate ion depends on the temperature, pressure, and salinity (Figure 26; Dickson, 1990a; Millero, 1995). Empirical data calculated from Millero (1995) and Dickson (1990a) show that an increase in the salinity of water reduces the pK_B (K_B is the dissociation constant of boric acid; Figure 26). Figure 27 illustrates the changes in the boron species distribution from freshwater salinity $(pK_B = 9.2)$ to seawater salinity $(pK_B = 8.6 \text{ at } 25 \degree \text{C})$. The higher pK_B values under low salinity conditions implies a higher



Figure 26 Modeling of the variations of the boric acid dissociation constant (expressed as pK_B^* values) as a function of salinity and temperature. Note that the pK_B^* value decreases with salinity and temperature. Empirical data were calculated from Millero (1995) and Dickson (1990a).

proportion of the borate ion in solution at pH below 9, and thus salinization will lead to a lower fraction of boric acid for a given pH (Figure 26).

Numerous experimental studies have shown that the adsorption of boron on oxides and clay minerals increases with pH at a maximum range of 8–9. The increase of adsorption with pH has led to the suggestion that the magnitude of borate ion (B(OH)₄⁻⁻) adsorption onto oxides and clay minerals is higher than that of the uncharged boric acid (Keren and Gast, 1981; Keren and Oconnor, 1982; Keren and Sparks, 1994; Keren et al., 1981; Mezuman and Keren, 1981). In contrast, Su and Suarez (1995) argued that uncharged boric acid is also adsorbed onto positively charged surfaces at low pH, and that the maximum adsorption of boric acid to form trigonally coordinated surface species occurs at a pH closer to the pK_B value of boric acid. Under higher pH conditions, the concentrations of hydroxyl ions increase and compete with borate ions for adsorption sites (Su and Suarez, 1995).

Experimental studies have also shown that boron adsorption onto oxides and clay minerals increases with ionic strength (Goldberg et al., 1993; Keren and Sparks, 1994; McBride, 1977). The effect of ionic strength suggests a mechanism involving an adsorption through an outer-sphere complex (McBride, 1977), which is salinity-dependent. However, it was found that this salinity effect is not universal and an innersphere adsorption mechanism applies for goethite, gibbsite, and kaolinite minerals while an outer-sphere adsorption (i.e., salinity-dependent) mechanism occurs for adsorption onto montmorillonite and bulk soils (Goldberg et al., 1993).

As shown in **Figure 27**, a rise in salinity will increase the fraction of borate ion in solution in the pH range of 7.5–9. Thus, a higher fraction of borate ion, which seems to be more effectively adsorbed, could result in overall higher boron retention with salinity. Since boron adsorption is associated with isotopic fractionation in which ¹¹B tends to incorporate preferentially into the trigonal species while ¹⁰B is selectively fractionated into the tetrahedral form, selective removal of ¹⁰B



Figure 27 Modeling of the distribution of boron species boric acid and borate as a function of pH under low salinity conditions ($pK_B^* = 9.2$ at 25 °C) and seawater salinity ($pK_B^* = 8.6$ at 25 °C). Note that an increase in the salinity increases the fraction of borate ion for a given pH and increases the overall reactivity of boron with oxides and clay minerals. Data were calculated from Millero (1995) and Dickson (1990a).

 $(OH)_4^-$ to the solid phase results in enriched ¹¹B/¹⁰B ratios in the residual solution (Palmer et al., 1987; Spivack et al., 1987; Vengosh and Spivack, 2000). Consequently, despite the increase of boron concentration with salinity, in many cases, the salinization phenomena are accompanied by an increase in boron adsorption with lower boron to chloride ratios and higher δ^{11} B values relative to the expected theoretical mixing relationships between saline and freshwater end members. This was demonstrated in studies of seawater intrusion and salinization by wastewater (Vengosh et al., 1994), salinization of groundwater in the Salinas Valley in California (Vengosh et al., 2002), and in the Mediterranean coastal aquifer of Israel (Vengosh et al., 1999b).

11.9.7.3 Naturally Occurring Radionuclides and Salinity

Groundwater may contain naturally occurring radionuclides produced during the decay of 238U, 235U, and 232Th (see Chapter 11.6). Uranium (U) is a source of kidney toxicity as well as alpha radiation (US Environmental Protection Agency, 2000). High concentrations (activities) of naturally occurring radium (Ra), a decay product of ²³⁸U and ²³²Th, in drinking water increase the risks of developing osteosarcoma (bone cancer) and other health problems (Cohn et al., 2003; US Environmental Protection Agency, 2000). High levels of Ra in groundwater have been reported in reduced (Cecil et al., 1987; Vinson et al., 2009), acidic (Cecil et al., 1987; Dickson and Herczeg, 1992; Herczeg et al., 1988; Szabo and Zapecza, 1987; Vinson et al., 2009), and thermal waters (Kitto et al., 2005; Sturchio et al., 1993), as well as in low-saline fossil groundwater such as the Nubian Sandstone (Disi) aquifer in Jordan (Vengosh et al., 2009). Yet, the most common phenomenon is the high correlation between radium abundance and salinity (Carvalho et al., 2005; Hammond et al, 1988; Kraemer and Reid, 1984; Krishnaswami et al., 1991; Moatar et al., 2010; Moise et al., 2000; Otero et al., 2011; Raanan et al., 2009; Sturchio et al., 2001; Tomita et al., 2010 ; Vinson, 2011). Most of these studies have shown that the radium adsorption coefficient is decreased with increasing salinity, probably due to competition with other dissolved cations for adsorption sites (Dickson, 1990b; Krishnaswami et al., 1991; Sturchio et al., 2001; Webster et al., 1995).

A field-based experiment of MgCl₂ brine injection into fractured metamorphic and granitic rocks from the Hubbard

Brook Experimental Forest in New Hampshire, USA, resulted in a large release of 226 Ra (from near zero to 1200 dpm l⁻¹) from ion-exchange sites on the fracture surfaces. This brine injection experiment demonstrated that when transient cation solutions are introduced to an aquifer system as part of salt water flow in an aquifer (e.g., seawater or brine intrusion, road salts applications, migration of leachates from landfills), significant Ra mobilization can occur from the aquifer rocks to groundwater (Wood et al., 2004).

In addition to salinity, the chemical composition of saline water also controls the retardation of Ra and the relationship with salinity (Tomita et al., 2010; Vinson, 2011). For example, sulfate-rich saline water is associated with Ra co-precipitation with secondary barite minerals, whereas reduced conditions trigger Ra mobilization from adsorbed sites due to reductive dissolution of Fe and Mn oxides in which radium is highly retained (Vinson, 2011). The control of both salinity and the redox state on Ra activity has been shown in several studies (e.g., Cecil et al., 1987; Sturchio et al., 2001; Vinson et al., 2009) and is illustrated in the case of the saline groundwater from the Cretaceous carbonate aquifer (Judea Group) in the Negev, Israel (unpublished data), that shows a linear correlation of ²²⁶Ra with salinity and a reverse correlation with dissolved oxygen (Figure 28).

11.9.7.4 Trihalomethanes and Salinity

Chlorine disinfection is widely employed in municipal water systems. Elevated chloride and bromide contents in supply waters can lead to the formation of toxic disinfection byproducts, such as trihalomethanes (THMs), and specifically brominated THMs (e.g., bromodichloromethane – BDCM), during the chlorine disinfection process. The extent to which chlorine disinfection results in the formation of these



Figure 28 ²²⁶Ra activity (decay per minute) versus total dissolved salts (mg I^{-1}) and dissolved oxygen (mg I^{-1}) in groundwater from the Lower Cretaceous carbonate aquifer (Judea Group) in the Negev, Israel. Note that the increase of ²²⁶Ra activity with salinity is parallel to the inverse relationship with dissolved oxygen. Data from unpublished results, Duke University.

byproducts depends on the content and type of organic matter present, the quantity of chlorine used, pH, temperature, and reaction time (Chowdhury et al., 2010b). Epidemiological and toxicological studies have reported that brominated THMs such as BDCM are more carcinogenic than their chlorinated analogs (Krasner et al., 2002; Miltner et al., 2008; Nobukawa and Sanukida, 2000; Pressman et al., 2010; Richardson, 2008, 2009; Richardson and Ternes, 2005; Richardson et al., 2002, 2003, 2007). The US EPA set MCL values of 80 µg l⁻¹ for total THMs and BDCM and 10 µg l⁻¹ for bromate in drinking water, and has initiated the Stage 2 Disinfectants and Disinfection Byproducts Rule (Stage 2 Disinfectants and Disinfection Byproducts rule; US Environmental Protection Agency, 2012). In Canada, the regulatory limit is 16 µg l⁻¹ for BDCM (Health Canada, 2007).

Several studies have shown that the bromide content and Br/Cl of treated water play an important role in the generation of brominated THMs (Chowdhury et al., 2010a,b; Heller-Grossman et al., 2001; Richardson et al., 2003; Uyak and Toroz, 2007; Xue et al., 2008). Experimental increases in the bromide ion concentration of treated water resulted in increasing rates of total THM formation, with higher BDCM and dibromochloromethane (DBCM) compounds and lower chloroform formation. A threefold increase of bromide content (from 40 to $120 \,\mu g \, l^{-1}$) caused an increase in BDCM content (Chowdhury et al., 2010b).

The Sea of Galilee (Lake Kinneret) in Israel is an interesting natural case study with respect to these byproducts as the lake water is the major drinking water source for Israel (through the National Water Carrier) and the salt budget of the lake is controlled by the discharge of saline groundwater with high Br/Cl ratios, such as the Tiberias Hot Spring with chloride contents of 19000 mg l^{-1} and Br/Cl~0.005 (Kolodny et al., 1999; Nishri et al., 1999; Stiller et al., 2009). The salinity of the lake has fluctuated during the last decades due to variations in precipitation and water inflows coupled with human activities (e.g., pumping rates; Figure 13(b)). Studies in the early 2000s monitored chloride content of \sim 280 mg l⁻¹, total organic carbon (TOC) concentrations ranging between 4 and 6 mg l^{-1} , and high bromide ion concentrations (1.9 mg l^{-1} ; Br/ $Cl \sim 3 \times 10^{-3}$). The combination of hydrophilic organic matter and high bromide contents resulted in high concentrations of THMs in Lake Kinneret water (summer = 606 μ g l⁻¹), in which 96% of total THMs is in the form of brominated THMs, mostly as bromoform and dibromoacetic acid (Heller-Grossman et al., 2001; Richardson et al., 2003). Thus, high bromide levels in the source water can cause a significant shift in speciation to bromine-containing byproducts (Richardson et al., 2003).

Since the Br content and Br/Cl ratio of potable water play a significant role in the formation of brominated THMs, the origin and type of the saline waters that is involved in salinization of freshwater resources could also affect the occurrence and distribution of brominated THMs in chlorinated water. For example, salinization with a brine with a chloride content of ~100000 mg l⁻¹ into a freshwater reservoir at a dilution factor of ~350 would keep the chloride content below the WHO recommendation for drinking water of 250 mg l⁻¹ (Figure 29). However, the Br/Cl ratio of the original brine would control the expected bromide contents in the salinized water. Three types of brines with identical chloride content of ~100000 mg l⁻¹ are



Figure 29 Modeling the dilution of a brine with chloride content of $\sim 100\,000$ mg l⁻¹ upon three different brine sources: (1) evaporated seawater such as the Appalachian brine from the eastern United States with Br/Cl = 4×10^{-3} (Osborn and McIntosh, 2010; Warner et al., 2012); (2) fivefold evaporated seawater below halite saturation with marine Br/Cl = 1.5×10^{-3} ; and (3) brine originated from halite dissolution with low Br/Cl = 0.1×10^{-4} . Mixing simulations show that dilution of the brine to the drinking water threshold of chloride = 250 mg l⁻¹ would result in differential bromide contents in the diluted water, based on the original Br/Cl ratios of the parent brines.

considered: (1) an Appalachian brine from the eastern United States with Br/Cl $=4 \times 10^{-3}$ (Osborn and McIntosh, 2010; Warner et al., 2012); (2) fivefold evaporated seawater below halite saturation with marine $Br/Cl = 1.5 \times 10^{-3}$; and (3) brine originated from halite dissolution with low $Br/Cl = 0.1 \times 10^{-4}$. Mixing simulations of these three brine types show significant bromide variations; at the drinking water threshold of chloride = 250 mg l^{-1} , dilution with the Appalachian brine, evaporated seawater, and halite dissolution yields bromide contents of 2.5, 0.9, and 0.05 mg l^{-1} , respectively (Figure 29). Consequently, dilution of brine with a high Br/Cl ratio would be sufficient to generate potable water based on the chloride standard, but with high bromide contents that could trigger generation of highly toxic brominated THMs during chlorination of the salinized potable water. The nature and mechanism by which the saline waters originated (e.g., evaporation of seawater beyond halite saturation, dissolution of halite, domestic wastewater) will control the Br/Cl ratios of the brine and consequently the bromide content of the salinized water. The bromide factor therefore increases the health risks associated with the formation of toxic brominated THMs.

11.9.7.5 Salinity and Toxic Algae Bloom

Salinization of surface water could trigger harmful algae blooms toxic to fish. One of the most frequent causes of fish kills is the bloom of *Prymnesium parvum*. The *P. parvum* is a haptophyte alga, which is distributed worldwide. This alga is tolerant of large variations in temperature and salinity, and is capable of forming large fish-killing blooms (Baker et al., 2007, 2009;

Sager et al., 2008; Southard et al., 2010). This saltwater alga produces a potent toxin that is capable of killing fish, mussels, and salamanders (Sager et al., 2008). Studies of P. parvum blooms in lakes along the Brazos River in Texas, USA, have shown that large fish-killing blooms occurred when the freshwater inflows were low and the salinity was high (Roelke et al., 2011). In addition to the Brazos Basin in Texas, major fish kills, directly associated with P. parvum blooms, occurred in the Colorado, Red, and Rio Grande basins in the United States between 1981 and 2008, with an estimate of 34 million fish kills and an estimated economic loss of almost \$13 million (Southard et al., 2010). The maximum growth of P. parvum occurs under specific environmental conditions such as temperature, salinity, and light. While P. parvum has been found in water with a range of salinity (TDS from 1000 to 100000 mg l^{-1}), it was found that the maximal cell concentrations occurred at 26 °C and TDS of about 20000 mg l^{-1} , about 60% of seawater salinity (Baker et al., 2007). Furthermore, the chemical composition of the saline water, particularly the abundance of cations, and the pH control the production of the toxins; under high pH conditions, toxins form, while at pH < 7, they are minimized and fish kills will not occur (Sager et al., 2008).

One of the recent significant fish kills that occurred directly from blooming of *P. parvum* and high salinity was the massive fish, salamander, and mussel kill on Dunkard Creek in September 2009. The Dunkard Creek watershed lies along the border of West Virginia and Pennsylvania, USA (Reynolds, 2009). The saline water discharged to the Dunkard Creek had TDS of about 23 000 mg l^{-1} , and was composed of Na–Cl–SO₄ ions with low concentrations of Ca²⁺ and Mg²⁺ (data from Reynolds, 2009). This composition is not consistent with the expected chemistry of produced water associated with oil and gas wells (e.g., high Ca^{2+}), or with water associated with coalbed methane production (high HCO_3^- , low SO_4^{2-}). The combined high chloride (6120 mg l^{-1}) and sulfate (10800 mg l^{-1}) contents suggest an artificial blend probably from multiple sources. Yet, the impact of the discharged saline water on the blooming of P. parvum and associated fish kill in Dunkard Creek indicates that discharge of saline effluents can have devastating effects on ecological systems (Reynolds, 2009).

11.9.8 Elucidating the Sources of Salinity

Elucidating salinity sources in water resources is crucial for water management, model prediction, and remediation. Yet, the variety of salinization sources and processes makes this a difficult task. Ground- and surface water salinization can result from point sources (e.g., leakage or discharge of domestic wastewater) or nonpoint sources (e.g., agriculture return flows, irrigation with sewage effluent). Salinization can result from geologic processes such as natural saline-water flow from adjacent or underlying aquifers (Alcalá and Custodio, 2008; Bouchaou et al., 2008; Faye et al., 2005; Herczeg et al., 2001; Hsissou et al., 1999; Kloppmann et al., 2001; Maslia and Prowell, 1990; Mehta et al., 2000a,b; Sami, 1992; Sánchez-Martos and Pulido-Bosch, 1999; Sánchez-Martos et al., 2002; Shanyengana et al., 2004; Vengosh and Benzvi, 1994; Vengosh et al., 1999b, 2002, 2005; Warner et al., 2012). Alternatively, salinization can be induced by direct anthropogenic

contamination or combined effects such as seawater intrusion. The multiple salinity sources therefore present a real challenge to water agencies and regulatory bodies.

The key to tracing salinity sources is the assumption that the chemical composition of the original saline source is preserved during the salinization process (i.e., conservative nature of the dissolved constituents). Due to the large differences in the solute content between saline waters and freshwaters, the chemical composition of the contaminated water mimics the composition of the saline source. However, the original composition of the saline source can be modified via water–rock interactions. For example, the composition of seawater is significantly modified by base-exchange reactions as it intrudes into coastal aquifers. Consequently, diagnostic tracers must be conservative. Nonetheless, nonconservative tracers are also useful in delineating salinization sources as long as the possible modification processes are understood.

Often, the chemical composition of salinized water does not point to a single source or salinization mechanism, given overlaps and similarities in the chemical compositions of different saline sources. For example, the Na/Cl ratio can be a good tracer to distinguish marine (e.g., seawater intrusion with Na/ Cl<0.86) from nonmarine or anthropogenic sources (Na/ $Cl \ge 1$). However, the reactivity of Na⁺ in the unsaturated zone can reduce the Na/Cl ratio even in a nonmarine setting (e.g., DeSimone et al., 1997; Kass et al., 2005; Stigter et al., 1998; Vengosh and Keren, 1996). It is therefore essential to use assemblages of diagnostic chemical and isotopic tracers for accurate delineation of the salinity sources. Mazor (1997) and Herczeg and Edmunds (2000) reviewed most of the common geochemical tools that can be used to identify the different salinity sources of solutes. In general, dissolved constituents in salinized water can potentially be derived from (1) mixing between meteoric water and saline water such as seawater, connate brines, and hydrothermal waters trapped within or outside the aquifer; (2) dissolution of evaporites; (3) mineralization due to weathering of the aquifer minerals; (4) accumulation and leaching of salts in the unsaturated zone derived from long-term deposition of atmospheric fallout; or (5) anthropogenic contamination derived from sewage (domestic or industrial) effluents, deicing, agricultural return flows, oil- and gas-produced waters, and effluents from coal mining and coal ash leaching. Each of these sources has a unique and distinctive chemical and isotopic composition. While using individual tracers can provide useful information on these saline sources, integration of multiple geochemical and isotopic tracers can help resolve multiple salinity sources and provides a more robust and reliable evaluation of salinization processes (Alcalá and Custodio, 2008; Banner and Hanson, 1990; Böhlke, 2002; Boschetti et al., 2011; Bouchaou et al., 2008, 2009; Farber et al., 2004; Gattacceca et al., 2009; Hosono et al., 2010, 2011; Jørgensen and Banoeng-Yakubo, 2001; Kim et al., 2003; Langman and Ellis, 2010; Lu et al., 2008; Lucas et al., 2010; Millot and Negrel, 2007; Millot et al., 2007, 2010, 2011; Moller et al., 2008; Moore et al., 2008b; Otero et al., 2011; Sánchez-Martos and Pulido-Bosch, 1999; Sánchez-Martos et al., 2002; Sultan et al., 2008; Vengosh et al., 2002, 2005, 2007; Widory et al., 2004, 2005).

A summary of the geochemical and isotopic characteristics of some of these sources is given in **Table 2**. This section explores the use of assemblages of geochemical tracers, with

| Source | TDS (g l ⁻¹) | Na/Cl (molar ratio) | SO₄/CI (molar ratio) | Br/Cl (×10 ⁻³ , molar ratio) | B/Cl (×10 ⁻³ , molar ratio) | δ ¹¹ Β (‰) | δ ³⁴ S (‰) | ³⁶ Cl/Cl (×10 ⁻¹⁵) |
|--|-----------------------------|---------------------------|----------------------------|---|--|--------------------------|--------------------------|--|
| Seawater | 35 | 0.86 | 0.05 | 1.5 | 0.8 | 39 | 21 | <5 |
| Relics of evaporated seawater (brines) | >35 | <0.86 | < 0.05 | >1.5 | <0.8 | >39 | >21 | <5–100 |
| Evaporite dissolution | >1 | 1 | $\gg 0.05$ | <1.5 | <0.8 | 20-30 | <21 | <5 |
| Hydrothermal water | 0.2 to >1 | >1 | ≫0.05 | <1.5 | >5 | 0 ± 5 | ≪21 | <5 |
| Domestic wastewater | ~1 | >1 | >0.05 | <1.5 | 5 | 0–10 | 6–10 | 50->100 |
| Agricultural return flow | 0.5–5 | >1 | $\gg 0.05$ | <1.5 | >0.8 | 20–30 | | 50->100 |

 Table 2
 Typical chemical and isotopic characteristics of major saline sources

particular emphasis on the systematics of conservative (Br/Cl) and nonconservative (e.g., Na/Cl) elements, stable isotopes ($\delta^{18}O_{H_2O}$ and $\delta^{2}H_{H_2O}$), radioactive tracers (^{36}Cl and ^{129}I), and isotopes of dissolved constituents in the water ($\delta^{11}B$, $^{87}Sr/^{86}Sr$, $\delta^{34}S_{SO,4}$ and $\delta^{18}O_{SO,4}$).

The most common tracers that have been extensively used for delineating salinity sources are halogen ratios, due to the basic assumption that halogens behave conservatively in aquifer systems. In particular, the bromide to chloride ratio has been used extensively to delineate salinization processes (Alcalá and Custodio, 2008; Andreasen and Fleck, 1997; Cartwright et al., 2004, 2006, 2007a, 2009; Davis et al., 1998; Dror et al., 1999; Edmunds, 1996; Edmunds et al., 2003; Farber et al., 2004, 2007; Fontes and Matray, 1993; Freeman, 2007; Herczeg and Edmunds, 2000; Hsissou et al., 1999; Hudak and Blanchard, 1997; Katz et al., 2011; Kolodny et al., 1999; Leybourne and Goodfellow, 2007; Mandilaras et al., 2008; Matray et al., 1994; Mazor, 1997; Panno et al., 2006; Vengosh and Pankratov, 1998; Warner et al., 2012). Figure 30 illustrates the possible variations of Br/Cl and B/Cl ratios for different salinity sources. While several salinity sources have distinctive low Br/Cl ratios (e.g., wastewater, deicing, evaporite dissolution) relative to other sources with high Br/Cl ratios (brines evolved from evaporated seawater, animal waste, coal ash), possible overlaps may occur. Furthermore, bromide may not always behave as a conservative tracer, as laboratory-controlled adsorption experiments have shown some bromide retention at pH < 7 that can lead to modification of Br/Cl ratios during water transport in clay-rich systems (Goldberg and Kabengi, 2010).

The second layer in the evaluation of a salinity source is using different cations to chloride ratios such as Na/Cl and Ca/ Cl ratios. For example, seawater intrusion into coastal aquifers is associated with an inverse correlation between Na/Cl and Ca/Cl due to base-exchange reactions, resulting in low Na/Cl and high Ca/Cl ratios relative to seawater values (Appelo, 1994; Appelo and Geirnart, 1991; Appelo and Postma, 2005; Appelo and Willemsen, 1987; Custodio, 1987a,b, 1997; Jones et al., 1999). In contrast, wastewater and nonmarine salinity sources typically have Na/Cl > 1. This distinction may be biased, however, since the original Na/Cl ratio can be modified by water-rock interaction and base-exchange reactions that would reduce the Na/Cl ratio of saline water in nonmarine settings; hence, additional tracers are required.

Other common conservative tracers for salinization studies are the stable isotopes of the water molecule, oxygen ($\delta^{18}O_{H,O}$)



Figure 30 Elucidation of saline sources by using the variation of B/Cl versus Br/Cl ratios. Note the expected geochemical distinction between seawater, evaporated seawater, brines (e.g., Dead Sea), hydrothermal fluids, sewage effluents, agricultural drainage (e.g., Salton Sea), and evaporite dissolution.

and hydrogen ($\delta^2 H_{H_2O}$) isotopes (see Chapter 7.10). The use of stable isotopes of oxygen and hydrogen for tracing salinity sources in surface water may be complicated by evaporation effects that will result in enrichment of ¹⁸O_{H,O} and ²H_{H,O} combined with low $\delta^{18}O_{H_2O}$ / $\delta^2H_{H_2O}$ ratios relative to the original composition of the saline water. However, natural or artificial recharge of saline surface water into an aquifer can be identified by distinctive enriched 18OH,O and 2HH,O compositions. This distinction was used to trace the distribution of saline-treated wastewater and imported water from the Sea of Galilee that are artificially recharged into the Mediterranean coastal aquifer of Israel. Both wastewater and imported water are characterized by high $\delta^{18}O_{H_{2}O}$ and $\delta^{2}H_{H_{2}O}$ values that are different from those of the regional groundwater and thus the stable isotope variations can be used to monitor the mixing of the external water in the aquifer (Vengosh et al., 1999b).

While dilution of saline water would create small changes in the solute ratios (e.g., Br/Cl) due to the relatively high concentration of the solutes in the saline source relative to freshwater, the original $\delta^{18}O_{H,O}$ and $\delta^{2}H_{H,O}$ values of saline sources would be completely modified by mixing (dilution) with meteoric water (e.g., Banner et al., 1989; Bergelson et al., 1999; Hanor, 1994; Warner et al., 2012). Nevertheless, stable isotopes of oxygen and hydrogen in water can be used to evaluate mixing relationships in the case of seawater intrusion (Jones et al., 1999; Yechieli et al., 2000) or reflect agricultural return flows (Davisson and Criss, 1993; Kass et al., 2005). It is also possible to use the stable isotopes for detecting the origin of salinity derived from mixing with diluted saline water (e.g., residues of evaporated seawater, formation waters) that were diluted by freshwater with low $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ values, as opposed to salinization from direct seawater intrusion with higher $\delta^{18}O_{H,O}$ and $\delta^{2}H_{H,O}$ values. For example, Herczeg et al. (2001) showed that groundwaters in the Murray-Darling Basin have low $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ values relative to possible mixing between meteoric water and seawater, thus suggesting that the salinity of the groundwater in the basin is derived from atmospheric fallout with stable isotope meteoric composition and not from seawater intrusion. Similarly, Bergelson et al. (1999) showed that saline springs that emerge from the Sea of Galilee in the Jordan Rift Valley have low $\delta^{18}O_{H,O}$ and $\delta^{2}H_{H,O}$ values to account for direct evaporated brine and must therefore reflect multiple dilution stages of the original hypersaline brines. Finally, anthropogenic saline sources, such as domestic wastewaters that are treated or stored in open reservoirs, are often enriched in ¹⁸O and ²H, which can be used to trace their presence in contaminated groundwater (Vengosh et al., 1999b).

Radioactive isotopes of ³⁶Cl and ¹²⁹I that behave conservatively in the hydrological system are also important tools for studying salinization processes (see Chapter 7.14). Since 1952, atmospheric thermonuclear testing has significantly changed the ³⁶Cl budget in the atmosphere. The atmospheric ³⁶Cl fallout was several magnitudes higher than prenuclear flux, particularly between 1952 and 1970. Hence, the nuclear ³⁶Clpulse is an important hydrological tracer that is preserved in the hydrological system and its signal is modified only by dispersion and natural decay of ³⁶Cl (half-life~301000 years; Phillips, 2000). Modern meteoric chloride is characterized by a high ³⁶Cl/Cl ratio that is preserved during evaporative concentration and recycling of salts via precipitation-dissolution (Phillips, 2000). In contrast, other saline sources such as road salts and oilfield brines have significantly lower ³⁶Cl/Cl ratios. The distinction between meteoric and groundwater chloride (Figure 31) was used by several studies to estimate the relative proportion of meteoric and subsurface chlorine sources in the Jordan Valley and the Dead Sea (Magaritz et al., 1990; Yechieli et al., 1996), the closed basins in Antarctica (Lyons et al., 1998), and Lake Magadi of the East African Rift (Phillips, 2000).

Similarly, ¹²⁹I is a naturally occurring, cosmogenic and fissiogenic isotope ($T_{1/2}$ =15.7 My; Fabryka-Martin, 2000; Fabryka-Martin et al., 1991). Like ³H, ¹⁴C, and ³⁶Cl, ¹²⁹I was produced in bomb tests, but in greater abundance above the natural level. While some of the other anthropogenic radionuclides have returned to near prebomb levels, ¹²⁹I in the surface environment continues to be elevated due to subsequent emissions from nuclear fuel reprocessing facilities, and is transported via the atmosphere on a hemispheric scale. Modern meteoric waters are expected to have a large ¹²⁹I/¹²⁷I ratio (>1000 × 10⁻¹²) relative to that in old groundwater (<10⁻¹²; Moran et al., 1999, 2002). By combining the isotopic ratios



Figure 31 Schematic illustration of the expected ³⁶Cl/Cl variation versus the reciprocal of chloride (I g^{-1}) upon salinization by: (1) surface evaporation; (2) seawater intrusion; and (3) mixing with brines and/or dissolution of evaporites. Data were integrated from Magaritz et al. (1990), Yechieli et al. (1996), and Phillips (2000). The relatively high ³⁶Cl/Cl ratio in the Dead Sea suggests mixing with young meteoric chloride (Yechieli et al., 1996).

(³⁶Cl/Cl, ¹²⁹I/I) Ekwurzel et al. (2001) discriminated between different saline sources in the Souss-Massa Basin in Morocco, and particularly between modern saline recharge and older saline groundwater (Figure 32).

Using conservative tracers such as Br/Cl, $\delta^{18}O_{H,O}$ and ${}^{36}Cl/$ Cl ratios, it is possible to discriminate river salinization processes (Figure 33). Recycling and evaporation of meteoric salts by in-stream river salinization would result in increasing $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ values with flow distance, but the Br/Cl and ³⁶Cl/Cl ratios in the river would not be expected to change with increasing salinity (Figure 33). River salinization via discharge of agricultural return flow would likely increase the $\delta^{18}O_{H_2O}$ values and may change the Br/Cl ratio, but the ${}^{36}Cl/Cl$ would not be changed (i.e., short-term recycling of modern meteoric chlorine with a high ³⁶Cl/Cl ratio). However, in dryland environments the long-term storage of chlorine in the subsurface can be expected to buffer the original ³⁶Cl/Cl ratio. Dissolution of halite deposits and formation of saline groundwater can be expected to form saline groundwater with a low Br/Cl ratio (e.g., Rio Grande Basin; Phillips et al., 2003; Mills et al., 2002) and a low ³⁶Cl/Cl would ratio. In contrast, an increase of the Br/Cl ratio with salinity reflects discharge of saline groundwater that originated from mixing with relics of evaporated seawater that are entrapped in the basin (e.g., Jordan River; Farber et al., 2004, 2005, 2007). In such a scenario, the ³⁶Cl/Cl ratio is also expected to be low (Figure 33).

While conservative tracers can provide some indication of the solute sources, reactive tracers are as valuable, as they can



Figure 32 Elucidation of saline sources by using the variation of ³⁶Cl/Cl and ¹²⁹l/¹²⁷l ratios. Note the isotopic distinction between modern meteoric water and agricultural return relative to formation water, evaporite dissolution, and seawater. Arrows represent possible extended ranges. Data from Ekwurzel et al. (2001) and Moran et al. (2002).

provide essential information on both the original solutes and possible modifications upon interactions with the host sediments/rocks of the investigated aquifer. One example is the boron isotope ratio, which can be used as an indicator of both the solute sources and interaction with oxides and clay minerals in the aquifer rocks. The δ^{11} B values vary significantly from low values in nonmarine brines (e.g., Qaidam Basin, Tibet; $\delta^{11}B = 0$ to +10%; Vengosh et al., 1995) and anthropogenic sources such as coal (δ^{11} B as low as -70%; Williams and Hervig, 2004) and coal ash leachates ($\delta^{11}B = -15\%$; Ruhl et al., 2010), to high ratios in evaporated seawater $(\delta^{11}B=55\%; Vengosh et al., 1992)$ and in the Dead Sea $(\delta^{11}B = 57\%; Vengosh et al., 1991b)$. Yet, boron tends to be adsorbed onto clay minerals and oxides, particularly under high salinity conditions (see Section 11.9.7.2). During the adsorption process, the light isotopes, in the form of B (OH)₄⁻, incorporate preferentially into adsorbed sites whereas the residual dissolved boron in the form B(OH)₃ is enriched in ¹¹B. The magnitude of the boron isotope fractionation between the boron species has been debated; earlier studies have utilized the theoretical fractionation factor of 19% (α_{B3-B4} = 1.0193) proposed by Kakihana et al. (1977) while later theoretical (Byrne et al., 2006; Liu and Tossell, 2005) and experimental (Klochko et al., 2006) studies have suggested a larger fractionation of 27.2‰ ($\alpha_{B3-B4} = 1.0272$). Adsorption experiments conducted by Palmer et al. (1987) also suggested a larger isotope fractionation of about 30% between adsorbed and dissolved boron. In contrast, boron mobilization from rocks is not associated with isotopic fractionation and the mobilization of boron from a typically lower δ^{11} B composition of rocks reduces the δ^{11} B values of the water.

Taking into account the possible isotopic modification upon water-rock interactions, boron isotopes can be used to trace salinization processes and to delineate multiple salinity sources (Figure 34; Vengosh and Spivack, 2000). Increasing numbers of studies (Barth, 1998; Farber et al., 2004; Forcada and Evangelista, 2008; Katz et al., 2009; Kloppmann et al., 2009; Kruge et al., 2010; Leenhouts et al., 1998; Naftz et al., 2008; Rabiet et al., 2005; Ruhl et al., 2010; Vengosh and Spivack, 2000; Vengosh et al., 1994, 2002, 2005; Widory et al., 2004, 2005) have utilized these variations to detect the origin of saline groundwater, such as seawater intrusion into coastal aquifers with high δ^{11} B values and low B/Cl ratios, as opposed to anthropogenic contamination with significantly lower δ^{11} B values and high B/Cl ratios, such as wastewater and leachates from coal and coal ash. Figure 34 illustrates the B/Cl and boron isotope variations of some of the major salinity sources and shows the conspicuous differences between marine sources (e.g., seawater intrusion, evaporated seawater, connate brines, oil and gas brines) with high δ^{11} B values relative to wastewater, geothermal water, and contamination derived from leaching of coal and coal ash. During water transport and reactivity with oxides and clay minerals in the aquifer, the original isotopic fingerprints of the different end members will *always* be modified toward higher δ^{11} B values and lower B/Cl ratios due to the isotopic fractionation associated with boron retention. These modifications can mask the original isotopic fingerprints of the salinity sources but in many cases the *range* of the δ^{11} B values of the salinized groundwater will still be useful to distinguish different salinity sources. For example, in spite of isotopic fractionation associated with seawater intrusion and wastewater contamination, the δ^{11} B ranges of groundwater salinized from these two sources would be distinguishable (Vengosh et al., 1994).

The strontium isotope ratio is another sensitive tracer to delineate the origin of saline water, the type of rock source, and the impact of weathering processes (see Chapter 7.11). Due to the absence of isotopic fractionation, the isotopic composition of strontium mobilized from rocks during weathering is identical to that of the rock and thus strontium isotope geochemistry is a powerful tool for delineating solutes and salinization sources. Numerous studies have utilized strontium isotopes to detect the flow paths of groundwater in different aquifers (Banner and Hanson, 1990; Banner et al., 1989; Bullen et al., 1996, 1997; Katz and Bullen, 1996; Smith et al., 2009; Starinsky et al., 1980, 1983a,b; White et al., 1999), the composition of exchangeable strontium in clay minerals (Armstrong et al., 1998; Johnson and DePaolo, 1994; Vengosh et al., 2002), salinization from upflow of the Middle Devonian Marcellus brines in northeastern Appalachian basin (Warner et al., 2012), salinization from produced water from coal bed methane production (Brinck and Frost, 2007; Campbell et al., 2008), the origin of dissolved strontium in rivers (Farber et al., 2004; Moore et al., 2008b; Singh et al., 1998), mineralization of schist rocks with radiogenic Sr isotope ratios along the margin of the Lakhssas Plateau in the Anti-Atlas Mountains of southwestern Morocco (Ettayfi et al., 2012), and the interaction between groundwater, lake water, and aquifer minerals (Katz and Bullen, 1996; Lyons et al., 1995).

In carbonate or calcareous sand aquifers, the strontium isotopic composition of saline groundwater should mimic that of the host aquifer rocks. In cases where they are dissimilar, the groundwater must have interacted with external rock sources and thus must have flown in a different aquifer. For example, saline groundwater from central Missouri, USA, has high ⁸⁷Sr/⁸⁶Sr ratios that are considerably more radiogenic than the host Mississippian carbonates. The high ⁸⁷Sr/⁸⁶Sr



Figure 33 Schematic illustration of possible Br/Cl (a), $\delta^{18}O_{H_2O}$ (b), and ${}^{36}Cl/Cl$ (c) variations upon different river salinization scenarios: (1) surface evaporation of the river water; (2) recycling of salts via formation of agricultural return flow and discharge to the river; (3) discharge of external groundwater to the river with brine or old formation water components (i.e., high Br/Cl); and (4) discharge of external groundwater salinized by dissolution of evaporite deposits.

ratios suggested deep subsurface migration and water-rock interaction with Paleozoic and Precambrian strata (Banner et al., 1989). Similarly, the ⁸⁷Sr/⁸⁶Sr ratios of saline groundwater from the Mediterranean coastal aquifer of Israel are considerably lower than the 87Sr/86Sr ratios of the Pleistocene carbonate aquifer matrix, indicating an external source for the formation of the saline groundwater (Vengosh et al., 1999b). The flow of external saline water with a different ⁸⁷Sr/⁸⁶Sr ratio is therefore an important tool to delineate salinization processes. Several studies have used this approach, such as the cases of the Nubian Sandstone aquifer in the Negev, Israel (Vengosh et al., 2007), the Jordan River (Farber et al., 2004), the coastal aquifer of North Carolina (Vinson, 2011; Woods et al., 2000), the Oconee River Basin in the Piedmont region of northeastern Georgia (Rose and Fullagar, 2005), the RAK aquifer in southern Saudi Arabia (Sultan et al., 2008), the Lower

Rio Grande in the New Mexico–Texas border region, USA (Moore et al., 2008b), the saline water in the Anti-Atlas Mountains of southwestern Morocco (Ettayfi et al., 2012), and the Souss-Massa Basin in Morocco (Bouchaou et al., 2008).

Strontium isotopes can also be used to trace salinization by agricultural return flow. Böhlke and Horan (2000) showed that some fertilizers and hence agricultural recharge have high radiogenic ⁸⁷Sr/⁸⁶Sr ratios, significantly different from those of natural strontium acquired by water–rock interactions in the aquifer. Although denitrification and carbonate dissolution may alter the strontium isotopic ratio in redox conditions, the association of distinctive ⁸⁷Sr/⁸⁶Sr ratios and nitrate concentrations suggests that the Sr composition is controlled by the input of fertilizers in groundwater (Böhlke and Horan, 2000).

The sulfur $(\delta^{34}S_{SO_4})$ and oxygen in sulfate $(\delta^{18}O_{SO_4})$ isotope variations in salinized groundwater can provide additional



Figure 34 Elucidation of saline sources by using the variation of δ^{11} B versus B/Cl ratios. Note the expected geochemical distinction between seawater, evaporated seawater, brines (e.g., Dead Sea), and saltwater intrusion with typically high δ^{11} B values relative to hydrothermal fluids, sewage effluents, evaporite dissolution, and contamination from coal and coal ash leachates with significantly higher B/Cl ratios and lower δ^{11} B values.



Figure 35 Variations of sulfur isotope ratio in sulfate ($\delta^{34}S_{SO_4}$) in different possible saline sources. Note the large range of $\delta^{34}S_{SO_4}$ values in marine evaporites that reflect the secular variations of $\delta^{34}S_{SO_4}$ in seawater with time and the high $\delta^{34}S_{SO_4}$ value of seawater relative to nonmarine and anthropogenic sources. Sulfate reduction processes are expected to increase the $\delta^{34}S_{SO_4}$ values in the residual sulfate.

information on the salinity sources. Seawater has distinctive isotopic characteristics ($\delta^{34}S_{SO_4} = +21\%$; $\delta^{18}O_{SO_4} = +9.5\%$) relative to nonmarine salinity sources, typically with lower $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values (Figure 35). High sulfate in non-coastal groundwater could be derived from oxidation of reduced inorganic sulfur components with low $\delta^{34}S_{SO_4}$ and

 $\delta^{18}O_{SO_4}$ values (-30% to +5%; -10% to +5%, respectively), or from dissolution of sulfate deposits. The isotopic ratios of marine gypsum vary with geological age and range from +10%to +35‰ and +9‰ to +20‰ for $\delta^{34}S_{SO}$ and $\delta^{18}O_{SO,\prime}$ respectively. Sulfate reduction causes isotopic fractionation in which the heavy isotopes, ³⁴S and ¹⁸O, become enriched in the residual sulfate-depleted water. Consequently, seawater intrusion and hypersaline brines are characterized by low SO4/Cl ratios and high $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ values due to sulfate reduction processes (Kim et al., 2003; Krouse and Mayer, 2000; Moore et al., 2008b; Oulhote et al., 2011; Raab and Spiro, 1991; Sanz et al., 2007; Yamanaka and Kumagai, 2006). Examples for salinization of groundwater from dissolution of evaporite sulfate deposits include the Nubian Sandstone aquifer of the Negev, Israel (Vengosh et al., 2007) and the Hueco Bolson aquifer, located within the Trans-Pecos Texas region and the primary water resource for El Paso, Texas, USA, and Juarez, Mexico (Druhan et al., 2008).

Anthropogenic sources such as domestic wastewater $(\delta^{34}S_{SO}, \text{ of } -0.5\% \text{ to } 14.3\%; \text{ Houhou et al., } 2010; \text{ Torssander}$ et al., 2006), fertilizers (-2.1% to +1.6%; Szynkiewicz et al., 2011), animal manure (+2.7%; Szynkiewicz et al., 2011), and industrial waste (+1-8%; Cortecci et al., 2002) have high sulfate (high SO₄/Cl ratios) with low $\delta^{34}S_{SO_4}$ characteristics (Figure 35). The $\delta^{34}S_{SO}$ data (range of -1.6% to +0.9%) from the Rio Grande River in New Mexico and western Texas, USA, showed that the high sulfate content in the river was derived from local fertilizers and not from the associated Paleozoic evaporite rocks that are characterized by higher $\delta^{34}S_{SO_4}$ values (Szynkiewicz et al., 2011). Overall, while different saline sources can have distinctive sulfur isotopic fingerprints (Figure 35), under anaerobic conditions sulfate reduction can mask the original isotopic signature, and the $\delta^{34}S_{SO}$ and $\delta^{18}O_{SO}$ values of the salinized groundwater will *always* be higher than the expected mixing relationships between the freshwater and the saline sources.

11.9.9 Remediation and the Chemical Composition of Desalination

As the world experiences explosive population growth, increasing demands for food and energy are associated with depletion of worldwide water resources and degradation of water quality. About 70% of the world's freshwater is utilized, particularly for irrigated agriculture. In order to meet global food demands, agricultural production will have to increase by twofold or threefold during the coming decades and the exploitation of freshwater resources will further increase (Gleick, 1994, 1998; Hanasaki et al., 2008a,b ; Hern and Feltz, 1998; Kim et al., 2009 ; Oki and Kanae, 2006; Vorosmarty et al., 2000). The expected increase in the human population during this century (8-12 billion by the year 2050; Roush, 1994) will increase demands for freshwater and cultivation of marginal land. Furthermore, projections for future renewable water resources in arid and semiarid areas such as the Middle East and northern Africa are alarming; climate change coupled with projected increasing water demand are likely to amplify the already profound water shortage in these regions Sowers et al., 2011. The Intergovernmental Panel on Climate Change (IPCC) (Christensen et al., 2007) and other independent studies predict

a significant reduction in precipitation in the Middle East and northern Africa by the next century (Alpert et al., 2008; Arnell, 1999; Conway and Hulme, 1996; Evans, 2008; Milly et al., 2005; Sánchez et al., 2004; Suppan et al., 2008). The combination of reduced recharge, enhanced evaporation, and pumping beyond replenishment capacity will likely cause severe and adverse environmental impacts, and in particular increasing salinization of water resources.

In principle, two technical solutions can be adopted by water agencies facing long-term salinization of water resources dilution and desalination. Dilution is the cheapest solution for pollution, which depends on the availability of freshwater resources. In many depleted or salinized aquifers, artificial recharge or irrigation of imported water occurs from areas of relatively high water abundance: for example, the northern-southern water transport in California, USA; the flow of snowmelt and rivers from the Atlas Mountains to the sub-Sahara Draa and Ziz basins in Morocco for irrigation of oases; and the transport of water from the Sea of Galilee in Israel through the National Water Carrier for artificial recharge in the Mediterranean coastal aquifer. This import and use of external water sources compensates, at least temporarily, for overexploitation and salinization of aquifers. Artificial recharge of external water will modify the oxygen and deuterium isotopic compositions of the natural groundwater. In some cases, where the recharge water is derived from upstream and higher elevation, the recharge will result in lower $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ values. This was demonstrated by the recharge of the Colorado River aqueduct water into the Pacific coastal aquifer of Orange County, California (Davisson et al., 1999; Williams, 1997). In contrast, in cases where the recharge water is derived from open-surface reservoirs with evaporation (e.g., recharge of Salinas River, California; Vengosh et al., 2002), lakes (e.g., recharge of imported water from the Sea of Galilee into the Mediterranean coastal aquifer, Israel; Vengosh et al., 1999b), and wastewater treated in open basins (Vengosh et al., 1999b), the $\delta^{18}O_{H,O}$ and $\delta^{2}H_{H,O}$ values are expected to be significantly higher than those of the natural groundwater. Given the water shortage, interbasin transfers are, however, a less feasible solution for most water-scarce regions.

Desalination, in contrast, could be the ultimate solution for providing potable water to water-scarce countries. The water crisis in the Middle East, for example, could be resolved primarily by large-scale desalination of seawater and brackish water (Glueckstern, 1992). In 1998, 12500 desalination units around the world produced about 23 million cubic meters per day (Glueckstern and Priel, 1998). A decade later (2009), 14451 desalination plants globally produced almost 60 million cubic meters per day of desalted water (International Desalination and Water Reuse, 2011), and under-construction and planned desalination plants are expected to generate an additional 11 and 25 million cubic meters per day of desalted water in the near future, respectively (data from desaldata.com updated to November 2010; Windler, 2011). Until 2000, the capacity of new installed desalination plants fluctuated between 1 and 2 million cubic meters per year, but since 2000, the capacity of newly installed desalination plants has increased rapidly to 6-7 million cubic meters per year

(International Desalination and Water Reuse, 2011). One of the critical factors that led to the accelerated rates of desalination is the significant improvement in reverse osmosis (RO) membrane technology, replacing older technologies such as thermal desalination. By 2009, about half of the global desalted water was produced using RO desalination technology and newer desalination facilities are entirely based on membrane technology (Greenlee et al., 2009). Nonetheless, Saudi Arabia, which is currently the world leader in desalination with approximately 26% of global production capacity, almost entirely uses thermal desalination. The United States on the other hand, which is ranked second and produces 17% of the world's desalted water, uses predominantly (~70%) RO desalination technology (Greenlee et al., 2009). The world's largest RO desalination plant was installed in Israel in 2005 with a production capacity of $330\,000 \text{ m}^3 \text{day}^{-1}$ (Dreizin, 2006; Kronenberg, 2004; Lokiec and Kronenberg, 2003; Sauvet-Goichon, 2007). Israel is expected to expand its desalination capacity so that it becomes the primary source for the domestic sector; it has already developed new desalination capacity of 345 million cubic meters per year and is planning to double this to 660 million cubic meters per year by 2013 (data from desaldata.com updated to November 2010; Windler, 2011).

Consequently, the chemical composition of future water resources in the twenty-first century is likely to reflect these human interventions – the creation of 'new water' from desalination. The rapid worldwide increase in desalination production generates new types of water that are added to the natural hydrological cycle through leakage, irrigation, and recycling by wastewater irrigation. The Anthropocene Era is therefore characterized by generating new 'man-made water.' Man-made water has different chemical and isotopic characteristics from natural waters. Given that RO is the leading desalination technology, the review of the geochemistry of desalted water is focused here on the effect of RO desalination.

The chemistry of RO desalted water depends on (1) the source water that is used for desalination, which can range from seawater to brackish to saline groundwater with a large spectrum of chemical compositions (Greenlee et al., 2009); (2) the ion selectivity through the membranes, which depends on ion mass, size, charge, and reactivity (Kloppmann et al., 2008b; Mukherjee and Sengupta, 2003); and (3) posttreatment processes that shape the chemistry of the produced water (Birnhack et al., 2011). While the composition of seawater is uniform, desalination of brackish to saline groundwater could generate desalted water with different chemical and isotopic compositions relative to natural waters. The most conspicuous difference is the stable isotope composition of desalted water; desalination generates low-saline water with $\delta^{18}O_{H,O}$ and $\delta^2 H_{H,O}$ values that are identical to those of the saline water source. Thus, desalination of seawater generates freshwater with $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ of seawater, which are significantly different from the depleted ${}^{18}O_{H_2O}$ and ${}^{2}H_{H_2O}$ composition of meteoric water. For example, the stable isotope signatures of RO desalted freshwater from the Ashkelon desalination plant in Israel ($\delta^{18}O_{H_2O} \sim +2\%$; $\delta^2H_{H_2O} \sim +12\%$; Figure 36) and the Sabkha C desalination plant in Eilat, Israel ($\delta^{18}O_{H_2O} \sim 0\%$; $\delta^2 H_{H,O} \sim +2\%$), are clearly different from the stable isotope compositions of fresh meteoric water (Kloppmann et al.,



Figure 36 $\delta^2 H_{H_20}$ versus $\delta^{18} O_{H_20}$ values of reverse osmosis (R0) desalted seawater and the Global Meteoric Water Line (Craig, 1961). The Anthropogenic Line lies on a possible mixing relationship between natural waters along the meteoric water line (arrow) and the desalted seawater. Future formation of a large volume of desalted seawater is expected to cause infiltration (e.g., leakage, reuse) of man-made freshwater with high $\delta^2 H_{H_20}$ and $\delta^{18} O_{H_20}$ values relative to natural meteoric waters with lower $\delta^2 H_{H_20}$ and $\delta^{18} O_{H_20}$ values.

2008b). Consequently, recharge of freshwater originating from desalination either by leakage in the urban environment or wastewater irrigation would have $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ values that lie along a mixing line between the natural and seawater values (Figure 36). The slope of the *Anthropogenic Line* depends on the $\delta^{18}O_{H_2O}$ and $\delta^2H_{H_2O}$ values of the meteoric water in the local area and will always be lower than those of natural meteoric lines with a slope <8 (Figure 36).

The second factor that controls the chemistry of RO desalted water is the preferential permeability of ions through the RO membrane. Ion transport through the membrane depends on ion mass, size, charge, and reactivity (Mukherjee and Sengupta, 2003). The rejection by the RO membrane is higher for heavier molecules; thus, the molar Na/Cl ratio is modified from 0.86 in seawater to 0.94 in desalted water (Table 1; data from Kloppmann et al., 2008b). The preferential selection by the RO membrane of double-charged ions (Ca^{2+} , Mg^{2+} , SO_4^{2-}) over single-charged ions (Cl⁻, Na⁺) also modifies the original chemical composition and ionic ratios of the desalted water. Thus, desalted seawater is modified into an Na-Cl freshwater type (Cl+Na/TDI~0.93, in equivalent units) and the Ca/Cl, Mg/Cl, SO₄/Cl, and Ca/Na ratios of RO desalted water are significantly lower (by fivefold) relative to those in the original seawater (Table 1). Similarly, nanofiltration membranes, with a negatively charged hydrophobic rejection layer, tend to selectively reject multivalent ions but have low rejection efficiency for monovalent ions (Kharaka et al., 1996, 1997).

Perhaps one of the most conspicuous ion selections that are associated with RO desalination is the selective transport of noncharged species such as boric acid $(B(OH)_3^0)$ and arsenic acid $(H_3AsO_3^0)$ relative to the rejection of charged species. Pretreatment processes typically reduce the pH of the saline water source in order to reduce scaling, and consequently boron exists mostly in the form of uncharged boric acid (see Figure 27 for the dependence of boron species on pH). For processed seawater (pH < 6.5) and saline groundwater from North Carolina (pH 7.8), it was calculated (based on salinity, pH, and pressure) that boric acid forms 99% (Kloppmann et al., 2008b) and 93% (Vinson, 2011) of the total boron, respectively. The noncharged nature of boric acid generates differential permeability of boron species through the RO membranes in which boric acid is not rejected as effectively as other, charged, ions. As a result, boron is enriched in desalted water with conspicuously high B/Cl ratios (Cengeloglu et al., 2008; Geffen et al., 2006; Georghiou and Pashafidis, 2007; Hyung and Kim, 2006; Kloppmann et al., 2008b; Mane et al., 2009; Ozturk et al., 2008; Parks and Edwards, 2005; Prats et al., 2000; Sagiv and Semiat, 2004; Tu et al., 2011; Vinson et al., 2011). The B/Cl of desalted water can reach 0.4 (Kloppmann et al., 2008b) relative to 8×10^{-4} in seawater, a 500-fold enrichment.

Given that boron isotope fractionation depends on the species distribution in which the heavy boron isotope ¹¹B tends to be enriched in boric acid, RO desalination can also induce isotopic fractionation. Under low pH desalination, where boric acid is the dominant species of boron, no isotope fractionation is expected, and thus the boron isotope composition of the desalted water will be identical to that of the saline source. This was demonstrated for both seawater (Kloppmann et al., 2008b) and brackish groundwater (Vinson et al., 2011) during RO desalination. In contrast, under high-pH desalination, where ¹¹B-depleted borate ion is rejected by the RO membrane, selective transport of boric acid species through the membrane will induce isotopic fractionation, which will result in ¹¹B-enriched desalted water (Kloppmann et al., 2008b). The Ashkelon RO desalination plant (Dreizin, 2006; Kronenberg, 2004; Lokiec and Kronenberg, 2003; Sauvet-Goichon, 2007) includes four cascade desalination stages, operating both at high- and low-pH conditions (Gorenflo et al., 2007), which reduce boron concentrations of the desalted water below 0.4 mg l⁻¹. At pH 9.5, where borate ion composes 95% of the dissolved boron, the desalted water is highly enriched in ¹¹B ($\delta^{11}B = 58\%$) relative to seawater (39%; Kloppmann et al., 2008b).

In addition to boron, the absorption of noncharged arsenic by the RO membrane also depends on the prevalence of charged As species in the saline water source. Arsenic speciation in water depends on oxidation state and pH. Under reducing conditions, arsenic occurs as arsenite (As(III)) in which the uncharged H₃AsO₃⁰ is the dominant species at pH below 9. Under oxic conditions, arsenate (As(V)) species are stable, particularly the monovalent species $H_2AsO_4^-$ (pH < 6.5) and the divalent species $HAsO_4^{2-}$ (pH > 6.5). Consequently, RO rejection for the charged As(V) in oxygenated water is more effective (George et al., 2006; Geucke et al., 2009; Moore et al., 2008a, Oreskovich and Watson, 2003; Walker et al., 2008). Desalination of reduced brackish to saline groundwater in which arsenic occurs as the reduced species arsenite (As(III)) therefore requires an additional treatment system to remove arsenic, as demonstrated in desalination of groundwater from the coastal aquifer of North Carolina (Vinson et al., 2011).

The third process that shapes the composition of desalted water is posttreatment of desalted water. Permeates after RO desalination contain low dissolved constituents and thus low buffering capacity that make the water very soft with low Ca²⁺ and Mg²⁺ contents (Birnhack et al., 2011; Delion et al., 2004;

Lahav and Birnhack, 2007). Such soft supply water could trigger corrosion of pipes (Sarin et al., 2004), a concern for older homes with lead-solder piping. In addition, several studies have shown an inverse relationship between magnesium content in drinking water and the pathogenesis of cardiovascular diseases (Mason, 2011). Furthermore, some studies have identified adverse effects on soils irrigated with desalted water (Lahav and Birnhack, 2007; Yermiyahu et al., 2007). Consequently, the Israeli Ministry of Health mandates specific water-quality characteristics for desalinated water before distribution in the drinking water system that include alkalinity as $CaCO_3 > 80 \text{ mg l}^{-1}$, Ca^{2+} between 80 and 120 mg l⁻¹, and pH < 8.5 (Birnhack et al., 2011).

In order to increase the alkalinity, posttreatment of RO desalted water could include (1) direct introduction of chemicals (e.g., hydrated lime - Ca(OH)₂, calcium salts); (2) blending with seawater or brackish groundwater; and (3) reaction with a calcite or dolomite rock matrix that will result in dissolution of Ca²⁺, Mg²⁺ (for dolomite), and HCO₃⁻ into the desalted water. In order to accelerate the carbonate dissolution, either CO2 or H2SO4 are added, followed by pH adjustment using NaOH base (Birnhack et al., 2011). These posttreatment techniques will change the composition of the desalted product. For example, in the Ashkelon desalination plant in Israel, addition of H₂SO₄ results in high Ca²⁺ and SO₄²⁻ contents relative to the RO permeate water, whereas calcite dissolution by carbon dioxide, as in the Larnaca desalination plant in Cyprus, resulted in moderate Ca²⁺ enrichment without any change in the conspicuously low SO₄/Cl ratio that characterizes the RO chemical fractionation (Kloppmann et al., 2008b). Nevertheless, the distinctive $\delta^{18}O_{H_2O_1}$, $\delta^2H_{H_2O_1}$, B/Cl, and $\delta^{11}B$ signatures associated with RO desalination are not affected by posttreatment processes and can be distinguished from natural water sources (Kloppmann et al., 2008b).

In addition to desalination of seawater and brackish groundwater, wastewater is another potential source that can be reused upon desalination. Since the dissolved inorganic constituents of sewage effluents are not removed during first and secondary sewage treatment procedures (Vengosh and Keren, 1996; Vengosh et al., 1994), high levels of salinity in treated water is one of the major limiting factors for using treated wastewater for irrigation (Rebhun, 2004). Desalination of treated wastewater could therefore provide an additional adequate water source upon removal of salts, organic matter, and pharmaceuticals (Deegan et al., 2011; Glueckstern and Priel, 1997; Glueckstern et al., 2008; Harussi et al., 2001; Ozaki and Li, 2002; Priel et al., 2006, 2009; Rebhun, 2004). Similar to RO desalination of seawater, the unique chemical and isotopic characteristics of wastewater are retained and even reinforced during desalination. This includes the stable isotope composition ($\delta^{18}O_{H,O}$ and $\delta^{2}H_{H,O}$) of treated wastewater that is typically enriched relative to groundwater (Vengosh et al., 1999a) and boron enrichment with a distinctive δ^{11} B range of 0–10% (Kloppmann et al., 2008a; Vengosh and Spivack, 2000; Vengosh et al., 1994, 1999a,b). For example, low-pH desalination of wastewater from Flanders, Belgium, showed desalted wastewater with high $\delta^{18}O_{H_2O}$ and $\delta^2 H_{H_2O}$ values and high boron with high B/Cl ratios and low δ^{11} B values of ~0% (Kloppmann et al., 2008a).

Finally, the formation of new water from desalination also generates saline effluents that could become an undesirable

salinization source. Seawater RO desalination plant recovery is typically limited to 40-65% of the volume of the inlet saline water and consequently the TDS levels of brines from seawater RO plants are usually in the range of 65000-85000 mg l⁻¹. The actual brine salinity will therefore be determined by the ratio of the permeate flow rate to feed flow rate (Voutchkov, 2011). For example, the RO desalination plant in Larnaka, Cyprus, generates brines with TDS of 74200 mg l^{-1} relative to Mediterranean seawater with TDS of 41125 mg l^{-1} , a concentration factor of 1.8 (data from Kloppmann et al., 2008b). In contrast, desalination of lower-salinity brackish groundwater or wastewater will allow larger fractional recoveries of 75-90% of the inlet water, which will result in larger concentration factors of 4-10 (Voutchkov, 2011). For example, the TDS of brines generated from desalination of brackish groundwater in Nitzna (Negev), Israel, was $\sim 40000 \text{ mg l}^{-1}$, relative to 4630 mg l^{-1} in the inlet water, a concentration factor of 8.6 (data from Kloppmann et al., 2008b). In addition to salts, brines from RO desalination may contain acids, bases, phosphates, and organic polymers due to the use of scale inhibitors (Voutchkov, 2011). Most of the coastal RO desalination plants dispose of their brines through ocean outfall (e.g., Ashkelon, Israel; Larnaka, Cyprus). RO brines are also disposed to the ocean via discharge canals from power plants in which the cooling water is blended with the RO brines, thus reducing the salinity of the discharged water (Voutchkov, 2011). Yet, in noncoastal areas, disposal of RO brines could become a limiting factor due to the large potential salinization effects of the brines. In areas where the brackish groundwater has high levels of radioactivity, such as the Nubian Sandstone aquifers of the Middle East (Vengosh et al., 2009), RO desalination would reject the charged radium nuclides but the residual brines would become enriched in radium (Rosenberg and Ganor, 2009).

The chemical and isotopic compositions of RO brines reflect the geochemical fractionation that occurs during RO desalination (Kloppmann et al., 2008b), particularly for constituents that are rejected or selected by the RO membrane. While the ratios of the major elements and isotopic compositions of stable oxygen and hydrogen in RO brines mimic the compositions of the inlet saline waters, dissolved constituents that are selectively transferred to RO permeates become depleted in the residual brines. For example, the B/Cl ratio of RO brines would drop to lower than the original saline water sources. This was demonstrated in brine compositions from the Eilat (Israel) desalination plant where brines in different sections of the desalination plant had lower B/Cl ratios relative to the saline inlet water (e.g., $B/Cl = 6 \times 10^{-4}$ in Sabkha C brine relative to inlet seawater with B/Cl ratio = 8×10^{-4}). The isotopic composition of boron in low-pH RO desalination brine will not be modified and will mimic the isotopic composition of the saline inlet water (Kloppmann et al., 2008b). Consequently, brines originated from RO desalination of seawater are expected to have low B/Cl ratios ($<8 \times 10^{-4}$) and marine isotope ratio ($\delta^{11}B = \sim 39\%$), which differ from the composition of saltwater intrusion due to elemental boron depletion and ¹¹B enrichment ($<8 \times 10^{-4}$; $\delta^{11}B > 39\%$; Figure 34) associated with boron adsorption during seawater intrusion (Vengosh et al., 1994).

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