

# 9.09

## Salinization and Saline Environments

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### 9.09.1 INTRODUCTION

One of the most conspicuous phenomena of water-quality degradation, particularly in arid and semi-arid zones, is salinization of water and soil resources. Salinization is a long-term phenomenon, and during the last century many aquifers and river basins have become unsuitable for human consumption owing to high levels of salinity. Future exploitation of thousands of wells in the Middle East and in many other water-scarce regions in the world depends, to a large extent, on the degree and rate of salinization. Moreover, every year a large fraction of agricultural land is salinized and becomes unusable.

Salinization is a global environmental phenomenon that affects many different aspects of our life (Williams, 2001a,b): changing the chemical composition of natural water resources (lakes, rivers, and groundwater), degrading the quality of water supply to the domestic and agriculture

sectors, contribution to loss of biodiversity, taxonomic replacement by halotolerant species (Williams, 2001a,b), loss of fertile soil, collapse of agricultural and fishery industries, changing of local climatic conditions, and creating severe health problems (e.g., the Aral Basin). The damage due to salinity in the Colorado River Basin alone, for example, ranges between \$500 and \$750 million per year and could exceed \$1 billion per year if the salinity in the Imperial Dam increases from  $700 \text{ mg L}^{-1}$  to  $900 \text{ mg L}^{-1}$  (Bureau of Reclamation, 2003, USA). In Australia, accelerating soil salinization has become a massive environmental and economic disaster. Western Australia is “losing an area equal to one football oval an hour” due to spreading salinity (Murphy, 1999). The annual cost for dryland salinity in Australia is estimated as AU\$700 million for lost land and AU\$130 million for lost production (Williams *et al.*, 2002). In short, the salinization process has become pervasive.

Salinity in water is usually defined by the chloride content ( $\text{mg L}^{-1}$ ) or total dissolved solids content (TDS,  $\text{mg L}^{-1}$  or  $\text{g L}^{-1}$ ), although the chloride comprises only a fraction of the total dissolved salts in water. The Cl/TDS ratio varies from 0.1 in nonmarine saline waters to  $\sim 0.5$  in marine-associated saline waters. Water salinity is also defined by electrical conductivity (EC). In soil studies, the electrical conductivity and the ratio of  $\text{Na}/\sqrt{(\text{Ca} + \text{Mg})}$  (SAR) are often used as an indirect measure of soil salinity. In addition to chloride, high levels of other dissolved constituents may limit the use of water for domestic, agriculture, and industrial applications. In some parts of Africa, China, and India, for example, high fluoride content is associated with saline groundwater and causes severe dental and skeletal fluorosis (Shiklomanov, 1997). Hence, the “salinity” problem is only the “tip of the iceberg,” as high levels of salinity are associated with high concentrations of other inorganic pollutants (e.g., sodium, sulfate, boron, fluoride), and bioaccumulated elements (e.g., selenium, and arsenic) (see Chapter 9.03).

The World Health Organization (WHO) recommends that the chloride concentration of the water supply for human consumption should not exceed  $250 \text{ mg L}^{-1}$ . Agriculture applications also depend upon the salinity level of the supplied water. Many crops, such as citrus, avocado, and mango, are sensitive to chloride concentration in irrigation water (an upper limit of  $250 \text{ mg L}^{-1}$ ). In addition, long-term irrigation with water enriched with sodium results in a significant reduction in the hydraulic conductivity and hence the fertility of the irrigated soil. Similarly, the industrial sector demands water of high quality. For example, the high-tech industry requires a large amount 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 a variety of applications.

The salinity problem is a global phenomenon but it is more severe in water-scarce areas, such as arid and semi-arid zones. The increasing demand for water has created tremendous pressures on water resources that have resulted in lowering water level and increasing salinization. For example, in the Middle East salinity is the main factor that limits water utilization, and future prospects for water use in Israel, Palestinian Authority, and Jordan are overshadowed by the increasing salinization (Vengosh and Rosenthal, 1994; Salameh, 1996). The salinity problem has numerous grave economic, social, and political consequences, particularly in cross-boundary basins that are shared by different communities (e.g., Salinas Valley California; Vengosh *et al.*, 2002a), friendly states (e.g., salinization of the Colorado River along Mexico-US border;

Stanton *et al.*, 2001), and hostile states (e.g., the Jordan River, Vengosh *et al.*, 2001; Aral Basin, Weinthal, 2002; Euphrates River, Beaumont, 1996; and the Nile River, Ohlsson, 1995).

Salinization of water resources also affects agricultural management. The type of irrigation water and its quality determine the salinity and fertility of the soil and eventually the quality of the underlying water resource. The use of treated wastewater or other marginal water (e.g., brackish water) depends on the salinity and the chemical composition of the water. Treated wastewater with high contents of chloride, sodium, and boron is suitable only for salt-tolerant crops and requires special treatment of the soil. Finally, high boron in irrigation water and consequently in soil water is also an important limiting factor for crops, as boron is an essential micronutrient for plants but becomes toxic at high levels (typically  $>0.75 \text{ mg L}^{-1}$  in irrigation water).

This chapter investigates the different mechanisms and geochemistry of salinization in different parts of the world. The role of the unsaturated zone in shaping the chemical composition of dryland salinization is discussed. Special emphasis is on the anthropogenic effects and to man-made fluids and reused water, such as treated wastewater and agricultural drainage water. Two anthropogenic salinization cycles are introduced—the agricultural and the domestic cycles. Some useful geochemical fingerprinting tracers are also included for defining the sources of salinity. Finally, the chemical composition of future water resources is predicted, based on the chemical and isotopic fractionation associated with remediation and desalination.

## 9.09.2 RIVER SALINIZATION

More than one-half of the world's major rivers are being seriously depleted and polluted, degrading and poisoning the surrounding ecosystems, and threatening the health and livelihood of people, who depend on them for drinking water and irrigation. Rivers are being depleted because the global demand for water is rising sharply. The problem will be further aggravated by the need to supply food, drinking water, and irrigation waters for an additional two billion people on Earth by 2025 (Serageldin, 2000). The World Commission on Water for the twenty-first century (Serageldin, 2000) defines the most stressed rivers as: the Yellow River in China, Amu Darya and Syr Darya in Central Asia, Colorado River in the western USA, the Nile River in Egypt, Volga River in Russia, Ganges River in India, and the Jordan River in the Middle East.

Salinization of surface waters occurs mainly due to a combination of natural and anthropogenic processes. In the natural setting, particularly in the

dryland environment, salts are deposited on the ground, stored in the subsurface, and 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 1). About 50% of arid land is located in “endorheic” regions whence 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, which have no outlets.

Salinization of rivers also occurs due to human intervention, e.g., diversion of upstream natural flow, dam construction, and consequently significant reduction of natural flow discharge. For example, the Amu Darya and Syr Darya rivers in Central Asia were almost desiccated due to the diversion of water for cotton irrigation in the former Soviet Union (Weinthal, 2002). The estimated historical annual flow in these two rivers is  $122 \times 10^9 \text{ m}^3$ . By the mid-1980s, the Amu Darya and Syr Darya no longer flowed to the Aral Sea (Micklin, 1988, 1992).

In a classic paper, Pillsbury (1981) described how recycling of salts via irrigation and agricultural return flow controls the salinity of downstream rivers in arid zones. Once the natural salt balance is disturbed and salts begin to accumulate, either in the unsaturated zone or in drainage waters, the salinity increases. 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 back to the river (Pillsbury, 1981). Similarly, the rise of the salinity in the Nile Delta has been attributed to a disturbance of the natural salts balance after the construction of Assuan dam and the reduction of the natural outflow of salts from the Nile River to

the Mediterranean Sea. About  $50 \times 10^9 \text{ m}^3$  of the Nile water is used for irrigation, from which the recycling of drainage water increases the salinity of the northern part close to the outlets to the Mediterranean Sea (Kotb *et al.*, 2000). Saline drainage water is also the primary source of salinity of the Euphrates and Tigris rivers in Iraq (Robson *et al.*, 1983; Fattah and Abdul Baki, 1980), coupled with sewage pollution (Mutlake *et al.*, 1980; Al-Muhandis, 1977), and reduction of the discharge of the river. Since the mid-1960s, Turkey has embarked on a large-scale program for the development of southeastern Turkey using water as the main agent of change (Beaumont, 1996). The Southeastern Anatolian Project (GAP) with the giant Ataturk dam is one of the largest water projects in the world. It utilizes more than  $13 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$  from the Euphrates and Tigris rivers for irrigation. Consequently, the annual flow of the rivers reduced by 30–50% (of an annual natural discharge of  $\sim 30 \times 10^9$ ; Beaumont, 1996). Massive irrigation in Syria and Iraq has resulted in the formation of saline agricultural return flows that are mixed with local shallow groundwater and then discharged back to the downstream sections of the river. As a result, the salinity of the Euphrates River, close to its confluence into the Persian Gulf, is higher than  $3,000 \text{ mg L}^{-1}$  (Robson *et al.*, 1983; Fattah and Abdul Baki, 1980).

In the dryland environment, river salinization occurs as a response to land clearing of deep-rooted natural vegetation, which accelerates recharge rates and causes groundwater tables to rise. 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 Murray River (Herczeg *et al.*, 1993). Large-scale clearing of natural vegetation and its replacement by annual

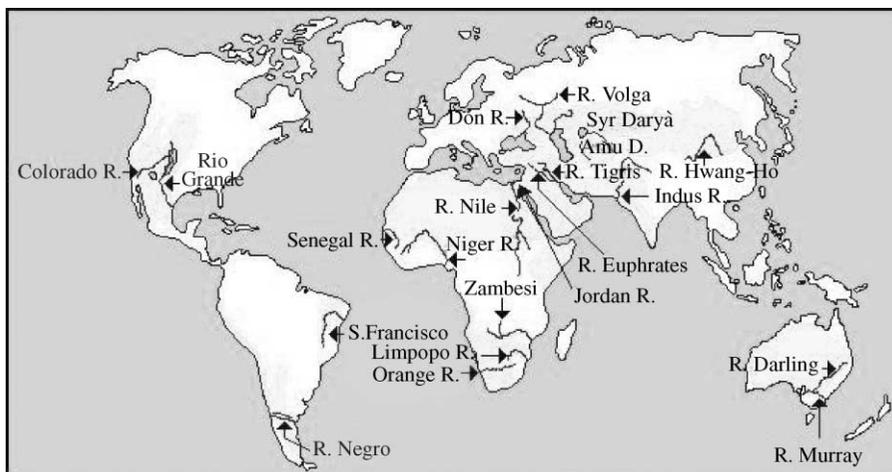


Figure 1 Major river systems and arid and semi-arid regions of the world.

crops and pastures has increased the amount of water leaking through the unsaturated zone. Excess irrigation has also increased groundwater levels (Williams *et al.*, 2002 and references there in). The rise of saline groundwater and mobilization of salts stored in the unsaturated zone has formed saline seepages that discharge to streams and the soil surface, which affects runoff salinity. In the Murray River in South Australia (Table 1) water salinity has been gradually increasing since the 1950s, and the 2000–2001 salinity level exceeded international water standards (defined as  $800 \mu\text{s cm}^{-3}$ ) for  $\sim 10\%$  of the year (Williams *et al.*, 2002; Jolly *et al.*, 2000). In the Sandspruit River, a tributary of Berg River in the semi-arid western Cape Province of South Africa, salinization of the river (TDS range from  $4,500 \text{ mg L}^{-1}$  to  $9,000 \text{ mg L}^{-1}$ ) is also attributed to accumulation and leaching of salts from the soil. Salt mass-balance estimations suggest that the salts are derived from both recycling of meteoric aerosols and soil leaching (Flugel, 1995).

A different type of river salinization in a dryland environment is represented by the Jordan River Basin along the border between Israel and Jordan. A 10-fold reduction of surface water flow in the Jordan River ( $(50\text{--}200) \times 10^6 \text{ m}^3$  today relative to  $\sim 1,400 \times 10^6 \text{ m}^3$  in historical times) and intensification of shallow groundwater discharge resulted in the salinization of the Jordan River. During August 2001, the salinity of the southern end of the Jordan River, just before its confluence into the Dead Sea, reached  $11 \text{ g L}^{-1}$ , a quarter of the Mediterranean seawater salinity. Based on Na/Cl, Br/Cl,  $^{87}\text{Sr}/^{86}\text{Sr}$ ,  $\delta^{11}\text{B}$ ,  $\delta^{34}\text{S}_{\text{sulfate}}$ , and  $\delta^{18}\text{O}_{\text{water}}$ . ( $\delta^{11}\text{B} = [({}^{11}\text{B}/{}^{10}\text{B})_{\text{sample}} / ({}^{11}\text{B}/{}^{10}\text{B})_{\text{NBS-SRM-951}} - 1] \times 10^3$ ),  $\delta^{34}\text{S}_{\text{sulfate}} = [({}^{34}\text{S}/{}^{32}\text{S})_{\text{sample}} / ({}^{34}\text{S}/{}^{32}\text{S})_{\text{VCDT}} - 1] \times 10^3$ , and  $\delta^{18}\text{O}_{\text{water}} = [({}^{18}\text{O}/{}^{16}\text{O})_{\text{sample}} / ({}^{18}\text{O}/{}^{16}\text{O})_{\text{SMOW}} - 1] \times 10^3$ ) whereas NBS SRM 951, VCDT, and SMOW are international standards (Coplen *et al.*, 2002) variations, the salinity rise of the southern section of the Jordan River (Table 1; Figure 2) was attributed to the discharge of saline groundwater (Vengosh *et al.*, 2001). It was suggested that the shallow saline groundwater was formed by mixing of saline groundwater originated from leaching of local saline sediments and deep hypersaline brines. Likewise, the salinity of the Rio Grande River increases to  $\sim 2,000 \text{ mg L}^{-1}$  along a distance of 1,200 km. The parallel decrease of the Br/Cl ratio of the salinized river implies discharge of saline groundwater that has interacted with halite deposits (Phillips *et al.*, 2002).

Salinization of rivers can also occur in temperate climatic zone owing to direct anthropogenic contamination. For example, the Rhine River suffers from the discharge of potash mine drainage brines since the opening of potash mines  $\sim 100$  yr 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 natural load of less than  $5 \text{ kg s}^{-1}$  to more than  $300 \text{ kg s}^{-1}$  in the 1960s (Meybeck and Helmer, 1989). Another example is the Arno River in northern Tuscany that is polluted by wastewaters, which has resulted in a downstream increase of  $\text{Na}^+$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$  ions with a characteristic sulfur isotopic composition (Cortecci *et al.*, 2002).

In sum, there are four major sources of soluble salts in river basins: (i) meteoric salts; (ii) salts derived from water–rock interaction (e.g., dissolution of evaporitic rocks); (iii) salts derived from remnants of formation water entrapped in the basin; and (iv) anthropogenic salts (e.g., wastewater effluents). 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.

### 9.09.3 LAKE SALINIZATION

Naturally occurring salt lakes reflect hydrological equilibrium states that have been developed during geological time (see Chapter 5.13). The wide range of chemical composition of natural salt lakes reflects a variety of sources: salts that are derived from the evolution of freshwater inflows (e.g., Great Salt Lake, Utah; Spencer *et al.*, 1985), hydrothermal fluids (Qaidam Basin, China; Vengosh *et al.*, 1995), remnants of evaporated seawater (Dead Sea, Israel; Starinsky, 1974; Stein *et al.*, 1997), and accumulation of marine aerosols over an exposed continent (Lake Eyre, Australia; Chivas *et al.*, 1991; Vengosh *et al.*, 1991a; Herczeg *et al.*, 2001). Human-induced activities may modify the natural conditions, as in the case of the Dead Sea. The diversion of natural tributaries has significantly reduced the inflows, which has resulted in a sharp decrease in the water level of the Dead Sea. Every year the water level of the Dead Sea drops by a meter (Yeichieli *et al.*, 1998; Salameh and Naser, 1999). In contrast, the term *lake salinization* used here refers to direct anthropogenic activity and the ongoing transformation of freshwater lakes into salt lakes.

In principle, the diversion of water from one basin to another or the use of natural river inflows are the basic processes that lead to lake salinization. The consequences can be devastating: for example, the diversion of  $\sim 100\%$  of the water from the Amu Daryà and Syr Daryà rivers in central Asia to grow cotton and other crops led to the desiccation of the Aral Sea, a fivefold increase in its water salinity ( $59 \text{ g L}^{-1}$  during 1991

**Table 1** Chemical composition of saline water from various sources. The ion concentrations are reported in mg L<sup>-1</sup>, whereas the ionic ratios are molar.

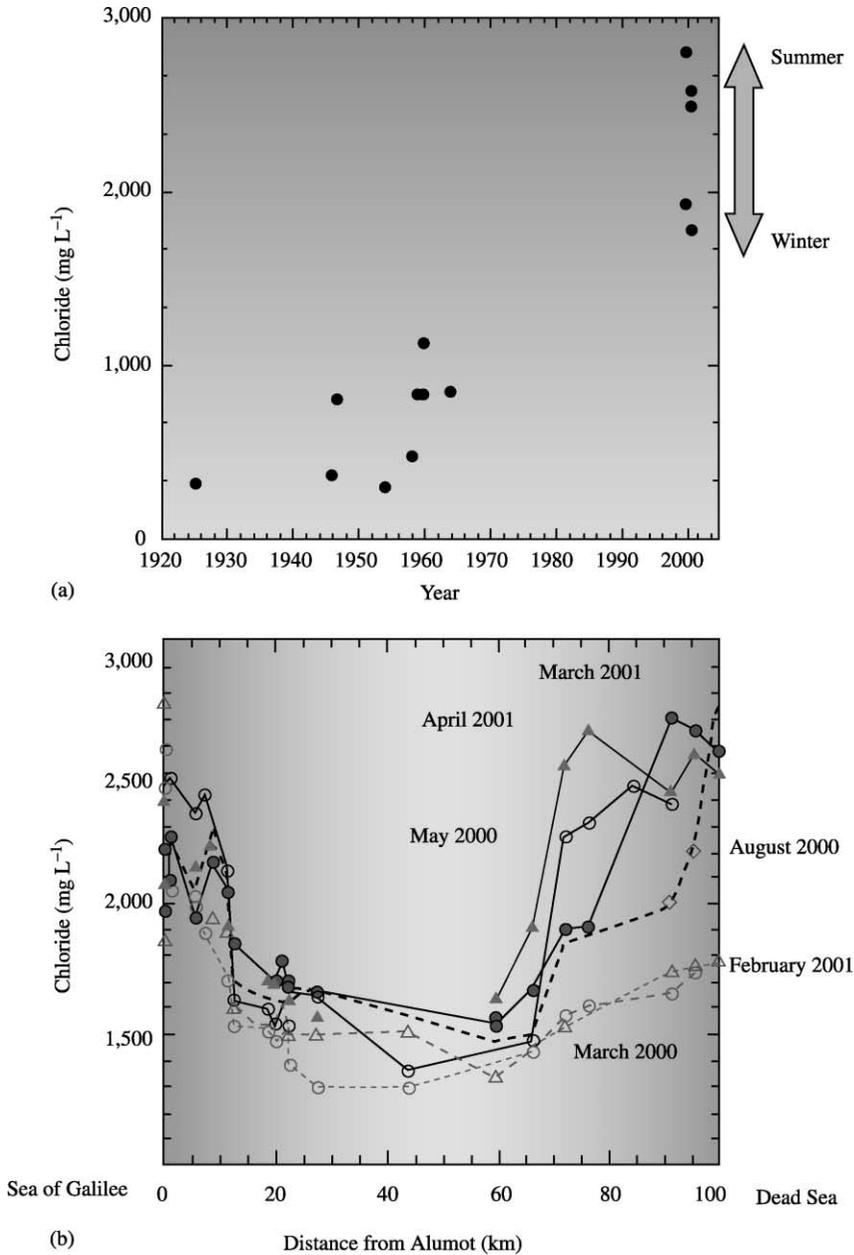
<i>Site</i>	<i>Source</i>	<i>TDS</i>	<i>Ca</i>	<i>Mg</i>	<i>Na</i>	<i>K</i>	<i>Cl</i>	<i>SO<sub>4</sub></i>	<i>HCO<sub>3</sub></i>	<i>NO<sub>3</sub></i>	<i>Br</i>	<i>B</i> (ppb)	<i>Na/Cl</i>	<i>SO<sub>4</sub>/Cl</i>	<i>Br/Cl</i>	<i>B/Cl</i> ×10 <sup>-3</sup>	
<i>Seawater (Red Sea)</i>		41,390	418	1,442	12,396	516	23,290	3,077	161		75.6	5.3	0.86	0.05	1.5	0.8	
<i>Freshwater river</i>																	
	Amzon River	1	39	5.2	1.0	1.5	0.8	1.1	1.7	20		6	2.1	0.6		18.2	
	Orinoco River	1	35	3.3	1.0	1.5	0.7	2.9	3.4	11		2	0.8	0.4		27.1	
	Mississippi (1905)	1	216	34	8.9	11	2.8	10.3	25.5	116			1.7	0.9			
	Mackenzie	1	211	33	10.4	7	1.1	8.9	36.1	111		12	1.2	1.5		4.4	
	Danube	1	307	49	9	9	1	19.5	24	190			0.7	0.5			
	Congo	1	34	2.4	1.4	2	1.4	1.4	1.2	13.4		3	2.2	0.3		7.2	
	Zambeze	1	58	9.7	2.2	4	1.2	1	3	25			6.7	1.1			
<i>Saline river</i>																	
	Murray River, South Australia	2	448	21	17	101	6	171	38	94	0.4		0.91	0.08	1.1		
	Jordan River (south end)	3	1,109	545	705	23,00	170	5,370	1,650	254	20	81	2,800	0.66	0.11	6.7	1.7
	Tigris River (Baghdad, 1977)	4	521	64	21.7	47.7		82.6	66.5	238	10		200	0.89	0.3		8.7
<i>Saline Lakes</i>																	
	Salton See (1989)	5	40,700	950	1,300	11,000	220	17,000	10,000	185	13	12,000	1.0	0.22	0.3	2.3	
	Aral Sea (1991)	6	59,120	1,020	3,600	14,600	640	22,650	16,180	430			0.99	0.26			
	Caspian Sea	7	12,385	340	700	3,016	88	5,233	3,008				0.89	0.2			
	Dead Sea, Rift valley	8	337,800	17,600	42,120	41,300	7,600	224,200	280	200	4,500	54,690	0.28	0.005	10	0.8	
<i>Seawater intrusion</i>																	
	Coastal aquifer, Israel	9		980	245	2,830	22	6,304	470	206	21.3	950	0.69	0.03	1.5	5.0	
	Salinas Valley, California	10		410	126	450	12	1,670	212	62	5.4	245	0.42	0.05	1.5	4.8	

(continued)

**Table 1** (continued).

<i>Site</i>	<i>Source</i>	<i>TDS</i>	<i>Ca</i>	<i>Mg</i>	<i>Na</i>	<i>K</i>	<i>Cl</i>	<i>SO<sub>4</sub></i>	<i>HCO<sub>3</sub></i>	<i>NO<sub>3</sub></i>	<i>Br</i>	<i>B</i> (ppb)	<i>Na/Cl</i>	<i>SO<sub>4</sub>/Cl</i>	<i>Br/Cl</i>	<i>B/Cl</i> ×10 <sup>-3</sup>
<i>Saline plumes and upcoming of brines</i>																
Coastal aquifer, Israel (Beer Toviyya)	11	2,560	176	97	545	3.9	1,125	143	370	98	3.5	508	0.75	0.05	1.4	1.5
Ogallala aquifer, Texas	12	67,530	1,460	388	23,850	32	36,120	5,610	41		6.2		1.0	0.06	0.07	
Dammam aquifer, Kuwait	13	4,062	470	138	635	15.2	1,241	1,189	77	8		1,500	0.77	0.35		3.9
Jordan Valley, Jericho, Cenomanian aquifer	14	8,270	490	580	1,700	110	4,950	105	275	62	83		0.52	0.02	7.4	
Pleistocen aquifer	14	3,100	156	208	590	84	1,372	295	363	29	10		0.66	0.16	3.3	
Groundwater associated with freezing process																
Sweden	15	18,200	3,690	31	2,850	12	11,100	522	7		79		0.39	0.02	3.1	
Finland	15	14,400	3,900	13	1,500	7	8,900	1	21		77		0.25	<0.01	3.8	
<i>Agricultural drainage</i>																
San Joaquin Valley, California	16	4,580	192	242	952		499	2,650		44		5,940	2.9	1.9		3.9
Mendota, San Joaquin Valley, California	17	14,280	438	285	3,720	3.1	1,210	8,350	250	25	3.4		4.7	2.5	1.2	
Imperial Valley, California	5	6,715	310	330	1,420	19	1,200	3,000	383	53			1.9	0.9		
Imperial Valley, California	5	8,250	560	320	1,700	24	2,600	2,700	342	5	2.3	1,700	1.0	0.4	0.4	2.0
<i>Wastewaters</i>																
Dan Reclamation Project, Israel (1993)	18	1,300	80	30	264	34.2	361	112.5	420		0.4	500	1.1	0.11	0.5	6
Orleans, Cape Cod, Massachusetts	19	1,700	440	0.3	100	30	950	19	134	30		200	0.16	0.007		0.7

Sources: 1. E. K. Berner and R. A. Berner (1987); 2. Herczeg *et al.* (1993); 3. Vengosh *et al.* (2001); 4. Mutlak *et al.* (1980); 5. Schroedar and Rivera, (1993); 6. Linnikov and Podberezny (1996); 7. Peeters *et al.* (1999); 8. Starinsky (1974). 9. Vengosh *et al.* (1994); 10. Vengosh *et al.* (2002a); 11. Vengosh *et al.* (1999); 12. Mehta *et al.* (2000a); 13. Al-Ruwaith (1995); 14. Marie and Vengosh (2001); 15. Bein and Arad (1992); 16. Mitchel *et al.* (2000); 17. Kharaka *et al.* (1996); 18. Vengosh and Keren (1996); 19. DeSimone *et al.* (1997).

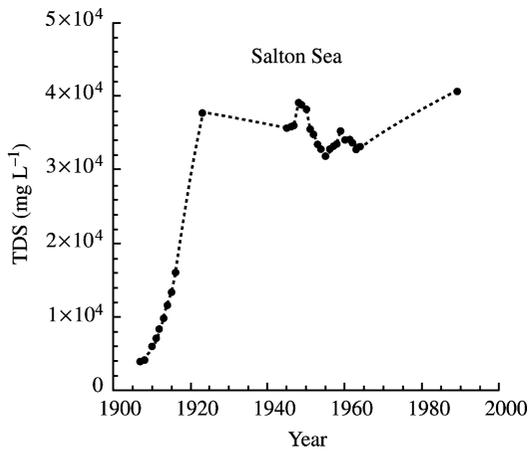


**Figure 2** Salinization of the Jordan River. (a) Evolution of the chloride content during the twentieth century as recorded in Abdalla Bridge, the southern point of the Jordan River before its entry into the Dead Sea. (b) Chloride variation transects along the Jordan River. Distance in km refers to the beginning of the river flow (Alumot dam) below the Sea of Galilee (source [Vengosh et al., 2001](#)).

([Linnikov and Podberezny, 1996](#)), destruction of the fisheries industry, and accelerating health problems in the region ([Micklin, 1988, 1992](#)). Finally, draining saline agricultural return flow from the Imperial Valley in Southern California during the twentieth century into the permlinal lake of the Salton Sea ([Figure 3](#)) resulted in salt accumulation and the creation of salt lake with a salinity of  $43 \text{ g L}^{-1}$  ([Schroeder et al., 1991, 2002](#); [Schroeder and Rivera, 1993](#); [Hely et al., 1966](#); [Amrhein et al., 2001](#)). The salinity rise of a lake may

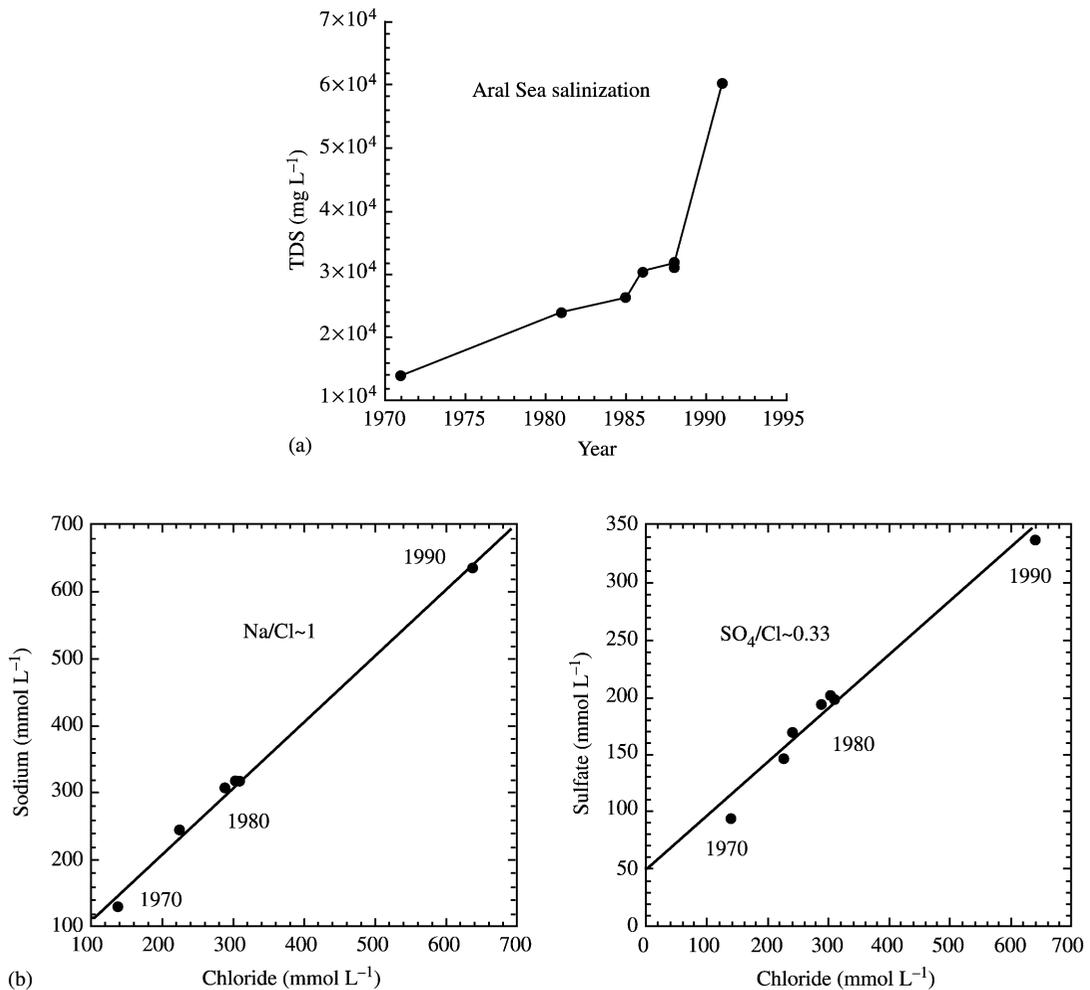
lead to a dramatic change in the ecological system and change in the species composition (e.g., rise of brine shrimp), which in turn will also modify the food chain mechanism in the lake, and consequently the bioaccumulation of toxic elements such as selenium (see [Chapter 9.02](#); [Glenn et al., 1999](#)).

Two types of lake salinization are considered. The first type is the imbalance between evaporation and water inflow, usually due to the diversion of freshwater discharge. This is demonstrated

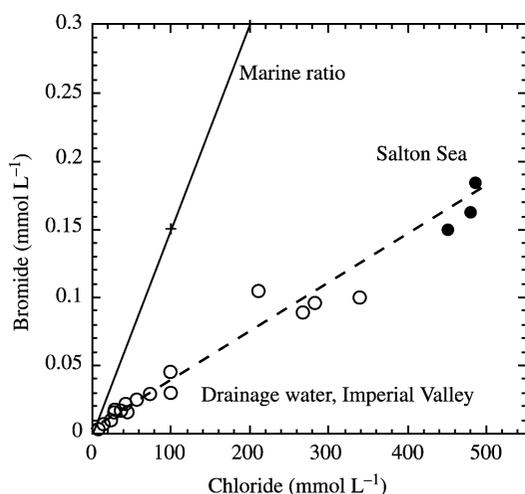


**Figure 3** Historical salinization of the Salton Sea (California, USA) during the twentieth century (sources: Schroeder *et al.*, 1991; Schroeder and Rivera, 1993; Amrhein *et al.*, 2001).

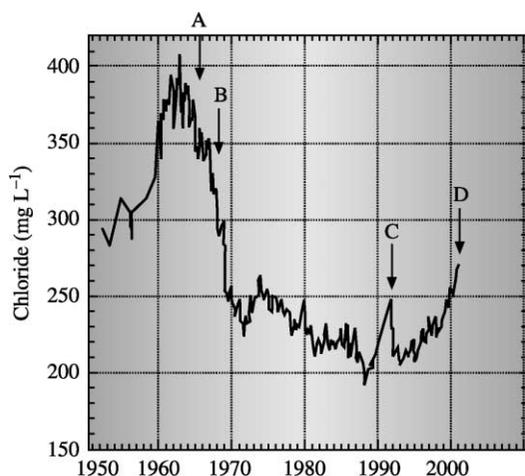
in the case of the Aral Sea (Table 1), where the chemical composition of the brackish water during early stages of salinization (salinity of  $14 \text{ g L}^{-1}$  in 1971) is identical to that of brines during later stages (salinity of  $56 \text{ g L}^{-1}$  during 1991; Figure 4; Linnikov and Podberzny, 1996). The second type of lake salinization is related to saline inflow coupled with evaporation within the lake. The source of the saline inflow can be anthropogenic, as in the case of the Imperial Valley in California, where agricultural return flow with a salinity of  $1\text{--}3 \text{ g L}^{-1}$  flows into the Salton Sea (Table 1; Figure 5). Alternatively, natural saline springs (salinity up to  $40 \text{ g L}^{-1}$ ) flow to the Sea of Galilee (Figure 6) in the northern Jordan Valley and control the chemical composition of the lake (salinity of  $\sim 0.5 \text{ g L}^{-1}$ ; Kolodny *et al.*, 1999; Nishri *et al.*, 1999). In both cases, the chemical composition of the saline inflows dominates the composition of the salinized lake.



**Figure 4** Salinization of Aral Sea. (a) The rise of the salinity during the 1970s and 1980s. (b) Sodium and sulfate versus chloride concentrations (in  $\text{mmol L}^{-1}$ ) as measured in the lake during different times. Note the linear relationships between the different ions, indicating that the initial chemical composition of the saline lake was not modified during the salinization process (source: Linnikov and Podberzny, 1996).



**Figure 5** Bromide versus chloride concentrations (in  $\text{mmol L}^{-1}$ ) of agricultural drainage waters (open circles) and the 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, inferring that the lake was originated from agricultural drainage inflow. The Br/Cl ratios are lower than the marine ratio, indicating dissolution of halite mineral (sources Schroeder *et al.*, 1991; Schroeder and Rivera, 1993; Amrhein *et al.*, 2001).



**Figure 6** Historic evolution of the chloride content (in  $\text{mg L}^{-1}$ ) of Sea of Galilee, Israel. The variations of the salinity of the lake reflect human operational stages: (i) during the mid-1960s the salinity increased due to the damming of the natural outflow of the lake; (ii) diversion of the saline springs that emerge to the lake (point A) initiated reduction of the salinity, followed by major flood events (point B) during the late 1960s; (iii) low level of the salinity marinated during the 1970s to 1990s as a result of a salt balance between freshwater input, saline water discharge, and pumping; and (iv) drought years (points C and D) resulted in significant reduction of the lake level and extensive evaporation and consequently salinization of the lake (data from the archive of the Hydrological Service, Israel).

In addition to the reduction of freshwater discharge, the fate and the rate of future salinization of lakes depends on the chemical composition of the lakes (see Chapter 5.13). Precipitation of minerals (Hardie and Eugster, 1970) and the activity of the saline water form important negative feedbacks that limit salt accumulation in the lakes. In this respect, the saturation level of calcite, gypsum, and halite in brines can determine the salinity and composition of the residual brines. In the Salton Sea, the lake water has a total salinity of  $43 \text{ g L}^{-1}$  and is oversaturated with respect to calcite, which controls the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  level of the lake. Biologic activity, sulfate reduction processes, and base-exchange reactions ( $\text{Na}^+$  removal) add additional dissolved  $\text{Ca}^{2+}$ , which enhances calcite precipitation (Amrhein *et al.*, 2001). At higher salinity levels, such as in the Dead Sea (Table 1) with a salinity of  $340 \text{ g L}^{-1}$ , the low water activity and thus the low vapor pressure of the hypersaline brines imposes low evaporation rates. Yechieli *et al.* (1998) predicted that despite 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 (Yechieli *et al.*, 1998). In sum, while the rate of salinization is rapid during the early stages of salinization, it decreases at evolved stages due to salt precipitation and the low water activity of the brines. As the salinity increases, the rate of lake salinization is expected to decrease.

## 9.09.4 GROUNDWATER SALINIZATION

### 9.09.4.1 Seawater Intrusion

Salt-water intrusion is one of the most widespread and important processes that degrade water quality to levels exceeding acceptable drinking and irrigation water standards, and endanger future water exploitation in coastal aquifers. This problem is intensified by large population growth, and the fact that  $\sim 70\%$  of the world population occupies the coastal plain zones. Human activities (e.g., pumping, agriculture, reuse of wastewater) increase the rate of salinization (Jones *et al.*, 1999). Salt-water intrusion into coastal aquifers has been identified in the eastern Atlantic (Meisler *et al.*, 1985; Wicks *et al.*, 1995; Wicks and Herman, 1996) and the western Pacific (Izbicki, 1991, 1996; Todd, 1989; Vengosh *et al.*, 2002a) coasts of the USA. Seawater intrusion occurs even under extremely humid climatic conditions, as in the Jeju volcanic island in South Korea, where the annual average rainfall is  $\sim 1,870 \text{ mm}$  and the estimated groundwater recharge is  $1.4 \times 10^9 \text{ m}^3 \text{ yr}^{-1}$ .

Although the groundwater withdrawal in the volcanic island is only 5% of the estimated replenishment, Br/Cl and  $\delta^{18}\text{O}$  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). As a result of global warming, a rise of sea level could lead to seawater intrusion in similar volcanic islands in the Pacific and further salinization of their groundwater.

Fossil seawater that represents past invasions into coastal aquifers accompanying rise in sea level can be documented by the apparent old age inferred by the  $^{14}\text{C}$  and  $^3\text{H}$  data of saline waters as reported in Germany (Hahn, 1991), Belgium (De Breuck and De Moor, 1991), India (Sukhija, 1996), and Israel (Yecheili *et al.*, 2001).

In many coastal aquifers around the world, modern seawater intrusion commonly occurs owing to extensive freshwater withdrawals. Ocean water itself has a salinity of 35 g L<sup>-1</sup> (TDS), while internal seas have higher (e.g., Mediterranean Sea, Red Sea; TDS ~40 g L<sup>-1</sup>) or lower salinities. Nevertheless, seawater has a uniform chemistry due to the long residence time of the major constituents. There is a predominance of Na<sup>+</sup> and Cl<sup>-</sup> with a molar ratio of 0.86, an excess of Cl<sup>-</sup> over the alkali ions (Na + K), and Mg<sup>2+</sup> greatly in excess of Ca<sup>2+</sup> (Mg/Ca = 4.5–5.2; Table 1). Seawater has also a uniform Br/Cl ( $1.5 \times 10^{-3}$ ),  $\delta^{18}\text{O}_{\text{water}}$  (0–1‰),  $\delta^{34}\text{S}_{\text{sulfate}}$  (21‰),  $\delta^{11}\text{B}$  (39‰), and  $^{87}\text{Sr}/^{86}\text{Sr}$  (0.7092) values. In contrast, the chemical compositions of fresh groundwaters is highly variable, though typically they are composed of Ca–Mg–HCO<sub>3</sub>. In most cases Ca<sup>2+</sup> dominates over Mg<sup>2+</sup>. The most striking phenomenon that characterizes seawater intrusion into coastal aquifers is the difference between the chemical composition of the saline water associated with salt-water intrusion and the theoretical mixture of seawater with groundwater (Jones *et al.*, 1999). In many cases, the saline water has a Ca-chloride composition (i.e., the ratio of Ca/(SO<sub>4</sub> + HCO<sub>3</sub>) > 1) with low ratios of Na<sup>+</sup>, SO<sub>4</sub><sup>2-</sup>, K<sup>+</sup>, and B to chloride relative to modern ocean water (Table 1).

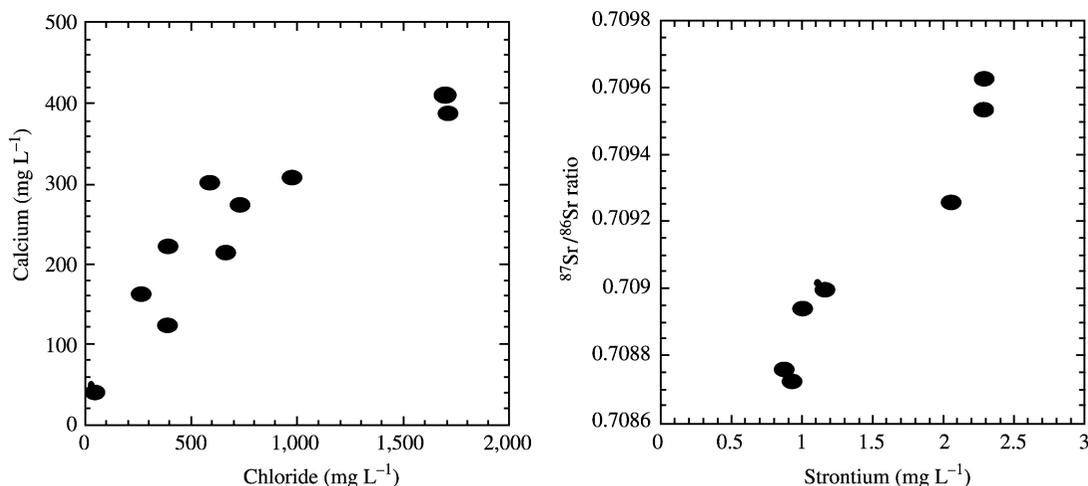
The geochemical modification of seawater intrusion has been attributed to base-exchange reactions with the aquifer rocks (Sayles and Mangelsdorf, 1977; Appelo and Willemsen, 1987; Appelo and Geimart, 1991; Appelo and Postma, 1993). Typically, cation exchangers in aquifers are clay minerals, organic matter, oxyhydroxides, and fine-grained rock materials, which have mainly Ca<sup>2+</sup> adsorbed on their surfaces. When seawater intrudes into a coastal freshwater aquifer, Na<sup>+</sup> replaces part of the Ca<sup>2+</sup> on the solid surfaces. As a result, Na<sup>+</sup> is taken up by the solid phase, Ca<sup>2+</sup> is released, the solute composition changes from a Mg-chloride into a

Ca-chloride type water, the Na/Cl ratio decreases, and the (Ca + Mg)/Cl ratio increases (Custodio, 1987, 1997; Custodio *et al.*, 1993; Appelo and Postma, 1993; Jones *et al.*, 1999). Under such conditions, the relative enrichments in calcium and magnesium, normalized to chloride concentrations, should be balanced by the relative depletion of sodium (i.e.,  $\Delta(\text{Ca} + \text{Mg}) = -2\Delta\text{Na}$  molar units; Vengosh *et al.*, 2002a). Together with Ca<sup>2+</sup>, exchangeable Sr<sup>2+</sup> is released to the dissolved phase (Johnson and Depaolo, 1994). The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of adsorbed strontium can therefore affect the isotopic composition of strontium in the saline groundwater. In Salinas Valley, California, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the salinized water increases with the Ca<sup>2+</sup> content (Figure 7), indicating a contribution of a high  $^{87}\text{Sr}/^{86}\text{Sr}$  source from the clays (Vengosh *et al.*, 2002a). In contrast, in the basaltic aquifer of Jesu island in South Korea, the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios show conservative relationships with salinity and reflect a mixing between seawater and local groundwater (Kim *et al.*, 2003). Flushing of the mixing zone by freshwater results in an opposite reaction: an uptake of Ca<sup>2+</sup> and Mg<sup>2+</sup> by the exchangers with concomitant release of Na<sup>+</sup>. This is reflected in an increase of the Na/Cl ratio and a decrease of the (Ca + Mg)/Cl ratio, and formation of an Na–HCO<sub>3</sub> water type (Appelo, 1994).

Finally, seawater intrusion is also characterized by high  $\delta^{34}\text{S}_{\text{sulfate}}$  (>20‰) and  $\delta^{11}\text{B}$  (>39‰) values that are associated with low SO<sub>4</sub>/Cl and B/Cl ratios below the marine ratios (0.05 and  $8 \times 10^{-4}$ , respectively). The relative depletion of sulfate and  $^{34}\text{S}$  enrichment is attributed to sulfate reduction along the salt–freshwater interface (Krouse and Mayer, 2000). The removal of dissolved boron is explained via adsorption onto clay minerals in which  $^{10}\text{B}$  is adsorbed preferentially onto the clays and the residual saline groundwater becomes enriched in  $^{11}\text{B}$  (Vengosh *et al.*, 1994).

#### 9.09.4.2 Mixing with External Saline Waters

Many studies of regional aquifer systems show the general sequence of major ion evolution from low-salinity Ca–Mg–HCO<sub>3</sub> type to saline Na–SO<sub>4</sub>–Cl groundwater along a hydraulic gradient (Mazor, 1997; Herczeg *et al.*, 1991, 2001; Hendry and Schwartz, 1988). The ratio of Na<sup>+</sup> and Cl<sup>-</sup> 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 Milk River Formation, Alberta, western Canada (Hendry and Schwartz, 1988; Herczeg and Edmunds, 2000). The gradual increase of salinity and the chemical modification towards



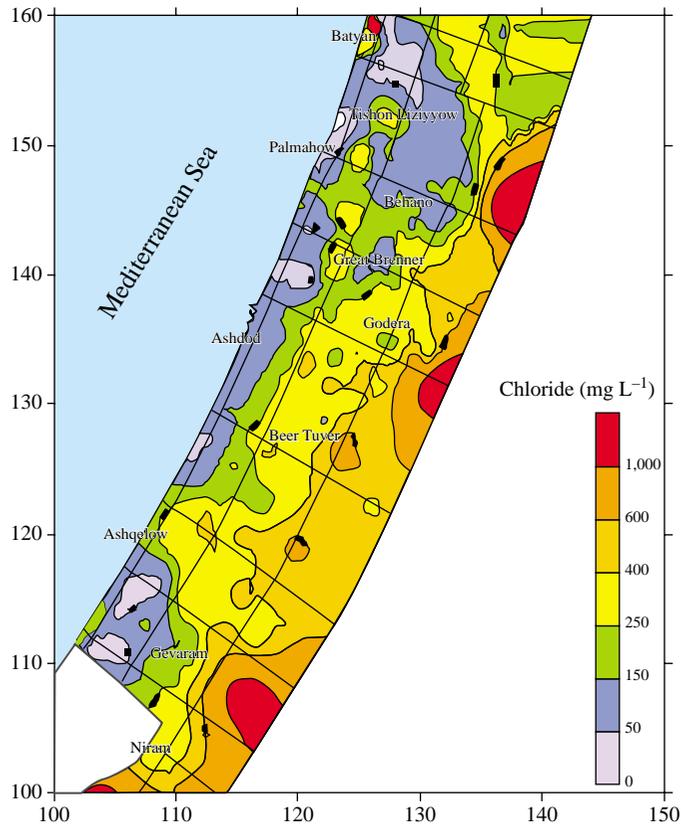
**Figure 7** The variations of chloride, calcium, strontium (in mg L<sup>-1</sup>), and <sup>87</sup>Sr/<sup>86</sup>Sr ratios during intrusion of seawater into the coastal aquifer of Salinas Valley, California, USA. Note the linear relationships between all constituents, which indicates conservative mixing relationships between freshwater and modified seawater. These relationships suggest that base-exchange reactions occur at early stage of seawater intrusion and that Sr in exchange sites has a high <sup>87</sup>Sr/<sup>86</sup>Sr ratio (source Vengosh *et al.*, 2002a).

predominance of chloride and sodium ions is a result of several possible processes: (i) advection and diffusion of saline fluids entrapped in an aquitard that is connected to an active aquifer and (ii) 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 the Milk River Formation, Alberta, western Canada. Hendry and Schwartz (1988) hypothesized that the salinity increase is derived from diffusion of solute from an 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 solute and a gradual increase of salinity (Herczeg and Edmunds, 2000).

Likewise, salinization of many aquifers is induced by intrusion of underlying or adjacent saline groundwater or saline-water flow from adjacent or underlying aquifers (e.g., Magaritz *et al.*, 1984; Maslia and Prowell, 1990, Vengosh *et al.*, 1999, 2002a,c; Sanchez-Martos and Pulido-Bosch, 1999; Sanchez-Martos *et al.*, 2001; Kloppman *et al.*, 2001; Hsissou *et al.*, 1999). For example, in the upper Floridan 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 cross-formational flow from underlying evaporite units (Mehta *et al.*, 2000a,b). Saline plumes formed from uprising of saline groundwater are also the major source of

salinity in the Mediterranean coastal aquifer of Israel (Table 1 and Figure 8; Vengosh *et al.*, 1999). Salinization of groundwater is one of the critical water-quality problems in the Gaza Strip, where the salinity of groundwater exceeds the salinity level of international drinking water. The major source of the salinity is the natural flow of saline groundwater from the eastern part of the aquifer. The rate of flow and salinization have been accelerated due to over-exploitation in the Gaza Strip (Vengosh *et al.*, 2002c).

The impact of salinization is particularly conspicuous in aquifers where the freshwater is not renewable (i.e., fossil; see Chapter 5.15). Numerous studies have shown that groundwater resources across the Sahara and the Sahel region in northern Africa and in the arid zones of the Middle East are fossil and reflect paleorecharge during Late Pleistocene periods of higher humidity (e.g., Cook *et al.*, 1992; Cook and Herczeg, 2000; Phillips, 1994; Edmunds and Gaye, 1994; Gaye and Edmunds, 1996; Edmunds and Droubi, 1998; Edmunds *et al.*, 1999, 2001). Typically, fresh paleowaters overlie saline dense water bodies. With geological time, a fragile hydraulic equilibrium has been established between the two water bodies. Drillhole construction and groundwater abstraction affect this delicate hydrological balance. Exploitation of paleowaters, with no possibility of modern replenishment, can lead to rapid salinization of the groundwater resources. In the Middle East, salinization of fossil groundwater has devastating effects since in some cases they are the only source of potable water (Vengosh and Rosenthal, 1994).

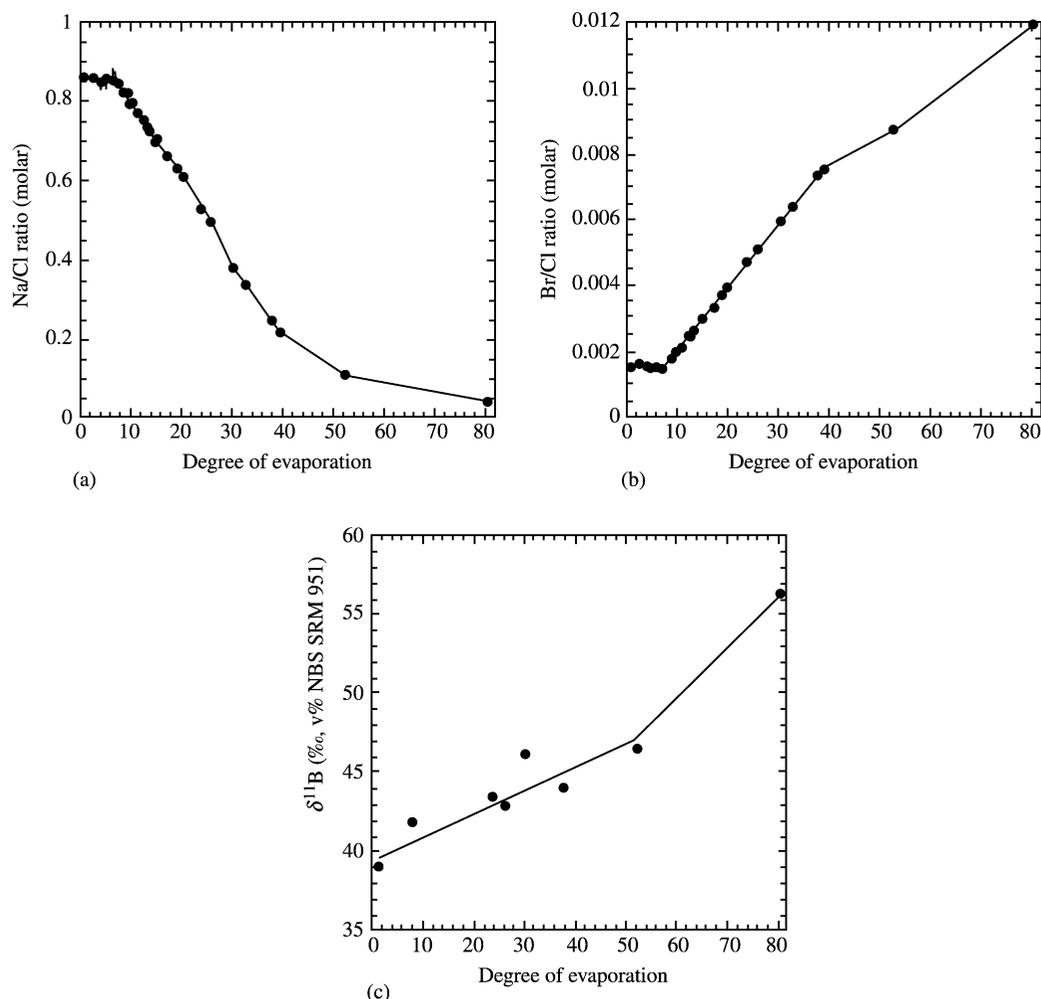


**Figure 8** Chloride (in  $\text{mg L}^{-1}$ ) distribution in groundwater from the central and southern part of the Mediterranean coastal aquifer of Israel. Note the saline plumes in the central and eastern parts of the aquifer.

For example, in the Damman carbonate aquifer in Bahrain, over-exploitation has resulted in a drop of the piezometric surface by 4 m and an increase in the salinity by over  $3 \text{ g L}^{-1}$  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 over-exploitation (Edmunds and Droubi, 1998). In Israel, the abstraction of brackish paleowater from the Lower Cretaceous Nubian sandstone aquifer in areas along the Rift Dead Sea Valley has resulted in the intrusion of Ca-chloride brine and the salinization of the associated groundwater. In South Jordan the fossil (i.e.,  $^{14}\text{C}$  ages of  $\sim 1.3 \times 10^4$  yr) freshwaters of the Disi–Mudawwara aquifer have been extracted since the early 1970s, which has resulted in a non-recoverable lowering of water levels by 20 m. The fresh groundwater body of Disi–Mudawwara aquifer is hydraulically interconnected with the overlying aquifer, in particular with the saline bearing of the Khrein confining unit. As such, early signs of salinization have already been recorded in the Disi–Mudawwara aquifer (Salameh, 1996). The future utilization of this valuable water resource, which is the only available freshwater

resource in Jordan, thus primarily depends upon the rate and extent of the salinization process.

In this section, the chemical and isotopic compositions of different types of saline groundwater are examined. These include residual evaporated seawater entrapped as formation water, saline water generated by evaporite dissolution, and hydrothermal water. Residual evaporated seawater is typically characterized by a Ca-chloride composition ( $\text{Ca}/(\text{SO}_4 + \text{HCO}_3) > 1$ ) with an Na/Cl ratio below seawater ratio value,  $\text{Br}/\text{Cl} \geq$  seawater ratio ( $1.5 \times 10^{-3}$ ), relative depletion of sulfate ( $\text{SO}_4/\text{Cl} < 0.05$ ),  $\delta^{34}\text{S}_{\text{sulfate}} \geq 20\text{‰}$ , and  $\delta^{11}\text{B} \geq 39\text{‰}$  (Figure 9; Starinsky, 1974; Carpenter, 1978; Carpenter *et al.*, 1974; McCaffrey *et al.*, 1987; Wilson and Long, 1993; Vengosh *et al.*, 1992; Raab and Spiro, 1991). Marine brines can be derived from relics of evaporated seawater that was modified by water–rock interaction (e.g., dolomitization) and sulfate reduction (Starinsky, 1974; Stein *et al.*, 1997). 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 large difference in salinity between the brines and the freshwater. Consequently, the dilution factor has



**Figure 9** Variations of Na/Cl, Br/Cl, and  $\delta^{11}\text{B}$  values during evaporation of seawater. Degree of evaporation is defined as the ratio of Br in the solution at different stages of evaporation to the initial Br in seawater (sources McCaffrey *et al.*, 1987; Raab and Spiro, 1991; Vengosh *et al.*, 1992).

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 residual evaporated seawater (>10-fold; Starinsky, 1974) are in hydrological contact with overlying fresh groundwater (Vengosh and Rosenthal, 1994; Marie and Vengosh, 2001). Once the natural hydrological balance is disturbed due to exploitation of the overlying fresh groundwater, the salinization process starts. In the Jericho area in the southern Jordan Valley, rapid rates of salinization due to rising underlying brines are found in wells located near the major Rift faults (Marie and Vengosh, 2001). The high salinity of the brines (>100 g L<sup>-1</sup>; Starinsky, 1974) indicates that only a small fraction of brine is required to cause devastating salinization in overlying freshwater resources.

An additional source of salinity in polar areas is residual brines derived from the freezing of seawater (Nelson and Thompson, 1954; Herut *et al.*, 1990; Richardson, 1976; Marison *et al.*, 1999; Bottomley *et al.*, 1999; Yaqing *et al.*, 2000). Bein and Arad (1992) showed that deep saline groundwaters in Sweden and Finland have low Na/Cl and high Br/Cl ratios. Based on their chemical composition, it was argued that the saline waters are remnants of frozen seawater formed during the last glaciation, followed by dilution with meteoric water (Bein and Arad, 1992).

Dissolution of evaporite minerals in sedimentary basins is also a common cause of salinization. This type of salinization occurs 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 (Rosenthal *et al.*, 1998), and the Great Artesian Basin in

Australia (Love *et al.*, 2000; Herczeg *et al.*, 1991). In case of halite dissolution, salinity typically increases along flow lines with a predominance of  $\text{Na}^+$  and  $\text{Cl}^-$  ions,  $\text{Na}/\text{Cl} \sim 1$ , and  $\text{Br}/\text{Cl} <$  seawater ratio (e.g., the Ogallala Formation; Table 1; Mehta *et al.*, 2000a,b). Salinization can also be due to the dissolution of marine sulfate as in Pinawa, Canada (Nesbitt and Cramer, 1993) and the Salinas Valley, California (Vengosh *et al.*, 2002a). Typically, gypsum dissolution produces saline water with  $\text{Ca}/\text{SO}_4 \sim 1$ . However, the dissolution of gypsum can also be associated with  $\text{Ca}^{2+}$  uptake on exchange substrates displacing  $\text{Na}^+$  to the solution. The residual water has an  $\text{Na}-\text{SO}_4$  composition (Nesbitt and Cramer, 1993). Dissolution of evaporitic sulfates would affect the sulfur isotopic composition of the water. The  $\delta^{34}\text{S}_{\text{sulfate}}$  values of marine sulfate varied over geological time with a maximum near +35‰ in the Cambrian and less than +10‰ in the Permian. In contrast, oxidation of sedimentary sulfides, which are significantly depleted in  $^{34}\text{S}$  relative to oceanic sulfates, would result in low  $\delta^{34}\text{S}_{\text{sulfate}}$  values with typical range of -30‰ to +5‰ (Krouse and Mayer, 2000).

Finally, salinization of groundwater can result from mixing with hydrothermal saline fluids. Thermal fluids, both in marine and nonmarine settings, are often characterized by high salt content. In western Turkey, for example, the salinity of thermal water is in the range 2–66  $\text{g L}^{-1}$ , with a high content of boron (>50  $\text{mg L}^{-1}$ ; Vengosh *et al.*, 2002b). In Mexico City, thermal water affects the quality of local groundwater (Edmunds *et al.*, 2002). In addition to chloride content, thermal waters are often enriched in sodium, boron, fluoride, arsenic, and other contaminants that present threat to the associated freshwater resources.

### 9.09.5 SALINIZATION OF DRYLAND ENVIRONMENT

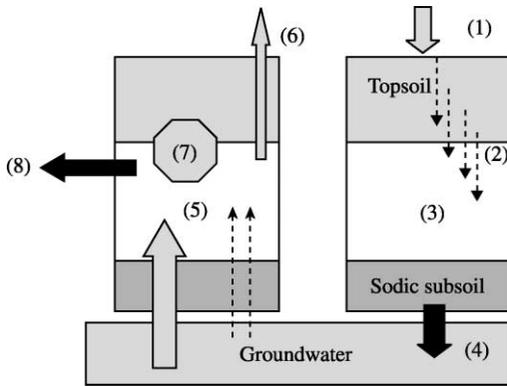
Salinity in dryland environment is a natural phenomenon derived from a long-term accumulation of salts on the ground and a lack of adequate flushing in the unsaturated zone. Salt accumulation and efflorescent crusts have been documented in the upper unsaturated zone (e.g., Gee and Hillel, 1988; Nativ *et al.*, 1997; Leaney *et al.*, 2003) and in fracture surfaces (Weisbrod *et al.*, 2000) in many arid areas. The salt formation has been attributed to surface evaporation (Allison and Barnes, 1985), wetting and drying cycles (Drever and Smith, 1978), soil capillarity, and capillarity transport of water and salts from the bulk rock matrix towards fracture surfaces (Weisbrod *et al.*, 2000).

In the western United States, recharge typically occurs along surrounding highlands and

groundwater flows towards the basin centers. Along the flow path the salinity of the groundwater increases by several orders of magnitude by both salt dissolution and extensive evaporation (Richter *et al.*, 1993). The chemistry of the residual saline groundwater is primarily controlled by the initial freshwater composition and the subsequent saturation with respect to typical minerals (calcite, gypsum, sepiolite, halite; Hardie and Eugster, 1970; Eugster and Jones, 1979). Evaporation and mineral precipitation control the salinity of groundwater in Deep Spring Lake (Jones, 1965), Death Valley (Hunt *et al.*, 1966), and the Sierra Nevada Basin (Garrels and MacKenzie, 1967).

While the source of the salts is natural, the process of salinization in dryland environment refers to human intervention. The most widespread phenomenon of dryland salinization is the response to land clearing and replacing the natural vegetation with annual crops and pastures. The natural vegetation in the arid and semi-arid zone uses any available water and, thus, the amount of water that leaks below the root zone is minimal, estimated to be 1–5  $\text{mm yr}^{-1}$  in South Australia (Allison *et al.*, 1985). Over thousands of years, salts have accumulated in the unsaturated zone, and the salt discharge to the saturated zone was balanced 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 leaking beneath the root zone and increased the rate of salt discharge to the underlying groundwater (Williams *et al.*, 2002 and references therein). The salts that were stored in the root zone were flushed into the unsaturated and saturated zone, causing salinization of the underlying groundwater. Leaney *et al.* (2003) predicted that the salt flux from the unsaturated zone in the Murray–Darling Basin of South Australia (with soil salinity up to  $1.5 \times 10^4 \text{ mg L}^{-1}$ ) would increase the salinity of the shallow groundwater ( $\sim 1,000 \text{ mg L}^{-1}$ ) by a factor of 2–6. The combination of increasing groundwater tables and salt fluxes in the unsaturated zone has caused devastating effects in the dryland environment. This was demonstrated in North America (Miller *et al.*, 1981), Argentina (Lavado and Taboada, 1987), India (Choudhari and Sharma, 1984), and South Africa (Flugel, 1995). However, the most dramatic large-scale salinization process occurs in the dryland environment of Australia (Allison *et al.*, 1985, 1990; Williams *et al.*, 2002; Peck and Hatton, 2003; Leaney *et al.*, 2003; Fitzpatrick *et al.*, 2000; Herczeg *et al.*, 1993, 2001).

The Australian case is used here to describe the chemical evolution of solutes in the dryland environment. The dryland salinization cycle (Figure 10) is a complex process that begins with salt accumulation on the ground,



**Figure 10** The dryland salinization cycle (the Australian model): (1) salt accumulation and precipitation of minerals; (2) selective dissolution and transport of soluble salts in the vadose 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 (after Fitzpatrick *et al.*, 2000).

evaporation, total desiccation, precipitation–dissolution of carbonate minerals, incongruent silicate mineral reactions, and precipitation–dissolution of gypsum and halite minerals (Hardie and Eugster, 1970; Eugster and Jones, 1979). The salts that accumulate in the soil are flushed into the vadose zone. Two factors control the flushing: the mineral solubility and the physical properties of soil. The differences in mineral solubilities cause chemical separation along the unsaturated zone: the higher the solubility of the mineral, the longer the travel of the salts that are derived from its dissolution. This process is also known as wetting and drying and involves the complete precipitation of dissolved salts during dry conditions and subsequent dissolution of soluble salts during wet conditions (Drever and Smith, 1978). This results in an uneven distribution of ions along the unsaturated zone:  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{HCO}_3^-$  tend to accumulate at relatively shallow depths,  $\text{SO}_4^{2-}$  at intermediate depths, and  $\text{Na}^+$  and  $\text{Cl}^-$  are highly mobilized to greater depths of the unsaturated zone. The  $\text{Na}/\text{Ca}$  ratio varies along the travel route of solutes in the vadose zone;  $\text{Ca}^{2+}$  is removed by the precipitation of carbonate minerals, whereas the concentration of  $\text{Na}^+$  remains constant, or even increases by dissolution of halite. In addition, the mobilization of  $\text{Na}^+$  triggers base-exchange reactions;  $\text{Na}^+$  is adsorbed on clays and oxides, but the newly generated  $\text{Ca}^{2+}$  released from adsorbed sites is removed by the precipitation of soil carbonate.

The final chemical composition of the solutes generated in the dryland environment depends on the initial fluid composition. In Australia, the

solutes are derived from marine aerosols that are deposited on the soil (Herczeg *et al.*, 2001 and references therein). Carbon-14 ages of soil solution reveal that most of the recharge occurred during wet climatic periods more than  $2 \times 10^4$  yr ago (Leaney *et al.*, 2003). Consequently, with thousands of years of salt accumulation and numerous cycles through the unsaturated zone, the saline groundwater in the dryland environment has become “marine like” with  $\text{Na}/\text{Cl}$  and  $\text{Br}/\text{Cl}$  ratios identical to that of seawater (Herczeg *et al.*, 1993, 2001; Mazor and George, 1992). The Australian salts lakes, which represent groundwater discharge zones, are characterized by marine chemical and isotopic (sulfur and boron) compositions superimposed by internal lake processes (Chivas *et al.*, 1991; Vengosh *et al.*, 1991a). If the initial solutes are derived from water–rock interactions induced by the generation of acids from  $\text{CO}_2$  accumulation and oxidation of organic matter in the soil, the final product is different. The “nonmarine” signature of the saline groundwater and salt lakes in the western USA reflects the role of water–rock interaction in shaping the chemical composition of both initial and evolved groundwater in the arid zone of the USA (Hardie and Eugster, 1970; Eugster and Jones, 1979).

The second factor that controls salinization of dryland 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 the downward movement of water and salts, leading to a saline zone (Fitzpatrick *et al.*, 2000). The accumulation of salts in soil can therefore be natural, due to the decrease of soil permeability (referred to as “subsoil transient salinity”; Fitzpatrick *et al.*, 2000) or anthropogenic due to the rise of saline groundwater as evidenced in South Australia (Allison and Barnes, 1985; Allison *et al.*, 1990; Herczeg *et al.*, 1993). As much as the leaching process in the vadose zone controls the salinity of the underlying shallow groundwater, the soil chemistry is also influenced by the chemistry of the rising groundwater (Cox *et al.*, 2002). The selective leaching process affects the composition of underlying groundwater. In some cases, recharged groundwater is controlled by marine aerosols and/or halite dissolution and has a typical predominance of  $\text{Na}^+$  and  $\text{Cl}^-$  (e.g., Cox *et al.*, 1996). In other cases, the solubility of gypsum produces saline water enriched in sulfate.

These two groundwater types exercise a direct control on the chemistry of secondary saline soils (Cox *et al.*, 1996; Fitzpatrick *et al.*, 2000). The rising of  $\text{Na}-\text{Cl}$  groundwater creates halite dominant soils, where chloride is the dominant anion. The rising of sulfate-enriched groundwater

creates three types of soils: (i) gypsic soil—under aerobic conditions and saturation with calcium sulfate; (ii) sulfidic soil—under anaerobic conditions and sufficient quantities of bacteria that use the oxygen associated with sulfate and produces pyrite; and (3) sulfuric 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 (Fitzpatrick *et al.*, 2000).

The differentiation of soil permeability when soil becomes clogged with clay and mineral precipitation causes lateral flow of saline soil water and shallow groundwater towards low-lying areas. The final stage of the dryland cycle is salinization of adjacent streams and rivers. 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 10).

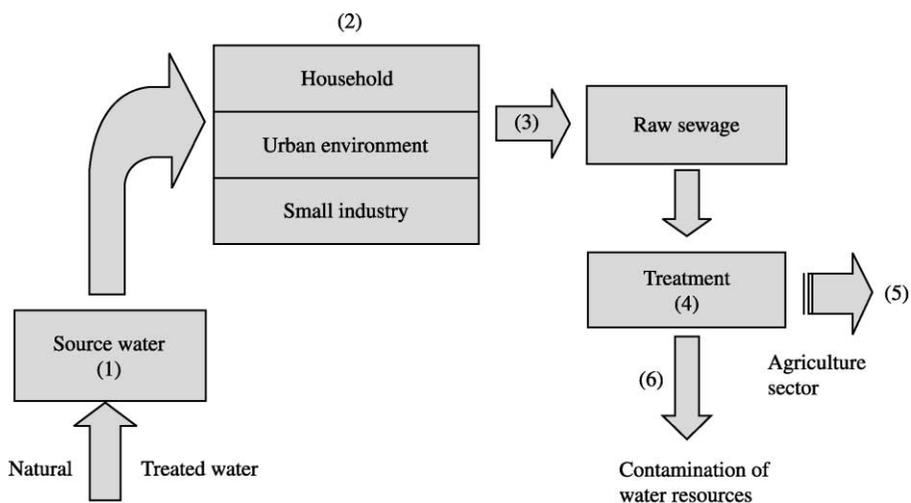
### 9.09.6 ANTHROPOGENIC SALINIZATION

#### 9.09.6.1 Urban Environment and Sewage Salinization

Two major sources of salinity are important in the urban environment: sewage and road salt. The salinity of domestic wastewater is derived from both the salinity of the source water supply to the municipality and the salts added directly by humans (Figure 11). This includes the use of detergents, washing powders, and salts. In Israel, for example, the average net human contributions of chloride, sodium, and boron to domestic wastewater are 125 mg, 120 mg, and 0.6 mg,

respectively, per liter of wastewater (Hoffman, 1993; Vengosh *et al.*, 1994). Chloride is derived from salts used in dishwashers and for refreshing ion-exchange columns, while sodium is also derived from detergents. First and secondary treatments of sewage, which form the most common procedure for sewage purification, do not remove the inorganic constituents, and consequently even treated sewage is relatively saline. In Israel the chloride content of domestic sewage effluent is between  $300 \text{ mg L}^{-1}$  and  $400 \text{ mg L}^{-1}$  (Vengosh *et al.*, 1994; Harussi *et al.*, 2001). In water-scarce areas, treated sewage is an important water source that substitutes for freshwater irrigation. It is expected that future utilization of treated domestic sewage will become the major source for irrigation water in the western United States, Israel, and Jordan. The saline wastewater can affect soil salinity (Beltran, 1999) and the composition of underlying groundwater in phreatic aquifers (Ronen *et al.*, 1987; Vengosh and Keren, 1996; DeSimone *et al.*, 1997; Stigter *et al.*, 1998; Gavrieli *et al.*, 2001). In addition, direct pollution by sewage affects both the organic and inorganic composition of contaminated groundwater.

The typical chemical composition of saline domestic sewage is presented in Table 1. The use of household NaCl salt and detergents enriched in sodium and boron results in  $\text{Na/Cl} > 1$ , a low Br/Cl ratio (i.e.,  $\text{Br/Cl} < \text{seawater ratio}$  due to halite dissolution; Vengosh and Pankratov, 1998), and a high B/Cl ratio ( $> \text{seawater ratio of } 8 \times 10^{-4}$ ). Detergents are enriched in boron due to the addition of Na-borate (derived from natural borate minerals) used as a bleaching agent (Waggott, 1969; Raymond and Butterwick,



**Figure 11** The domestic 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; and (6) contamination of water resources.

1992). Since Na-borates are mined from natural borate deposits (mainly in the western USA, Turkey, and China), they have typical boron isotopic compositions ( $\delta^{11}\text{B}$  range of 0–10‰; Vengosh *et al.*, 1994). The anthropogenic sulfate is also isotopically distinguished, as indicated by the pollution of the Arno River in northern Tuscany with a distinctive sulfur isotopic ratio ( $\delta^{34}\text{S} = 6\text{--}8\text{‰}$ ; Cortecchi *et al.*, 2002).

Another source of urban salinization is the use of road de-icing salts. Salt has been used for road de-icing for several decades, particularly in the eastern and northeastern states in the United States and Canada. The use of road salt improves fuel efficiency and reduces accidents; at the same time, it causes salinization of associated groundwater. In 1990, more than 10.5 Mt of salt were used for road de-icing (Richter *et al.*, 1993). Brine generated in storage piles of salt (Wilmoth, 1972) and from the dissolution of salts that are applied directly to the roads (Howard and Beck, 1993; Williams *et al.*, 1999) can contaminate water resources. If salt is applied as a powder, its particles may become airborne and transported for considerable distances downwind (Jones and Hutchon, 1983; Richter *et al.*, 1993).

The most common road de-icing practice is to apply pure sodium chloride to main urban roads and highways. Calcium chloride is also used but not as frequently, since it is more expensive and is known to make road surfaces more slippery when wet (Richter *et al.*, 1993). Hence, the most important geochemical signal of road de-icing is typically an Na–Cl solution with an Na/Cl ratio close to unity (Table 1; Howard and Beck, 1993). The use of calcium chloride results in contamination with Ca-chloride solutions with an Na/Cl  $\ll$  1.

#### 9.09.6.2 Agricultural Drainage and the Unsaturated Zone

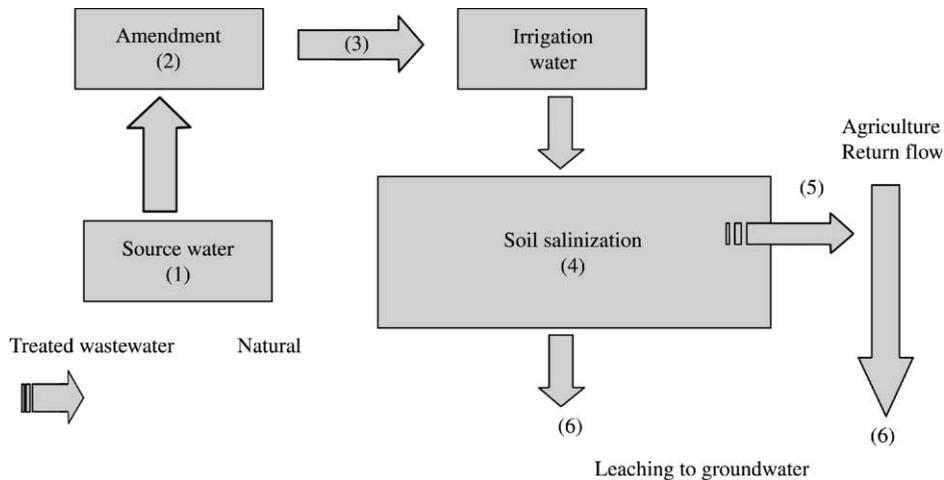
A survey of the quality of drainage water in the western United States shows that the drainage waters are typically saline, with elevated concentrations of selenium, boron, arsenic, and mercury (Hern and Feltz, 1998). In San Joaquin Valley, Salinas Valley, and the Imperial Valley in California, drainage waters are highly saline and contaminate the associated ground- and surface waters. The salinity of agriculture return flow is derived from two principal sources: added commercial chemicals (e.g. nitrogen fertilizers, gypsum, dolomite, and boron compounds), and the nature of the soil in which the irrigation water flows. In the western US, the occurrence of selenium in the drainage water is attributed to mobilization from oxidized alkaline soils derived predominantly from seleniferous marine sediments (Hern and Feltz, 1998; Grieve *et al.*, 2001; see Chapter 9.03). As a result, agricultural

contaminants have caused significant changes in groundwater geochemistry and have induced water–rock interactions (Bölke, 2002).

The salinity of agricultural return flow depends on the balance between the amount of salt entering the soil and the amount of salt that is removed. A change from natural vegetation to agricultural crops and application of irrigation water adds salt to the system. Approximately 60% of the supplied irrigation water is consumed by growing crops, but the salts remain in the residual solution as they are not consumed by evaporation and transpiration. Consequently, adequate drainage is one of the key factors that determines soil salinization; nevertheless, the nonreactivity of the soluble salts (i.e., conservative and not consumed by the sediments) makes them a long-term hazard.

The salinity of agricultural return flow is also derived from the salinity of the soil. In arid and semi-arid areas the natural salinity of the soil is high, and thus the flushing with irrigation water enhances the dissolution of stored salts. Moreover, the selenium and boron anomalies associated with agricultural return flow in the San Joaquin Valley (Kharaka *et al.*, 1996) and the Imperial Valley (Glenn *et al.*, 1999) in California are directly derived from leaching the local soil. The soil reactivity is also enhanced by the composition of the irrigation water and added fertilizers. As high salinity is associated with high sodium content, exchangeable sodium replaces exchangeable calcium. As a result of this interaction, the soil becomes impermeable. The “sodium hazard” is expressed as “sodium adsorption ratio” (SAR), which represents the relative activity of sodium ions in exchange reactions with soil. Typically, irrigation water with SAR values higher than 10 are considered to be a sodium hazard (e.g., San Joaquin Valley; Mitchel *et al.*, 2000). In cases of high SAR values coupled with heavy soil, gypsum is applied to improve the physical properties of soil. The agricultural drainage salt generation during irrigation of crops in San Joaquin Valley in California exceeds  $6 \times 10^5$  t annually and accumulates at a rate that is causing serious concern for the environment and the local agricultural industry (Jung and Sun, 2001).

The chemical composition of agricultural drainage (Figure 12) is influenced by the quality of the water source. In many water-scarce areas, the only available water for irrigation is the treated (usually only secondary treatment) domestic sewage. Hence, the end product of urban waste (Figure 11) can be the initial water for the agriculture cycle. Other types of marginal waters (e.g., brackish waters) may also affect the composition of the initial stage of the agricultural cycle. The second factor that determines the



**Figure 12** 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; and (6) contamination of water resources.

chemistry of the agriculture cycle is fertilizers and other types of ammandates that are added to the irrigation water. Nitrate is the dominant ion contributed by fertilizers. Bölke (2002) showed that artificial fertilizer is the largest nonpoint source of nitrogen in rural areas. This reflects the global increase in the use of nitrogen fertilizer since the middle of the twentieth century. Nitrate derived from fertilizers has relatively low  $\delta^{15}\text{N}_{\text{nitrate}}$  values ( $-4\text{‰}$  to  $+3\text{‰}$ ; Kendall and Aravena, 2000 and references therein). Note that  $\delta^{15}\text{N}_{\text{nitrate}} = [({}^{15}\text{N}/{}^{14}\text{N})_{\text{sample}}/({}^{15}\text{N}/{}^{14}\text{N})_{\text{AIR}} - 1] \times 10^3$ ; AIR refers to  $\text{N}_2$  in air (Coplen *et al.*, 2002). Other important forms of nitrogen applied to crops are urea,  $\text{CO}(\text{NH}_2)_2$ , ammonia ( $\text{NH}_3$ ), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), and animal manure (Bölke, 2002).

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 (Bölke, 2002), and gypsum, which is used in heavy soil with irrigation water having high SAR values in order to neutralize the exchangeable  $\text{Na}^+$  in the soil (e.g., Salinas valley, California; Vengosh *et al.*, 2002a). In addition, application of KCl results in chloride contamination and use of Na-borate or Ca-borate fertilizers in boron-depleted soil contribute boron (Komor, 1997). The use of soil fumigants such as ethylene dibromide (EDB) (Bölke, 2002) can lead to degradation and release of bromide to groundwater, as demonstrated in shallow groundwater underlying strawberry cultivation in Salinas Valley, having conspicuously high Br/Cl ratios (Vengosh *et al.*, 2002a).

Another source of salinity that is associated with agricultural activity is animal waste, which

includes cattle (Goody *et al.*, 2002; Hao and Chang, 2002, Harter *et al.*, 2002) and swine manure (Krapac *et al.*, 2002). Hao and Chang (2002) and Krapac *et al.* (2002) showed that, following long-term manure application, the salinity of soil and underlying groundwater increase significantly. Manure is characterized by high concentrations of chloride ( $1,700 \text{ mg L}^{-1}$  in swine manure), sodium ( $840 \text{ mg L}^{-1}$ ), potassium ( $3,960 \text{ mg L}^{-1}$ ), and ammonium with  $\delta^{15}\text{N}$  values  $>9\text{‰}$  (Krapac *et al.*, 2002). The combination of a high K/Cl ratio, a high nitrogen concentration (ammonium that is transformed into nitrate in the unsaturated zone), and high  $\delta^{15}\text{N}_{\text{nitrate}}$  make it possible to trace the impact of animal wastes on the quality of the underlying groundwater.

The third stage in the agriculture cycle (Figure 12) 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 (this is also true for contamination by wastewater and de-icing salts). Microbial oxidation of ammonium releases protons ( $\text{H}^+$ ) that generate acidity along with nitrate in soils (Bölke, 2002) and induce dissolution of calcium carbonate minerals. 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 US, groundwater recharged beneath fertilized fields has a unique Ca–Mg– $\text{NO}_3$  composition with positive correlations between nitrate and other inorganic constituents such as  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{K}^+$ , and  $\text{Cl}^-$  (Hamilton *et al.*, 1993; Hamilton and Helsel, 1995). In the Gaza Strip of the Mediterranean

coastal aquifer, dissolution of the aquifer matrix is reflected by the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios of nitrate-rich groundwater (Vengosh *et al.*, 2002c).

Using irrigation water enriched in sodium with high SAR values triggers ion-exchange reactions (Stigter *et al.*, 1998). 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. Nonetheless, the uptake of  $\text{Na}^+$  and release of  $\text{Ca}^{2+}$  (and  $\text{Mg}^{2+}$ ) is a major geochemical modifier associated with transport of irrigation water in the unsaturated zone. The Na/Cl ratio is a good indicator for the efficiency of the base-exchange reactions; low ratios (i.e., below the original value of the irrigation water) reflect continuation of exchange reactions, whereas an increase of 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). Gavrieli *et al.* (2001) showed that irrigation with calcium-rich water causes an opposite reaction, in which  $\text{Na}^+$  is released and the residual groundwater has an Na/Cl ratio higher than that of the irrigation water. Similarly, the ability of the clay minerals to adsorb reactive elements (e.g., boron and potassium) is limited, and over long-term recharge or irrigation, the capacity of adsorption decreases (Vengosh and Keren, 1996; DeSimone *et al.*, 1997; Stigter *et al.*, 1998). In most cases, the potassium level in groundwater is low, and the K/Cl ratios in agricultural recharge are less than unity due to adsorption of potassium onto clay minerals (Bölke, 2002).

Leaching of the soil also contributes contaminants to the drainage waters (Johnson *et al.*, 1999; Sun, 2001; Tedeschi *et al.*, 2001; Gates *et al.*, 2002). The drainage waters of Imperial Valley and the Salton Sea in Southern California are characterized by  $\text{Na}/\text{Cl} > 1$ , high  $\text{B}/\text{Cl}$  and  $\text{SO}_4/\text{Cl}$  (ratios higher than in seawater) and typically low  $\text{Br}/\text{Cl}$  ratio (Table 1; data from Schroeder and Rivera, 1993). The  $\text{Br}/\text{Cl}$  ( $(3-4) \times 10^{-4}$ ) in the drainage water is one order of magnitude lower than seawater ( $1.5 \times 10^{-3}$ ) or atmospheric ( $>1.5 \times 10^{-3}$ ) ratios (Figure 5; Davis *et al.*, 1998). This suggests that halite dissolution in the soil can be an important component of the salinity associated with agriculture return flow in the Imperial Valley.

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 results in accumulation of  $\text{HCO}_3^-$  and  $\text{Ca}^{2+}$  due to dissolution of the carbonate matrix of the host aquifer. In addition, the contents

of sulfate and nitrate are expected to rise and to be conservatively transported in the unsaturated zone. Thus, the typically high  $\text{SO}_4/\text{Cl}$  and the high nitrate level, which represents the original composition of the irrigation water, are preserved. In contrast, under anaerobic conditions, sulfate and nitrate reduction enhances calcium carbonate precipitation, and hence sulfate (by sulfate reduction), nitrate (denitrification), and calcium (precipitation) are removed along the flow in the unsaturated zone (Gooddy *et al.*, 2002). In this case, the original chemical signature of the agricultural return flow is modified: the residual groundwater becomes relatively depleted in sulfate and nitrate concentrations with high  $\delta^{34}\text{S}_{\text{sulfate}}$  and  $\delta^{15}\text{N}_{\text{nitrate}}$  values relative to the irrigation water.

### 9.09.7 SOIL SALINIZATION

Soil salinization is a major process of land degradation that decreases soil fertility and is a significant component of desertification processes in the world's dryland (Thomas and Middleton, 1993). The World Bank states that soil salinization caused by inappropriate irrigation practices affects  $\sim 60$  Mha, or 24% of all irrigated land worldwide. In Africa, salinization accounts for 50% of irrigated land (Thomas and Middleton, 1993; Ceuppens and Wopereis, 1999). Increasing soil salinization is also occurring in India, Pakistan, China, and Central Asia (Wichelns, 1999). In Egypt,  $\sim 35\%$  of the agricultural land suffers from salinity (Kotb *et al.*, 2000; Kim and Sultan, 2002). Soil salinization is the first stage of environmental destruction caused by salinity, and is related to river and lake salinization. For example, the diversion of the Amu Darya and Syr Darya rivers not only caused a significant desiccation of the Aral Sea, but also caused salinization of associated agricultural land (Weinthal, 2002). In Australia, soil salinization is the most severe environmental problem of the continent, causing a dramatic change in landscape, industry, and the future of farmland (Dehaan and Taylor, 2002).

The accumulation of soluble salts in soil occurs when evaporation exceeds precipitation, and salts are not leached but remained in the upper soil layers in low-lying areas. Natural soil salinization, called "primary salinization," occurs in arid and semi-arid climatic zones. "Secondary salinization" is the term used to describe soil salinized as a consequence of direct human activities (Fitzpatrick *et al.*, 2000; Dehaan and Taylor, 2002).

Salinization of soil results from a combination of evaporation, salt precipitation and dissolution, salt transport, and ion exchange (Shimajima *et al.*, 1996). Excessive salinity in soil leads to toxicity in 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 (Hillel, 1980; Bresler *et al.*, 1982; Frenkel *et al.*, 1978; Ramoliya and Pandey, 2003). The quality of the irrigation water is also a major contributor to soil salinity. Irrigation with marginal waters (e.g., brackish water, wastewater) with a high content of soluble salts directly affects soil salinity (Sparks, 1995). For example, in the Nile Delta the highly saline drainage water is the principal source of soil salinization, and extensive irrigation without an adequate drainage system causes soil salinization (Kotb *et al.*, 2000).

In shallow groundwater conditions, water and dissolved salts move by capillary action to the soil surface. When the water evaporates at the surface, the salts are left behind. The excess salts cause many types of crops to wither and die. The salts prevent plant roots from making use of water in the soil. Plant roots absorb water from the soil through the process of osmosis. Osmosis moves water from an area of lower salt (higher water) concentration to an area of higher salt concentration. The salt concentration inside a normal plant cell is ~1.5%, so that water moves into root cells. In saline soils, the concentration of salt in the soil water can rise above 1.5% and prevent osmosis from moving water into the roots. This may cause water to move out of the roots, thereby dehydrating the plant (Poljakoff-Mayber and Gale, 1975).

Soil salinization is often associated with sodic soil. Natural or anthropogenic accumulation of sodium in the system leads to gradual replacement of divalent cations with  $\text{Na}^+$  on the exchange complex of clay minerals. The increased level of adsorbed  $\text{Na}^+$  causes the soil to become dispersed, which significantly reduces the soil porosity and permeability. This is a major problem for drainage of soil water and salt flush in the unsaturated zone. The predominance of  $\text{Na}^+$  in the exchange phases occurs due to both high levels of  $\text{Na}^+$  in the soil water and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  precipitating as carbonate and sulfate minerals. In Australia, natural sodic soils, which are defined as soils in which the exchangeable sodium percentage is greater than 15%, are associated with saline soil ( $\text{EC} > 8 \text{ dS m}^{-1}$ ; Fitzpatrick *et al.*, 2000). Sodic soils also develop under irrigation of water enriched in sodium (e.g., wastewater), which requires special reclamation measures such as using gypsum or  $\text{CaCl}_2$  salts to remove the exchangeable  $\text{Na}^+$  (Bresler *et al.*, 1982).

### 9.09.8 WETLAND SALINIZATION

More than one-fourth of the world's wetlands and more than 50% of the wetlands in the United States have been lost owing to their salinization.

The destruction of wetlands has reduced the diverse assemblages of millions of waterfowl and shorebirds. Present and future water projects and salinization induced by agricultural and urban uses of water pose a threat to the bird populations in wetlands. Moreover, salinization is likely to harm the birds' reproductive capacity and place further stresses on their diversity (Williams, 2001a,b). Wetland destruction has been particularly devastating in arid zones. Half of Nevada's wetlands have been lost during the last 200 years (Titus and Richman, 2000). Inland wetland salinization occurs in the Tavlas de Daimiel National Park of Spain (Berzas *et al.*, 2000), which is a unique wetland area with a wide floral and faunal diversity, rich in many migratory birds. The wetland virtually dried up and salinized due to the use of its source waters (Berzas *et al.*, 2000).

Coastal wetland salinization is caused by a significant decrease of river discharge, diversion of freshwater for irrigation network, and upstream seawater intrusion under the influence of the tide (Zalidis, 1998). Indeed, salinization of low-lying coastal or deltaic plains is the most striking process that threatens the future of global wetlands. Coastal wetlands, those of southern United States, Southeast Asia, China, and northern Australia, are vulnerable to saltwater intrusion. Their vulnerability is likely to increase with the expected sea-level rise during the next century due to global warming. Even in near-pristine environments, such as the mouth of the Yukon and Kuskokwim rivers in northern Alaska, salinization due to sea-level rise threatens to destroy the diverse freshwater habitat. In northern Australia, saltwater intrusion has been identified in the extensive low-lying coastal plains, particularly in the Lower Mary River area, changing the system from a predominantly freshwater wetland environment to one dominated by saltwater. The dramatic environmental changes that have taken place in the Lower Mary River since the early 1950s could be a possible analogue to the more widespread salinization that will accompany future sea-level rise (Mulrennan and Woodroffe, 1998). EPA studies (Titus and Richman, 2000) estimated that sea level is likely to rise by 90 cm along the US coast by the middle of next century. Consequently, low-lying areas 1.5 m below sea level would be flooded by spring high tides. A survey of the coastal levels along the coastal plain of the US reveals that the areas most vulnerable to sea-level rise are those of North Carolina, Louisiana, the Florida Everglades, and virtually all barrier islands and coastal wetlands. The most striking finding is that in North Carolina, an area equivalent to that of the Netherlands is expected to be flooded by seawater (Titus and Richman, 2000).

### 9.09.9 ELUCIDATING THE SOURCES OF SALINITY

Identifying the origin of salinity in water is crucial for water management, model prediction, and remediation. Yet the variety of salinization sources makes this task difficult. Ground- and surface-water salinization can result from point sources (e.g., leakage or recharge of domestic wastewater) or nonpoint sources (e.g., agriculture return flows, irrigation with sewage effluent). Salinization can be derived from natural (geo-genetic) processes such as seawater intrusion or saline-water flow from adjacent or underlying aquifers (e.g., Maslia and Prowell, 1990; Vengosh *et al.*, 1999, 2002a; Sanchez-Martos and Pulido-Bosch, 1999; Sanchez-Martos *et al.*, 2001; Kloppman *et al.*, 2001; Hsissou *et al.*, 1999). Alternatively, salinization can also be induced by direct anthropogenic contamination. The multiple salinity sources therefore present a real challenge to water agencies and regulatory bodies.

The key for tracing salinity sources is the assumption that the chemical composition of the original saline source is preserved during the salinization process. Due to the large differences between the solute content of saline 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 once it is masked by water–rock interactions. For example, the composition of seawater is significantly modified as it intrudes into coastal aquifers. Consequently, diagnostic tracers, in order to be useful, must be conservative. The overlap and similarity of the chemical composition of different saline sources makes the tracing task even more difficult. For example, the Na/Cl ratio can be a good tracer for distinguishing marine (e.g., seawater intrusion with Na/Cl < 0.86) from nonmarine or anthropogenic sources (Na/Cl ≥ 1). However, the reactivity of Na<sup>+</sup> in the unsaturated zone can reduce the Na/Cl ratio even in nonmarine settings (e.g., Vengosh and Keren, 1996; DeSimone *et al.*, 1997; Stigter *et al.*, 1998; Gavrieli *et al.*, 2001). 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 geochemical tools that are useful for discriminating between different sources of solutes in groundwater systems. The source of solutes in the salinized environment can be derived from (i) mixing of meteoric water with saline water such as seawater, connate fluids, and hydrothermal waters trapped within or outside the aquifer; (ii) dissolution of evaporites left behind after the last seawater or brine retreat; (iii) weathering of the aquifer minerals;

(iv) accumulation of salts derived from long-term deposition of atmospheric fallout; (v) sewage (domestic or industrial) contamination; and (vi) salinization by agricultural return flows. Each of these sources has a unique and distinctive chemical and isotopic composition. The integration of geochemical and isotopic tracers can be used to help resolve these multiple sources. Summary of the geochemical characteristics of these sources is given in Table 2.

Reactive species are important tools to evaluate the level of interaction with the host sediments/rocks of the investigated aquifer. Strontium isotopes are an excellent tracer to delineate the type of rock source and weathering process (see Chapter 5.12), the flow path of groundwater in a watershed of different lithological compositions (e.g., Starinsky *et al.*, 1980, 1983; Banner and Hanson, 1990; Banner *et al.*, 1989; Bullen *et al.*, 1996), the composition of exchangeable strontium in clay minerals (Johnson and Depaolo, 1994; Armstrong *et al.*, 1998; Vengosh *et al.*, 2002a), the origin of dissolved strontium in rivers (Singh *et al.*, 1998; Vengosh *et al.*, 2001), 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 of lack of similarity, the groundwater must interact with external rock sources. For example, saline groundwaters from central Missouri, USA have high <sup>87</sup>Sr/<sup>86</sup>Sr ratios that are considerably more radiogenic than the host Mississippian carbonates. The high <sup>87</sup>Sr/<sup>86</sup>Sr ratios reflect deep subsurface migration and water–rock interaction with Paleozoic and Precambrian strata (Banner *et al.*, 1989). Similarly, the <sup>87</sup>Sr/<sup>86</sup>Sr ratios of saline groundwaters in the Mediterranean coastal aquifer of Israel are considerably lower than that of the aquifer carbonate matrix, indicating an external source for the saline groundwaters (Vengosh *et al.*, 1999).

Strontium isotopes can also be used to trace salinization by agricultural return flow. Bölke and Horan (2000) showed that some fertilizers, and hence agricultural recharge, have a high radiogenic <sup>87</sup>Sr/<sup>86</sup>Sr ratio, which differs significantly from that of strontium acquired by water–rock interactions in the aquifer. Although denitrification and carbonate dissolution may alter the strontium isotopic ratio, the association of distinctive <sup>87</sup>Sr/<sup>86</sup>Sr ratios and nitrate concentrations may indicate the impact of fertilizers on groundwaters (Bölke and Horan, 2000).

In contrast, other tracers can be considered as universal—i.e., their use is not related to the specific local geology or hydrological system.

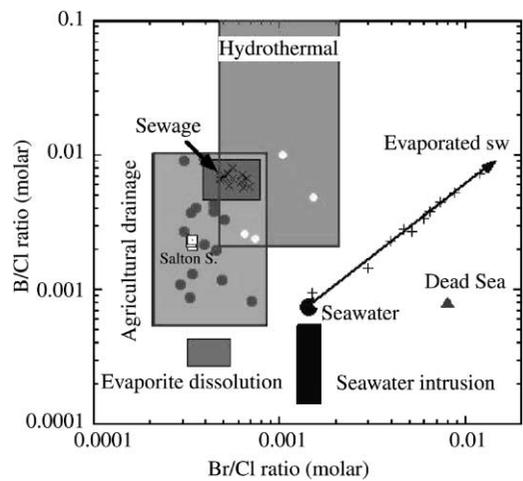
**Table 2** Typical chemical and isotopic characteristics of major saline sources.

Source	TDS (g L <sup>-1</sup> )	Na/Cl (molar ratio)	SO <sub>4</sub> /Cl (× 10 <sup>-3</sup> )	Br/Cl molar ratio (× 10 <sup>-3</sup> )	B/Cl molar ratio (× 10 <sup>-3</sup> )	δ <sup>11</sup> B (per mil)	δ <sup>34</sup> S (per mil)	<sup>36</sup> Cl/Cl (10 <sup>-15</sup> )
Seawater	35	0.86	0.05	1.5	0.8	39	21	<5
Replies of evaporated seawater (brines)	>35	<0.86	>0.05	>1.5	<0.8	>39	>21	<5–100
Evaporite dissolution	>1	1	≧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 to >100
Agricultural return flow	0.5–5	>1	≧0.05	<1.5	>0.8	20–30	>21	50 to >100

In this respect, the Br/Cl (Edmunds, 1996; Davis *et al.*, 1998; Vengosh and Pankratov, 1998), B/Cl, δ<sup>11</sup>B (Bassett, 1990; Bassett *et al.*, 1995; Palmer and Swihart, 1996; Vengosh *et al.*, 1991a,b, 1992, 1994; Vengosh and Spivack, 2000), δ<sup>34</sup>S<sub>sulfate</sub> (Krouse and Mayer, 2000), <sup>36</sup>Cl/Cl (Phillips *et al.*, 1986; Phillips, 2000; see Chapter 5.15), and δ<sup>18</sup>O<sub>water</sub> (see Chapter 5.11) variations can be used to discriminate between multiple salinity sources. The variations of some of these tracers are presented in Figures 13 and 14. A clear distinction is shown between marine sources such as seawater intrusion or marine-derived brines (e.g., Dead Sea), nonmarine (e.g., evaporite dissolution), and anthropogenic (e.g., sewage effluents, agricultural return flows) sources.

The use of boron and sulfur isotopes is constrained by their reactivity in the hydrological system. Boron tends to be adsorbed on clay minerals and oxides, particularly under highly saline conditions. During the adsorption process <sup>10</sup>B(OH)<sub>4</sub><sup>-</sup> is incorporated preferentially into adsorbed sites, whereas the residual dissolved boron in the form of B(OH)<sub>3</sub> is enriched in <sup>11</sup>B. The magnitude of the boron isotope fractionation varies between 20‰ and 30‰, and as a result seawater and evaporated brines have δ<sup>11</sup>B values >40‰ (60‰ in the Dead Sea; Figure 15; Vengosh *et al.*, 1991a,b, 1992, 1994; Vengosh and Spivack, 2000).

The sulfur (δ<sup>34</sup>S<sub>sulfate</sub>) and oxygen in sulfate (δ<sup>18</sup>O<sub>sulfate</sub>) isotope variations provides a distinction between seawater (δ<sup>34</sup>S<sub>sulfate</sub> = 21‰; δ<sup>18</sup>O<sub>sulfate</sub> = 9.5‰), evaporated seawater (>21‰), dissolution of marine sulfate minerals



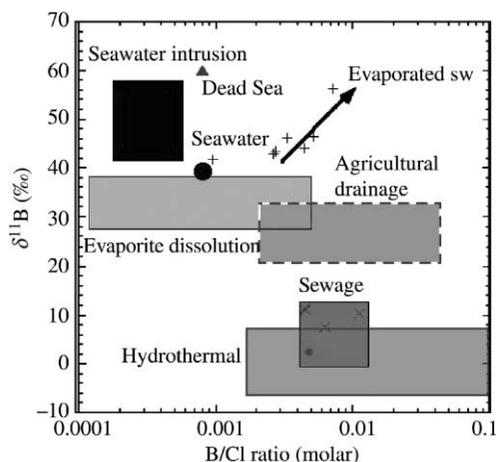
**Figure 13** Elucidation of saline sources by using the variations of Br/Cl and B/Cl ratios. Note the expected geochemical distinction between seawater, evaporated seawater, brines (e.g., Dead Sea), hydrothermal fluids, sewage effluents, agricultural drainage (e.g., Salton Sea), and evaporite dissolution.

(depends on time of deposition with a range of +10–35‰ and +9–20‰), fertilizers (+6–11‰), domestic sewage (6–8‰), and sulfate derived from the oxidation of reduced inorganic sulfur components (–30 to +5‰; –10‰ to +5‰; Krouse and Mayer, 2000, and references therein). However, the  $\delta^{34}\text{S}_{\text{sulfate}}$  values are modified by sulfate reduction and the residual sulfate becomes enriched in  $^{34}\text{S}$  and  $^{18}\text{O}$ .

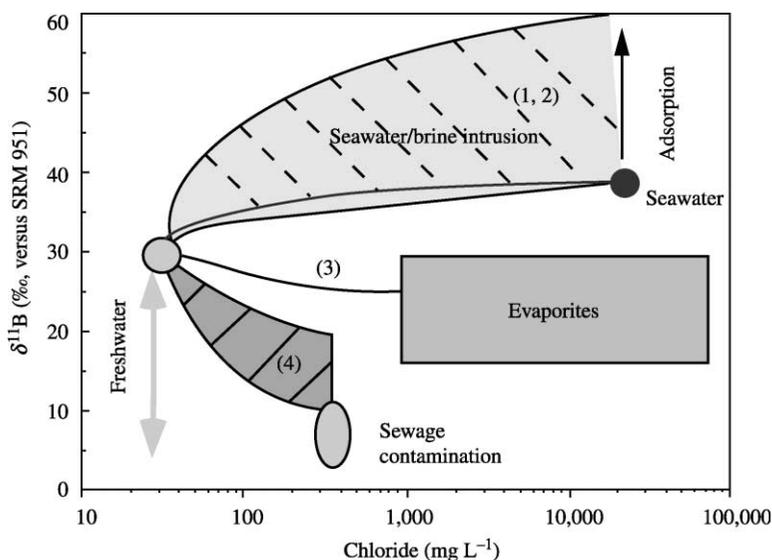
The use of the stable isotopes of oxygen and hydrogen for tracing the origin of salinity is straightforward in the case of river salinization,

but it is more problematic in groundwater studies. In many cases, the original  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values of the saline sources are completely modified by mixing (dilution) with meteoric water (e.g., Banner *et al.*, 1989; Hanor, 1994; Bergelson *et al.*, 1999). Nevertheless, the  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values can be used to calculate mixing relationships in the case of seawater intrusion (Jones *et al.*, 1999; Yechieli *et al.*, 2001) or reflect agricultural return flows (Davisson and Criss, 1993). It is also possible to use the stable isotopes for detecting the origin of saline groundwater: remnant of diluted evaporated seawater and formation waters are characterized by low  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values relative to direct seawater intrusion. For example, Herczeg *et al.* (2001) showed that groundwater in the Murray Basin is depleted in  $^{18}\text{O}$  and  $^2\text{H}$  relative to possible mixing between meteoric water and seawater. This indicates that the salinity of the groundwater in the Murray Basin is derived from atmospheric fallout, not from direct seawater intrusion. Similarly, Bergelson *et al.* (1999) showed that the saline springs that emerge at the Sea of Galilee in the Jordan Rift valley have low  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values to account for direct seawater intrusion and must reflect dilution of hypersaline brines. Finally, anthropogenic saline sources, such as domestic wastewater that is treated or stored in open reservoirs, are enriched in  $^{18}\text{O}$  and  $^2\text{H}$ , and thus can be used to trace their impact on contaminated groundwater (Vengosh *et al.*, 1999).

The radioactive isotopes  $^{36}\text{Cl}$  and  $^{129}\text{I}$  behave conservatively in the hydrological system and are important tools for studying salinization processes. Since 1952, atmospheric thermonuclear testing



**Figure 14** Elucidation of saline sources by using the variations of B/Cl and  $\delta^{11}\text{B}$  values. Note the expected geochemical distinction between seawater, evaporated seawater, brines (e.g., Dead Sea), hydrothermal fluids, sewage effluents, agricultural drainage, and evaporite dissolution.



**Figure 15** Schematic illustration of the expected boron isotope variations upon salinization by (1) seawater intrusion; (2) mixing with brines; (3) dissolution of marine evaporites; and (4) mixing with sewage effluents. Note the enrichment in  $^{11}\text{B}$  associated with adsorption process (sources Vengosh *et al.*, 1992, 1994).

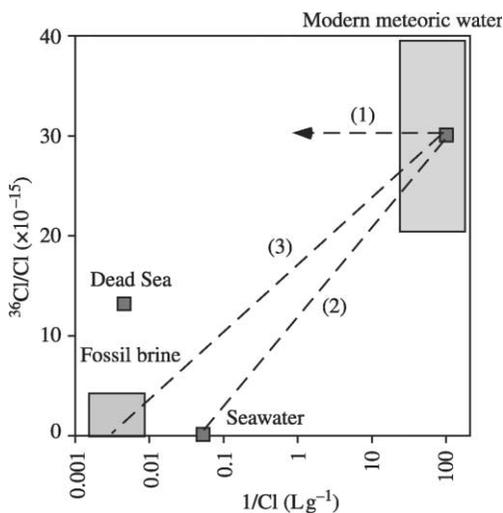
has significantly changed the  $^{36}\text{Cl}$  budget of the atmosphere. The atmospheric  $^{36}\text{Cl}$  fallout was several orders of magnitudes higher than normal flux, particularly between 1952 and 1970. Hence, the bomb  $^{36}\text{Cl}$ -pulse is an important hydrological tracer that is preserved in the hydrological system. Its signal is modified by dispersion and natural decay of  $^{36}\text{Cl}$  (half-life  $\sim 3.01 \times 10^5$  yr; Phillips, 2000, and references therein). Meteoric chloride is therefore characterized by a high  $^{36}\text{Cl}/\text{Cl}$  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  $^{36}\text{Cl}/\text{Cl}$  ratios. The distinction between meteoric and groundwater chloride (Figure 16) has been used in several studies to estimate the relative proportion of meteoric and subsurface chlorine sources in the Jordan Valley and Dead Sea (Paul *et al.*, 1986; Magaritz *et al.*, 1990; Yechieli *et al.*, 1996), closed basins in Antarctica (Lyons *et al.*, 1998), and Lake Magadi of the East African Rift (Phillips, 2000).

Similarly,  $^{129}\text{I}$  is a naturally occurring, cosmogenic, and fissiogenic isotope ( $T_{1/2} = 15.7$  Myr; Fabryka-Martin *et al.*, 1991; FabrykaMartin, 2000). Like  $^3\text{H}$ ,  $^{14}\text{C}$ , and  $^{36}\text{Cl}$ ,  $^{129}\text{I}$  was produced in bomb tests, but in greater abundance above the natural level. While some of the other anthropogenic radionuclides have returned to near pre-bomb levels in the surface environment, the  $^{129}\text{I}$  level continues to be elevated due to emissions from

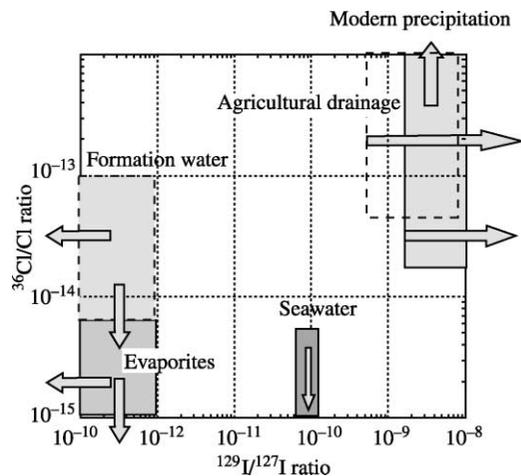
nuclear fuel reprocessing facilities, which are transported via the atmosphere on a hemispheric scale. Modern meteoric waters are expected to have large  $^{129}\text{I}/^{127}\text{I}$  ratios ( $>1,000 \times 10^{-12}$ ) relative to that in old groundwater ( $<10^{-12}$ ; Moran *et al.*, 1999, 2002). By combining the values of the isotopic ratios  $^{36}\text{Cl}/\text{Cl}$  and  $^{129}\text{I}/^{127}\text{I}$ , Ekwurzel *et al.* (2001) were able to discriminate between different saline sources in the Souss-Massa Basin in Morocco, particularly between modern saline recharge and saline groundwater (Figure 17).

Geochemical tracers are useful for delineating the sources of salinity in groundwater systems; they can also be used for studying river salinization (Herczeg *et al.*, 1993; Vengosh *et al.*, 2001; Cortecchi *et al.*, 2002; Phillips *et al.*, 2002; Mills *et al.*, 2002). River salinization can be derived from surface evaporation along the river flow, recycling of meteoric salts via irrigation and formation of agricultural return flows, discharge of saline groundwater derived from the dissolution of evaporites or from mixing with remnants of formation waters, and from anthropogenic contamination like discharge of sewage effluents.

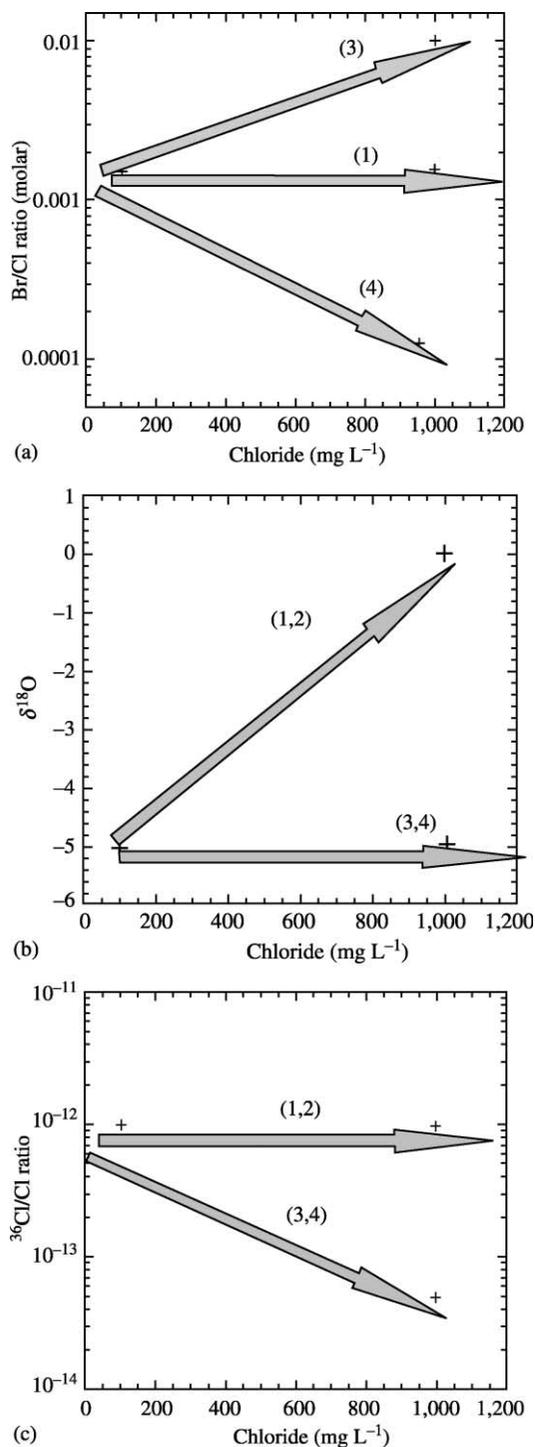
Each of these sources is characterized by identifiably different chemical and isotopic compositions. Hence, the different salinization processes induce different chemical and isotopic changes in the salinized river. By using conservative tracers of  $\text{Br}/\text{Cl}$ ,  $\delta^{18}\text{O}_{\text{water}}$ , and  $^{36}\text{Cl}/\text{Cl}$  ratios, it is possible to discriminate between these processes (Figure 18). Recycling of meteoric salts by in-stream river salinization results in



**Figure 16** Schematic illustration of the expected  $^{36}\text{Cl}/\text{Cl}$  variations versus reciprocal of chloride ( $\text{L g}^{-1}$ ) upon salinization by: (1) surface evaporation; (2) seawater intrusion; and (3) mixing with brines and/or dissolution of evaporates. The relatively high  $^{36}\text{Cl}/\text{Cl}$  ratio in the Dead Sea suggests mixing with meteoric chloride (Yechieli *et al.*, 1996) (sources Magaritz *et al.*, 1990; Yechieli *et al.*, 1996; Phillips, 2000).



**Figure 17** Elucidation of saline sources by using the variations of  $^{36}\text{Cl}/\text{Cl}$  and  $^{129}\text{I}/^{127}\text{I}$ . Note the isotopic distinction between modern meteoric water and agricultural return relative to formation water, evaporite dissolution, and seawater. Arrows represent possible extended ranges (sources Ekwurzel *et al.*, 2001; Moran *et al.*, 2002).



**Figure 18** Schematic illustration of possible Br/Cl (a),  $\delta^{18}\text{O}_{\text{water}}$  (b), and  $^{36}\text{Cl}/\text{Cl}$  (c) evolution scenarios upon river salinization: (1) surface evaporation (and/or evapotranspiration) 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.

increasing  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values with flow distance due to evaporation, but the Br/Cl and  $^{36}\text{Cl}/\text{Cl}$  ratios in the river are not expected to change with increasing salinity (Figure 18). Salinization via agricultural return flow is likely to increase the  $\delta^{18}\text{O}_{\text{water}}$  values and may change the Br/Cl ratio, but the  $^{36}\text{Cl}/\text{Cl}$  is not changed (i.e., short-term recycling of modern meteoric chlorine with a high  $^{36}\text{Cl}/\text{Cl}$  ratio). However, in dryland environment the long-term storage of chlorine in the subsurface buffers the original  $^{36}\text{Cl}/\text{Cl}$  ratio. Dissolution of halite deposits and the formation of saline groundwater are expected to form saline groundwater with a low Br/Cl ratio (e.g., Rio Grande Basin; Phillips *et al.*, 2002; Mills *et al.*, 2002) and a low  $^{36}\text{Cl}/\text{Cl}$  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 is entrapped in the basin (e.g., Jordan River; Vengosh *et al.*, 2001). In such a scenario, the  $^{36}\text{Cl}/\text{Cl}$  ratio is also expected to be low. Finally, sewage pollution increases the salinity, nitrate (with  $\delta^{15}\text{N}_{\text{nitrate}} > 10\text{‰}$ ), boron ( $\delta^{11}\text{B} < 10\text{‰}$  in domestic sewage; Vengosh *et al.*, 1994), and sulfate ( $\delta^{34}\text{S}_{\text{sulfate}} < 0\text{‰}$  in industrial areas; Cortecchi *et al.*, 2002) levels in the contaminated river.

#### 9.09.10 REMEDIATION AND THE CHEMICAL COMPOSITION OF TREATED WATER RESOURCES

As the world experiences an explosive population growth of 50%, demands for food production will result in the conversion of prime agricultural land to urban uses and the conversion of more marginal lands to agricultural uses. At the turn of the twenty-first century, 70% of the world's freshwater is used for irrigated agriculture. In order to meet global food demands, agricultural production will have to increase by two- to threefold during the next few decades, and the exploitation of freshwater resources will increase further (Hern and Feltz, 1998). The expected increase of the human population during the next century (8–12 billion by the year 2050, relative to the population of over 6 billion at the end of the twentieth century; Rouch, 1994) will increase the demands for freshwater and cultivation of marginal land, and is likely to cause severe adverse environmental impacts such as salinization of the over-exploited water resources and direct contamination by agricultural drainage water (Bölke, 2002).

In principle, two solutions can be adopted by water agencies facing long-term salinization of water resources—dilution and desalination. Dilution is the cheapest solution for pollution,

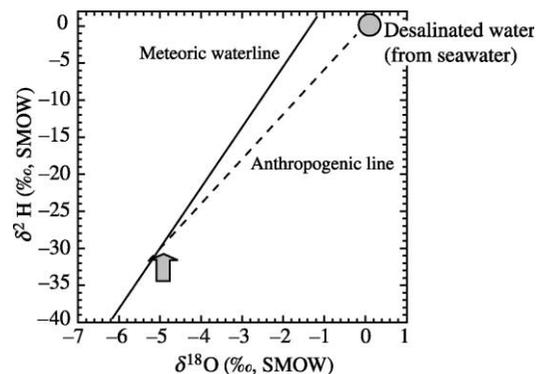
given the availability of freshwater resources. In many depleted or salinized aquifers, artificial recharge of imported water compensates for over-exploitation or reduces salinization rate. Artificial recharge modifies the oxygen and deuterium isotopic composition of the natural groundwater. In some cases where the recharge water is derived from upstream and higher elevations, the recharge causes lower  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values (e.g., the recharge of the Colorado River aqueduct in Orange County, California; [Davisson et al., 1999](#); [Williams, 1997](#)). In contrast, in cases where the recharge water is derived from open reservoirs (e.g., recharge of the Salinas River, California; [Vengosh et al., 2002a](#)) or lakes (recharge of imported water from the Sea of Galilee into the Mediterranean coastal aquifer in Israel; [Vengosh et al., 1999](#)), their  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values are significantly higher than that of the natural groundwater. Interbasin transfers are, however, no longer a possible solution for most water-scarce countries.

Desalination, in contrast, is the ultimate solution for the long-term sustainability of water-poor countries. The water crisis in the Middle East, for example, can only be resolved by large-scale desalination of seawater and brackish water ([Glueckstern, 1992](#)). By 1998,  $1.25 \times 10^4$  desalination units around the world produced about  $23 \times 10^6 \text{ m}^3 \text{ d}^{-1}$  ([Glueckstern and Priel, 1998](#)). In Saudi Arabia, 35 desalination plants were built to produce potable water from seawater and brackish water using multistage flush system (MS) and reverse osmosis (RO). Presently, Saudi Arabia is the largest producer of desalinated water in the world with a water production of  $\sim 1,000 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$  ([Abderrahmann, 2000](#)). In Israel, desalinated seawater is expected to produce about one-fifth ( $500 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ ) of the country's annual water use during the 2000s. In California, desalination of wastewater is one component of the overall water management scheme for continued exploitation of a stressed coastal aquifer as demonstrated in Orange County south of Los Angeles. Desalination of secondary treated wastewater and recharge into the aquifer is used simultaneously with the recharging of the external source (Colorado River) and continued pumping of the aquifer supply water to local inhabitants and agriculture section ([Orange County Water District, 1994](#)).

The chemical composition of water resources in the twenty-first century is likely to reflect these human interventions: the creation of new water and the contamination of the depleted water resources. RO has become the cheapest and hence most frequently used technique for desalination ([Glueckstern and Priel, 1998](#)). The generation of desalinated water is associated with chemical transformations that are controlled by the prefer-

ential selectivity of RO membrane. The ion selectivity through the membrane depends on their masses, size, charge, and reactivity. Rejection by RO membrane is stronger for heavier ions, thus the Na/Cl ratio is modified from 0.86 in seawater to 0.94 in desalinated water ([Table 1](#); data from [Vengosh et al., in preparation](#)). The preferential selection by reverse osmosis membranes of doubly charged ions ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ ) over singly charged ions ( $\text{Cl}^-$ ,  $\text{Na}^+$ ) also modifies the original chemical composition and ionic ratios of the desalted water. Thus, desalted water is modified into an Na–Cl water type ( $\text{Cl} + \text{Na}/\text{TDI} \sim 0.93$ , in equivalent units), and the Ca/Cl, Mg/Cl,  $\text{SO}_4/\text{Cl}$ , and Ca/Na ratios of RO desalted water are fivefold lower 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](#)). Finally, the RO rejection of uncharged boric acid is low, which results in enrichment of boron in desalinated water (B/Cl ratio of  $2 \times 10^{-2}$  relative to  $8 \times 10^{-4}$  in the original seawater) with a seawater isotopic signature ( $\delta^{11}\text{B} \sim 39\%$ ; [Vengosh et al., in preparation](#)).

The  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values of desalinated seawater are identical to those in seawater ([Vengosh et al., in preparation](#)). Consequently, recharge of freshwater derived from desalination either by direct leakage in the urban environment or via wastewater irrigation would have  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values that lie along a mixing line between the natural and seawater values ([Figure 19](#)). The slope of the *anthropogenic line* depends on the  $\delta^{18}\text{O}_{\text{water}}$  and  $\delta^2\text{H}$  values in the local area and is always lower than that of the natural meteoric line ([Craig, 1961, Gat, 1974](#)).



**Figure 19**  $\delta^2\text{H}$  versus  $\delta^{18}\text{O}_{\text{water}}$  values of reverse osmosis desalted seawater and the global meteoric waterline ([Craig, 1961](#)). The anthropogenic line lies on a possible mixing relationship between natural waters along the meteoric waterline (arrow) and the desalted seawater. Future formation of a large volume of desalted seawater expects to cause infiltration (e.g., leakage, reuse) of freshwater with high  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values relative to natural replenishment.

Post-treatment of desalinated water usually increases the  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  (interaction with lime) contents of the water supply to the municipality. In some cases, the addition of sulfuric acid increases the sulfate content in the post-treated water. Nevertheless, the extremely high  $\delta^{18}\text{O}_{\text{water}}$ , B/Cl, and  $\delta^{11}\text{B}$  values are not affected, so that desalinated water can be distinguished from natural water sources (Vengosh *et al.*, in preparation).

In addition to creating new water, anthropogenically induced salinization modifies the chemical composition of natural water resources. Meybeck and Helmer (1989) showed that polluted rivers are systematically enriched in  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{SO}_4^{2-}$ , and  $\text{NO}_3^-$ , relative to pristine rivers. The salinization of future water resources is expected to be derived primarily from contamination by domestic wastewater and agricultural return flow. First and secondary sewage treatments (the common sewage treatment) do not affect the inorganic chemical composition of treated wastewater (Vengosh *et al.*, 1994). The reuse of treated sewage in agriculture and the release of domestic wastewater into natural water resources will change the chemical composition of the environment. As of early 2000s,  $\sim 450 \times 10^9 \text{ m}^3$  of wastewater are globally discharged into rivers, streams, and lakes every year (Hinrichsen and Tacio, 2002). In the Middle East, reuse of domestic treated sewage is becoming one of the important water sources, given the depletion of natural water resources. In Israel, about  $300 \times 10^6 \text{ m}^3$  of treated sewage is used annually for irrigation (Blitz *et al.*, 2000). The impact of effluents enriched in sodium, sulfate, and boron are expected to modify the soil salinity (e.g., increase of sodicity), the composition of the unsaturated zone, and consequently the underlying groundwater resources. Long-term application and numerous cycles of reused wastewater are likely to affect the underlying water resources.

The second major source of salinization that is expected to shape environmental chemistry is agricultural return flow. Based on studies of irrigation drainage in the western United States, Hern and Feltz (1998) predicted that the future use of marginal land for agriculture is expected to form saline drainage effluents enriched in selenium, boron, and arsenic. Hence, the composition of drainage water (e.g., Imperial Valley, California; Table 1) is expected to affect the soil, the unsaturated zone, and the associated water resources. The bioaccumulation of selenium is turning out to be one of the most severe environmental hazards in the western United States (Hern and Feltz, 1998). Boron enrichment in soil and contaminated water will reduce soil productivity for certain crops and will increase

boron levels in contaminated water. Consequently, future salinization of water resources due to the increasing contribution of agricultural return flows will have much wider environmental implications.

In conclusion, the human impact on the salinity of the environment has caused dramatic changes in the chemical composition of soil and water resources. The continued stress on land and water resources has shifted the natural balance and has accelerated the natural salinization process, particularly in arid and semi-arid climatic zones. In addition, direct anthropogenic salinization is expected to modify the environment. The inorganic chemical composition of the pristine environment is now diminishing.

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