

# Origin and distribution of saline groundwaters in the upper Miocene aquifer system, coastal Rhodope area, northeastern Greece

C. P. Petalas · I. B. Diamantis

**Abstract** This paper describes the origins and distribution of saline groundwaters in the coastal area of Rhodope, Greece. The aquifer system includes two aquifers within coarse-grained alluvial sediments in the coastal part of the study area. Two major water-quality groups occur in the study area, namely  $\text{Ca}^{2+}$ -rich saline groundwater and  $\text{Ca}^{2+}$ -poor, almost fresh groundwater. The main process controlling the groundwater chemistry is the exchange of calcium and sodium between the aquifer matrix and intruding seawater. The natural salt water in the study area is probably residual water that infiltrated the aquifer system during repeated marine transgressions in late Pleistocene time. Seawater intrusion into the coastal aquifer system occurs as a result of overpumping in two seawater wedges separated vertically by a low-permeability layer. The rate of intrusion averages 0.8 m/d and is less than expected due to a decline of the aquifer's permeability at the interface with the seawater. The application of several hydrochemical techniques (Piper and Durov diagrams;  $\text{Na}^+/\text{Cl}^-$ ,  $\text{Ca}^{2+}/\text{Cl}^-$ ,  $\text{Mg}^{2+}/\text{Cl}^-$ , and  $\text{Br}^-/\text{Cl}^-$  molar ratios;  $\text{Ca}^{2+}/\text{Mg}^{2+}$  weight ratio; and chloride concentrations), combined with field observations, may lead to a better explanation of the origin of the saline groundwater.

**Résumé** Ce papier décrit les origines et la distribution des eaux souterraines salées de la zone côtière du Rhodope (Grèce). Le système aquifère est constitué de deux aquifères dans les alluvions grossières de la zone littorale de la région d'étude. Deux groupes principaux de qualité d'eau sont observés dans cette région, une eau souterraine salée riche en  $\text{Ca}^{2+}$ , et une eau souterraine presque douce pauvre en  $\text{Ca}^{2+}$ . Le processus

principal contrôlant le chimisme de l'eau souterraine est l'échange de calcium et de sodium entre la matrice de l'aquifère et l'eau marine de l'intrusion. L'eau salée naturelle dans cette région est probablement une eau fossile provenant d'intrusions dans l'aquifère durant les transgressions marines répétées au Pléistocène récent. L'intrusion marine dans le système aquifère littoral résulte du pompage excessif dans deux biseaux salés séparés verticalement par un niveau à faible perméabilité. La vitesse de progression de l'intrusion est en moyenne de 0,8 m/jour ; elle est inférieure à la valeur prévue pour une décroissance de la perméabilité de l'aquifère à l'interface avec l'eau marine. L'utilisation de plusieurs techniques hydrochimiques (diagrammes de Piper et de Durov, rapports molaires  $\text{Na}/\text{Cl}$ ,  $\text{Ca}/\text{Cl}$ ,  $\text{Mg}/\text{Cl}$  et  $\text{Br}/\text{Cl}$ , rapport massique  $\text{Ca}/\text{Mg}$  et concentrations en chlorures), associées aux observations de terrain, peuvent contribuer à une meilleure explication de l'origine de l'eau souterraine salée.

**Resumen** Se describen los orígenes y la distribución de las aguas subterráneas salinas en la zona costera de Rhodope, Grecia. El sistema acuífero en la zona de estudio incluye dos acuíferos formados por sedimentos aluviales de grano grueso. Aparecen dos tipos de agua en la zona de estudio: agua salina, rica en  $\text{Ca}^{2+}$ , y agua dulce, pobre en  $\text{Ca}^{2+}$ . El principal proceso que controla el quimismo es el intercambio de calcio y sodio entre el acuífero y el agua de intrusión marina. El agua salada presente de manera natural es probablemente agua residual procedente de las repetidas transgresiones marinas que tuvieron lugar en el Pleistoceno superior. La intrusión marina se debe probablemente a la sobre-explotación de dos cuñas marinas, separadas verticalmente por una capa de baja permeabilidad. La velocidad de intrusión es de 0.8 m/d, menor de la esperada por una reducción de la permeabilidad en la interfaz. La aplicación de diversas técnicas hidroquímicas (diagramas de Piper y Durov, relaciones  $\text{Na}^+/\text{Cl}^-$ ,  $\text{Ca}^{2+}/\text{Cl}^-$ ,  $\text{Mg}^{2+}/\text{Cl}^-$ ,  $\text{Br}^-/\text{Cl}^-$  y  $\text{Ca}^{2+}/\text{Mg}^{2+}$ , y concentraciones de cloruro) podrán dar lugar a una mejor explicación del origen de la salinidad.

Received, May 1997  
Revised, May 1998, December 1998  
Accepted, February 1999

C. P. Petalas (✉) · I. B. Diamantis  
Geotechnical Division, School of Civil Engineering  
Demokritos University of Thrace  
Xanthi, 67100 Greece  
Fax: +541 22540  
e-mail: jdiam@demo.cc.duth.gr

**Key words** Greece · hydrochemistry · salt-water/fresh-water relations · coastal aquifers · groundwater quality

**Introduction**

During the last decade, increasing attempts to understand the origin of saline aquifer systems have been undertaken, in order to formulate appropriate strategies to prevent or minimize salt-water intrusion. The problems associated with natural saline groundwater, salt-water intrusion, and upconing of saline water in pumping wells are major concerns in many coastal aquifers of Greece (Lambrakis et al. 1995, 1997; Kallergis et al. 1997). Both vertical and lateral intrusion occurs, usually caused by overpumping. This paper describes the hydrogeochemical evolution of groundwater in the coastal area of Rhodope. Locations are shown in *Figure 1*.

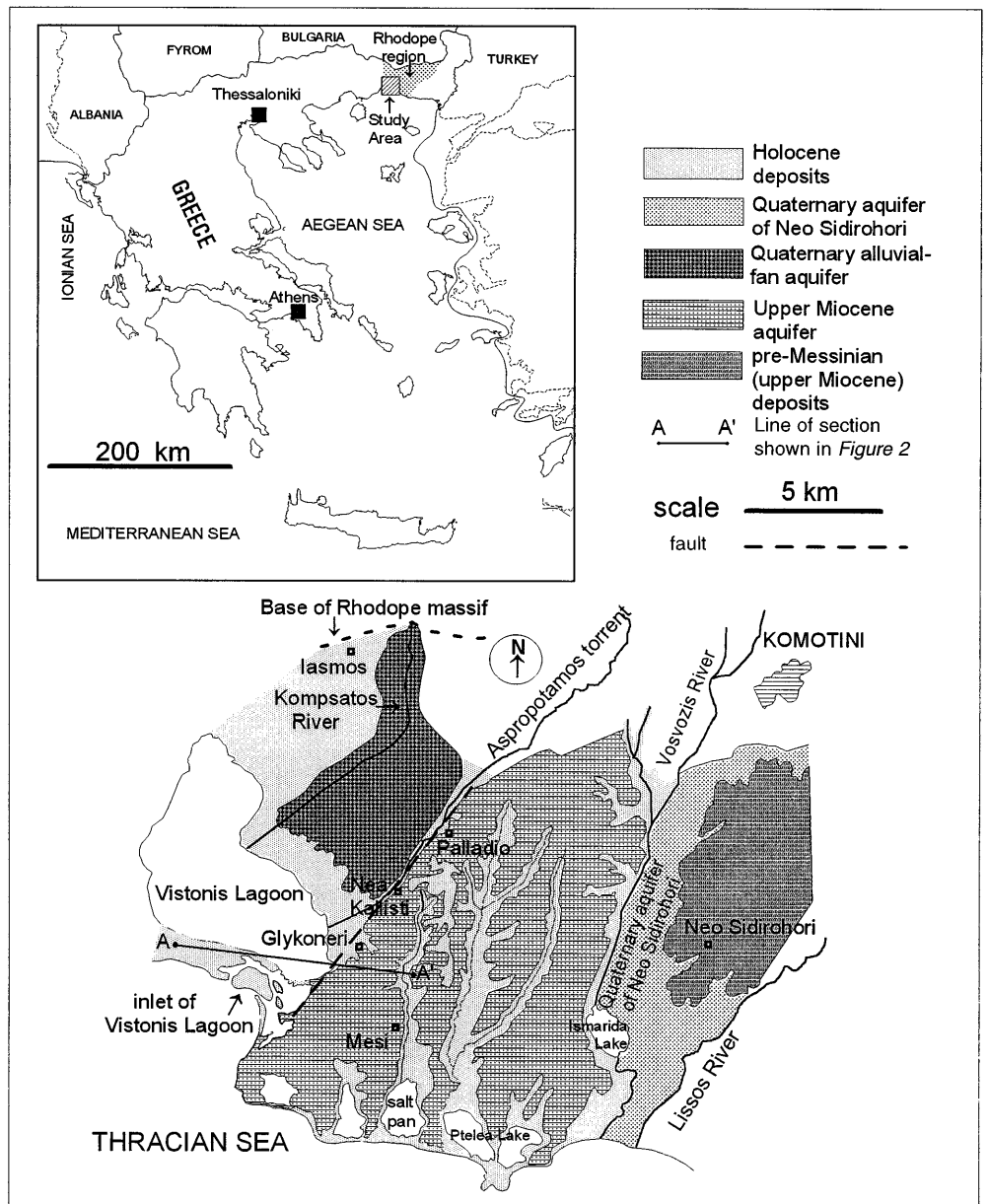
The first attempt to identify sources of salinity in the groundwater of the Rhodope area was made by deter-

mining the chloride–bicarbonate ratio, or Revelle coefficient, and by an electrical-conductivity study of widely distributed groundwater samples (Diamantis and Petalas 1989). This report is the result of studies undertaken from 1989–95, which utilized geophysical techniques, hydrogeology, hydrochemistry, and groundwater modeling techniques.

The Rhodope aquifer system provides about  $35 \times 10^6$  cm<sup>3</sup>/yr of high-quality water mainly for agriculture but also for domestic use in the prefecture of Rhodope. The aquifer system is physically complex, and it was not certain whether saline intrusion occurred in the 1970s.

The study area includes the alluvial coastal plain at the base of the Rhodope massif bounded on the north by the base of the Rhodope massif, on the west by the River Kompsatos and Vistonis Lagoon, on the east by

**Figure 1** Location and hydrogeology of the Rhodope area



the River Lissos, and on the south by the Thracian Sea (Figure 1). The study area has low relief and mostly gentle slopes. The regional annual precipitation, one of the sources of fresh-water recharge to the coastal aquifers, ranges from 329–844 mm. The average annual precipitation is 628 mm. Most precipitation is lost through runoff and evapotranspiration. The climate of the area is Mediterranean with hot and dry summers.

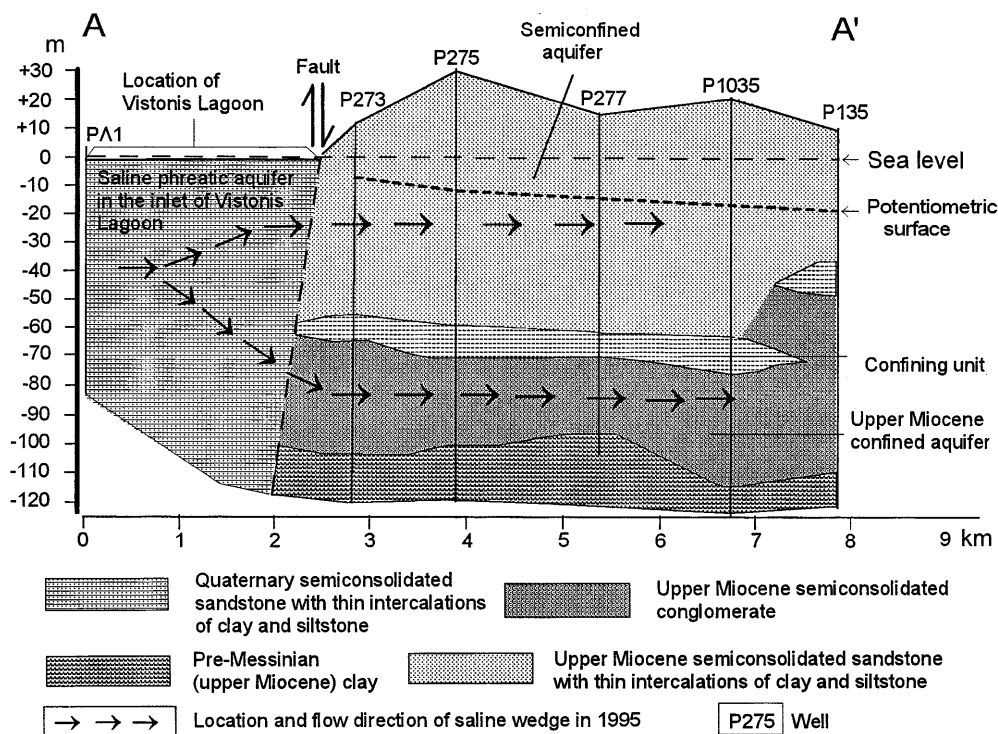
Water has been pumped from the aquifer system at an ever-increasing rate for many years; recently, withdrawal has exceeded the maximum quantity of water that can be continuously withdrawn from the Rhodope aquifer system without adverse effects (Petalas and Diamantis 1993), particularly in the Glykoneri area adjacent to the inlet of the Vistonis lagoon (Figure 1). The objectives of this investigation were to identify: (1) the sources of water input; (2) the chemistry of the various waters of the aquifer system and the areal distribution of chloride; and (3) the control of the water chemistry of the salt-water/fresh-water mixing zone by water-rock interactions during 1978–95. This paper also describes the aquifer system, its significance to regional water resources, the completed salinity study, and implications for aquifer management and regional water-resource planning.

Prior to agricultural development in the area, high inland groundwater levels imposed a strong seaward gradient on groundwater flow. This seaward gradient impeded the inland movement of saline water into the aquifer system. In recent years, water levels have declined by 10–40 m in parts of the area, causing a reversal in the groundwater gradient.

## Geological Framework

The stratigraphic sequence in the study area ranges from Eocene to late Miocene in age and is composed mainly of interbedded marl, silt, clay, sandstone, and conglomerate. The hydrogeology is shown in Figure 2. The aquifer system consists mostly of upper Miocene alluvial deposits. At the base of the sequence is a wide-spread thick clay of late Miocene age. Overlying the clay throughout much of the region is an extensive alluvial deposit laid down in a braided-river sedimentary environment. The most important feature in the paleogeographic evolution of the study area since late Miocene time is the presence of a braided-river system in which coarse-grained sediments were deposited. Fine-grained sediments (e.g., lacustrine deposits) are negligible (about 3–5%). Little of the clay mineralogy of these sediments has been studied, and only in some cases, where continuous drill-core was available, have clay minerals been directly identified. About 60–80% of the upper Miocene sediments overlying the braided-river system (confined aquifer) in the study area are interbedded sandstone, siltstone, and clay in beds ranging from a few millimeters to tens of meters thick. These fine-grained sediments are mainly calcitic and montmorillonitic clays as well as smectites. The braided-river system contains locally abundant thin coal beds that range in thickness from 1 cm to 1 m (Petalas 1997). Thin evaporitic strata of negligible thickness and very restricted in extent also occur near the base of the braided-river system (Petalas and Diamantis 1993).

**Figure 2** Hydrogeological section of the upper Miocene aquifer system, Rhodope area, showing the location and direction of seawater intrusion. All of the unit shown as the upper Miocene aquifer is the saline part of this aquifer. Line of section shown in Figures 1 and 7



The tectonic evolution of the study area is directly related to the tectonic uplift of the Rhodope massif (of Alpine age) and development of the underlying Xanthi–Komotini sedimentary basin (of Tertiary age). Upper Miocene beds were deposited in the eastern part of this basin. During late Miocene time, pronounced rotational and compressional events resulted in general uplift of the region, accompanied by differential subsidence along northwest- and northeast-trending normal faults; this activity has continued into recent time (Koukouvelas and Doutsos 1990). Several faults in the study area are important controls on the occurrence and movement of groundwater in the area (Petalas 1997).

## Hydrogeology

The hydrogeologic character of the study area is described by Petalas and Diamantis (1993), based on data obtained from pumping tests, geophysical logs (resistivity, self-potential, and gamma-ray logs; temperature logs), an electrical-resistivity survey, and field work.

A lower confined aquifer is present in coarse-grained alluvial sediments in the upper Miocene part of the Rhodope alluvial system. An upper semiconfined aquifer, which commonly contains saline groundwater, is present in alluvial sediments (mainly sandstone) in a limited area along the coast. The semiconfined aquifer is separated from the underlying confined aquifer by a thick clay unit.

Three types of pumping wells occur in the study area, namely, screened wells that are open to either the confined or the semiconfined aquifers, but not both, and screened wells open to both the confined and semiconfined parts of the aquifer system. Well depths range from 50–140 m.

Groundwater recharge to both aquifers is by infiltration of surface runoff of the numerous streams crossing the area, from direct percolation of rainfall, from groundwater inflow along the western and northeastern boundaries, from infiltration of irrigation water, and from leakage from the overlying Quaternary aquifer of Neo Sidirochori. Most recharge occurs during December–April. However, most of the annual precipitation is lost through runoff and evapotranspiration. Recharge from the semiconfined aquifer into the underlying confined aquifer does not occur under natural conditions, but it may occur artificially because of leakage through improperly plugged boreholes.

Estimated recharge to the regional flow system within the upper Miocene clastic sediments averages about 44 mm/yr, based on a simulation of the flow system using a finite-difference computer model (Petalas 1997). Isotopic analysis of the groundwater shows that the surface runoff that recharges the upper Miocene aquifer system originates mostly from areas about 200–400 m above sea level (Petalas 1997).

Pumping-test results show that despite its heterogeneity the alluvial aquifer has a narrow range of transmissivity and hydraulic conductivity values (Petalas 1997). The hydraulic conductivity of that part of the aquifer where seawater intrusion is occurring was calculated from pumping tests to be  $18 \times 10^{-5}$  m/s. The pumping tests were performed only in the confined aquifer in fully penetrating wells with piezometers as observation wells. The distances of the piezometers from the pumping wells range from 100–250 m.

A saline phreatic aquifer of Quaternary age that ranges in thickness from 80–120 m occurs in the inlet of Vistonis Lagoon (Figure 1). This aquifer consists mostly of a semiconsolidated sandstone with thin intercalations of clay and siltstone, and is in hydraulic communication with the Rhodope aquifer system (Petalas and Diamantis 1995).

## Hydrochemistry

Water samples for chemical analysis were obtained from 22 wells in both the confined and semiconfined parts of the aquifer system. Each screened well is open to either the confined or the semiconfined aquifer but not both. Each well was pumped at least 12 h before a sample was collected. Table 1 summarizes chemical analyses of groundwater samples. The temperature, pH, and electrical conductivity of the groundwater samples were determined in the field at the time of collection of the samples. The electrical conductivity of saline groundwater normally ranges from 1000–36,000  $\mu\text{S}/\text{cm}$ . The electrical conductivity in groundwater samples from the fresh-water well fields (confined aquifer) ranges from 600–800  $\mu\text{S}/\text{cm}$  (Petalas and Diamantis 1995). An electrical-conductivity value greater than 1000  $\mu\text{S}/\text{cm}$  was considered to be indicative of saline-water intrusion and was used for mapping contaminated areas (Petalas 1997). The pH of fresh groundwater in the study area normally ranges from 7–8 (mean value 7.4); the pH of saline groundwater ranges from 6.6–7.7 (mean value 7.1). Groundwater temperature ranges from 20–28 °C, reflecting a higher than normal geothermal gradient (greater than 1 °C per 33 m of depth); most samples were  $22.5 \text{ °C} \pm 1$ .

During groundwater flow from the surrounding highlands toward the basin center, groundwater dissolves minerals from the rock units, resulting in an increase in total dissolved solids.  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from weathered silicate minerals are removed from solution by cation exchange and replaced by  $\text{Na}^+$  (Petalas 1997). The sodium that occurs on cation-exchange minerals (primarily clay minerals) probably originates from salt water or from weathered sodium-rich clay (Petalas 1997).

Most chemical evolution of subsurface water occurs in the unsaturated zone, between the land surface and the water table (Groenewold et al. 1981). Dissolution of calcite is the main source of  $\text{HCO}_3^-$  in groundwater.

**Table 1** Wells sampled and selective chemical analyses of groundwaters of the Rhodope area. Concentrations are in mg/L

Sample no.	S. E. C (μS/m)	Na <sup>+</sup>	K <sup>+</sup>	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Cl <sup>-</sup>	HCO <sub>3</sub> <sup>+</sup>	SO <sub>4</sub> <sup>2-</sup>	F <sup>-</sup>	NO <sub>3</sub> <sup>+</sup>	SiO <sub>2</sub>
PKMP	365	20.7	3.5	42.5	8.8	18.9	135.8	50.8	0.3	0.4	14.3
P603	780	56.2	4	83.7	21.8	74.4	321	12.5	0.1	8.3	26.3
PYP	720	11.2	1.9	69.4	4.1	89.6	259.2	14.8	0.4	4.2	29.8
PYA	290	11.2	1.3	32.1	7.2	8	102.7	36.4	0.2	3.2	13.5
PS	330	43	5.8	34.9	10.7	10.7	130.1	23.6	0.1	13.3	22.6
PYM	470	16.8	1.5	23.4	12.7	56.3	125.1	24.3	0.1	5.3	19.6
P960	310	53.7	6.5	29.2	7.6	7.3	122	28.8	0.1	2.8	18.1
P321	2820	130.9	2.1	337.8	62.5	811.8	225.3	225.3	0.4	38.1	27.9
P351	6990	372.2	2.5	808.3	147.5	2197.9	244	120	0.2	13.8	30.7
P319	7350	289.2	4.1	874.3	203.7	2384.7	222.6	94.2	0.3	12	31.5
P381	6700	76.4	3.4	887.3	235.8	2056.1	253.0	178.2	0.3	76	27.5
P827	11000	1023.8	1.8	992.1	351.4	3992.	240.8	283	0.3	42.5	31.1
P332	2250	95.5	2	246	55.9	577.7	251.9	19.2	0.3	15.3	31.7
P1019	6950	297.1	3	745.3	200	2162.5	195.2	75	0.3	39.6	29.8
P1018	2500	225.8	2.4	254.7	71.1	807.1	253.1	56.9	0.4	19.9	28.3
P345	5600	254.6	3.2	652.5	152.6	1761.8	219.2	108.6	0.3	43.3	30
P339	3500	229.6	2.7	372.5	77.9	1070.8	212.4	42.5	0.3	25.2	30.8
P313	2450	140.9	1.7	231.1	49.7	621.4	360.1	40.6	0.5	18.6	30.6
P317	1700	269.5	2.5	53.5	9.5	379.3	244	18.7	0.3	6	28.3
P337	1600	15.5	1.4	155.2	33.5	389.9	249.5	14.1	0.4	10.5	30.3
P338	2675	153.2	2.2	258	60.1	687.7	244	40.6	0.4	18.2	28.3
P270	4750	309.6	2.7	476.4	126.9	1453.4	213.5	123.9	0.5	36.5	30.6
P328	1600	115.5	1.4	155.2	33.5	389.9	249.5	14.1	0.4	10.5	30.3
P475	7100	259.1	3.9	871.1	198.7	2298.8	203.7	122.9	0.3	26.7	31.7
P1035	6100	163.7	3.2	769.2	178.7	1946.6	231.8	62.5	0.2	17.5	30
P478	3810	287	1.4	379.8	66.9	1028	323.3	93.3	0.2	43.5	30
P822	3100	157.1	2.5	347.9	68.9	912.5	180.1	58.1	0.3	25.8	29.5
P1104	1650	118.5	2.3	164	41.8	225.2	448.5	63.1	0.3	145.6	38
P114	4700	684.2	3.3	190.9	67.2	1293.9	280.6	156.2	0.5	37.3	28.3
P1049	2200	177.1	3.	170.8	52.3	537.2	257	53.1	0.36	18.3	31
P1041	2200	279.7	1.8	147	48.3	543.6	277.5	32.8	0.64	19.3	34.5
P1028	1400	159.2	2.2	77.9	26.3	258.8	298.9	31.9	0.56	9.1	32.1
Aliki	370000	77680.2	2502.4	1042.1	8521.7	139003.2	305.1	1052.5		5.0	
Vistonos	35000	4033.5	130.2	210.0	607.0	9077.8	184.3	10502.5		0.0	
Thracian Sea	7100	10457.0	350.3	489.0	1415.4	21417.8	167.2	2250.7		0.0	
Ptelea	97000	15436.5	540.4	681.4	2038.0	30495.6	189.1	2600.4		1.2	
PA1	70000.0	16428.6	377.2	1040.4	2172.8	30196.3	530.8	4680.2		1.8	18.8

Cation exchange of Ca<sup>2+</sup> for Na<sup>+</sup> on Na-montmorillonitic clay results when excess Ca<sup>2+</sup> from calcite dissolution is available in infiltrating water (Petalas 1997). Exchange of Ca<sup>2+</sup> for Na<sup>+</sup> results in an increase in dissolved Na<sup>+</sup> and further dissolution of calcite. Through the mechanism of cation exchange, high concentrations of Na<sup>+</sup> are generated in groundwater. High Na-HCO<sub>3</sub> water at depth in the study area is largely a result of the processes of sulfate reduction in the presence of coal beds (Petalas 1997). In the coal-bearing strata of the confined aquifer, where recharge is through predominantly clayey and silty flood-basin sediments, Na<sup>+</sup> is released from montmorillonitic clays. Dissolution of gypsum, a common mineral in those sediments, results in additional Na<sup>+</sup>-Ca<sup>2+</sup> exchange (Petalas and Diamantis 1993). Where sand and silty sand are predominant in the recharge area, the dominant ions in solution are Ca<sup>2+</sup> and HCO<sub>3</sub><sup>-</sup> (Petalas 1997). The dominant clay mineral of the overlying confined-aquifer sediments in the study area is sodium montmorillonite (Petalas and Diamantis 1993).

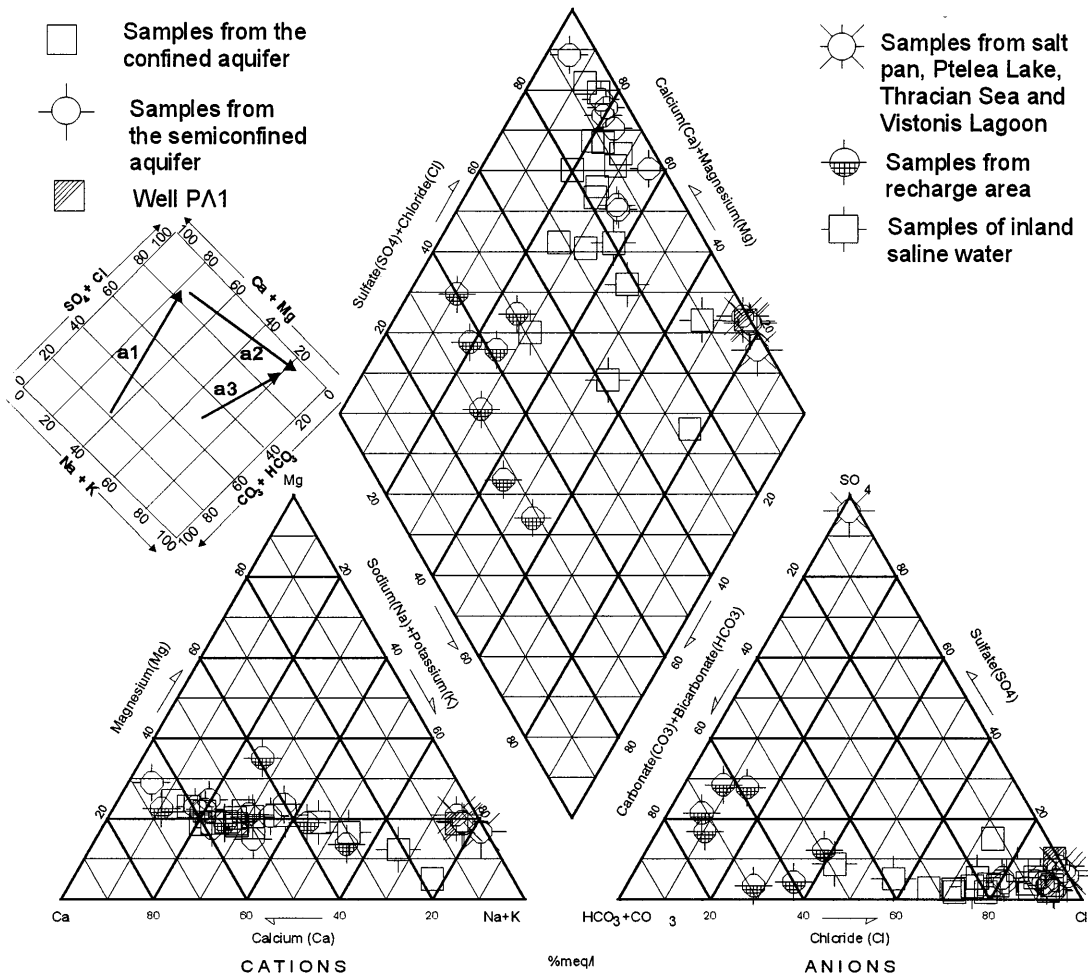
Two broad groups of groundwater, one highly saline and the other almost fresh, are recognized in the upper

Miocene aquifer. Ca<sup>2+</sup>-rich highly saline groundwater is present in both the semiconfined and the confined aquifers. The saline water in both aquifers is similar in composition, which suggests a common source. Ca<sup>2+</sup>-poor, fresh groundwater is present in most of the study area.

The concentrations of various ions in the groundwater at the sample sites are highly variable; however, many similarities also exist. Although the ionic content of groundwater of the study area is highly variable, the dominant anions are HCO<sub>3</sub><sup>2-</sup> and Cl<sup>-</sup> and the dominant cations are Na<sup>+</sup> and Ca<sup>2+</sup>. Water in the saline parts of the confined aquifer is generally the Ca<sup>2+</sup>-Cl<sup>-</sup> type. The SO<sub>4</sub><sup>2-</sup> concentration is normally very low.

The background (base line) chloride concentration of fresh water in the study area is about 138.2 mg/L. Concentrations as great as 544 mg/L occur at inland sites near Palladio and Nea Kallisti (Figure 1), far from the advancing plume of seawater. These values approximate the value of 600 mg/L that is used to indicate mixing of fresh water and seawater. An increase in the concentration of chloride helps to determine the position of an advancing front of intruding seawater. The





**Figure 4** Piper diagram based on data in *Table 1*

A sample from well P114, located inland (*Figure 3*) at a great distance from the advancing seawater front, is in the field of seawater of the Piper diagram and indicates mixing of fresh groundwater with seawater.

Local mixing of intruded seawater with fresh water along a borehole is characterized by simple mixing and evident only for a sample from the well P317 (confined aquifer; *Figure 3*). Groundwater samples from the fresh-water well fields (confined aquifer) are in the subarea of the diamond shape of the Piper diagram, where  $\text{SO}_4^- + \text{Cl}^-$  as well as  $\text{Ca}^{2+} + \text{Mg}^{2+}$  range from 30–70% (Petalas and Diamantis 1995), indicating that the aquifers are directly replenished by local precipitation and that slight mixing with brackish water occurs locally. As could be expected, almost all of the samples from the recharge area are in the field where  $\text{Na}^+ + \text{K}^+$  as well as  $\text{SO}_4^{2-} + \text{Cl}^-$  range from 0–50%.

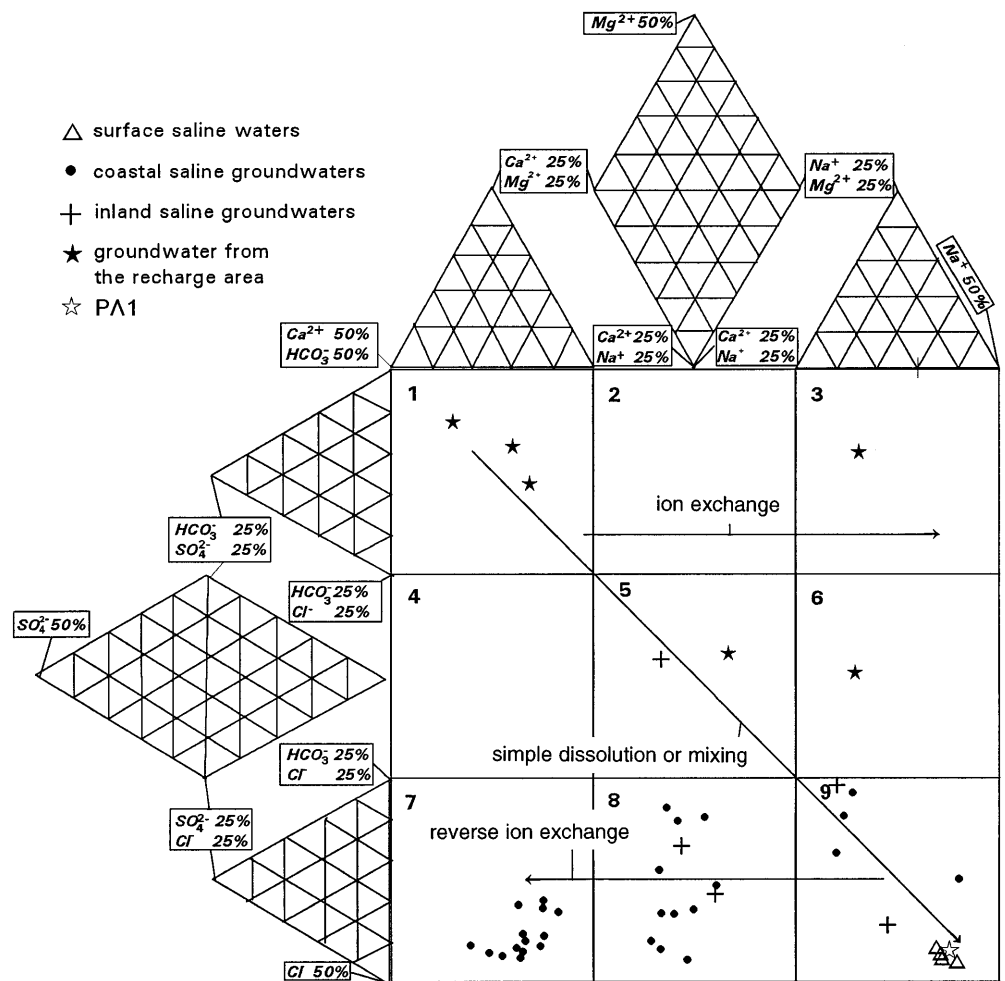
As shown in *Figure 5*, most samples of coastal saline groundwater plot in fields 7 and 8; in field 7,  $\text{Cl}^-$  and  $\text{Ca}^{2+}$  are dominant, and in field 8,  $\text{Cl}^-$  is dominant or no dominant cation is evident. These analyses may reflect reverse-ion exchange of  $\text{Na}^+ - \text{Cl}^-$  waters. Reverse-ion exchange, in which  $\text{Na}^+$  reduces preferen-

tially for  $\text{Ca}^{2+}$ , is a common feature of waters on the fringe of a saline intrusion (Lloyd and Heathcote 1985). The small number of coastal saline-water samples in field 9 in which  $\text{Na}^+ - \text{Cl}^-$  is dominant represents end-point water. In *Figure 5*, analyses of inland saline groundwater plot in fields 2, 5, and 9, which indicates waters exhibiting simple dissolution or mixing and possibly reverse-ion exchange. According to Howard and Lloyd (1983), in areas of recent seawater intrusion, water analyses predominantly show ion exchange, whereas in areas of old seawater intrusion the analyses reveal little or no evidence of ion exchange. Thus, the inland saline groundwater in the study area is considered to be the residual water of an old seawater intrusion.

Samples of groundwater from recharge areas (*Figure 5*) are dominated by  $\text{HCO}_3^{2-}$  and  $\text{Ca}^{2+}$ , as expected. Mixing of fresh water and saline water can occur in open boreholes that penetrate aquifers containing both types of water. If the hydraulic head in a fresh-water aquifer is higher than in the salt-water unit, fresh water will intrude into the saline formation.

To facilitate a sustainable water-resource management program for the Rhodope aquifer system, it is desirable to differentiate between modern and ancient seawater intrusions and between modern seawater

**Figure 5** Durov diagram (expanded) based on data in Table 1



intrusion and original formation water. Different residence times of the salt water within the aquifer may hold the key to distinguishing among these origins. Isotopic differentiation through the use of an isotope of tritium is one possible analytical tool for distinguishing old from new seawater. The tritium content of recent continental water is several tritium units (TU) greater than seawater in deep aquifers, which contain almost no tritium because of long residence times (Custodio 1987). Because the half-life of the tritium isotope is so short (12.4 yr), and because isotopic analyses reveal (Petalas 1997) a residence time of more than 20 yr for most water in both aquifers (confined and semiconfined), almost all water samples from the study area contain no tritium. Even seawater in the saline aquifer underlying Vistonis Lagoon (Figure 2) has a long residence time. As a consequence, the use of a tritium isotope to differentiate the various types of groundwater is not feasible in this area.

The average  $\text{Ca}^{2+}/\text{Mg}^{2+}$  weight ratio of 0.25 in seawater of the study area is very low compared to the characteristic average value of 4.0 in both saline and fresh groundwater of the study area (Petalas 1997). Ion exchange between intruding seawater and the rock matrix of the fresh-water aquifer results in an increase

in  $\text{Ca}^{2+}$  as compared to the amount in seawater. This increase in the  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ratio may be more pronounced in older waters than in modern waters (Sidenvall 1981). The average  $\text{Br}^-/\text{Cl}^-$  weight ratio in the saline groundwaters of the study area is approximately  $4.55 \times 10^{-3}$  (Petalas 1997), slightly greater than the average ratio in seawater of the study area ( $3.3 \times 10^{-3}$ ). Thus, the mixing of intruded seawater with fresh water caused only a slight change in the  $\text{Br}^-/\text{Cl}^-$  ratio. Bromide concentrations, probably due to the intrusion of seawater into the semiconfined and confined aquifers of the study area, average approximately 12.5 mg/L; the  $\text{Br}^-$  concentrations range from 3.9–43.5 mg/L.

According to Magaritz and Luzier (1985), groundwater samples containing less than 15% seawater are enriched in  $\text{Na}^+$ . As the percentage of seawater increases, the water becomes increasingly enriched in  $\text{Ca}^+$  and  $\text{Na}^+$  is depleted; thus  $\text{Na}^+$ , which is strongly selected by the exchanger (clay), displaces  $\text{Ca}^+$ , and clay minerals are enriched in  $\text{Na}^+$  (Sayles and Mangelsdorf 1977).

Boron was detected in some groundwater samples in the study area, and the fact that boron concentrations are higher in the higher temperature samples (Petalas



1997) may indicate the presence of hydrothermal water (Welch and Preissler 1986).

## Natural Saline Water

Natural saline groundwater, generally, is regionally occurring saline groundwater that underlies fresh-water aquifers. Salinization, indicated by an increase in TDS, is the most widespread form of water contamination. The effect of salinization is an increase in concentrations of specific chemical constituents as well as in overall chemical contents. Natural processes and human activities are potential sources of salinity. Mixing of different waters is often enhanced by human activities, e.g., improper drilling and well construction may create artificial connections between fresh-water aquifers and saline-water aquifers that are naturally separated by impermeable layers. Pumping of fresh water may change the direction of groundwater flow and cause salt-water encroachment into the pumped well. The presence of natural saline groundwater may generally be attributed to residual water from the time of deposition in a saline environment, solution of mineral matter, intrusion of seawater, or any mixture of the above (Richter and Kreitler 1993).

Natural saline groundwater is present in the study area. Salinization of fresh groundwater resources is occurring in much of the study area. Two potential sources of salt water have been identified: recent seawater intrusion and natural saline groundwater (brines; Petalas and Diamantis 1992).

As used in this study, natural saline water, or brine, is  $\text{Na}^+ - \text{Cl}^-$ -rich saline groundwater of probable marine origin, in the form of isolated pockets that are present at depths no greater than 150 m. The origin of brines in the area is generally not well understood. Natural saline groundwater was detected in the study area prior to the beginning of groundwater development in the mid-1970s. Natural saline water underlies fresh water in both aquifers in the southwestern part of the study area (the villages of Glykoneri and Mesi) and in the confined aquifer in the vicinity of Nea Kallisti and Palladio (Figure 1). In Nea Kallisti and Palladio, where abundant fresh water overlies saline water, no major problems of salt water mixing with fresh water occur. In contrast, in the southwestern part of the study area, drawdown of the potentiometric surface is so great that the fresh-water/salt-water interface has moved into the cones of depression of the individual wells, resulting in contamination of the wells. Unfortunately, it is almost impossible to obtain representative samples for chemical analyses and thus to identify natural saline water in this area. Only one sample, from well P114 (Table 1), is considered to be representative of natural saline groundwater. Also, the scarcity of reliable data makes it impossible to delineate precisely the chemical evolution of natural saline groundwater during the last two decades.

The occurrence of natural saline groundwaters may be related to (Petalas and Diamantis 1992):

1. Brines that originated as residual bittern brine solutions left after the precipitation of evaporites during the Messinian salinity crisis (Hsü et al. 1977); and
2. Slumping of sediments due to faulting that has exposed permeable units to landward intrusion of seawater

Two additional possible sources of salinity are (1) leaching of evaporitic strata; and (2) concentration of dissolved solids through membrane filtration.

Dissolution of salt in the subsurface may be the best explanation for sedimentary basin brines (Land 1987). Significant recharge pulses may dissolve this salt and flush it into groundwater. Leaching of evaporitic strata is ruled out owing to the fact that evaporitic strata in the study area are of negligible thickness and very restricted in extent. In addition, molar ratios of major chemical constituents, such as  $\text{Na}^+/\text{Cl}^-$ ,  $\text{Ca}^{2+}/\text{Cl}^-$  and  $\text{Mg}^{2+}/\text{Cl}^-$ , which can be used to differentiate an evaporation trend (1:1 slope) from a mixing trend (typically not a 1:1 slope), do not display a 1:1 slope.

Residual saline water generally does not occur within the shallow subsurface (<100 m) because of the normal flushing of formation water by precipitation through time (Richter and Kreitler 1993). Relatively young aquifers may still contain pockets of connate water where hydraulic gradients and hydraulic conductivities are low.

The salt water in the study area is probably residual water that infiltrated the aquifer during repeated marine transgressions that covered much of this area in late Pleistocene time (Perissoratis and Mitropoulos 1989). Apparently, insufficient time has elapsed for the salt water to have been flushed. The position of this mixing or transition zone varies in response to changes in either flow component, mostly in response to heavy pumpage of fresh water. This relict seawater varies in its composition, reflecting local recharge/discharge conditions.

In natural membrane filtration, basinal waters are forced through low-permeability shales, leaving a brine on the high-pressured side of the membrane. The waters apparently interact with clays, altering the concentrations of  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{B}^-$  (Sanders 1991). Haydon and Graf (1986) argue that  $\text{Ca}^{2+}$  must be retained by shale membranes preferentially relative to  $\text{Na}^+$  in virtually all natural sedimentary environments. According to Sanders (1991), membrane filtration apparently did not alter composition of the waters. Opponents of the salt-sieving theory note that: (1) sufficient pressure gradients are probably not generated in nature; (2) the chemistry of brines in shale-rich sections does not conform to expected patterns; and (3) a wide variety of formation-water types are observed in similar settings (Land 1987). Petrologic characteristics of the upper Miocene aquifer system indicate that it has never been subjected to such a pressure regime (Petalas and Diamantis 1993). Consequently, the probability is

very small that membrane filtration has been an active process in the study area.

## Seawater Intrusion

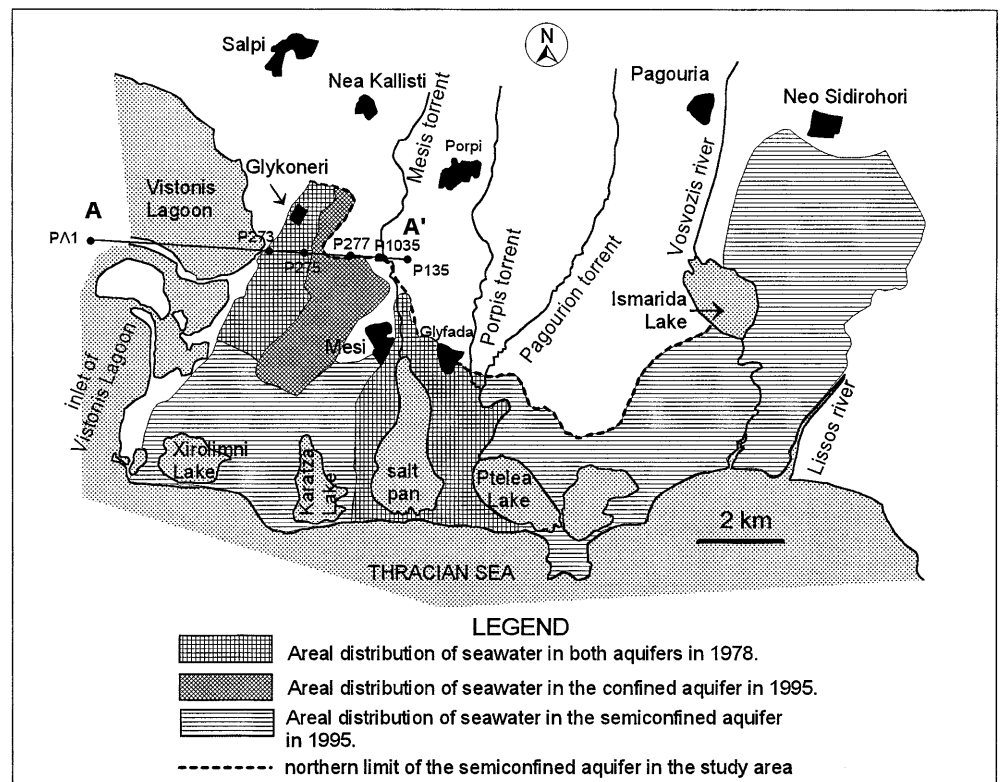
For seawater intrusion to occur, a permeable formation must be in hydraulic connection with seawater. Another necessary condition is that there be an inland gradient; that is, there must be a tendency for water to move inland from the seawater sources. Such an inland gradient normally would result from pumping at rates higher than the ability of the aquifers to supply fresh water from some inland source. These conditions have existed in the southwestern part of the study area since the mid-1970s. Seawater intrusion occurs in the coastal part of the Rhodope aquifer system as a result of widespread and dramatic decline in groundwater levels relative to mean sea level (Diamantis and Petalas 1989; Petalas and Diamantis 1993). Particularly since 1978, the groundwater level has declined substantially due to increasing rates of withdrawal. The main point of entry of saline water into the Rhodope aquifer system is the inlet of Vistonis lagoon. Also, some salt water enters the Rhodope aquifer system through the salt pan area, but this point of entry is of secondary importance for seawater intrusion. The extent of intrusion is shown in Figure 6.

Most research on confined coastal aquifers assumes that the aquifer is directly connected to the sea. Rela-

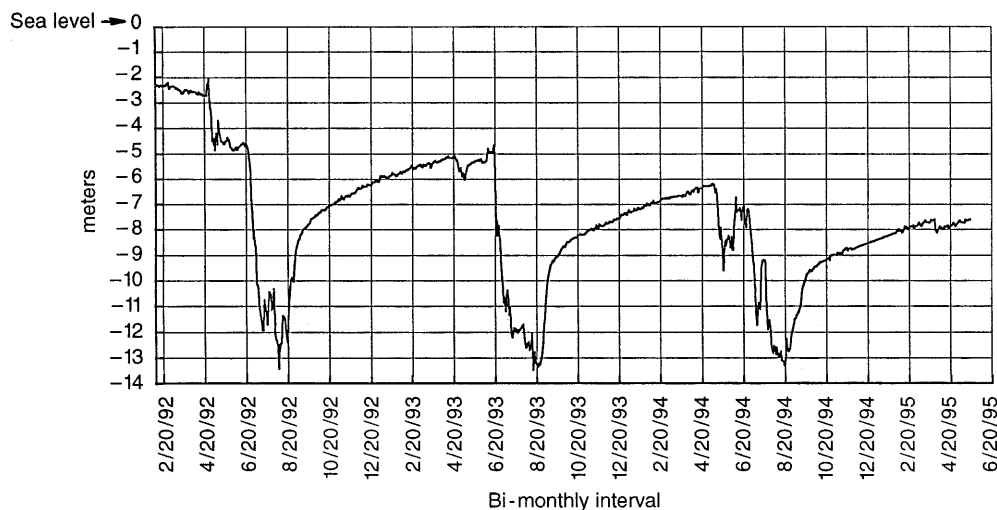
tively little attention has been paid to the problem of seawater intrusion in a layered aquifer system, such as the Rhodope system, that is not directly connected to the sea. In this study, the system was investigated to determine the influence of an aquifer in the inlet of Vistonis Lagoon between the main aquifer system and the sea. Only a few wells pump from this phreatic aquifer during the cold season, so the available data are very limited. Seawater intrusion was observed in the vicinity of Mesi and Glykoneri in 1975. At first, it was noted at a few specific isolated spots, each quite small in area, and where only fresh groundwater was being pumped from the Rhodope aquifer system. Then it spread out gradually, and by 1978 it covered a quite large area (Figure 6). By late 1989, a reconnaissance survey indicated a substantial increase in the area affected by seawater intrusion (Diamantis and Petalas 1989). A few years later, in 1995, conspicuous increases in the area of intrusion had occurred (Figure 6).

Wedges of seawater from the saline aquifer intrude into each of the two major aquifers; the lower wedge is the more extensive. The extent of seawater intrusion into the confined aquifer is also indicated by the distribution of chloride in Figure 3. In Figure 7, a characteristic hydrograph is shown for well P277 (Figure 3). The pronounced periods of drawdown, namely April–September, are related to heavy withdrawal for agriculture. The periods of recovery, namely October–March, are related to the periods of heavy rainfall with practically no groundwater pumpage. The average net annual decline was 1 m from 1978–95 in the

**Figure 6** Extent of seawater intrusion in the semiconfined and confined aquifers of the Rhodope aquifer system, 1978 and 1995



**Figure 7** Hydrograph of well P277, February 20, 1992, to May 20, 1995, in the saline part of the confined aquifer



confined aquifer. The lowest water level (30–40 m below mean sea level) occurs during July–August.

Excessive pumping in the study area has resulted in such large drawdowns of the water table and the potentiometric surface of the confined aquifer of the coastal part of the aquifer system, that the fresh-water/salt-water interface has moved into the cones of depression of many wells. Where fresh groundwater is underlain by saline water, pumping a well in the fresh groundwater zone causes the fresh-water/salt-water interface to rise. This upconing is in response to the pressure reduction on the interface due to drawdown of the water table around the well.

That the water chemistry of the mixing zone is so greatly modified by  $\text{Na}^+$ – $\text{Ca}^{2+}$  base exchange indicates that the connection with the sea is partially blocked. Because the water in the transition zone between fresh water and seawater is almost stagnant (Goldenberg et al. 1983), one can regard this zone as formation water (Magaritz and Luzier 1985). Based on experimental studies, Goldenberg et al. (1983) suggest that the permeability of sand aquifers may decrease at the interface between fresh water and seawater as a result (Magaritz and Luzier 1985) of the reaction between small amounts of clay in the sediments and solutions of various compositions passing through the sediments. The possibility that authigenic smectite, which is the major cause of the permeability reduction (Goldenberg 1985), can form in the aquifer, may indicate that even if the sediments did not originally contain smectite, reduced hydraulic conductivity would be expected given sufficient time (Magaritz and Luzier 1985). Smectite is a group name for a variety of swelling clays that have high cation-exchange capacity. Montmorillonite is one type of smectite and is common in the Rhodope aquifer system.

The rate of seawater intrusion is about 0.6 km/yr (Petalas 1997). This rate is based on the hydraulic characteristics of the confined aquifer, the fact that the confined aquifer receives steady underflow from the saline phreatic aquifer (constant-head boundary) and

the hydraulic-head gradients across the boundary. In 1978, seawater intrusion in the study area (Figure 6) was observed only in wells within 1.5 km of the coast (inlet of Vistonis lagoon), except in the Mesi area along the salt pan, where intrusion had progressed as much as 5.75 km from the coast; here the point of entry for seawater intrusion is the coast of Thracian Sea, south of the salt pan. Increased groundwater withdrawal advanced the position of the salt-water front to about 4.75 km from the coast, at an average rate of 0.8 m/d. In contrast, between 1978 and 1995, the landward movement of the salt water near the salt pan stopped. The hypothesis is that the intrusion is inhibited by a fault that acts as a barrier. Additional research is needed to solve this problem.

Considerable degradation of the fresh groundwater is caused by the presence of many improperly constructed or abandoned wells, namely, screened wells that are open to both aquifers in the study area. These wells represent conduits of groundwater contamination by artificially creating vertical communication between the hydrogeologically separated shallow semiconfined and lower confined aquifers. Heavy draft during the pumping season lowers the water levels in the producing zones below the water level in the upper aquifer, permitting poor-quality waters to enter the lower aquifer through well screens as well as through the open borehole itself. The lowering of the potentiometric surface has resulted in the abandonment of many wells due to water-quality degradation. In spite of the steady decline in groundwater quality during the last 25 yr, groundwater that is now saline (4000–12,000  $\mu\text{S}/\text{cm}$ ) continues to be used for agriculture.

## Conclusions

Identification of the geochemical processes that control the evolution of the groundwater chemistry is essential for predicting long-term groundwater quality in the

Rhodope aquifer system. These geochemical processes are carbonate dissolution, gypsum dissolution, and cation exchange. A combination of these processes produces water that is highly mineralized but generally suitable for agricultural and livestock use. Significant concentrations of  $\text{Na}^+$  are generated by cation exchange on sodic montmorillonitic clays. The mineralogy of sediments enclosing the aquifers is also a key factor in the chemical evolution of the groundwater. Degradation of groundwater quality may be minimized if these factors are understood and integrated in a management plan for the system.

Additional field information and well monitoring are needed to model the behavior of the zone of seawater intrusion more satisfactorily and to estimate the rate of movement of the fresh-water/salt-water interface. The study of the upper Miocene aquifer offers an opportunity to identify the complex of chemical and physical parameters in a coastal aquifer system, including various possible sources of saline groundwater that can degrade groundwater quality.

## References

- Appelo CAJ, Postma D (1993) Geochemistry, groundwater, and pollution. A.A. Balkema, Rotterdam
- Custodio E (1987) Hydrogeochemistry and tracers. In: Custodio E (ed) Groundwater problems in coastal areas. UNESCO, Studies and Reports in Hydrology 45, pp 213–269
- Diamantis IB, Petalas CP (1989) Seawater intrusion into coastal aquifers of Thrace and its impact on the environment. *Toxicol Environ Chem* 20–21:291–305
- Goldenberg LC (1985) Decrease of hydraulic conductivity in sand containing an interface between seawater and diluted suspension of clay. *J Hydrol* 78:183–189
- Goldenberg LC, Magaritz M, Mandel S (1983) Experimental investigation on irreversible changes of hydraulic conductivity in the seawater–freshwater interface in coastal aquifers. *Water Resour Res* 9:77–85
- Groenewold GH, Rehm BW, Cherry JA (1981) Depositional setting and groundwater quality in coal-bearing sediments and soils in western North Dakota. In: Ethridge FG, Flores RM (eds) Recent and ancient non-marine depositional environments: models for exploration. *SEPM Spec Publ* 31, pp 157–167
- Haydon PR, Graf DL (1986) Studies of smectite membrane behavior: temperature dependence, 20–180°C. *Geochim Cosmochim Acta* 50:115–121
- Howard KWF, Lloyd JV (1983) Major ion characterization of coastal saline groundwaters. *Ground Water* 21:429–437
- Hsü KJ, Montadert L, Bernoulli D, Cita MB, Erickson A, Garrison RE, Kidd RB, Melieres F, Muller C, Wright R (1977) History of the Mediterranean salinity crisis. *Nature* 267:399–403
- Kallergis G, Lambrakis NJ, Nokas-Zographos H (1997) Estimating of the refreshing time of the aquifers in the coastal and island regions. Proc 3rd National Congress of the Greek Committee for the Management of the Water, Greece, pp 225–228 (in Greek)
- Koukouvelas I, Doutsos T (1990) Tectonic stages along a traverse crosscutting the Rhodopian zone (Greece). *Geol Rundsch* 79:753–776
- Lambrakis NJ, Voudouris KS, Tiniakos LN, Kallergis G (1995) Impacts of simultaneous action of drought and overpumping on Quaternary aquifers of Glafkos basin (Patras region, western Greece). *Environ Geol* 29:209–215
- Lambrakis NJ, Nokas-Zographos H, Kallergis G (1997) The problems of salinization of the coastal aquifer due to the lack of an integral management of water resources. Proc 3rd National Congress of the Greek Committee for the Management of the Water, Greece, pp 199–205 (in Greek)
- Land LS (1987) The major ion chemistry of saline brines in sedimentary basins. In: Banavar JR, Koplik J, Winkler KW (eds) Physics and chemistry of porous media II. Ridgefield, Connecticut, Am Inst Phys Conf Proc 154, pp. 160–179
- Lloyd JW (1985) The hydrochemistry of the aquifers of north-eastern Jordan. *J Hydrol* 3:319–330
- Lloyd JW, Heathcote JA (1985) Natural inorganic hydrochemistry in relation to groundwater – an introduction. Clarendon Press, Oxford
- Magaritz M, Luzier JE (1985) Water–rock interaction and seawater–freshwater mixing effects in the coastal dunes aquifer, Coos Bay, Oregon. *Geochim Cosmochim Acta* 49:2515–2525
- Perissoratis C, Mitropoulos D (1989) Late Quaternary evolution of the Northern Aegean shelf. *Quat Res* 32:36–50
- Petalas CP (1997) Analysis of aquifer systems in the heterogeneous coastal plain of Rhodope region. PhD, University of Thrace, Department of Civil Engineering, Xanthi, Greece (in Greek)
- Petalas CP, Diamantis IB (1992) Techniques for identifying potential sources of groundwater salinization in the same aquifer system (The case of the coastal area of Rhodope, Greece). *Geol Soc Greece Bull* 27:5–16 (in Greek)
- Petalas CP, Diamantis IB (1993) Hydrogeological investigation of the aquifer system formed in the east part of Xanthi–Komotini sedimentary basin. Proc 2nd Hydrogeol Congr, Patras, Greece, pp 403–418 (in Greek)
- Petalas CP, Diamantis IB (1995) Investigation of the mechanism of seawater intrusion and hydrochemical conditions in the coastal aquifers of Rhodope. Proc 3rd Hydrogeol Congr, Iraklio, Greece, pp 323–334 (in Greek)
- Richter BC, Kreitler CW (1993) Geochemical techniques for identifying sources of ground-water salinization. CRC Press, Boca Raton
- Sanders LL (1991) Geochemistry of formation waters from the Lower Silurian Clinton Formation (Albion Sandstone), eastern Ohio. *AAPG Bull* 75:1593–1608
- Sayles FL, Mangelsdorf PC Jr (1977) The equilibration of clay minerals with seawater exchange reactions. *Geochim Cosmochim Acta* 41:951–960
- Sidenvall J (1981) Fossil groundwater of marine origin in the Uppsala area, Sweden. Proc 7th Salt Water Intrusion Meeting, Uppsala, Sweden, pp 40–44
- Welch AH, Preissler AM (1986) Aqueous geochemistry of the Bradys Hot Springs geothermal area, Churchill County, Nevada. US Geol Surv Water-Supply Paper 2290, pp 17–36