INTERNATIONAL ASSOCIATION OF HYDROGEOLOGISTS SELECTED PAPERS

5

Nitrates in Groundwater

Editors: Lidia Razowska-Jaworek
Andrzej Sadurski

Nitrate pollution and quality degradation of Ionian coastal groundwater (Southern Italy)

M. Polemio, P.P. Limoni, D. Mitolo, F. Santaloia and R. Virga
C.N.R. I.R.P.I., Bari, Italy

CHAPTER 17

Nitrate pollution and quality degradation of Ionian coastal groundwater (Southern Italy)

M. Polemio, P.P. Limoni, D. Mitolo, F. Santaloia and R. Virga
C.N.R. I.R.P.I., Bari, Italy

ABSTRACT: The chemical and physical characterization of groundwater described by the paper resulted from a careful analysis of: the aquifers lying in the Ionian coastal plain; of the relations between surface waters and groundwater and of the effects of anthropogenic factors on water quality. Two main types of aquifers have been recognized in the study area: one involving the marine terraces and alluvial deposits in the inland sectors, and the second one corresponding with the alluvial, marine and coastal deposits of the Ionian coastal plain. The quality of the entire groundwater system has been degraded by anthropogenic activities. This degradation is significant in terms of nitrate concentrations, which have increased considerably, especially in the years between 1990 and 2002. Two areas show a complex and serious degradation. The first area is located between the Agri and Cavone rivers, while the second one is located between the Basento and Bradano rivers. The total and fecal coliforms have been reported in high concentrations in the latter area, along with nitrogen cycle species and carcinogenic elements.

INTRODUCTION

The study area lies in the southernmost part of the Basilicata (or *Lucania*) region in Southern Italy, along the Ionian coastal plain, known as the *Piana di Metaponto* (Metaponto Plain), stretching across the central and lower valleys of the Sinni, Agri, Cavone, Basento and Bradano rivers (Figure 1).

Throughout the twentieth century, land reclamation works, the construction of more than ten dams and the introduction of modern irrigation systems have deeply modified the water cycle along the coastal plain. The area is farmed intensively and the quality of the groundwater is vital for the expansion of the tourist industry and for farming activities throughout the Ionian plain.

Attention has been focused on the shallow aquifer of the coastal plain, which is the most important in terms of practical utilization, as highlighted by Radina (1956). This aquifer is also the most subject to seawater intrusion and the risk of groundwater degradation (Polemio, Limoni, Mitolo *et al.* 2002b).

The geological and hydrogeological profile of the study area, as well as chemical and physical features and the quality of groundwater, have been inferred from an analysis of historical data concerning 1,130 boreholes (Polemio *et al.* 2002c). A monitoring programme was realized in a selected area during 2002, in order to evidence the trend of nitrate pollution.

The characterization of nitrate concentration variations and the general effect of anthropogenic factors on groundwater in terms of pollution, emphasize how important the issue of nitrate pollution is for these groundwater resources.

Extensive research has indicated that agricultural practices may cause nitrate contamination to be so high as to exceed the maximum acceptable level for drinking-water (Böhlke 2002). As a consequence, nitrate contamination of groundwater has become a global problem (Spalding and Exner 1993), commonly related to a variety of causes, not just intensive farming but also high density housing, low-efficiency sewerage and purification systems, and irrigation using sewage effluents, particularly in a region of mixed agricultural land uses such as the study area Voterdy. The increase in groundwater nitrate concentrations is a source of real concern as it may be associated with loss of fertility of the overlying soil, eutrophication when the groundwater discharges into the surface water, and potential health risks for animals and human beings.

Soil and groundwater contamination due to agricultural and livestock management practices should already be regarded as a serious environmental threat to the area under examination.

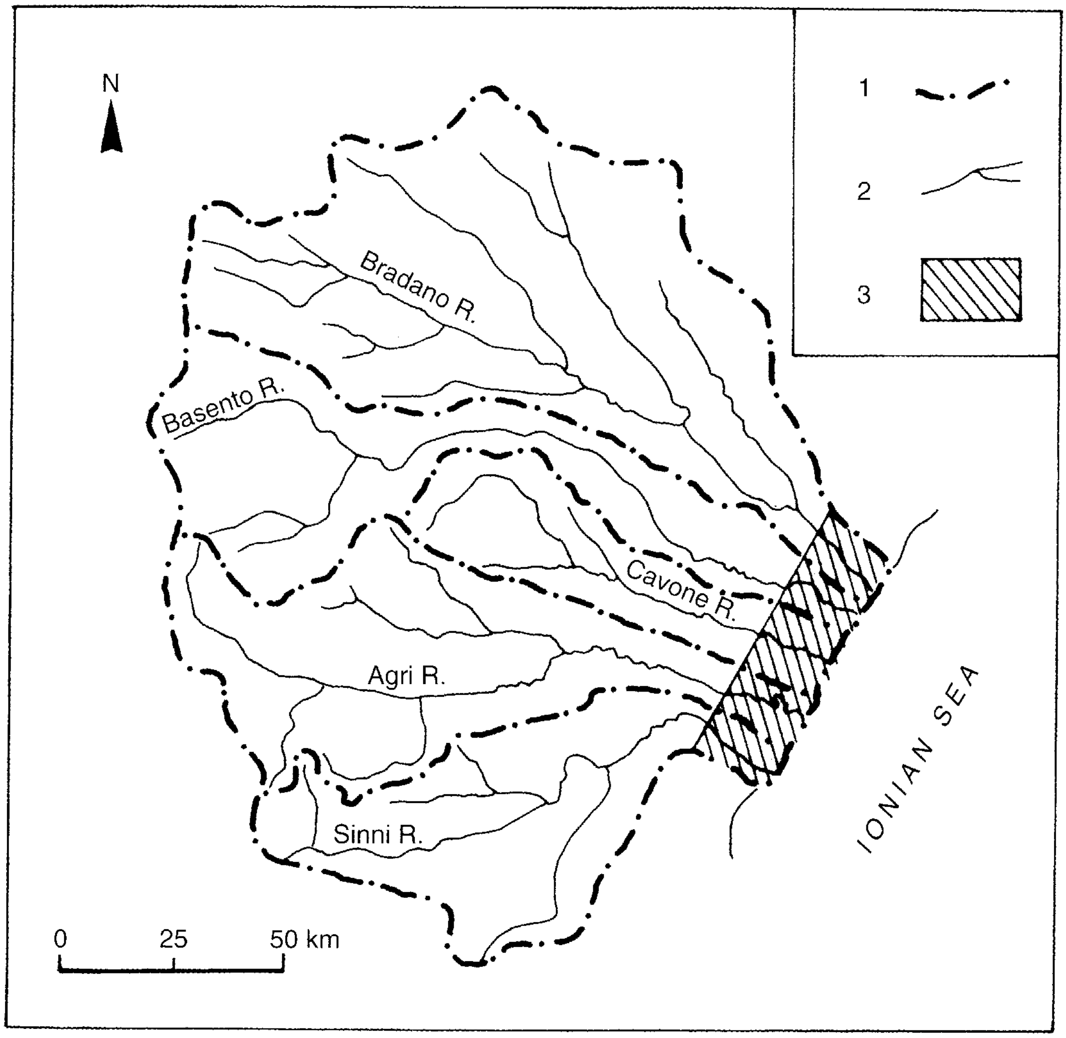

Figure 1. Study area and main rivers. 1) catchment's boundary; 2) main drainage network; 3) study area.

GEOLOGICAL AND HYDROGEOLOGICAL SET-UP

The Marine Terraced Deposits (regressive deposits consisting of sands, conglomerates and silts of the Middle–Upper Pleistocene age) overlying the Subapennine Clayey Formation (silty-clayey successions of the Late Pliocene?–Middle Pleistocene age) outcrop in the upland segments of the study area, while the alluvial, transitional, marine and coastal deposits (Holocene age) outcrop mainly in the coastal plain and along the rivers (Figure 2).

Based on lithological logs, the lithological profile of the shallow portions of the area has been accurately depicted (Figure 3). As regards the inland areas where marine terraces outcrop, three units have been identified below the topsoil (Figure 2). The upper unit consists of pebbles, locally cemented and dispersed in a sandy matrix, with sands and silty-clayey levels. The middle sandy unit, around 40 m thick, is composed of fine- to coarse-grained sands. Different clayey and silty-clayey strata, sandstone levels and gravelly lens are also widespread in this sandy unit. The third unit is represented by a clayey and silty-clayey succession.

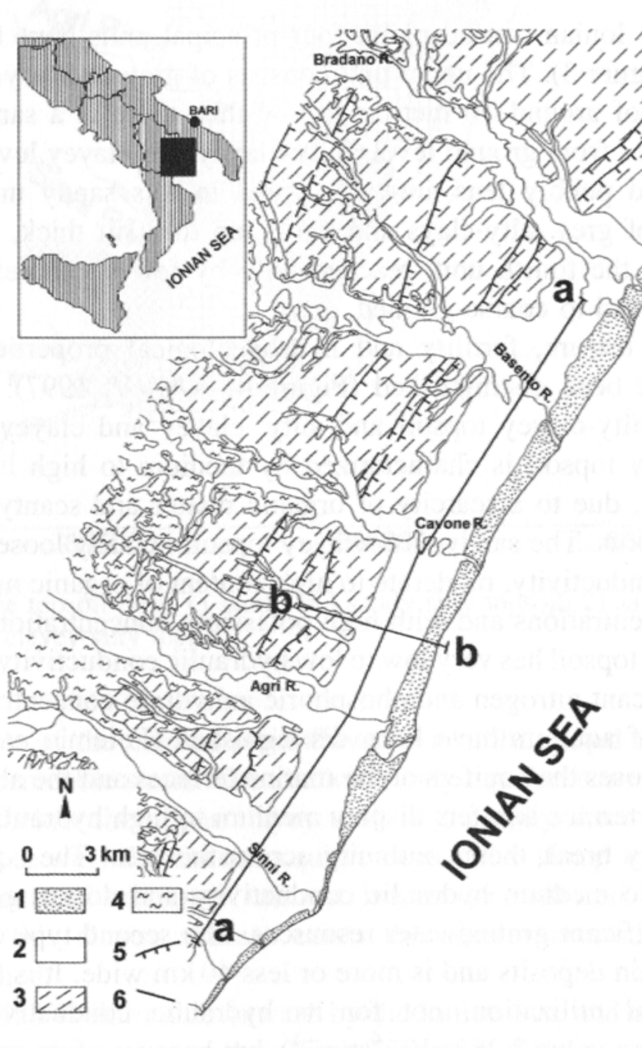

Figure 2. Schematic geological map of the study area. 1) coastal deposits; 2) alluvial, transitional and marine deposits; 3) Marine Terrace Deposits; 4) Subapennine Clays Formation; 5) marine terraced scarps; 6) lithological sections lines.

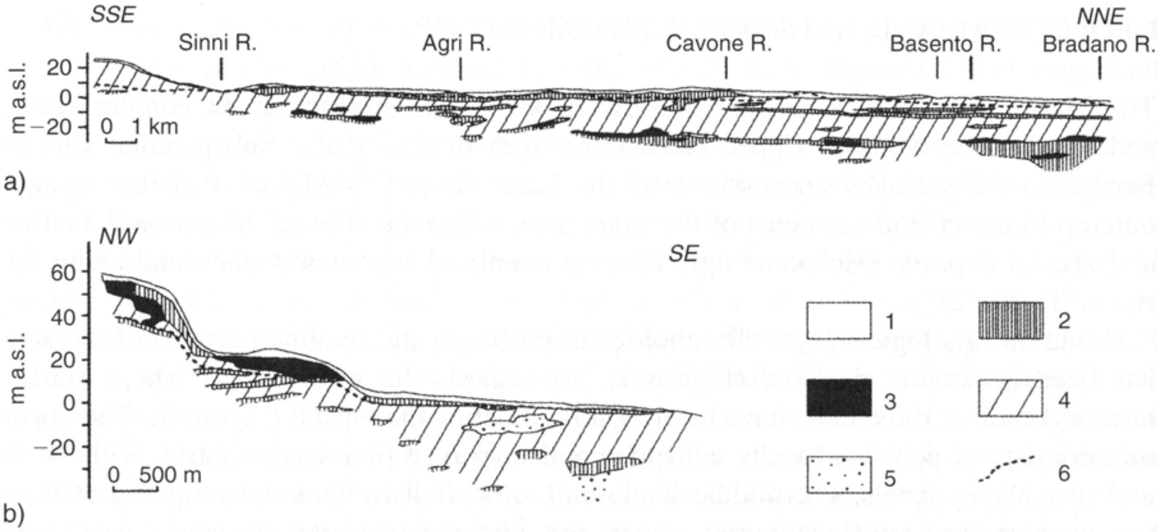

Figure 3. Schematic lithological sections. 1) soil; 2) clays or silty clays (yellow, brown, grey); 3) pebbles in a sandy and/or clayey matrix; 4) grey sands with clayey strata; 5) sands and/or silty sands; 6) piezometric surface (m a.s.l.).

With regard to the Ionian coastal plain, four principal units have been distinguished below the topsoil (Figure 3). The upper unit consists of grey and/or yellow clays, with a maximum thickness of around 10 metres. Below this, there is a sandy unit stretching down to 45–50 metres from ground level. Silty-clayey and clayey levels, gravelly sands and locally cemented pebbly lens are widespread in this sandy unit. The third unit consists essentially of grey silty-clays and clays, up to 30 m thick, locally with some pebbly lens. Finally, the fourth unit, reached only by few boreholes, consists of grey sands, from fine-grained to coarse-grained.

According to the texture, fertility and hydrogeological properties, three principal types of topsoil have been distinguished (Figure 4; AA.VV. 1997): sandy and sandy-silty topsoil, sandy-silty-clayey topsoil and silty, clayey and clayey-silty topsoil. The sandy and sandy-silty topsoil is characterized by medium to high hydraulic conductivity and low fertility, due to a scarcity of organic matter and scanty concentrations of nitrogen and phosphorus. The sandy-silty-clayey topsoil is fairly loose, with from low to medium hydraulic conductivity, moderate to high content of organic matter, low nitrogen and phosphorus concentrations and with high potassium concentration. The silty, brown clayey or clayey-silty topsoil has very low to low hydraulic conductivity, moderate organic matter content, and scant nitrogen and phosphoric anhydride concentrations.

Two main types of aquifers have been distinguished (Polemio *et al.* 2002a, 2002b, 2002c). The first encloses the aquifers of the marine terraces and the alluvial river valleys deposits. The marine terrace aquifers display medium to high hydraulic conductivity but river valleys regularly break their continuity across the area. The aquifers of the river valleys display low to medium hydraulic conductivity and do not generally permit an accumulation of significant groundwater resources. The second type of aquifer includes that of the coastal plain deposits and is more or less 40 km wide. It is the most important in terms of practical utilization, not for its hydraulic conductivity, which is not particularly high (mean value 2.28×10^{-4} m s^{-1}), but because of its extension, thickness, continuity across the plain and, also, because of its location, where the water demand is the highest one.

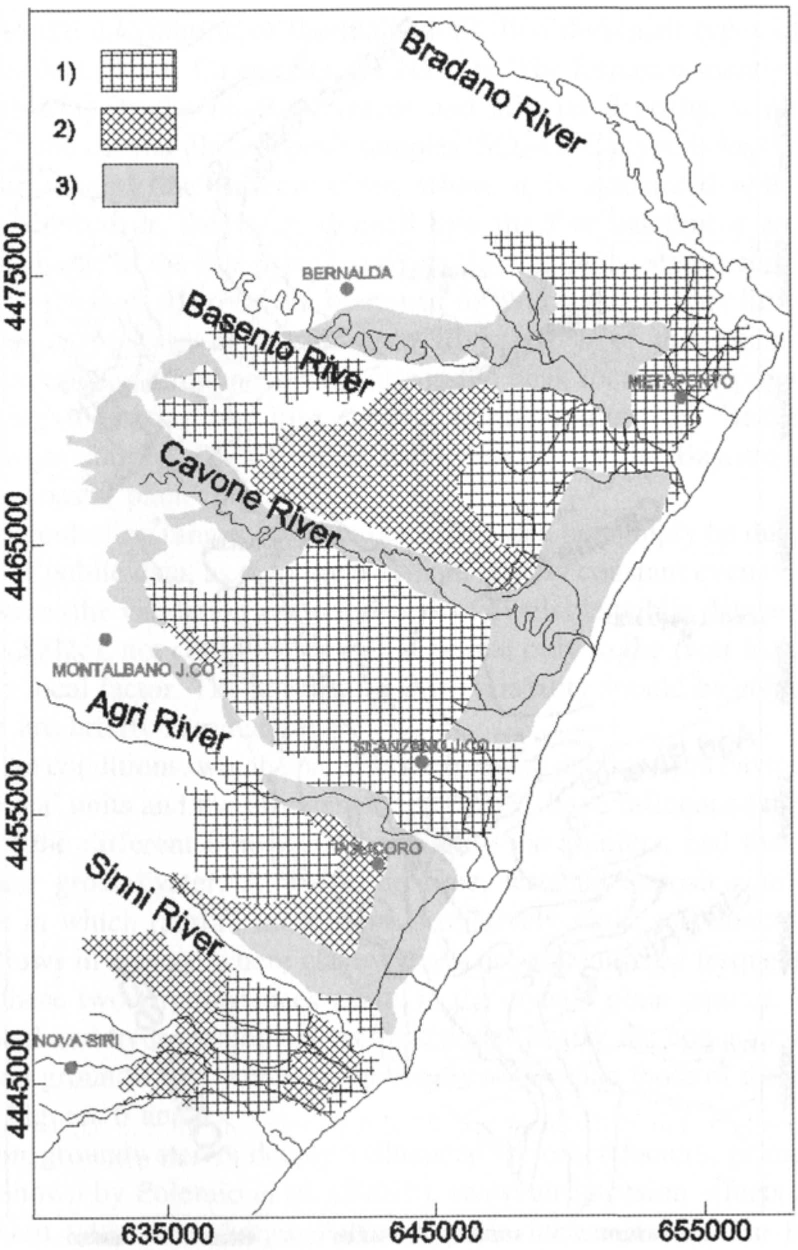

Figure 4. Map of the topsoil type. 1) sandy and sandy-silty topsoil; 2) sandy-silty-clayey topsoil; 3) silty, clayey and clayey-silty topsoil.

The groundwater of the coastal plain flows in a multilayered aquifer constituted by different sandy permeable strata. The shallow sandy aquifer, corresponding to the upper sandy unit, lying below the upper clayey unit, is generally the only one employed for practical uses. Moreover, the coastal aquifer does not outcrop everywhere due to the widespread presence of an upper, almost impervious stratum, 3 to 10 m thick. In particular, where this clayey stratum exists the aquifer is confined; otherwise it is generally unconfined.

The coastal aquifer is skirted downward by the Ionian Sea, and upward by the aquifers belonging to marine terraces or to the alluvial deposits of the river valleys. The shallow coastal aquifer is mainly recharged by the discharge from the upward aquifers (Figure 5) and by river leakage. As shown in Figure 3, the riverbeds in the coastal plain are almost

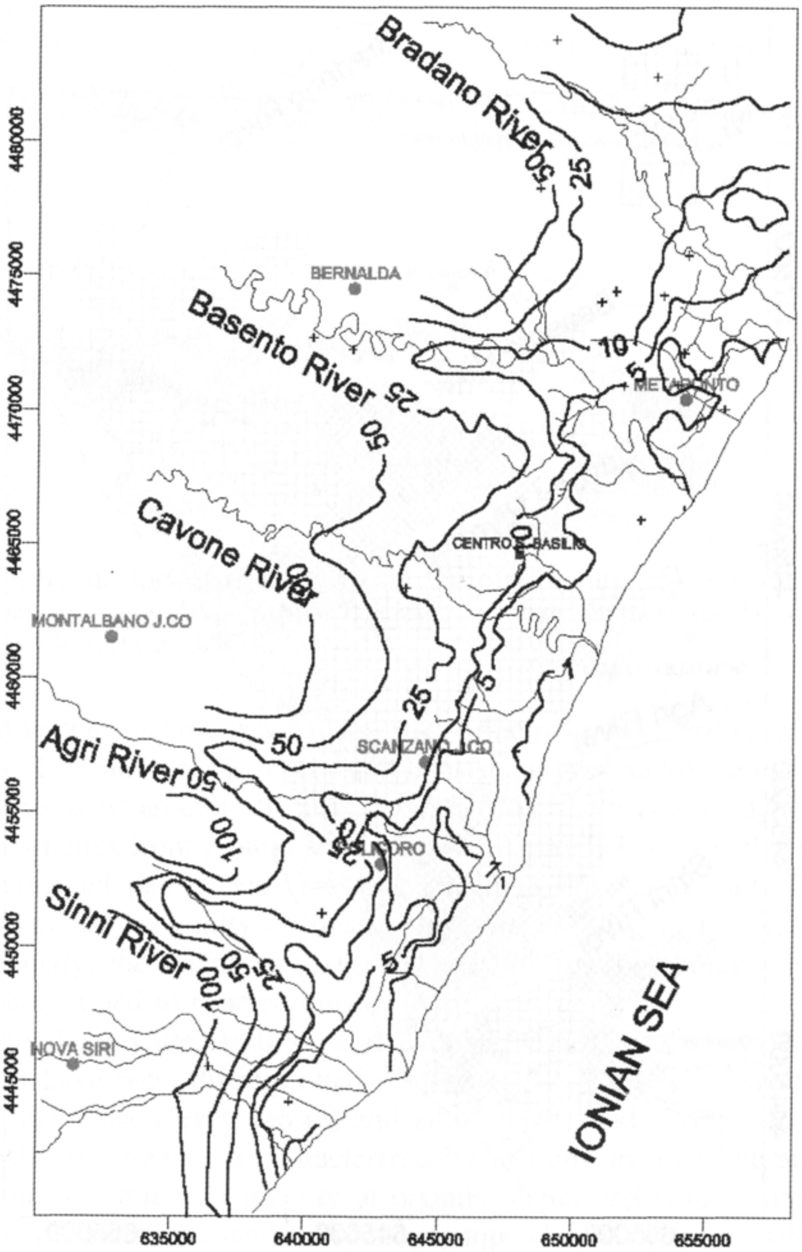

Figure 5. Piezometric map (m a.s.l.).

always deep enough to cut outcropping soils of low hydraulic conductivity, where they exist. Piezometric levels, near the riverbeds, are besides generally low enough to permit river leakage.

CHEMICAL AND PHYSICAL FEATURES OF THE GROUNDWATER

The chemical and physical characterization of the groundwater has been inferred from the analysis of different groundwater samples, taken from 158 wells which are uniformly distributed within the study area: 47 samples have been tapped from marine terraced deposits and 162 samples from alluvial and coastal deposits (coastal plain deposits). All the wells were sampled in 1990, and some were sampled also in 1999.

According to the distribution of the major ions, two dominant types of groundwater have been identified: HCO_3-Ca and SO_4-Cl-Na type. The former is mainly typical for the groundwater flowing in the marine terraces and alluvial deposits, while the latter is characteristic of the coastal plain deposit samples. SO_4-Cl-Ca type is less frequent except in the area surrounding the Basento river, where it is associated with the pollution detected there. Moreover, the water drained into the five catchment areas (Figure 1) supplies the discharge of the five principal rivers flowing in the study area. The discharge yield is particularly high for rivers in the basin of which impervious lithotypes outcrop extensively, as in the case of the Basento River (85% of the catchment area has impervious outcropping lithotypes). Considered the peak location of population density and of polluting industrial activities located in the region, the Basento river area represents a major hazard. On the other hand, leakage of the Basento river water is possible in the coastal plain (Figure 3).

The high concentration ranges of the major ions could not simply be due to differences in the sources of public data, as the ranges remain largely constant even on the basis of a single data source (the validation and references of available public data are described by Polemio *et al.* 2002c); nor could the pollution be due only to the river leakage, though it appears to be a local factor. The reasons for this variability should be connected to other factors, which are briefly summarized below.

First of all, the conditions, which characterize both the depositional environments of the various geological units and the lithogenetic processes, have influenced the geochemical composition of the different lithotypes constituting the aquifers, and thus the chemical features of their groundwater. At the same time, terraced deposit aquifers constitute recharge areas in which rainfall infiltration is relatively rapid and direct, and in which groundwater flows in a space where clayey levels are encountered frequently.

Neither of these two circumstances exists in the coastal plain aquifer. River leakage and geochemical and hydrogeological factors cannot justify the concentration ranges of the coastal plain groundwater, which are generally wider than those of the marine terrace groundwater (Figures 6 and 7).

Coastal plain groundwater is deeply influenced by other factors, primarily seawater intrusion. As shown by Polemio *et al.* (2002b), seawater intrusion affects a coastal strip that is 1–1.5 km wide on average. Anthropogenic factors could also be inferred to explain the high variability of the ion concentration. A relevant contribution is due to the widespread irrational procedures of irrigation and of fertilizer utilization and to the consequent water irrigation and chemical surpluses.

Irrigation is important in this semi-arid area because of the high rate of potential evaporation–transpiration, corresponding to a mean annual value of 860 mm (161% of the mean annual rainfall). The irrigation water is supplied by dams, built in the inner sectors of the main river basins and dating to the 1960s. Before using aqueducts, supplied by dams, the irrigation water used to be tapped by wells and today this practice still persists during drought periods, when the artificial lakes are largely empty (as is the currently the case).

In both cases an increasing load of salt mass, which is introduced by the irrigation water, and pollutants, which are added to the topsoil, mainly in the form of fertilizers but also pesticides, may cause a degradation of the quality of the fresh, pure groundwater system. During intensive groundwater exploitation (that is, in drought periods) the situation becomes more serious as the irrigation – distributing salt mass – is at least partly the cause of seawater intrusion (Polemio *et al.* 2002a, 2002b).

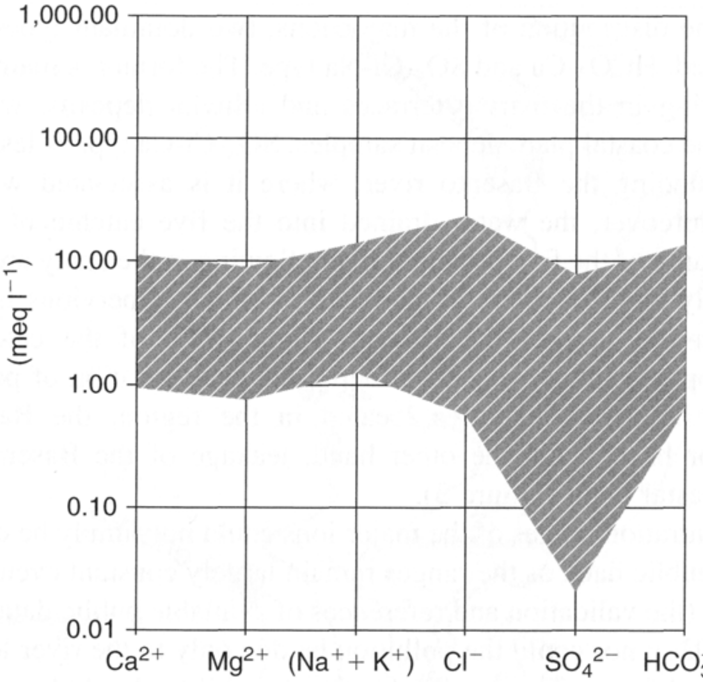

Figure 6. Schoeller diagram of the whole groundwater samples in the terraced marine aquifers.

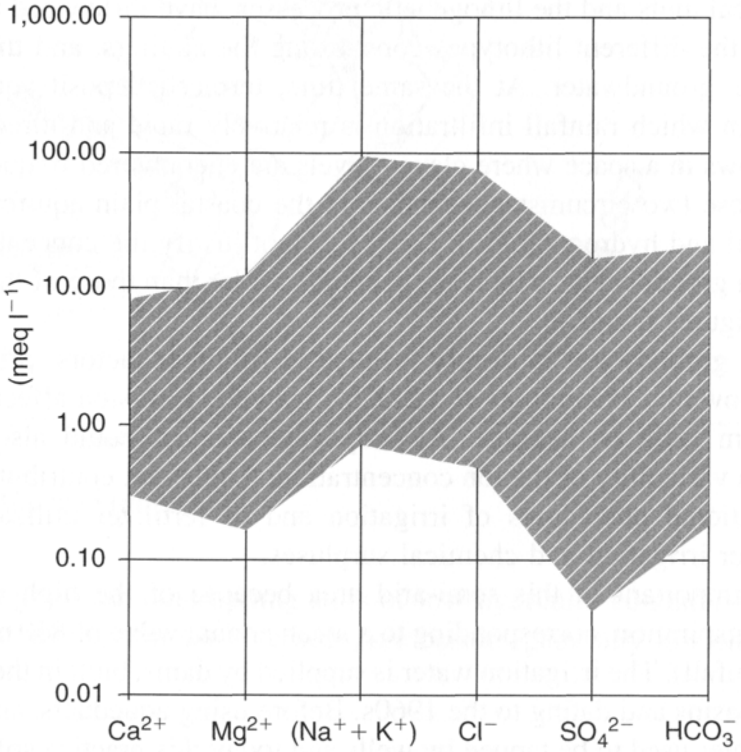

Figure 7. Schoeller diagram of the whole groundwater samples in the alluvial and coastal aquifers.

Another factor could be also related to the extremely low drainage capacity of the coastal plain, which is subjected to frequent and extensive seasonal pounding due to river flooding. The evaporation of the pounded waters may also be a further source of salts and pollutants, added to the system, as pointed out by Lopez *et al.* (1986).

Nitrate distribution and trend

The environmental impact of agricultural activities is becoming a serious problem, especially in industrialized countries. Eutrophication, for instance, as caused by high concentrations of nutrients in waters, represents one of the possible environmental impacts of agriculture and animal husbandry practices. In Italy, in the Northern Adriatic Sea, algal blooms have acquired the dimension of an ecological catastrophe since 1988 (AA.VV. 1997).

Nitrates represent one of the most important causes of water quality degradation, and nitrate losses from agricultural areas are generally larger than the losses from natural ecosystems.

In the study area, the direct contribution of anthropogenic factors to groundwater quality degradation is significant in terms of nitrate concentrations and other contaminants, as summarized by Table 1.

The major contaminant considered is nitrate, as it is generally the most significant, mobile and persistent agricultural contaminant (Böhkle 2002). The spatial trend of nitrate concentrations is shown in Figure 8; the trend is fairly high for the study area, which is characterized primarily by arable land and the intensive use of fertilizers. The mean value of the nitrate concentration is about $16\,mg\,l^{-1}$, but locally this chemical parameter may exceed $150\,mg\,l^{-1}$.

A close relationship has been detected between topsoil properties and spatial trend nitrate concentrations, and between nitrate concentrations and soil hydraulic conductivity. In fact, there are two areas most significantly subjected to nitrate contamination (Figure 8). The first is located between the Agri and Cavone rivers (along the coast between the mouth of the Agri river and the village of Scanzano Jonico, and inland between the village and the Cavone river). The second area is between the Basento and Bradano rivers in the coastal plain. In both these areas the topsoil, constituted by sandy and sandy-silty soils, shows the highest hydraulic conductivity (Figure 5). On the other hand, the above-mentioned natural scanty nitrogen concentrations in the topsoil do not justify the high nitrogenous compounds measured in the groundwater under examination.

The spatial trend for ammonia concentrations, reported in Figure 9, highlights the existence of two areas with concentrations in excess of $0.5\,mg\,l^{-1}$. The first area, characterized also by high nitrate concentrations, lies between the Sinni and the Agri rivers where two important towns are situated (Scanzano Jonico and Policoro). The second one is located near Metaponto.

The presence of nitrate seems to be related to an intense use of agricultural fertilizers and, in limited areas, to urban activities. In some groundwater samples, the high NH_4 concentrations measured seem to be distinctive of sewage leakages and polluting urban activities.

To evaluate the evolution over time of nitrate pollution, a test area was selected, between the Basento and Cavone rivers, and groundwater samples were taken from 34 wells of the coastal plain aquifer. The survey was realised during 2002 (Figure 10).

The 34 wells of the 2002 survey are uniformly distributed in the costal aquifer of the test area, while some of the 40 wells in the 1990 survey are also located in the terraced deposits.

As shown by nitrate maps (Figures 8 and 10), the nitrate ion is detected consistently and abundantly in the test area. The $25\,mg\,l^{-1}$ contour line of 1990 several times cuts the

Table 1. Statistical outline, listing the minimum, the maximum and the mean values of parameter selected to highlight the anthropogenic groundwater pollution of the whole Metaponto plain (1990 survey) and the test area (2002 survey). <DL: Less than detection limit.

Quality parameters	Terraced deposits – 1990			Coastal plain deposits – 1990			Coastal plain deposits – 2002		
	min	max	mean	min	max	mean	min	max	mean
Ammonia ($mg\,l^{-1}$)	<DL	24	1	<DL	50	3	1.30	21.27	8.40
Nitrate ($mg\,l^{-1}$)	<DL	68	16	<DL	183	16	2.95	92.72	29.70
Nitrate ($mg\,l^{-1}$)	<DL	21	1	<DL	<DL	<DL	/	/	/
Colonies at 22°C	800	3,200	1,201	800	3,500	2,375	/	/	/
Colonies at 36°C	120	2,500	686	450	2,500	1,463	/	/	/
Total coliforms (MPN/100 ml)	16	16	13	<DL	16	7	/	/	/
Fecal coliforms (MPN/100 ml)	2	6	4	<DL	16	4	/	/	/
Fecal streptococci (MPN/100 ml)	6	16	9	<DL	16	4	/	/	/
Strontium ($mg\,l^{-1}$)	<DL	21	1	<DL	<DL	<DL	/	/	/
Lithium ($mg\,l^{-1}$)	<DL	21	1	<DL	<DL	<DL	/	/	/
Fluorine ($mg\,l^{-1}$)	<DL	21	1	<DL	<DL	<DL	5.13	270.00	38.33
Iron ($mg\,l^{-1}$)	<DL	24	1	<DL	10	4	/	/	/
Manganese ($mg\,l^{-1}$)	<DL	21	1	<DL	<DL	<DL	/	/	/
Copper ($mg\,l^{-1}$)	21	35	20	15	52	48	/	/	/
Zinc ($mg\,l^{-1}$)	4.15	6.50	3.70	0.04	1.25	0.44	/	/	/
Arsenic ($mg\,l^{-1}$)	0.009	0.009	0.006	0.010	0.016	0.012	/	/	/

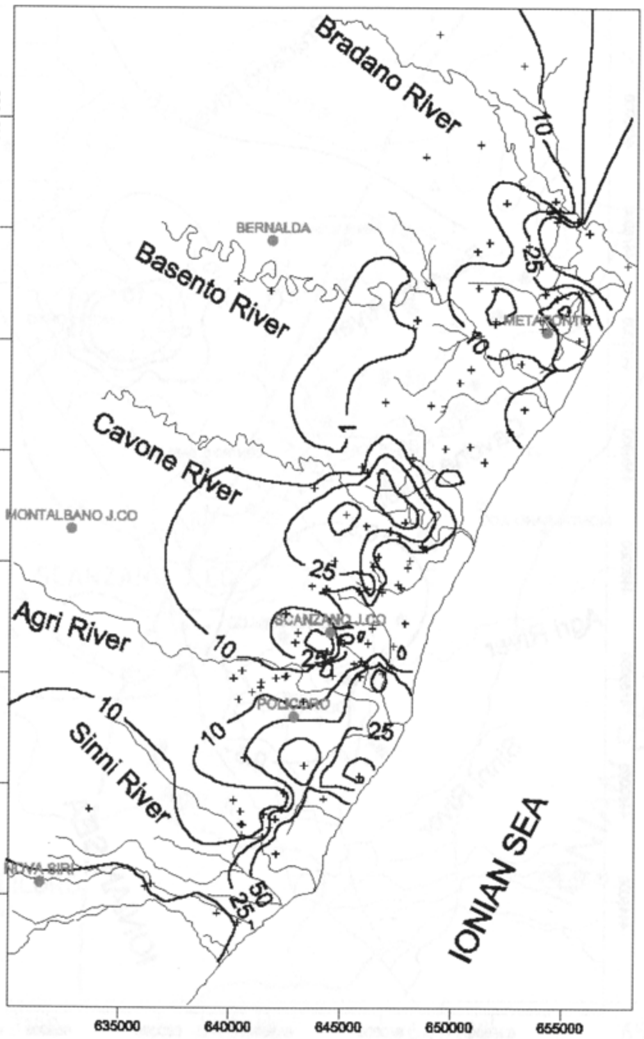

Figure 8. Map of nitrate groundwater concentration, year 1990 ($mg\,l^{-1}$).

limit between the terraced deposits and the coastal plain deposits, roughly corresponding to the railway line (Figure 10). Upward, the concentration is higher in the southern portion and lower in the remaining portion; downward, in the coastal plain aquifer, the concentration is lower.

The 25 $mg\,l^{-1}$ contour line of 2002 overlaps with the 1990 line only in the northern portion of the test site; in the central portion it has moved downward, while in the southern portion it is replaced by the 50 $mg\,l^{-1}$ contour line. In each point of the test area, the coastal aquifer display nitrate concentrations that are generally increased, somewhere significantly.

This result is a cause for considerable concern due to the dramatic increase in groundwater nitrate concentrations. The concentrations seem to have more than doubled

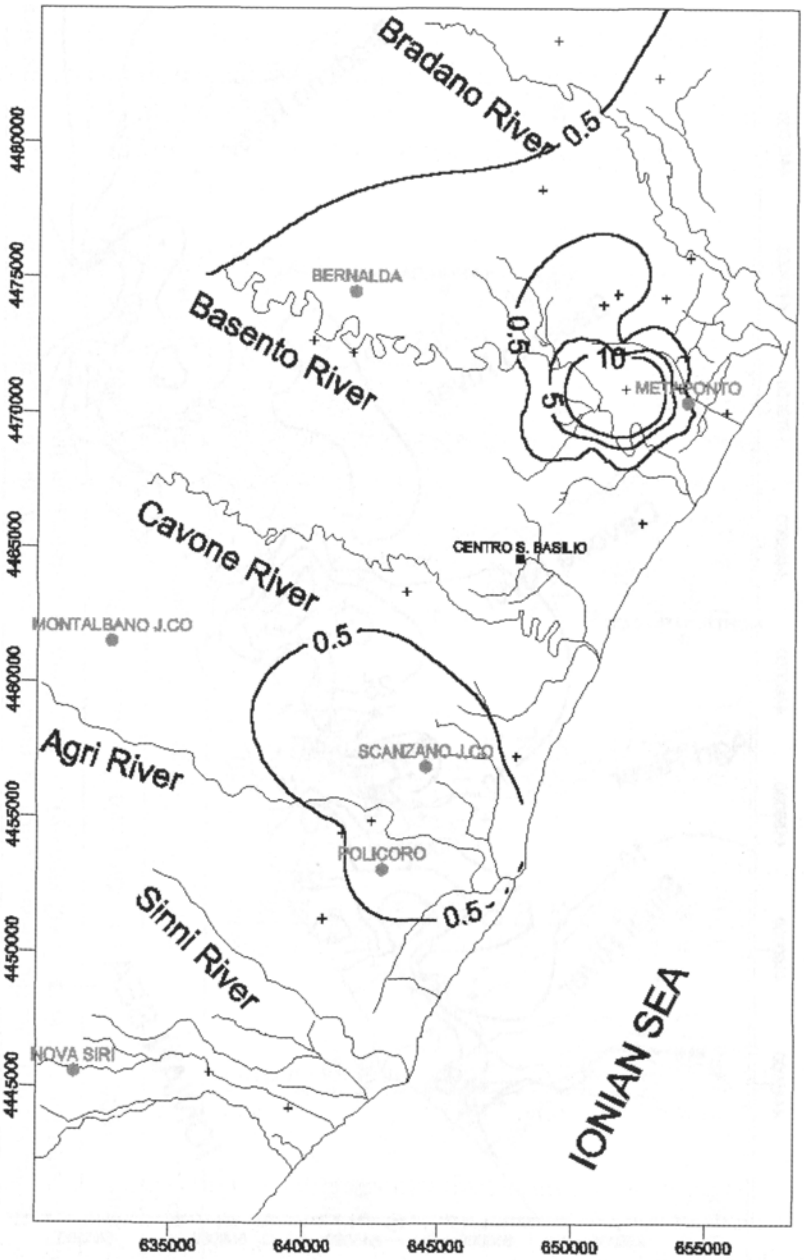

Figure 9. Map of ammonium groundwater concentration, year 1990 ($mg\,l^{-1}$).

in the coastal plain, not only where the topsoil is more permeable (Figure 4). If this trend were extrapolated to the whole study area the result would be devastating.

In the test area the statistical parameters (minimum, mean and maximum) rose significantly not only in terms of nitrate but also ammonia, between 1990 and 2002 (Figures 8–10 and Table 1).

Moreover, nitrate and ammonia are not the only source of risk. Widespread bacteriological pollution of the studied groundwater was also observed in the 1990 survey (Table 1). This phenomenon may be explained by the presence of several towns and villages, in addition to extensive livestock management practices, in the coastal plain.

The presence of metals such as Fe, Mn, Cu, As and Zn, detected in the groundwater, may be associated with urban waste water, polluted river leakage, direct recharge, mineral dissolution and anthropogenic activities.

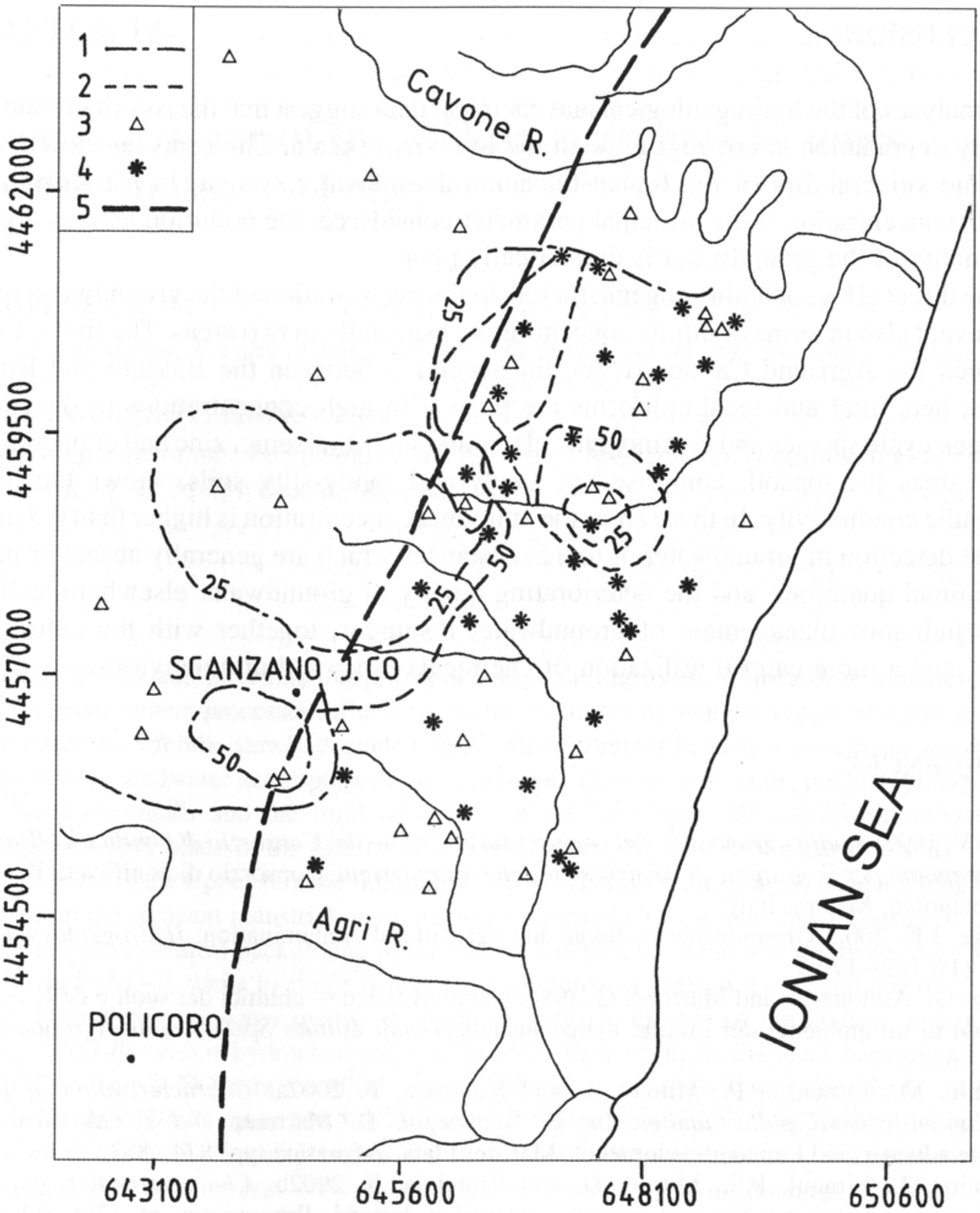

Figure 10. Map of nitrate concentration from 1990 to 2002 in the test area. 1) 1990 nitrate concentration (mg l^{-1}), 2) 2002 nitrate concentration (mg l^{-1}), 3) 1990 monitoring well, 4) 2002 monitoring well, 5) railway.

Moreover, the portion of coastal aquifer between the Bradano and the Basento rivers is characterized by a widely diversified concentration of contaminants. Total and fecal coliforms have been reported in high concentrations (exceeding 15 MPN/100 ml) along with nitrogen cycle species and carcinogenic elements, such as arsenic, zinc and copper. This phenomenon is suggestive of the poor groundwater quality caused by human activities. Indeed, the groundwater of this stretch of the Ionian coastal plain has been increasingly polluted by both the urban and industrial waste water discharged into the Basento river, which is interconnected to the downward groundwater system, and by a dense drainage network of reclamation works.

CONCLUSIONS

The analyses of the hydrogeological and chemical data suggest that the risk of groundwater quality degradation is not negligible in the Metaponto plain. The analysis show also the extreme vulnerability of the Ionian-Lucanian groundwater system. In particular, if the nitrate concentration is the principal parameter considered, the pollution level is high and the quality of the groundwater is dramatically poor.

The direct effect of anthropogenic factors to the deterioration of the groundwater quality is relevant also in terms of nitrate concentration, especially in two areas. The first is located between the Agri and Cavone rivers, the second is between the Basento and Bradano rivers; here total and fecal coliforms are present in high concentrations in the form of nitrogen cycle species and carcinogenic elements, such as arsenic, zinc and copper. In both these areas the topsoil, comprised of sandy and sandy-silty soils, shows the highest hydraulic conductivity. In these areas the ammonia concentration is higher than 0.5 mg l^{-1}.

The detection in groundwater of toxic substances which are generally absent or present in minimal quantities, and the deteriorating quality of groundwater elsewhere, call for a more judicious management of groundwater resources, together with the entire water cycle, and a more careful utilization of chemicals in agricultural activities.

REFERENCES

AA.VV. 1997: *Studio agronomico del comprensorio irriguo del Consorzio di bonifica di Bradano e Metaponto per la gestione delle risorse idriche a fini irrigui*. Consorzio di bonifica di Bradano e Metaponto, Matera, Italy.

Böhlke, J.K. 2002: Groundwater recharge and agricultural contamination. *Hydrogeology Journal 10* (1): 153–179.

Lopez, G., Ascione, S. and Marrone, G. 1986: Caratteri fisico – chimici dei suoli e delle acque di falda di un ambiente del litorale ionico lucano. *Annali Istituto Sperimentale Agronomico 17*: 49–65.

Polemio, M., Limoni, P.P., Mitolo, D. and Santaloia, F. 2002a: *Characterisation of Ionian-lucanian coastal plain aquifer*. In: E. Bocanegra, D. Martinez and H. Massone (eds): Groundwater and human development, Mar del Plata, Argentina, pp. 874–883.

Polemio, M., Limoni, P.P., Mitolo, D. and Santaloia, F. 2002b: *Characterisation of Ionian-lucanian coastal aquifer and seawater intrusion hazard*. Proceedings of 17th Salt Water Intrusion Meeting, Deft, Netherlands, pp. 422–434.

Polemio, M., Dragone, V., Limoni, P.P., Mitolo, D. and Santaloia, F. 2002c: *Extended report of CNR-CERIST unit on deliverables: first year of activity*. European research project 'CRYSTECHSALIN', VPQ of European Commission (RST-EESD), Brussels.

Radina, B. 1956: Alcune considerazioni geoidrologiche sulla fascia costiera jonica compresa fra i fiumi Bradano e Sinni. *Geotecnica 1*: 3–11.

Spalding, R.F. and Exner, M.E. 1993: Occurence of nitrate in groundwater. *Journal of Environmental Quality 22*: 392–402.