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ASSESSMENT OF VULNERABLE ZONES TO NITRATE POLLUTION: A STUDY CASE IN THE APULIA REGION

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SUMMARY- The excessive use of nitrogen fertilizers and pesticides in European countries has led to an increase in agricultural productivity but also to the groundwater contamination by nitrate. Therefore the aim of this study is to implement a vulnerability assessment methodology of a zone to nitrate pollution. The Sinistra Bradano situated on the western part of Taranto (south of Italy) was the case of application.

Focusing on this area, we produced the groundwater vulnerability map using the DRASTIC Model. This model produces a numerical value called DRASTIC Index which is derived from the overlay of seven thematic maps related to seven hydro-geologic factors which are: Depth to water, Recharge, Aquifer media, Soil media, Topography, Impact of the vadoze zone and the Hydraulic Conductivity. The obtained vulnerability map was characterized by high to very high vulnerability.

The groundwater chemistry showed that the maximum nitrate concentration found was 43.2 mg/l so all analyzed samples were under the threshold of 50 mg/l and only 21% of them fall in the medium class. This percentage of samples confronted with the vulnerability map fall in the very high vulnerable zones.

This actual nitrate concentration in groundwater was resulted from the application of the double of what is required as nitrogen fertilizers needs. Therefore, good agricultural practices are necessary to reduce and prevent further nitrate pollution.

Key words: Nitrogen fertilizers, nitrate pollution, DRASTIC model, vulnerability map, groundwater analysis.

RESUME L'utilisation excessive des engrais azotés et des pesticides dans les pays européens a mené à une augmentation de la productivité agricole mais également à la contamination des eaux souterraines par le nitrate. Par conséquent, le but de cette étude est d'appliquer une méthodologie d'évaluation de la vulnérabilité d'une zone à cette pollution. Le Sinistra Bradano situé sur la partie occidentale de Taranto (sud de l'Italie) était le cas d'étude.

Se concentrant sur ce secteur, nous avons produit la carte de vulnérabilité des eaux souterraines en utilisant le modèle DRASTIC. Ce modèle produit une valeur numérique appelée Index dérivé de l'intersection de sept cartes thématiques liées à sept facteurs hydrogéologiques qui sont : la Profondeur à la nappe, la recharge, le type d'aquifère, le type de sol, la topographie, l'impact de la zone vadose et la conductivité hydraulique.

La carte obtenue a été caractérisée par haute à très haute vulnérabilité.

La chimie des eaux souterraines a prouvé que la concentration maximum en nitrate était 43.2 mg/l. Ainsi, tous les échantillons analysés étaient sous le seuil de 50 mg/l et seuls 21% qui appartiennent à la classe moyenne. Ce pourcentage d'échantillons, confrontés avec la carte de vulnérabilité, vient dans la classe très haute sensibilité.

La concentration actuelle en nitrate dans les eaux souterraines a été le résultat de l'application du double de ce qui est exigé comme engrais azotés.

Par conséquent, les bonnes pratiques agricoles sont nécessaires pour réduire et empêcher plus de pollution par le nitrate.

Mots clés: Engrais azotés, pollution par le nitrate, le modèle DRASTIC, la carte de vulnérabilité, analyse des eaux souterraines.

INTRODUCTION

Year by year a few hundreds of thousands of tons of nitrogen infiltrate in water in the form of nitrate or of ammonium.

A considerable proportion of 55 % comes from nitrate rejections related to agricultural activities (GOUDOT, 2003). We find at the head of the list the use of manure in cultures but also the breeding of pig that is the origin of the liquid manures.

The strongest contents are observed either in the cereal zones and market gardening or in the intensive cattle-breeding areas where the production of farm manure often exceeds the capacities of purification of the grounds and the cultures. The diffuse rejections of agricultural origin on a permeable catchments area are mainly in question (Ruiz et al, 2000). Consequently different nitrate concentrations are detected in ground waters. They change from year to year in the same well or among wells in the same fields because it depends on many factors such as procedures of irrigation management, soil type, the depth to water table and the rate of precipitation. For example in France, a study done by the Organization of Cooperation of Economic Development (OCDE), had shown that the $NO_3 - N$ concentration in irrigation water can vary between 10 ppm and more on short distances.

Sensitive crops may be affected by nitrogen concentrations above 5 mg/l. Most other crops are relatively unaffected until nitrogen exceeds 30 mg/l (FAO. Irrigation water quality, P: 91).

Therefore the council of the European communities had implement the directive 91/ 676 / EEC of the December 1991 to establish a limit for nitrate concentration in groundwater equal to 50 mg/l. It mentions that " *it is necessary for member states to identify vulnerable zones and to establish and implement action programs in order to reduce water pollution from nitrogen*".

Groundwater vulnerability to pollution defined in agreement with the conclusions and recommendations of the international conference on "Vulnerability of Soil and Groundwater to Pollutants", held in 1987 (Duijvenbooden and Waageningh (Ed.), 1987), as "*The sensitivity of groundwater quality to an imposed contaminant load, which is determined by the intrinsic characteristics of the aquifer*".

Thus, through this research we will determine the degree of vulnerability on the western part of Taranto and evaluate the nitrate pollution of groundwater due to the intensive use of nitrogen fertilizers in this zone. It's an approach that aims to confront the vulnerability map generated by the DRASTIC model and nitrate concentrations found by analysis in order to put good agricultural practices relative to the actual situation.

STUDY SITE

This approach was implicated on the western part of Taranto situated in Apulia, Italy's boot heel, its southeastern most region. We focused our attention particularly on the Sinistra Bradano zone (Fig.1).

The climate in the study zone is typically Mediterranean: hot and dry. The precipitation is scarce and takes place only in the period between October and March and summer droughts are frequent.

MATERIALS AND METHODS

Aquifer vulnerability assessment using DRASTIC Model

DRASTIC model of aquifer vulnerability falls into the category of overlay and an index method, which is one of the most commonly, used categorical rating methods and was among the earliest methods used (National Research Council, 1993). It was developed by EPA, USA (Aller et. Al., 1987) which standardized system for evaluating ground water pollution potential of hydrogeologic settings. This model produces a numerical value called DRASTIC INDEX which is derived from the ratings and weights assigned to the parameters used in the model. DRASTIC is an acronym for the seven thematic maps used in the model. The seven thematic maps required are:

D	Depth to water: the more depth to water the lesser the chance for the contaminant to reach it as compared to shallow water table.
R	Recharge: it is the process through which the contaminant is transported to the aquifer and hence more the recharge more vulnerable the aquifer is.
A	Aquifer Media: it reflects the attenuation characteristics of the aquifer material reflecting the mobility of the contaminant through the aquifer material.
S	Soil Media: soil of different types have differing water holding capacity and influence the travel time of the contaminant
T	Topography: high degrees of slope increases runoff and erosion which is composed of the pollutant
I	Impact of vadose zone: it reflects the texture of the soil in the unsaturated zone above the water table
C	Hydraulic Conductivity: the amount of water percolating to reach the ground water through the aquifer is influenced by the hydraulic conductivity of the soil media

DRASTIC model defines weights, ranges and ratings for the classes associated with each of the above thematic maps.

- *Weights:* each DRASTIC factor has been evaluated with respect to the other to determine the relative importance of each factor. A relative weight ranging from 1 to 5.
- *Ranges:* each DRASTIC factor has been divided into either ranges or significant media types that have an impact on pollution potential.
- *Ratings:* each range for each DRASTIC factor has been assigned a rating which varies between 1 and 10 to be evaluated with respect to the others to determine its relative significance with respect to pollution potential.

These ratings and weights are used in arriving at the DRASTIC INDEX, which is calculated using the following formula:

$$\text{DRASTIC index} = D_r D_w + R_r R_w + A_r A_w + S_r S_w + T_r T_w + I_r I_w + C_r C_w \quad (1)$$

Where the capital letter indicates the corresponding map and the subscript "r" and "w" refer to the rating and weights respectively.

* Remark: It's notable that those maps do not include any data that quantify contaminant concentrations or chemical properties.

Weights of the critical factors

Weights relative to the seven critical factors are presented in *Table 2*. The proposed weights have been assigned by means of a Ranked pair wise Comparison Technique, resulting from analysis of case histories and expert judgments, and may not be changed.

Table 2. Weights of critical factors

Critical factors	weight
Depth of water	5
Net Recharge	4
Aquifer media	3
Soil media	2
Topography	1
Impact of the vadose zone	5
Hydraulic conductivity	3

It should be noted that the highest weights have been assigned to the factors affecting path way and length of an infiltrating contaminant/contaminated water from the ground surface to the water table.

Nitrate groundwater analysis

Nitrate was determined with ion chromatography method (Limbrick, 2003). It is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the resin. It's greatest utility is for analysis of anions for which there are no other rapid analytical methods. It is also commonly used for cations and biochemical species such as amino acids and proteins.

Water Analysis results will help us to determine its quality and put recommendations for use if it's necessary. Analyses were done on 32 samples distributed (Fig. 3) on the coastal part of Taranto.

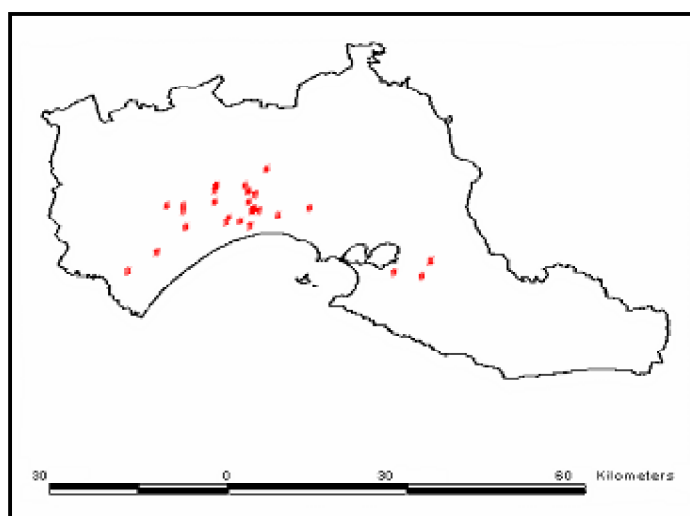


Fig. 3. Localization of water samples

RESULTS AND DISCUSSION

Determination of the study zone vulnerability to nitrate pollution using the DRASTIC model

Depth to water

Depth to water constitutes the thickness of ground that a contaminant must travel before reaching the water table. It consequently impacts on the degree of interaction between the percolating contaminant and subsurface materials (air, minerals, water) and, therefore, on the degree, extent, physical and chemical attenuation and degradation processes. In general, the aquifer potential

protection increases with depth to water. *Piezometric map of the Taranto region* was used to provide the depth to water map.

Corresponding indexes of different classes are shown in *Table 3*.

Table 3. Classes of Depth to water found in Sinistra Bradano aquifer

Class (m)	Index
0 - 2	10
5 - 10	7
10 - 20	4

The figure below shows the localization of different classes of water level in the study zone.

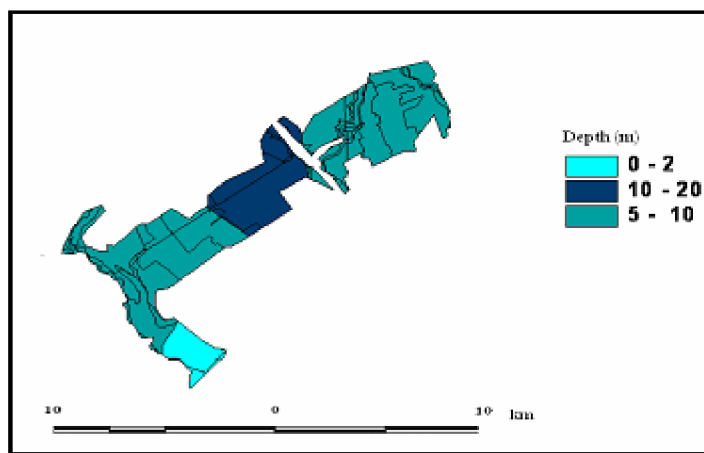


Fig. 4. Depth to water map of the Sinistra Bradano aquifer

Net recharge

The net recharge is defined as the amount of water from precipitation and artificial sources available to migrate down to the ground water. Recharge water is, therefore, a significant vehicle for percolating and transporting contaminants within the vadose zone to the saturated zone (Benedini et al., 1994). Net recharge is calculated on an annual basis by summing each monthly data obtained from: precipitation, artificial recharge, superficial run-off, ground moisture content, evaporation and plant transpiration (Added and Hamza, 2000). The algorithm allowing the net recharge calculation is:

$$R_i = (P_i + IR_i - r/O_i - \Delta ST_i - AET_i) \quad (2)$$

R_i = net recharge in the i th month (mm)

P_i = rainfall in the i th month (mm)

IR_i = artificial recharge in the i th month (mm)

r/O_i = superficial run-off in the i th month (mm)

ΔST_i = variation of the ground moisture content in the i th month (mm)

AET_i = actual evapotranspiration in the i th month (mm)

We found five classes of net recharge varying from 0 to more than 254 mm per year (*Table 4*).

Table 4. Classes of net recharge found in Sinistra Bradano aquifer

Class (mm)	Index
0 - 51	1
51 - 102	3
102 - 178	6
178 - 254	8
> 254	9

The distribution of percolation rates are shown in the recharge map below.

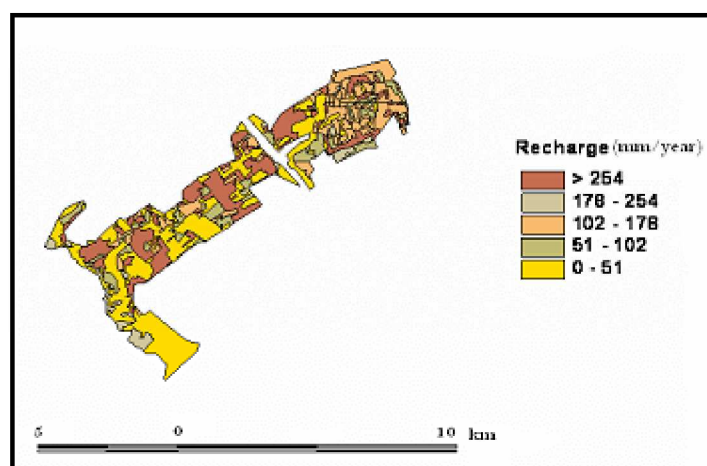


Fig. 5. Recharge map of the Sinistra Bradano aquifer

Aquifer media

The aquifer media refers to the portion of ground capable to yield water in pores. The contaminant attenuation of aquifer depends on the amount and sorting of fines. In general, the lower is the grain size; the higher can be assumed the attenuation capacity of aquifer media (Added and Hamza, 2000).

Using the geologic map of Taranto province we found seven classes and as shown in *Table 5* we attributed to them their corresponding indexes.

Table 5. Classes of aquifer lithology found in Sinistra Bradano

Class	Index
Sand, agglomerated sand and gravel	8
Gravel with some sand and silt	7
Clay, sand and gravel	5
Marly clay with variable components of silt and sand	3
Clayey and silty marl with sandy intercalation	3
Agglomerations, gravel and sand and alluvial limestone agglomerations	7
Sand, lime and gravel	7

The figure below presents those different geologic layers in the study zone.

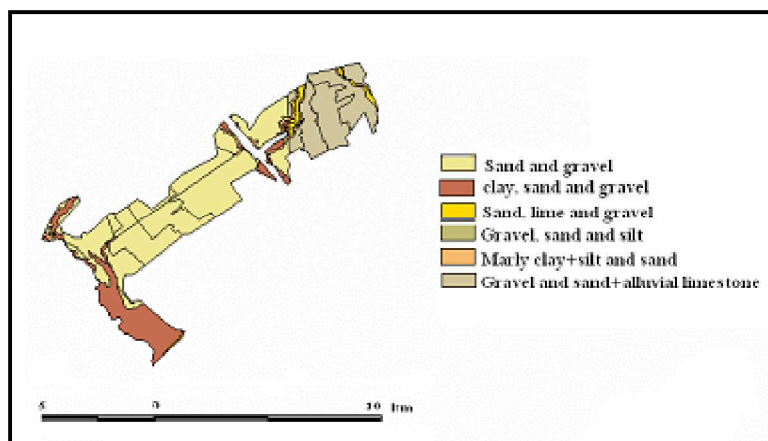


Fig. 6. Geologic map of the Sinistra Bradano aquifer

Soil media

Soil media is the uppermost and weathered part of the ground, which is characterized by significant biological activity and exchanges with the atmosphere. Soil cover characteristics influence the surface and downward movement of contaminants. The presence of fine grain size materials, such as clay, peat or silt, and the remarkable percentage of organic matter within the soil cover can decrease intrinsic permeability, and retard or prevent contaminant migration via physical - chemical processes (i.e., adsorption, ionic exchange, oxidation, biodegradation) (Added and Hamza, 2000). Soil cover characteristics of the study area were derived from the pedologic map and the indexes of soil classes were determined according to tables of DRASTIC model (*Table 6*).

Table 6. Classes of Soil cover characteristics found in Sinistra Bradano

Class	Index
sandy loam + Gravel	7
Sandy loam	6
Loamy sand	6
Sandy clay loam	4
Clay loam	3
sand	9

The pedologic map below shows that the major part of the zone is formed by sandy loam.

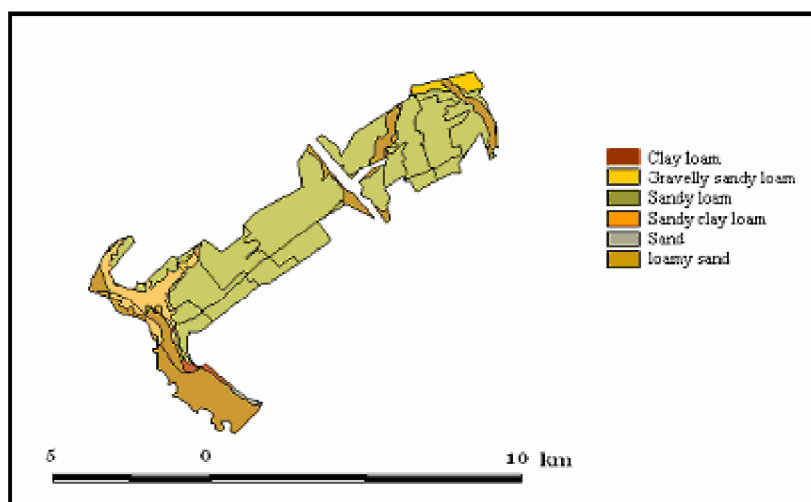


Fig. 7. Pedologic map of the Sinistra Bradano.

Impact of the vadose zone

The vadose zone is defined as the ground portion found between the aquifer and the soil cover in which pores or joints are unsaturated or only discontinuously saturated. The vadose zone influence on aquifer pollution potential, it is essentially similar to that of soil cover, depending on its permeability and on the attenuation characteristics of the media (Added and Hamza, 2000).

Information for the evaluation of this critical factor was obtained by the interpretation of geologic data. Since the depth to water is low and ranges between 1 and 20 m and the thickness of different layers is more than 10 m as shown in *Table 7* we estimate that the vadose zone is composed of the same layers of the aquifer media.

Table 7. Classes of vadose zone properties

Class	Index	Thickness (m)
Sand, agglomerated sand and gravel	8	30
Gravel with some sand and silt	7	limited
Clay, sand and gravel	5	15
Marly clay with variable components of silt and sand	3	1000
Clayey and silty marl with sandy intercalation	3	100
Agglomerations, gravel and sand and alluvial limestone agglomerations	7	9
Sand, lime and gravel	7	limited

Topography

Topography will give an indication on whether a pollutant will run off or remains on the surface long enough to infiltrate into the groundwater (Aller, Bennett, Petty and Hackett, 1987).

To obtain the slope map we used the iso-lines map of Taranto and using Arc GIS options we obtained the percentage slope map.

The western part of Taranto is more or less a plan surface therefore the slope in the Sinistra Bradano zone varies between 0 and 2% (Fig. 8).

Table 8. Topography classes

Class (%)	Index
0 - 2	10

We attribute the index 10 because this slope facilitates the contaminant infiltration.

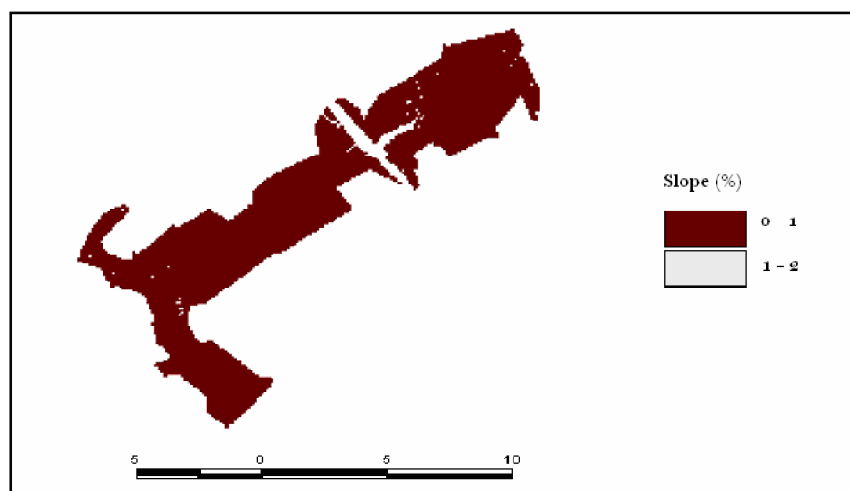


Fig. 8. Slope map of the Sinistra Bradano

Hydraulic conductivity

Aquifer hydraulic conductivity refers to the ability of the aquifer formation to transmit water. It depends on the amount and degree of interconnection between empty spaces inside the rock media (Added and Hamza, 2000). This critical factor controls the contaminant migration and dispersion from the injection point within the saturated zone and, consequently the plume concentration in the aquifer.

The hydraulic conductivity was determined by redefining the lithology classes of the aquifer following the tabled hydraulic conductivity varying with lithology.

Table 9. Hydraulic conductivity related to lithology in the study zone

Lithology	Class (m/d)
Sand, agglomerated sand and gravel	> 81
Gravel with some sand and silt	32 – 42
Clay, sand and gravel	32 – 42
Marly clay with variable components of silt and sand	10 – 20
Clayey and silty marl with sandy intercalation	10 – 20
Agglomerations, gravel and sand and alluvial limestone agglomerations	41 – 81
Sand, lime and gravel	32 – 42

As shown in the hydraulic conductivity map that the majority of the left part of the study zone has a hydraulic conductivity more than 81 m/d however it's between 41 – 81 m/d on the right part.

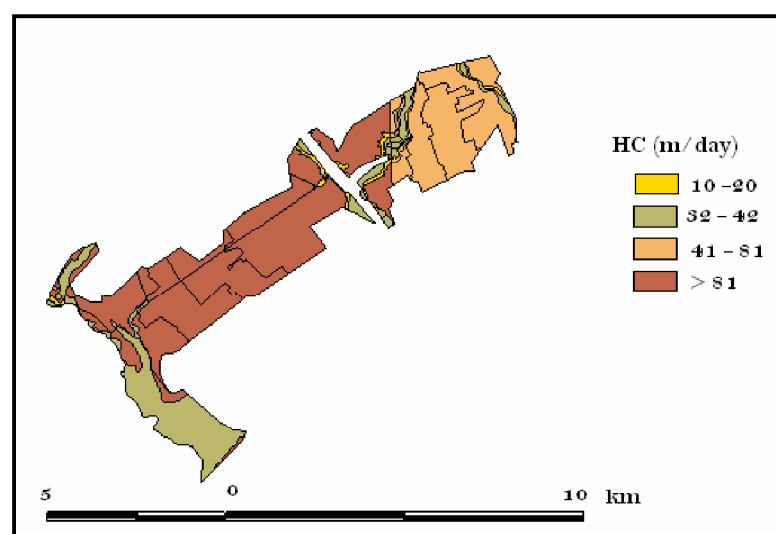


Fig. 9. Hydraulic conductivity map of the Sinistra Bradano

Ratings relative to different classes are summarized in the table below.

Table 10. Hydraulic conductivity indexes

Class (m/day)	Index
10 – 20	3
32 – 42	7
41 – 81	8
> 81	9

Hydrogeologic vulnerability of the aquifer

By determining and tabulating index values for each class, maps related to rating of each factor were constructed with GIS and converted to Grid type.

The aquifer pollution index for each grid sub-area was determined following this summation:

$$V = \sum P_i S_i \quad (3)$$

where:

V = Aquifer pollution potential index

P_i = weight of the i^{th} factor

S_i = index of the i^{th} factor

Values obtained represent a measure of the aquifer hydrogeologic vulnerability, ranging from a minimum value of 24 to a maximum of 226. The higher the computed value, the higher the hydrogeologic vulnerability to percolating contaminants. The degree of vulnerability can be determined, based on the following assessment criteria:

Low hydrogeologic vulnerability, if $V < 80$;

Medium hydrogeologic vulnerability, if $80 \leq V < 120$;

High hydrogeologic vulnerability, if $120 \leq V < 160$;

Very high hydrogeologic vulnerability, if $160 \leq V < 185$;

Extremely high hydrogeologic vulnerability, if $V \geq 185$.

the found indexes were classified according to the vulnerability assessment of the DRASTIC model, and we obtained three degrees of vulnerability as shown in the vulnerability map of Sinistra Bradano aquifer (Fig. 10). It shows high and very high degrees of vulnerability on the most zones.

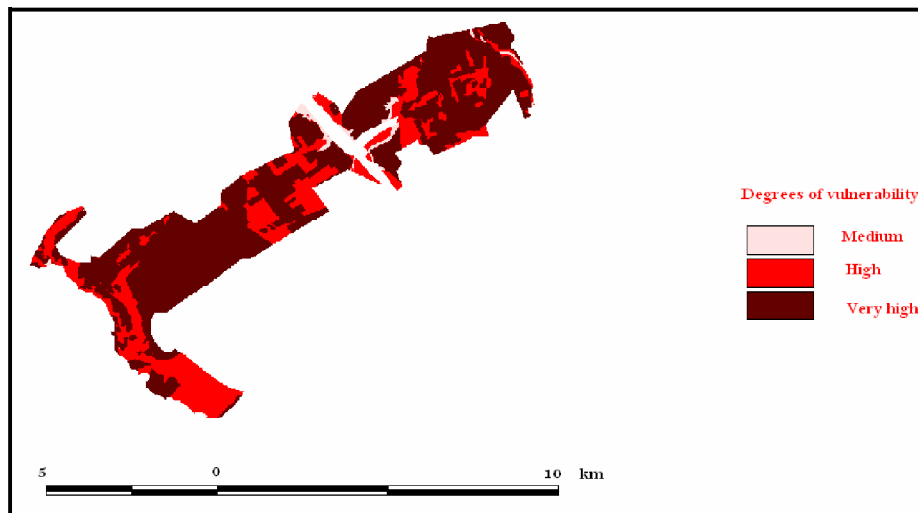


Fig. 10. Vulnerability map of the Sinistra Bradano

Nitrate concentration in groundwater

The table below presents different samples with according crops where were taken, date of sampling and nitrate concentration found.

Table 11. Nitrate concentration results

Code	Crop	Sampling	NO ₃ (mg/l)
W1	Citrus	3 –Oct - 05	5,5
W2	Citrus	3 –Oct - 05	2,6
W3	Citrus	3 –Oct - 05	4,8
W4	Citrus/olive	3 –Oct - 05	9,8
W5	Table grape	3 –Oct - 05	< 0.2
W6	Table grape	4 –Oct - 05	3,1
W7	Table grape	4 –Oct - 05	0,8
W8	Citrus	4 –Oct - 05	8,0
W9	Citrus	26 –Oct - 05	4,6
W10	Citrus	26 –Oct - 05	< 0.2
W11	Citrus	7 – Nov - 05	15,3
W12	Citrus	7 – Nov - 05	8,4
W13	Citrus/grape	7 – Nov - 05	11,5
W14	Citrus	7 – Nov - 05	4,7
W15	Citrus	7 – Nov - 05	10,7
W16	Citrus	7 – Nov - 05	13,1
W17	Citrus/olive/vegetables	14 – Nov - 05	3,3
W18	Citrus	14 – Nov - 05	8,7
W19	Table grape	14 – Nov - 05	4,9
W20	Citrus	1 – Feb - 06	18,5
W21	Citrus	1 – Feb - 06	21,6
W22	Table grape	8 – Feb - 06	28,3
W23	Table grape	8 – Feb - 06	2,7
W24	Table grape	15 – jun -06	31,3
W25	Table grape	15 – jun -06	3,2
W26	Citrus	15 – jun -06	19,7
W27	Citrus	6 – Jul - 06	22,0
W28	Table grape	6 – Jul - 06	43,2
W29	Citrus	6 – Jul - 06	< 0.2
W30	Citrus	6 – Jul - 06	10,4
W31	Citrus	6 – Jul - 06	12,1
W32	Citrus	6 – Jul - 06	5,9

In the interpretation of analysis results we concentrated on citrus and table grapes which are the most important crops in the zone and for which we have more samples.

The nitrate concentrations were grouped into one of three classes as shown in the table below: low (< 20 mg/l), medium (\geq 20 mg/l and < 50 mg/l) and high (\geq 50 mg/l).

Table 12. Nitrate concentrations categories

	Total number of wells	Wells in concentration categories		
		Low	Medium	High
Citrus	20	17	3	0
Grapes	9	6	3	0

This distribution shows that:

- The major part of wells present low nitrate concentrations (85 % of samples in citrus and 67 % of samples in grape) so they present a low risk to human health and environment.
- 33 % of samples taken in grape fields are in the medium range and are near from the limit of high range (43.2 %). Those concentrations are high enough to indicate the influence of this land use on the ground water pollution because of its important need of fertilizers.
- All nitrate concentrations found are under the threshold of 50 mg/l and only 21% of them fall in the medium class, this shows that the hazard of intensive quantities of used nitrogen fertilizers begins to appear.

Then we confronted the vulnerability map with nitrate concentration results to know the actual situation of zones defined as vulnerable but also to see to which vulnerability degree samples having important nitrate concentrations belong. For samples that don't fall in the study zone but are very near from it, we used the available vulnerability map of Apulia done some years ago. We found that all samples having important nitrate concentration fall in zones of very high vulnerability (Fig. 11). For the other samples which still have low concentrations is either because there isn't significant pollutant loading entering the subsurface or because of soil characteristics.

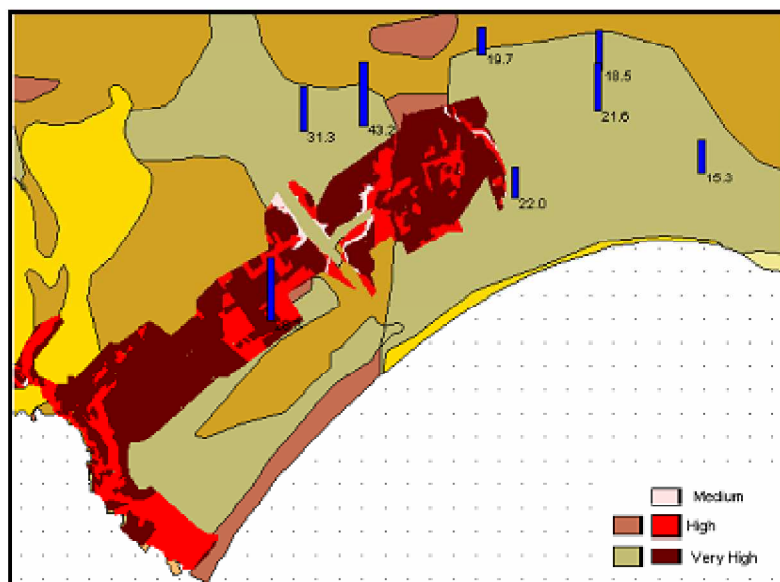


Fig. 11. Localization of samples having important NO₃ concentration on the vulnerability map

Comparison between applied quantities of N-fertilizers and nitrate concentrations in groundwater

In this part we studied the correlation between high application of nitrogen fertilizers and high nitrate concentration in groundwater.

Tables 13 and 14 below show the distribution of N – fertilizers during the vegetative cycle of citrus and table grapes. The optimum amendment of fertilizers for citrus should be 200 kg/ha/year and 180 kg/ha/year for table grapes (confirmed by the consortium of Stornara and Tara). However, in reality and with information given by the consortium of Taranto, this quantity is more or less the double for citrus (382.3 kg/ha/year) and 247 kg/ha/year for table grapes.

Table 13. Distribution of N - fertilizer through the vegetative cycle of citrus

Month	Amendment of N- fertilizer (kg/ha)
Beginning of Nov	45
Beginning of Mar	140
Beginning of Apr	23.1
Beginning of May	25.5
End Jul - Beginning of Aug	38.1
10 Aug	38.1
End of Aug	72.5
Total	382.3

Table 14. Distribution of N - fertilizer through the vegetative cycle of table grapes

Month	Amendment of N- fertilizer (kg/ha)
End of January	52,5
March	65
Apr	42
Beginning of June	28,5
End of June	28,5
Jul	22,5
Aug	8
Total	247

Studying the effect of this fertilization on the nitrate concentration in groundwater, we found that:

- *For citrus:* on two different soil types: sandy (S) and sandy loam (SL) soil the infiltration of the nitrate starts between October and November that means after harvesting as shown in the table below.

Table 15. Variation of NO₃ concentration with time and soil on citrus and table grapes fields

	Citrus		Table grapes	
	S	SL	S	SL
Oct - Nov	8.5	7.3	11.5	4
Feb	18.5	21.6	31.3	28.3
Jun - Jul	15.9	8.15	43.2	3.2

The NO₃ concentration becomes maximum in February on the two soil types; this comes after four rainy months (Fig. 13). This concentration decreases to 8,15 mg/l between Jun – Jul on a sandy loam soil. However, it stills high on sandy soil (15.9 mg/l). First because of the soil type, second because of the excess of irrigation in this period so those two factors together facilitate the percolation of nitrogen from the root zone to the water table.

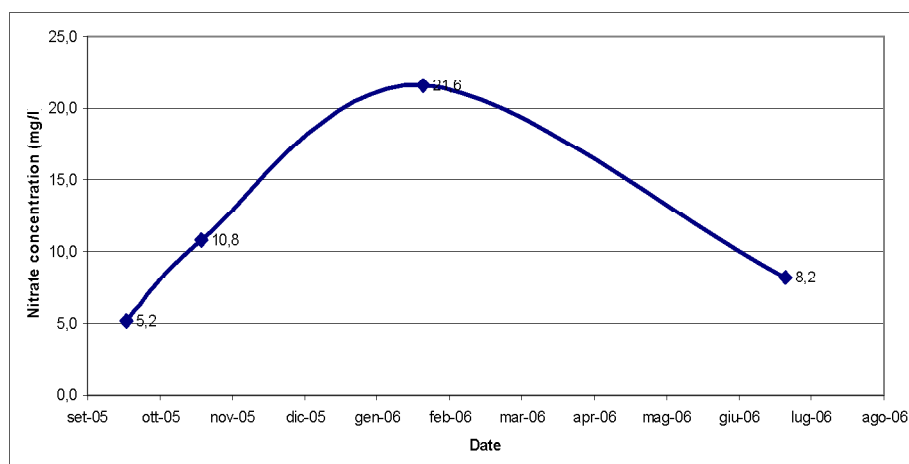


Fig. 12. Nitrate concentrations variation

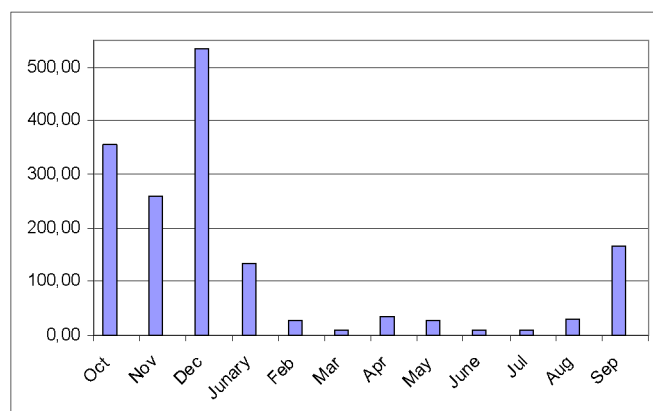


Fig. 13. Precipitation distribution

- *For the table grape:* Although the number of samples is low, we did the same reasoning and it was found that high nitrate concentration exists in February on a **SL** soil and in June – July for **S** soil (43.2 mg/l) as presented in the *Table 15* for the same reasons explained before.

CONCLUSION

The nitrate pollution in the Sinistra Bradano zone was characterized by the following results:

- The pollutant load, which is the quantity of fertilizers applied, depends on the crop pattern. In fact, 51% of the study zone is cultivated with citrus and vegetables and they consume around the double of fertilizers quantities that should be applied as it was confirmed by the consortium of Stornara and Tara. This is not the case of Table grapes but we should also keep in mind that groundwater nitrate concentration is affected by other factors including the water circulation: direction and sense and its capacity of transporting pollution. The latter depends on the flow velocity, viscosity and temperature. That's why we cannot say that if the N - fertilizers applied for citrus is higher than those for grapes we must find that the nitrate concentration under the first crop higher than on the second, but any result found is the intersection of many factors.
- Water analysis showed that all samples have a nitrate concentrations under the threshold of 50 mg/l and the maximum detected was 43.2 mg/l. we conclude that the zone doesn't present actually a high danger but since that it's high sensitive to nitrate pollution it incites us to preserve these zones by the application of good agricultural practice.

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