A PROBABILISTIC APPROACH TO ASSESS THE RISK OF GROUNDWATER QUALITY DEGRADATION.

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Abstract

In environmental sciences, the risk assessment methods focus on the most reliable techniques to quantify vulnerability and hazard, being the former defined as functionally related to the latter independent variables. With regard to groundwater systems, this chapter explores the possibility of assessing directly the environmental risk as a probability, avoiding to evaluate each of its components. Environmental risk is intended here as the probability of groundwater (i.e. the vulnerable natural system) quality degradation due to the uncontrolled spreading of nutrients on soils in agriculture (i.e. the hazardous event). Risk is formally defined as the probability of exceeding given thresholds of nitrate concentration, conditioned by values sampled within the considered groundwater system. Then, a probabilistic methodology is proposed, based on geostatistical, non-parametric, stochastic simulation, to estimate and spatialize such a risk. Finally, the methodology has been applied to the shallow aquifer of the "Tavoliere di Puglia" plain, located in Apulia, southern Italy, and characterized by intense agricultural activities and civil facilities.

Keywords

Environmental risk assessment; Groundwater; Nitrates; Geostatistics; Conditional sequential indicator simulation; Entropy.

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1. INTRODUCTION

The progressive reduction of natural water resources availability, due to the increasing demand for water in all sector and the ongoing climate changes, has the effect of qualitative and quantitative deterioration of this resource and launches a severe alarm aimed to protect and preserve such natural resources.

When considering Mediterranean areas, where predicted scenarios of climate change indicate trends to warmer and arid climate, problems of scarcity and degradation of quality of natural water resources become more severe. In such areas, the reduction in availability of water resources significantly influences sustainable growth. Human activities, in these areas, often produces threats for groundwater safety due to direct or incidental water overexploitation and pollution; the former is particularly critical nearby coastal areas, where it causes the groundwater hydraulic head lowering and seawater intrusion (Zaccaria et al., 2016). Furthermore, the almost total absence of perpetual surface watercourses, which characterizes the Mediterranean environments, forces water resource managers to draw to the more precious reservoir of the groundwater to satisfy water needs. Groundwater is the major source of worldwide freshwater supply, which is currently used to meet nearly half of the drinking water needs (Machiwal at al., 2018) and around 43% of the irrigation demand (Siebert et al. 2010). Considering what said, quantitative saving and qualitative safeguarding of water resources must be the main objective of any effective environmental policy that, in turn, often implies the assessment of the risk of quali-quantitative groundwater degradation.

The word 'risk' has two distinct meanings (Burton and White, 1980; Rue et al., 1999). In some contexts, it is considered as a threat that is an exposure to mischance or peril. In other contexts, risk is interpreted, more narrowly, as the possibility or chance of suffering an adverse consequence, or of encountering some loss (Duckett, 1983; Mishra and Sarkar, 2017).

Generally, according to Varnes (1984), *risk* is defined as functionally related to two independent variables: (i) the vulnerability V of the natural system, that is the degree of the intrinsic weakness of the considered system, and (ii) the hazard H associated to a specific (natural or human) event (Barca and Passarella, 2008), that is the possibility that a potentially detrimental event of given characteristics occurs in a given area, for a given time-period (IPCC, 2012). When assessing the hazard associated to an event, it is necessary to evaluate the temporal trend, frequency and spatial extent of the past events and determine the severity of the effects produced by them (deterministic approach). On the other hand, the elements contributing to the vulnerability of a natural system are sensitivity, adaptive capacity (resilience and

renewability) and weaknesses. A system is more or less sensitive to external events, depending on how it changes in response to it. The adaptive capacity measures the degree to which a natural system can adjust in response to changing external conditions. Depending on whether the adaptation occurs autonomously or it requires some sort of external intervention, it is usually named resilience or renewability, respectively. Finally, the presence of weakness points in a natural system can produce uncontrolled harmful effects in even very large areas.

Particularly, environmental risk is defined as the "actual or potential threat of adverse effects on living organisms and the environment by effluents, emissions, wastes, resource depletion, etc., arising out of an organization's activities." (Power and McCarty, 1998). Environmental exposures, whether physical, chemical, or biological, can induce a harmful response and may affect soil, water, air, natural resources or entire ecosystems, as well as the plants and animals - including humans - and the surroundings where they live (Mishra and Sarkar, 2017). The assessment of the environmental risk due to human activities is very important in order to plan and start actions aimed to reduce impacts, recreating the co–evolutionary process between human and natural components of the environment.

Concerning groundwater, this reservoir, even though somewhat protected by soil layers and vadose zone, is strongly subjected to various quantitative and qualitative risks due to human activities. The overexploitation of such a resource, often heavily reduces fresh water availability and worsen its qualitative status. In fact, it increases the risk of aquifer's salinization, particularly in coastal areas, where fresh water withdrawal from wells, causes an increase of the natural sea water intrusion. Furthermore, groundwater is often subjected to point type pollution, usually due to localized human activities, such as industrial sites, landfills and wastewater treatment plants, etc., to which chemical and microbiological type environmental risks are usually related. Finally, diffuse pollution of groundwater, such as the one due to nutrients spreading over the ground surface in agriculture, is one of the main groundwater degradation risks because of its intrinsic characteristic of affecting wide land areas.

In this chapter, a typical environmental risk is addressed, since it concerns the expected qualitative degradation of groundwater due to the possible increase of dissolved nitrates' concentration above critical thresholds. In fact, one of the most worrying causes of diffuse pollution of groundwater is the infiltration, through the unsaturated layers of the subsoil, of nutrients and fertilizers widely used in intensive agriculture (Goodchild, 1998; Liu et al, 2005; Almastri, 2007; Menció et al., 2016). Generally, nitrate is a low-toxic compound, but it becomes dangerous to human health when it reduced to nitrite. In fact, ingested nitrites from polluted

drinking waters can induce *blue baby syndrome*, by blocking the oxygen-carrying capacity of hemoglobin or also have a potential role in developing cancers of the digestive tract through their contribution to the formation of nitrosamines (Camargo and Alonso, 2006). Although nitrate in groundwater can derive from many sources, such as industrial, municipal, residential and agricultural sources, the largest cause of this kind of groundwater pollution, on a global scale, is the use of chemical fertilizers in agriculture (Haller et al., 2013). The contamination occurs by nitrogen leaching (that is the downward transport of nitrate by water percolating) from the soil to aquifers, when the amount of this nutrient contained in fertilizers greatly exceeds the nitrogen crop requirements (Libutti and Monteleone, 2017).

The need to control and mitigate the negative impact of nitrogen leaching from agricultural activities on water quality has prompted, in 1991, the European Union to adopt the Nitrates Directive 91/676/EEC (EU, 1991). The Directive sets the acceptable threshold of nitrate concentration in groundwater at 50 mg/l, and involves the definition of "Nitrate Vulnerable Zones" (NVZs) as large areas of land draining into waters, which exceed or are at risk of exceeding the threshold. The directive establishes mandatory action programs for these areas by means the adoption of a code for "Good Agricultural Practices" and providing training and information for farmers. Despite Nitrate Directive was issued and implemented long ago, the problems of nitrate pollution in the aquifers is still persistent throughout Europe (EEA, 2012) with many EU Member States whose groundwater quality monitoring stations exhibit NO3 concentration over 50 mg/l (EU, 2000; EU, 2006). Therefore, different methodologies have been implemented to support groundwater protection by nitrate pollution and its management (Kronvang et al. 2009; Bouraoui et al., 2009; Barca et al., 2015).

The scope of this work has then been to investigate ways of fusing information of different types and to implement a conditional stochastic simulation algorithm for risk assessment of groundwater quality degradation. The proposed method has been applied to the aquifer of the "Tavoliere di Puglia" located below the homonym valley in the northern part of the Apulia Region (south Italy).

2. MATERIALS AND METHODS

2.1 Methodological Framework

Considering groundwater systems pollution, vulnerability is rather easy to estimate because their transport characteristics do not change appreciably with time. However, hazard is difficult

to quantify since a number of time-dependent processes, involving several non-homogeneous variables, affects it. By its nature, this issue requires a probabilistic approach.

In fact, it allows risk of qualitative groundwater degradation to be assessed directly, overcoming the need of evaluating its components, separately, and represents a cost-effective and fast alternative to the deterministic methodologies (Burton and White, 1980; Duckett, 1983). This kind of approach to risk analysis allows using computational tools, based on setting critical thresholds of pollutant concentration according to given standards of groundwater quality (Passarella et al., 2002). In this contest, risk assessment is based on the estimation of variables, which are subject to extreme uncertainty. This uncertainty depends on both the intrinsic nature of the variables and the cost of obtaining information about them. Many chemical and geotechnical variables (major constituents, porosity, permeability, transmissivity, etc.), that may affect groundwater quality, can be assessed and quantified only based on sparse sampling and punctual field tests. This in turn requires spatial modelling of those variables that are deemed affecting groundwater quality.

Combinations of all variables at hand, interpreted as spatial random variables, describe the possible "states of nature". Providing multiple stochastic realizations of spatial variables can form the basis of quantitative risk assessment. Treating these realizations as possible realities, risk assessment consists essentially in observing the frequency (probability) with which specified criteria are exceeded or fail to be met (Dowd and Pardo-Iguzquiza, 2002).

Geostatistics is a set of probabilistic and statistical tools suitable to characterize and estimate attributes distributed in space (Castrignanò et al., 2000a). The complex spatial and temporal variability observed in the groundwater attributes, the multiplicity of the factors involved in the natural phenomena and the limited understanding of their complex interactions, are the main reasons for the shift from strictly deterministic modelling to a more statistical and probabilistic approach which asses the uncertainty of prediction (Castrignanò et al., 2000b).

In the Bayesian formalism, any early existing information about the considered variable is called *a-priori* distribution of the variable. Any additional information, which comes from taking into account the proximity of the observations through geostatistics, produces a change into the data distribution, called *a-posteriori* distribution, and affects the determination of the variable's uncertainty.

In the proposed case, average values of nitrate concentration measured in samples collected during eight monitoring campaigns carried out from 2007 to 2011, within the regional groundwater-monitoring network have been used as quantitative (measurements) *a-priori*

information, while hydro-geological and land use of the considered area have been used as qualitative (map) *a-priori* information.

The proposed approach of risk assessment is essentially based on this updating process of an *a-priori* distribution into an a-posterior distribution and will be discuss in detail hereinafter.

The main goal of a probabilistic approach consists in assessing uncertainty related to available information, which requires estimation of conditional distributions over the domain of interest (Castrignanò et al., 2007). Stochastic conditional simulation is an effective technique in this respect since it generates multiple realizations of the random variable over the domain of interest, which allows both a direct vision of spatial and temporal uncertainty and an assessment of joint conditional distributions (Castrignanò and Buttafuoco, 2004). Such simulations are conditional, because each realization honours the available data, and stochastic because the estimated spatial statistics are reproduced. The critical step of this approach is the estimation of conditional distributions, which can be realized in various ways since different stochastic simulation algorithms exist: Gaussian-related algorithms, which are more suited to continuous variables, and non-parametric indicator algorithms that are better suited to categorical variables. Given the objectives of this study, the indicator approach is more appropriate, even because it accounts for additional qualitative (soft) information. The conditional distributions at each node of a regular grid covering the domain can be estimated sequentially by indicator kriging, which is a non-parametric technique, not requiring any assumption about the type of data distribution function and is quite flexible to any experimental condition.

Differently, estimation procedures, such as kriging or splines, provide a unique image, which is optimal for some *a-priori* optimization criterion (minimum error variance or minimum curvature) but does not reproduce spatial statistics (histogram and variogram). Compared to stochastic conditional simulation, such estimated maps look more smoothed with elimination of the minima and maxima actually observed. They are therefore unsuitable for risk analysis where the extreme classes are generally of greatest interest.

Since geostatistical techniques are data driven, i.e. they rely on actual observations, their applications are severely constrained by the lack of data. In hydrogeological studies direct measurements of groundwater quality attributes are usually quite expensive and then rare. However, an appreciable amount of more qualitative though imprecise indirect information related to groundwater quality, as geological, pedological or geophysical maps, exists which could be effectively correlated with the actual attributes of interest. Therefore, when direct

information is sparse, poorer but more extensively accessible information should be used, in order to improve the prediction accuracy of the spatial attributes deemed influencing groundwater quality.

2.2 Probabilistic approach

To implement the probabilistic approach, the following steps are needed:

1. Record and analyse the existing sets of both quantitative (measurements) and qualitative (map units) information;
2. Code such information for quantitative use. The coding has to be flexible enough so that the various (both direct and indirect) types of information can be jointly processed. Moreover, it must be consistent with the probabilistic basic principles and techniques of geostatistics;
3. Define an algorithm for stochastic non-parametric simulation which provides multiple realizations of risk categories conditioned to the various types of information;
4. Post- process the simulations so to calculate synthetic indicators of the local risk of groundwater quality degradation and assess the level of uncertainty using the concept of entropy.

Each step will be individually described in detail.

2.2.1 Step 1

The data will be distinguished in quantitative and qualitative data. A quantitative datum corresponds to a precise measurement of the attribute(s) (nitrate) of groundwater quality at some well of known location. The uncertainty attached to this value is assumed negligible, and will not be considered in the following analyses. Using the terminology of Journel (1986) such data will be referred as *hard data*. All the other types of data, represented by maps (raster images), will be considered qualitative and called *soft data* by opposition to hard data (Journel, 1986).

2.2.2 Step 2

The variable to be simulated is categorical and represents the different risk levels (categories) of groundwater quality degradation. Each class corresponds to a particular interval of the attribute (nitrate) selected for characterizing groundwater quality. In particular, the thresholds of 10 mg/L and 50 mg/L have been used to define the three risk level categories. The former value refers to a guide value for a good groundwater quality, while the latter indicate the maximum allowable concentration of nitrates in groundwater for civil uses.

For both hard and soft data, the indicator formalism is used that was introduced in the field of spatial statistics by Switzer (1977) and later extended and developed by Journel (1983, 1986). Consider the *K* mutually exclusive categories s_k k= 1,…,K of the categorical variable, risk. This list of categories is intended to be exhaustive, which means that any location u belongs to one and only one of the *K* categories. Let i_k(u) be the indicator associated to the class s_k, which takes the value 1 if u ϵ s_k, 0 otherwise. The following relations express mutual exclusion and exhaustivity:

$$i_k(\mathrm{u})i'_k(\mathrm{u}) = 0, \quad \forall\, k \neq k' \tag{1}$$

$$\sum_{k=1}^{K} i_k(\mathrm{u}) = 1 \tag{2}$$

The auxiliary information (soft data) is coded as a set of prior distributions (relative frequencies) of each category of risk within each map unit. In order to synthetize the multiple auxiliary information, one combined map was obtained by overlapping the maps of each auxiliary variable.

2.2.3 Step 3

The stochastic simulation approach is based on conditional sequential indicator simulation procedure that enables to perform multiple simulations of a categorical variable. The simulations are constrained to adhere to all the hard information (conditional simulation) and the method does not correspond to a particular distribution model (model-free method). The procedure consists in evaluating the conditional probability of each category s_k at each location u as the conditional expectation of the corresponding indicator i_k(u), according to the following relation (Journel, 1983):

$$Prob\{I(\mathrm{u}) = 1|(n)\} = E\{I(\mathrm{u})|(n)\} \tag{3}$$

where (n) stands for conditional information.

Direct kriging of the indicator variable i_k(u) provides an estimate for the probability that s_k prevails at location u. Using simple indicator kriging (SIK) (Goovaerts, 1997) under the assumption of second order stationarity , the probability of the category s_k is estimated by the following relation:

$$Prob^*\{I_k(\mathrm{u}) = 1|(n)\} = p_k + \sum_{\alpha=1}^{n} \lambda_\alpha [I_k(\mathrm{u}_\alpha) - p_k] \tag{4}$$

where $p_k = E\{I_k(\mathrm{u})\} \in [0,1]$ is the prior marginal frequency of category s_k , calculated as proportion of data of type s_k from both hard and soft data, as described in step 2. The weights λ_α are calculated by the SIK system for each category or better by SI cokriging system taking into account the spatial correlations between the various categories (Wackernagel, 1996). However, the latter requires a multivariate consistent model of both direct and cross- indicator variograms of all categories s_k. Therefore, for sake of simplicity the model is built starting from the univariate model fitted to the experimental variogram of the most frequent category s_k and then tuning the sills of the other variograms according to the proportion of each category. Since it is assumed that the average proportions p_k of the K categories vary locally on the basis of the local auxiliary information, simple indicator kriging with varying local means (local proportions p_k's) (Goovaerts, 1997) is used. The approach consists in re-estimating these proportions from the indicator data available in the neighborhood of location u. As regards the calculation of these average proportions, taking into account all prior information from both hard and soft data, see step 2. The estimates may not necessarily lie between 0 and 1, therefore they are truncated to positive values and normalized *a-posteriori*. The next step requires defining any ordering of the K categories so to build a cumulative density function (cdf) of the probability interval [0, 1] with the following K intervals (Deutsch and Journel, 1998):

$$[0, p_1^*(\cdot)], [p_1^*(\cdot), p_2^*(\cdot) + p_1^*(\cdot)\,], \dots, \left[(1 - \sum_{k=1}^{K-1} p_k^*(\cdot)), 1\right] \qquad (5)$$

A random number p uniformly distributed in the interval [0, 1] is then drawn and the interval in which p falls determines the simulated category at location u. After updating all K indicator data with this new simulated value, the procedure proceeds to the next location u' along the random path until the output grid is completely filled with the simulated category. The arbitrary ordering of the K probabilities $p_k^*(\cdot)$ does not affect which category is drawn nor the spatial distribution of categories (Deutsch and Journel, 1998; Alabert and Massonnat, 1990). When the neighborhood search around a target node contains no data (neither hard data nor already simulated nodes), the simulation becomes non conditional and the simulated category is drawn from the theoretical proportions previously entered as prior information.

Completed the path, the next simulation will be generated repeating all the procedures described in step 3 but with its own random path so to avoid systematic errors in providing the different realizations (Alabert, 1987).

2.2.4 Step 4

This step is designed to perform statistical calculations on the results of stochastic indicator simulations corresponding to the risk category simulations. Running multiple simulations, at each node of the output grid superimposed on the study area several risk categories are generally generated, one for each realization (simulation). Using these multiple realizations, at each node the following numerical quantities can be calculated:

1. The probability of each category, simply by counting how many times each category occurs over the total number of realizations;
2. The most probable category, i.e. the one associated with the greatest probability;
3. The least probable category, i.e. the one associated with the least probability;
4. The corrected most probable category after Soares correction (Soares, 1992, 1998), which tries to compensate the failures of sequential indicator simulation to reproduce the global proportion of each category. The problem occurs when areas, where the categories of low proportion prevail, are under or over sampled by the random path at the beginning of simulation procedure. In this case, the simulated data tend to have biased proportions in all categories especially the ones with low proportions, from the beginning of simulation. The idea of the algorithm is to correct the local probabilities by adding for each category the deviation between the global prior probability and the corresponding global proportion obtained at each realization.
5. Local standardized entropy (Journel and Deutsch, 1993)at each location u, to assess the uncertainty attached to the categorical risk variable discretized in K categories with probabilities p_k, k= 1, …, K, according the following formula :

$$H(\mathrm{u}) = -\frac{\sum_{k=1}^{K}[lnp_k(\mathrm{u})]p_k(\mathrm{u})}{lnK} \qquad (6)$$

where p_k (u) is the probability of each category k of the location u previously determined at the point 1. The standardization of local entropy to the interval [0, 1] is obtained by dividing the common definition of entropy by its upper bound, lnK, corresponding to the uniform distribution with each category k characterized by the same probability $p_k = K^{-1}$. The above approach was implemented for the case study using three categories for the risk variable, defined at the step 2, and 1000 realizations deemed sufficient to stabilize the local probability of occurrence for each category.

3. CASE STUDY

3.1 Study Area

The study area belongs to the "Tavoliere di Puglia" (hereinafter simply referred as Tavoliere), the largest alluvial plain of Southern Italy which extends for about 2830 Km2 in the Northern Apulia Region. A wide and shallow aquifer is hosted in the sediment of alluvial plain (shallow porous aquifer of Tavoliere) (Figure 1). Tavoliere is characterized by an intensive agricultural activity, mostly consisting in durum wheat production, which requires large amounts of nitrate fertilizer, and vineyard, olive and fruit trees, which are also irrigated. Not by chance, most of the nitrate vulnerable zones of agricultural origin in Apulia fall in this area. In the last decades, the collected data, coming from the groundwater monitoring networks of Apulia Region, show the high level of pollution from nitrates often exceeding the standard values in most of the area, particularly following the periods of mineral fertilizer application. Then, in this area, intensive agricultural practices, based on non-rational use of chemicals, represent the critical event affecting the water quality standard. The regional groundwater-monitoring network of the shallow aquifer of Tavoliere consists of 49 quality monitoring wells and 63 quantity monitoring wells. The quality monitoring wells are all located in the downstream part of the aquifer on its eastern side where agriculture and anthropic activities are more widespread. No wells for water quality monitoring exist in the western part of the plain where piezometric level increases, while aquifer thickness and man activities decrease. In this view, the western boundary of the study area has been set at the average piezometric level of 100 m above sea level, as reported by the regional Water Protection Plan (Apulia Region, 2009).

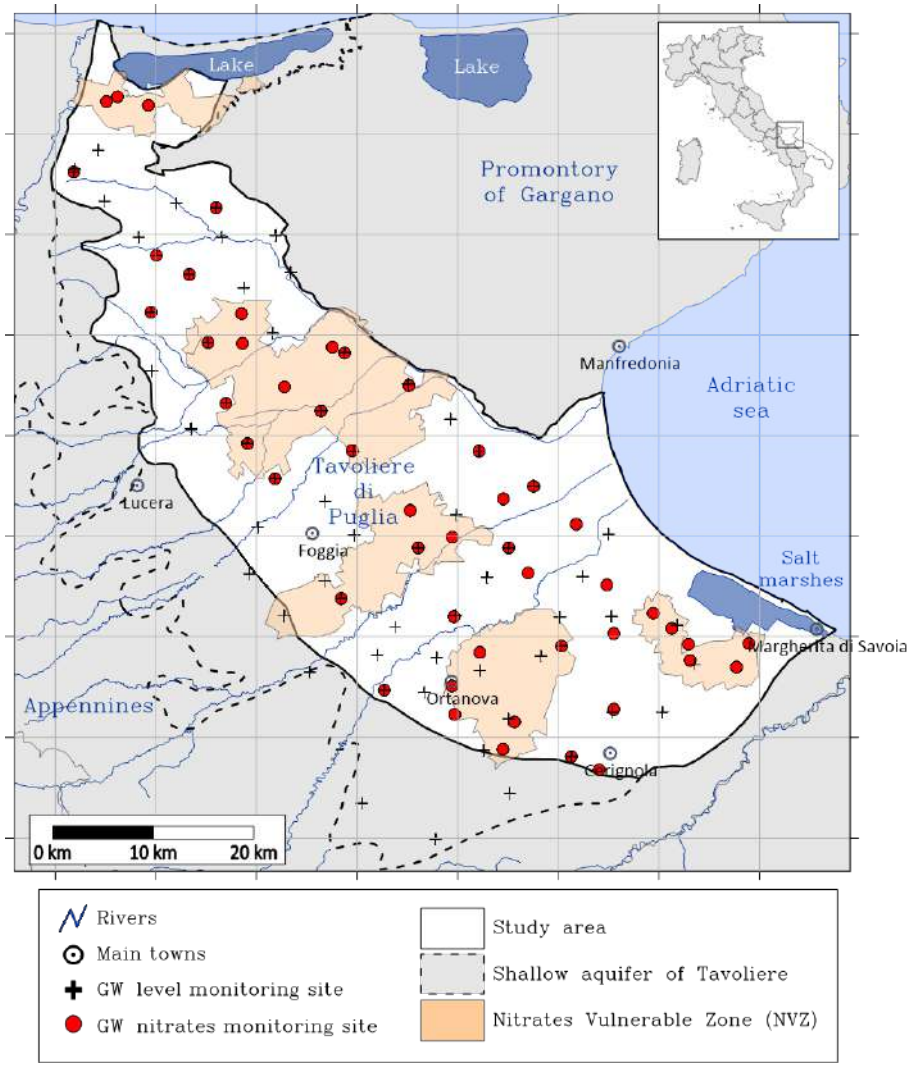


Figure 1: Study area, groundwater (GW) monitoring networks and Nitrates Vulnerable Zones (NVZ).

3.2 Geology

From the geological point of view, Tavoliere represents the Northern sector of the Bradanic Foredeep, bounded to the West by the Apennine Chain and to the East by the Apulian Foreland, locally represented by Gargano Promontory. Hundreds of meters thick, younger deposits cover the Cretaceous calcareous substratum belonging to Apulian Foreland, dislocated by graben-type structures toward the Apennines.

The older units (Pliocene – early Pleistocene) consist of shallow-marine carbonate deposits (Calcarenite di Gravina Fm) passing upward to a thick silty-clayey layer deposits of the argille subappennine Fm. A regional uplift phase of Bradanic Foredeep, combined with the glacioeustatic sea level changes which ,took place during Quaternary period, determined the sedimentation of terraced deposits, consisting of both continental and marine synthems grouped in Tavoliere super-synthem (Gallicchio et al., 2014) (Figure 2).

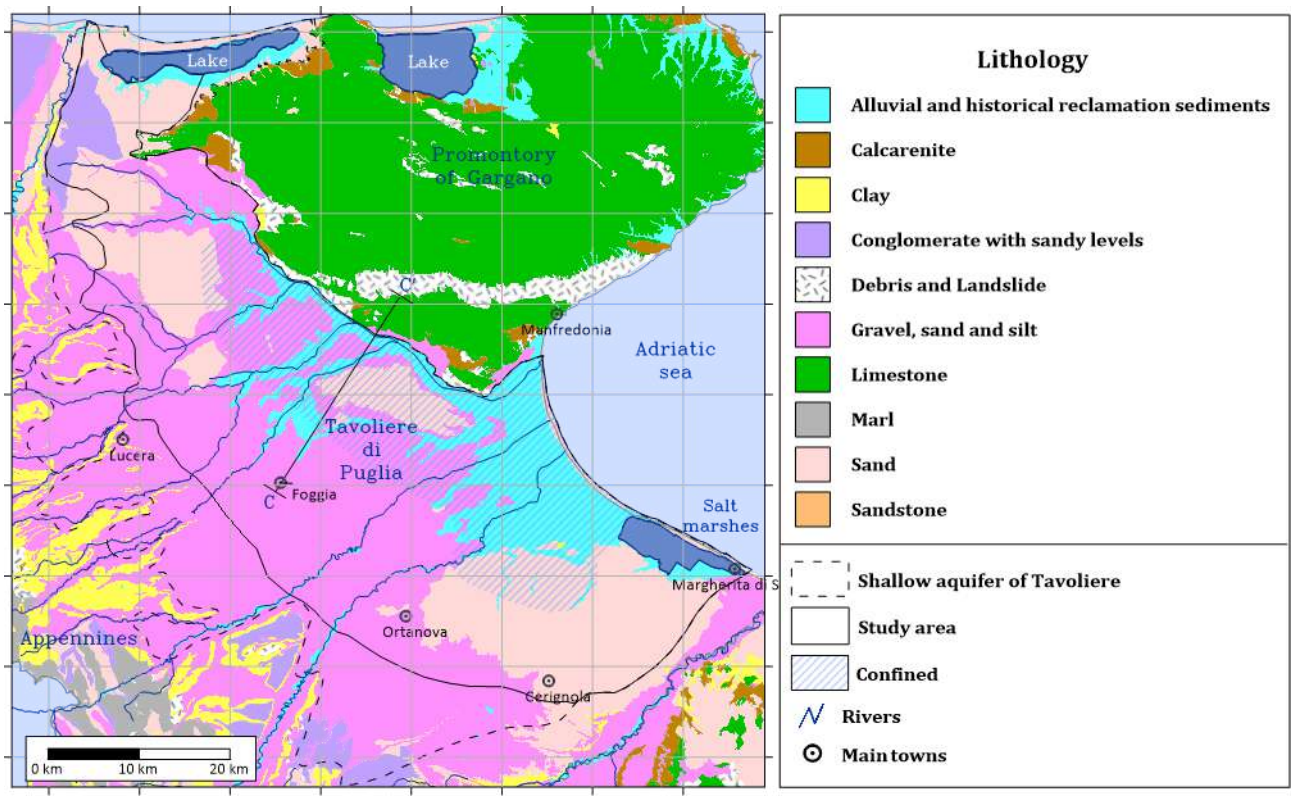


Figure 2: Lithological characteristics of the study area (Apulia Region, 2009).

Quaternary deposits, that widely outcrop all over the plain, are characterized by a variable thickness, generally increasing from the Apennines toward the eastern edge of the plain. The grain size and texture of these deposits also vary all over the area. In fact, the western sector of the plain is characterized by debris flow and coarse grained sediments deposited in alluvial fun settings, whereas the eastern one by gravel and sand-gravel deposited in braided alluvial plain setting. Changes in grain size and texture are also observed among deposits with different ages, being the older alluvial deposits coarser and poorly sorted compared to younger one.

3.3 Hydrogeology

According to the above outlined geological settings, three distinct aquifers can be detected from the bottom upwards (Figure 3): (a) the deep karst aquifer located in the cretaceous calcareous substratum, which can be found down to 300-600 m deep; (b) the deep porous aquifer located in the sandy portions within the argille subappennine Fm; (c) the shallow porous aquifer in the quaternary deposits.

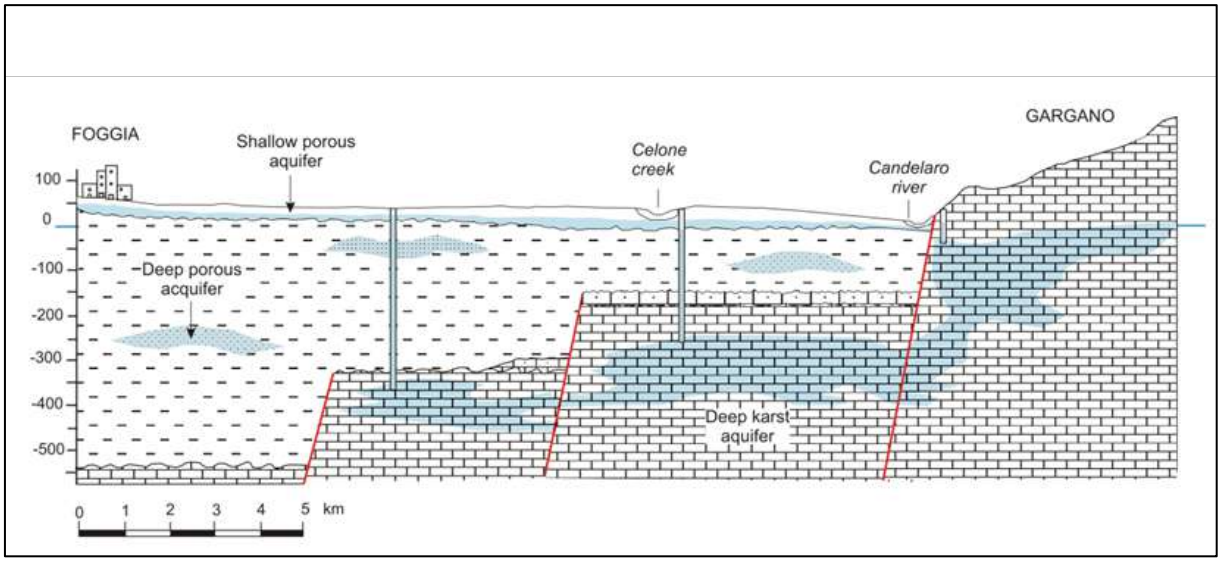


Figure 3: Cross section C-C': Hydrogeological complexes in Tavoliere area (Masciale et al., 2011, modified).

No vertical hydraulic connection exist among the three overlapping aquifers so that important differences are shown both in the flow patterns and in the geochemical features of groundwater (Maggiore et al., 1996). The shallow aquifer, defined as significant groundwater body by the Apulian Water Protection Plan, is the most exploited for agricultural uses, representing the main source of water supply in the area. Figure 2 shows the hydrogeological boundaries of Tavoliere shallow aquifer and the portion considered in this study. Due to its geological settings, it is a multy-layered aquifer, consisting of a complex alternation of alluvial gravel and sand lenses interbedded to sandy-loam and silty clay loam sediments. Nevertheless, due to limited lateral continuity of the confining beds, the different water-bearing layers are hydraulically interconnected to each other so that a single complex groundwater flow system results.

Moving to eastern sectors of the aquifer, clay and silt layers tend to prevail in the upper part of the sequence, confining the lower water-bearing layers and reducing the groundwater recharge. On the contrary, the coarse-grained sediments prevail in upstream sector of the aquifer, where the high permeability of these outcropping sediments allows direct groundwater recharge by infiltration of rain and surface water during the wet periods (Tadolini et al., 1989; Cotecchia, 1956; Maggiore et al., 1996). Consequently, groundwater flows in unconfined conditions in the upper part of the plain and in confined conditions in the middle-low part (Figure 2).

The groundwater flows mainly in the SW-NE direction under an average hydraulic gradient of about 0.5%. Proceeding towards the coast, due to the gradually deepening of the top of the clay formation, some aquifer layers are found below the sea level and they are affected by seawater intrusion.

Because of the intense exploitation of this aquifer, since the 1990s, regional water authorities have implemented different groundwater monitoring plans. The monitoring network was changed in the course of time regarding both the number of monitoring points and their locations. The large amount of data available for this aquifer, made it an ideal experimental field in the framework of several national and international research projects (Barca et al. 2006 a,b; Passarella et al. 2006; Lo Presti et al. 2010; Maggiore et al. 2005; Masciale et al. 2011) which have allowed to precisely assess the aquifer size, its quantitative status and hydrogeochemical characteristics. Moreover, observed seasonal fluctuations of water table recently led to reliable studies of the groundwater system balance and to an improved assessment of the fresh water availability (Passarella et al., 2017).

In this work, hydrogeology has been taken into account as auxiliary soft variables. In particular, hydrogeological information has been simplified by grouping the outcropping lithologies according to their hydraulic conductivity class, which affects leaching of contaminant in the subsoil and the time required to reach the water table. According to The Water Protection Plan of Apulia Region (Apulia Region, 2009) two main classes of hydraulic conductivity have been distinguished over the study area, which are low-medium and very low. The low-medium class corresponds to coarser grained sediments (well-graded gravel with silt and silty sandy) prevailing in the upstream sector of the aquifer, while the low class corresponds to finer grained layers (clay, silt and silty clay) tending to prevail in the downstream sector of the aquifer (Figure 4).

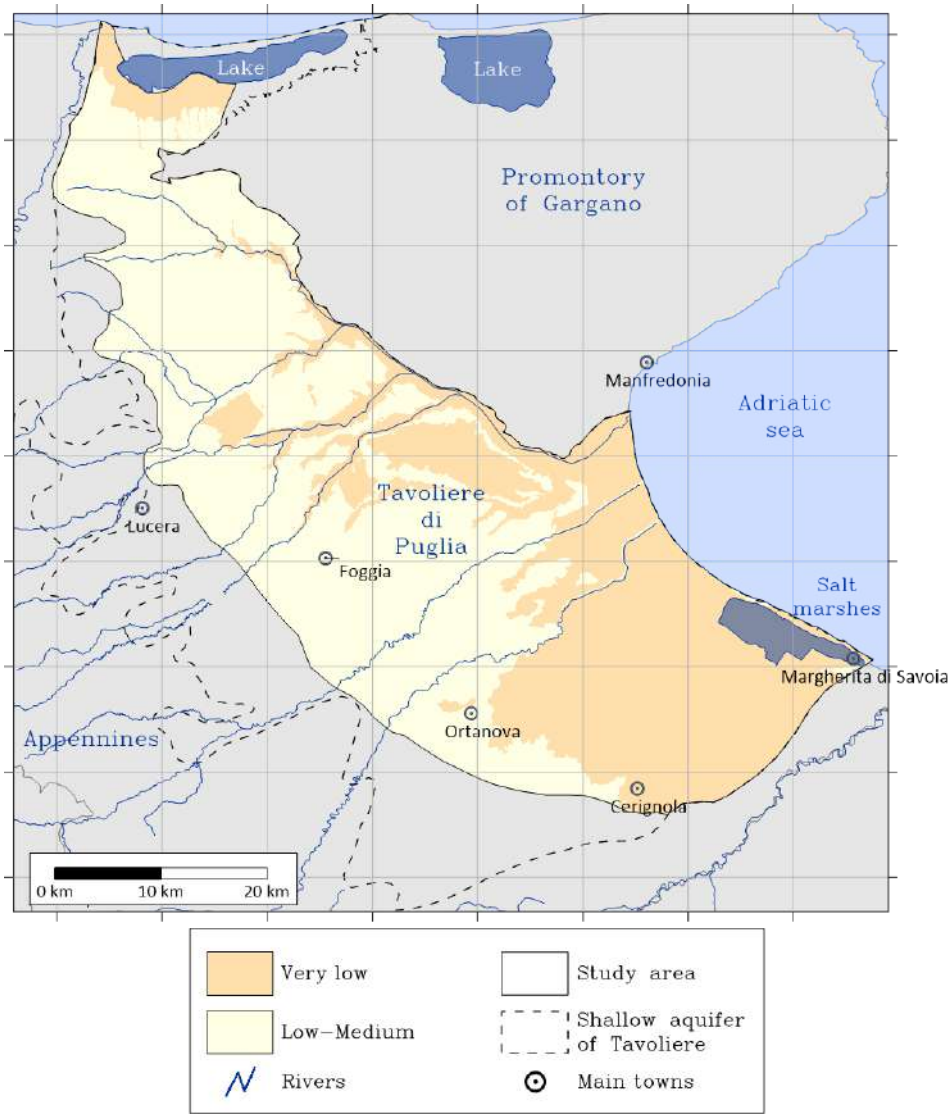


Figure 4: Simplified map of hydraulic conductivity classes over the study area (Apulia Region, 2009).

3.4 Land use

Land use of the study area was derived from the map, updated to 2011, available at the Territorial Information System (SIT) of Apulia Region, conforming to the specifications of the Corine Land Cover project (EEA, 2007; EEA, 2017). Most of Tavoliere's land covering (about 87%) is classified as agricultural area (Figure 5).

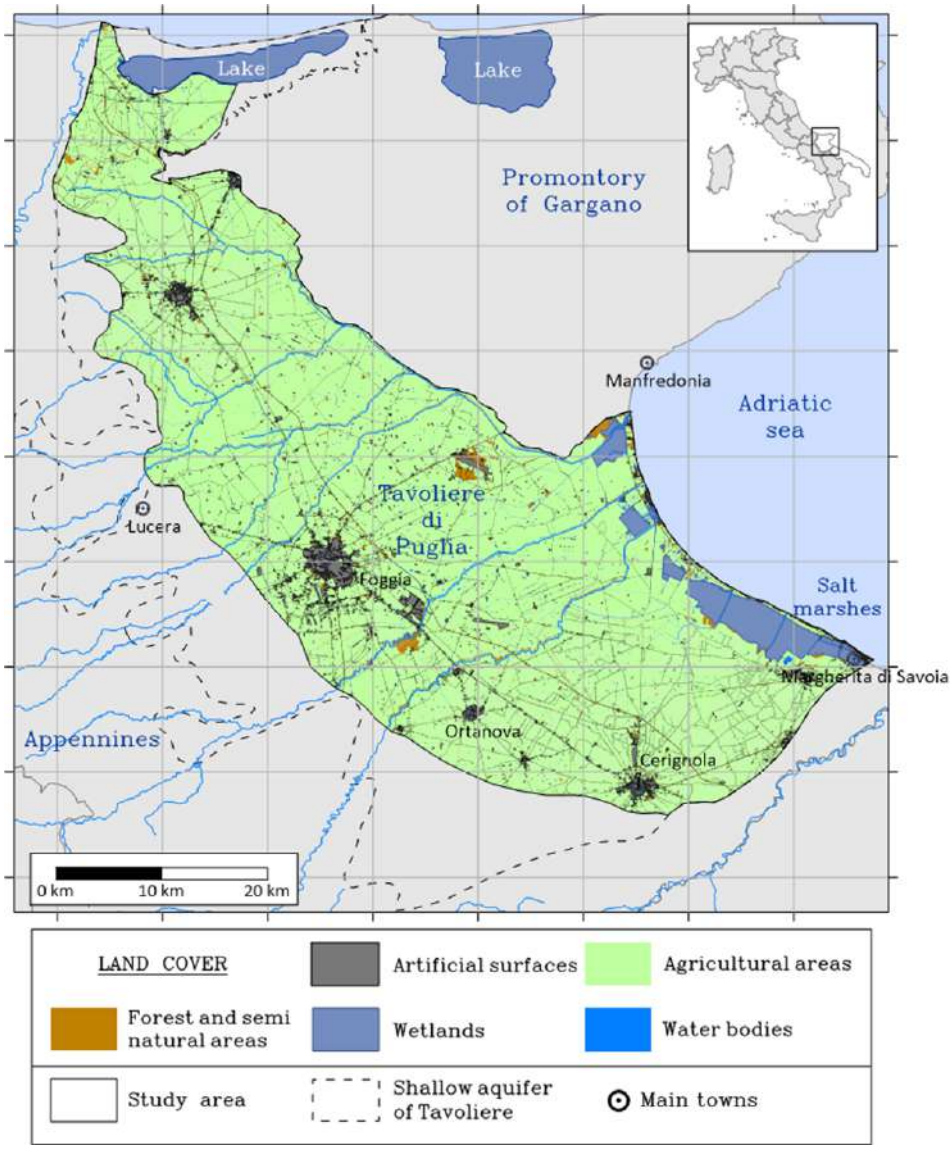


Figure 5: Land cover of the study area. (EEA, 2007; EEA, 2017).

At a more detailed level, the two main types of land cover in agricultural areas are arable land (67,4%) and permanent arboreal crops (20,7%), the latter made of vineyards, olive and fruit trees, that cover about 88% of the total area. The remaining part of the area is represented by heterogenous agricultural land (about 0.2%) artificial surfaces (about 5.8%), comprising infrastructures, human settlements and urban green areas, and natural and semi-natural environments (about 5.9%), comprising woods, wetlands, water bodies, natural pasture, natural vegetation, beaches and dunes (Figure 6).

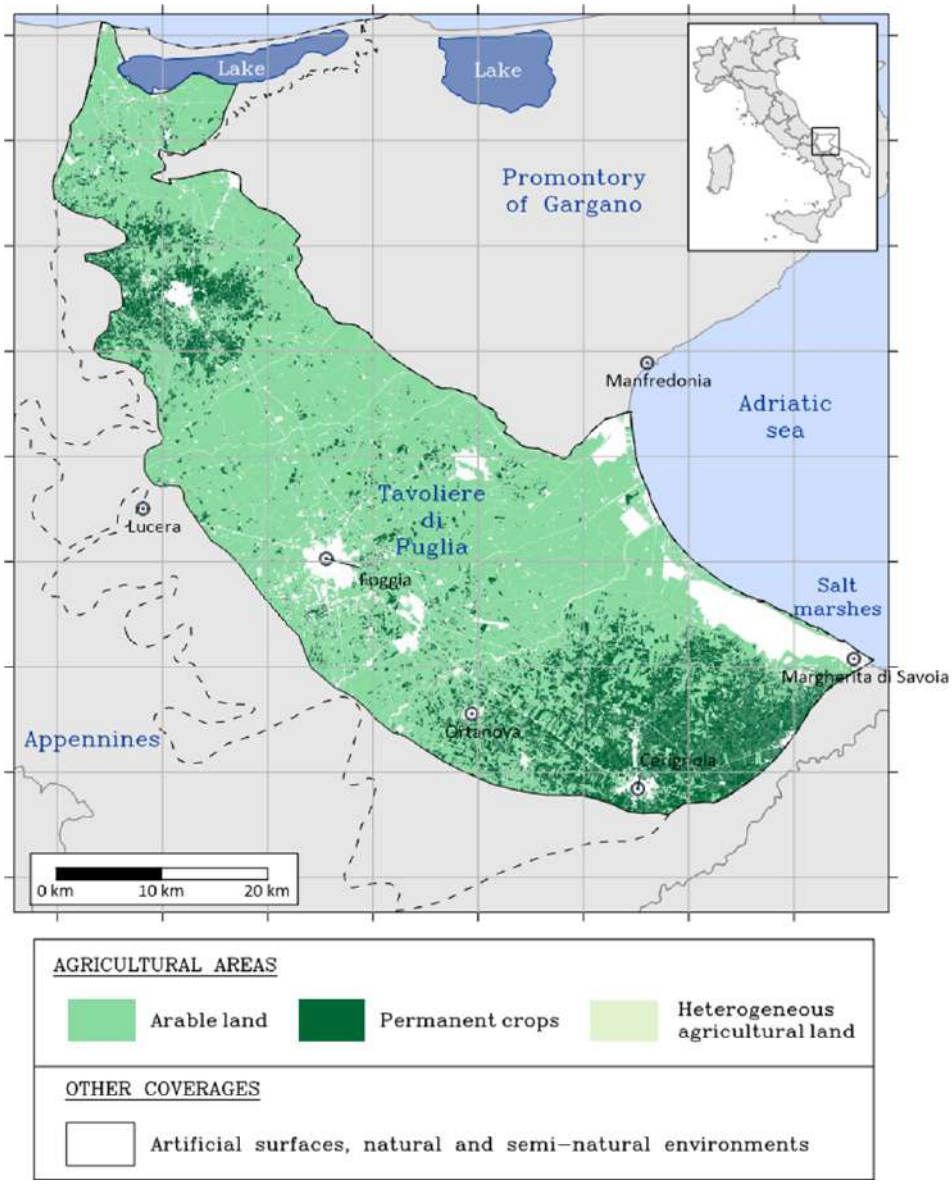


Figure 6: Agricultural sub-zones of the study area (EEA, 2007; EEA, 2017).

The paper deals with nitrate pollution of groundwater resources, which mostly comes from agricultural practices, where it is used as crop nutrient. Land use information then represent a precious information in terms of agricultural exploitation of the considered area. Considering the two prevailing agricultural categories in the study area, which is arable land and permanent crops, the land coverage was simplified in these two main classes as resulting from the Figure 7.

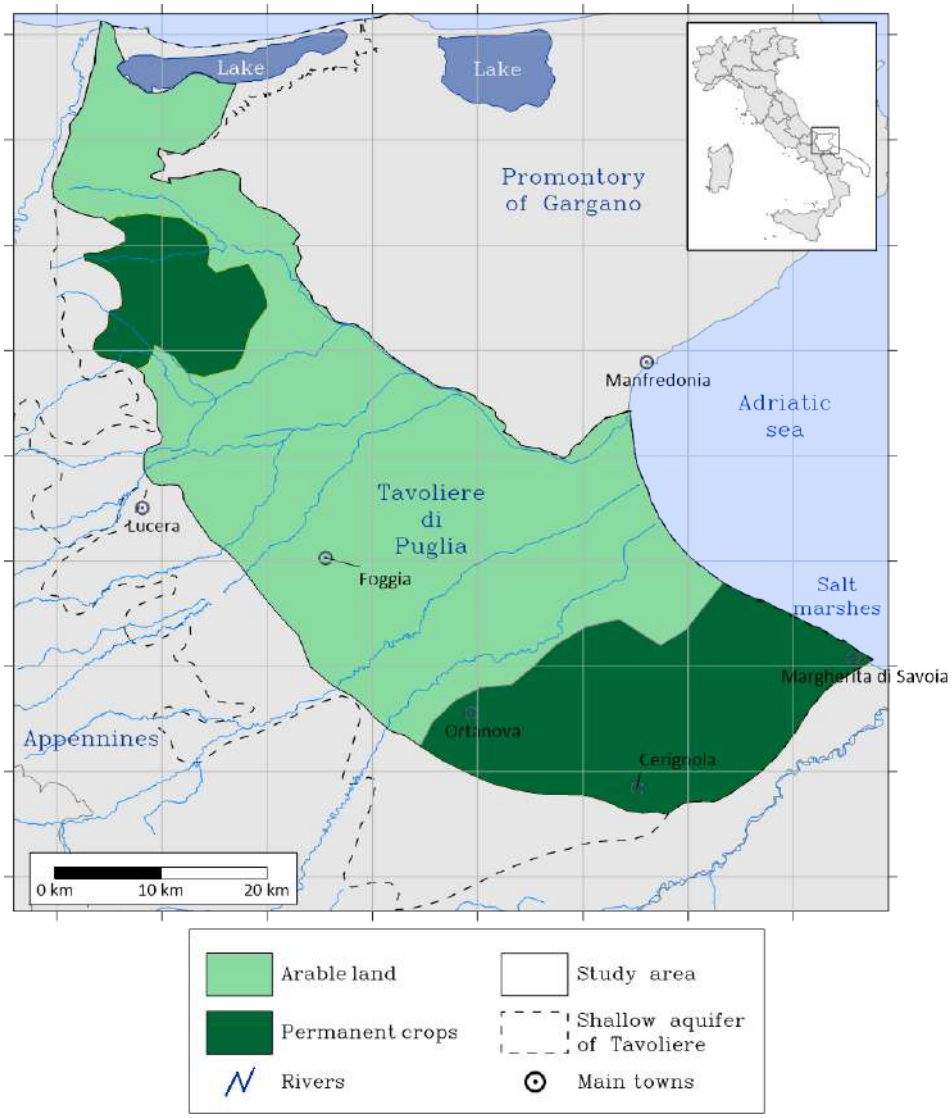


Figure 7: Simplified map of Land cover of the study area.

3.5 Nitrate data

Nitrate concentration data, used in this paper, have been provided by Apulia Region. 310 water samples were taken from 49 wells of the regional groundwater-monitoring network, established in 2007 within the project TIZIANO.

The samples were collected from autumn 2007 to spring 2011, for a total of eight seasonal monitoring campaigns named from t=6 months (6M-first campaign) to t=48 months (48M-last campaign). The spring campaigns correspond to the maximum water level of the aquifer while the autumn ones correspond to the minimum. Each water sample has been analysed and about 100 chemical and microbiological parameters were assessed per campaign, with different analytical methods. In particular, nitrates concentrations were measured by ion

chromatography (UNI 9813:1991). Three risk classes was set for increasing nitrate values: class 1 corresponding to $NO_3 < 10$ mg/L; class 2 corresponding to $10 \geq NO_3 < 50$ mg/L; class 3 corresponding to $NO_3 \geq 50$, that is the acceptable threshold of NO_3 concentration in groundwater set by Nitrates Directive 91/676/EEC.

4. RESULTS AND DISCUSSION

The technique described in the section 2.2 has been applied to the real data set with the goal to show the potential and the weakness of the approach but also to stress the importance of using qualitative/auxiliary information in addition to quantitative information.

The distribution of the three risk classes in the sample data set shows a clear prevalence of the highest risk class (class 3) over the other two (classes 1 and 2), with frequencies of 57%, 21% and 22%, respectively. These results, while highlighting the danger of qualitative degradation of the groundwater, do not give any spatial information on the location of the areas at greatest risk, which is crucial for the implementation of any recovery strategy. Due to this limitation of the 'classical statistical analysis', we turned to the geostatistical techniques of simulation.

A three-dimensional spatio-temporal model was adapted to the experimental variogram of indicator of the most frequent class (3). The model has been assumed isotropic in space, not having a sufficiently high number of locations to allow the calculation of directional variograms for the identification of any anisotropies in space. The resulting model included 3 structures: a nugget, a spherical spatial model with a range of 5000 m and a spherical temporal model with a range of 24 months (Table 1). Moreover, the resulting model is isotropic in space (total sill=0.25) and time (sill=0.095).

Table 1: Basic structure of the resulting spatio-temporal variogram model

S1	Nugget effect
	Sill = 0.099
S2	Spherical spatial
	Range = 5000.00m
	Sill = 0.150
S3	Spherical temporal
	Range = 24.00m
	Sill = 0.095

The results related to the ranges suggest that groundwater quality data can be considered associated (auto-correlated) within a spatial distance of 5000 m and a period of two years.

Obviously, these results strongly depend on the number and spatial-temporal displacement of the sample measurements (Barca et al., 2017). Given the small number of measurement sites, it is to be expected that the structural characteristics and prediction models will change with the set of sample data. This influence would obviously be less appreciable if a sufficiently exhaustive sample data set were available (approximately 100 samples within a range of 5000 m). For the reasons explained above, we have tried to compensate the missing primary information (nitrate concentration in groundwater) with the auxiliary (hydrogeologic and land cover) information but assumed strictly influential the first. The auxiliary information has been combined overlapping the two simplified maps of hydraulic conductivity and land cover shown in Figure 4 and
Figure 7. Figure 8 shows the resulting map.

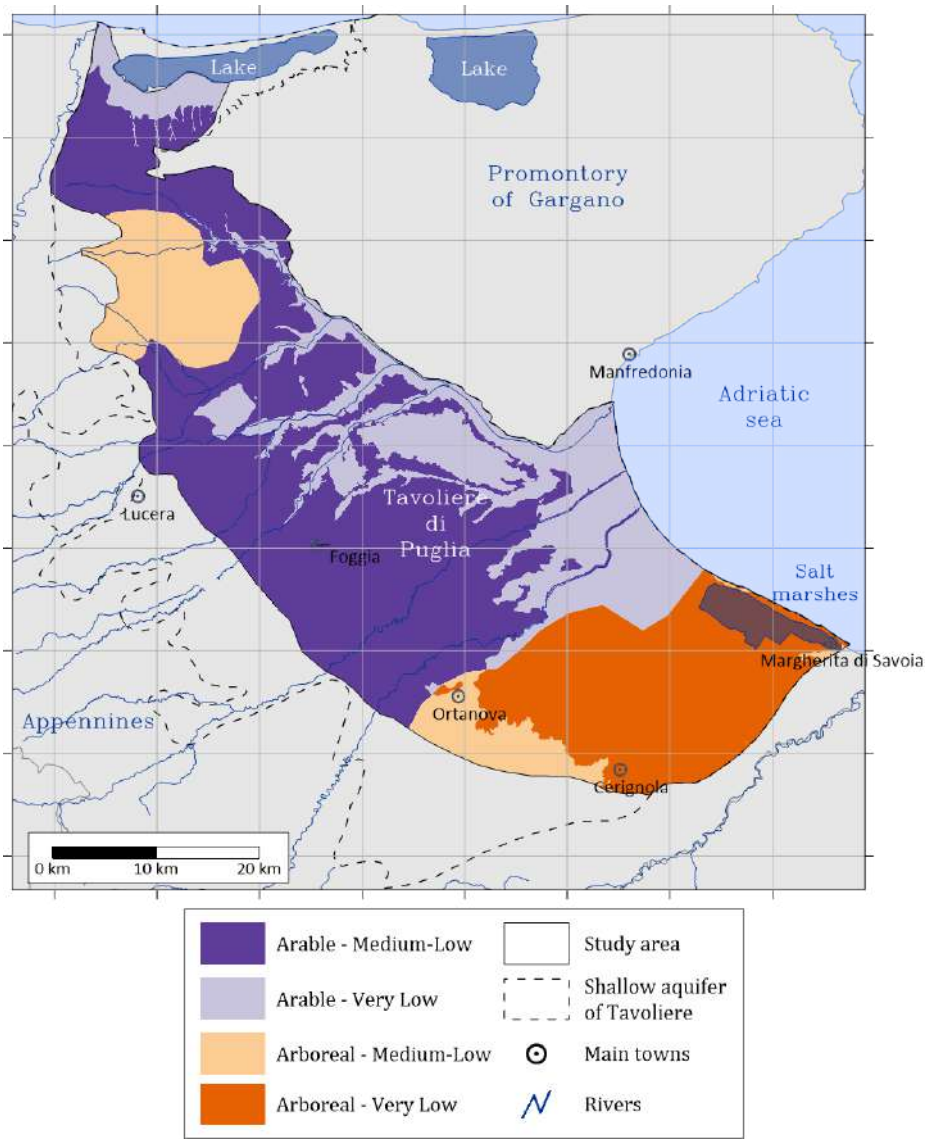


Figure 8: Final map obtained by overlapping the two auxiliary information (hydraulic conductivity classes and land cover.

Four different type of sub-areas can be identified: 1) areas characterized by the presence of arable land with a medium-low hydraulic conductivity class; 2) areas characterized by the presence of arable land with a very-low hydraulic conductivity class; 3) areas characterized by the presence of permanent crops with a medium-low hydraulic conductivity class; 4) areas characterized by the presence of permanent crops with a very-low hydraulic conductivity class.
Furthermore, even quantitative *a-priori* information has been considered in this study. As described at section 2.1, such information consists in the percent number of observed nitrate values belonging to each class over each of the areas of Figure 8, per monitoring campaign. As an example, Figure 9: A-priori probability maps of the three classes of risk at the first monitoring campaign.

shows the *a-priori* probability maps related to each nitrate threshold, obtained by crossing together quantitative and qualitative information, at the 6th month monitoring campaign. The choice of the 6th month, which is the first of the considered monitoring series, is due to the practical equivalence of all the probability maps during the entire observed period. This equivalence, in space and time of all the *a-priori* probability maps confirms the observed constant in space and persistent in time presence of nitrates within the considered aquifer.
More in detail, Figure 9: A-priori probability maps of the three classes of risk at the first monitoring campaign.

shows an almost equal probability of getting nitrates values in each of the three classes in the southeastern part of the study area, characterized by the presence of permanent crops with a very-low hydraulic conductivity class.
On the other side, the remaining parts of the study area exhibit a higher probability of exceeding the threshold of 50 mg/L, being this probability around 0.6 in the areas characterized by arable land and permanent crops with a medium-low hydraulic conductivity.
The probability increase until to 0.8 in the eastern most part of the study area, which is characterized arable land and very-low hydraulic conductivity.
This last zone is the most downstream part of the Tavoliere plain. It covers a wide portion of the coastal area and most of the riverbed proximity bands. The very low hydraulic conductivity of outcropping lithology does not allow nitrates concentration dilution by freshwater recharge. Furthermore, the riverbeds cut the outcropping sediments facilitating the infiltration of surface water, often rich of nitrates content due to soil leaching, towards the groundwater system.
By processing the proximal (spatial) information by the stochastic simulation techniques, the *a-priori* probability maps have been transformed into *a-posteriori* probability maps.

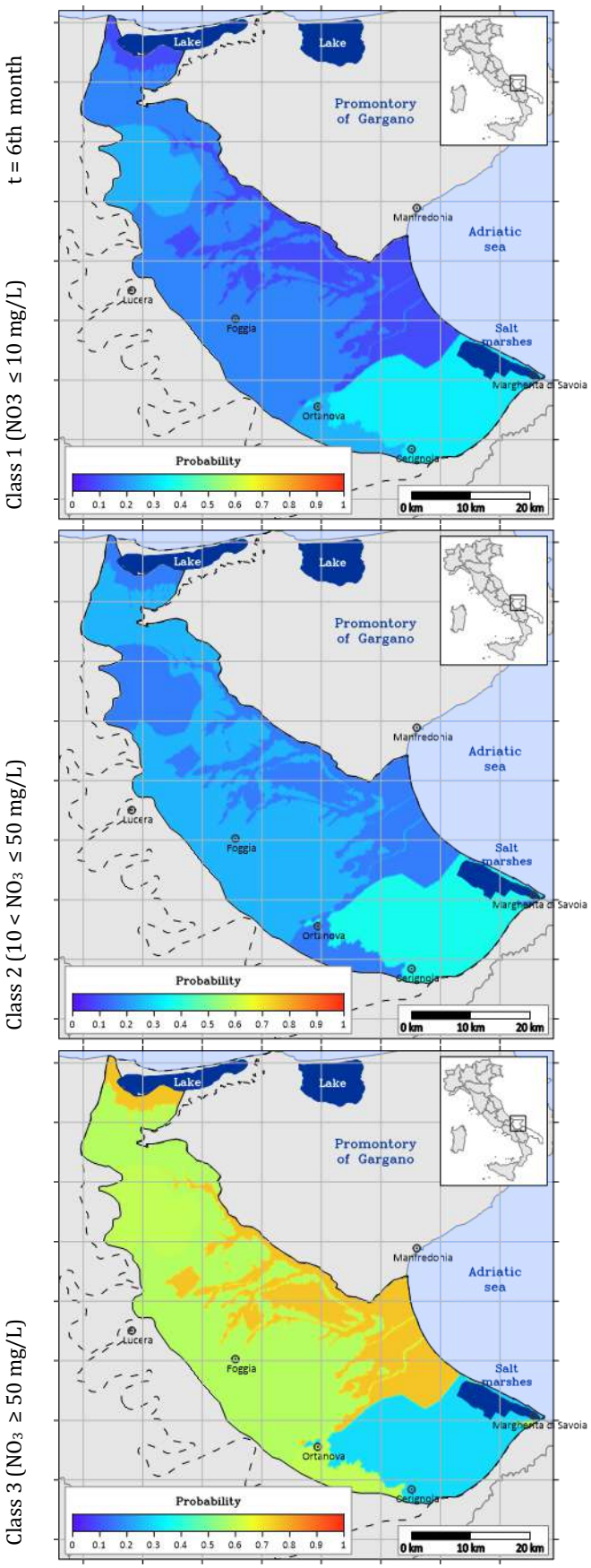

t = 6th month
Class 1 (NO3 ≤ 10 mg/L)
Class 2 (10 < NO3 ≤ 50 mg/L)
Class 3 (NO3 ≥ 50 mg/L)
Lake
Lake
Promontory of Gargano
Manfredonia
Adriatic sea
Lucera
Foggia
Salt marshes
Margherita di Savoia
Ortanova
Probability
0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1
0 km 10 km 20 km

Figure 9: A-priori probability maps of the three classes of risk at the first monitoring campaign.

Figure 10 shows the temporal evolution of the *a-posteriori* probability maps of occurrence of the three classes, provided by the proposed method.

From a visual inspection, it is clear that the areas, characterized by a certain level of risk, remain stable over time. This would indicate that the main cause of groundwater quality degradation, even being surely anthropogenic, is deep-seated over the area and rather permanent in time, at least during the observed period.

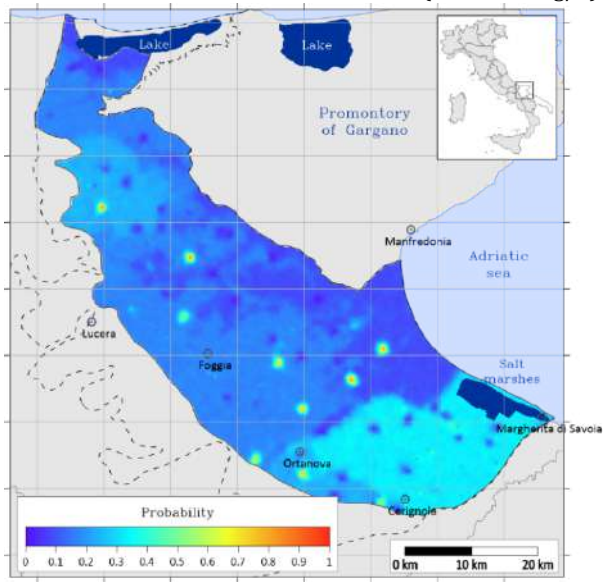
Sparse hot-spots which appears in the *a-posteriori* maps may have been caused by a low sampling density and a relatively short range with respect to the minimum sampling distance.

The comparison of Figure 9: A-priori probability maps of the three classes of risk at the first monitoring campaign.

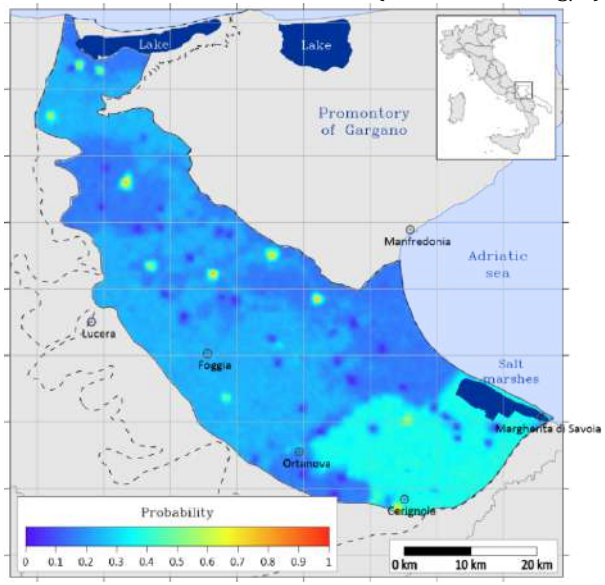
and Figure 10 evidences, the *a-priori* and *a-posteriori* maps are very similar apart from a greater variability of the latter obviously due to the additional proximal information.

As already described above with regard to the *a-priori* maps, the probability of occurrence of classes 1 and 2 ($NO_3 \leq 50$ mg/L) in the *a-posteriori* maps is confirmed, generally, very low and reaches its maximum, about 0.4, in the southeastern part of the study area, characterized by permanent crops and very-low hydraulic conductivity. At the same time, class 3 (NO3 ≥ 50 mg/L) reaches high probability values almost everywhere in the norther part, becoming particularly worrying, with values around 0.8, all along the eastern boundary.

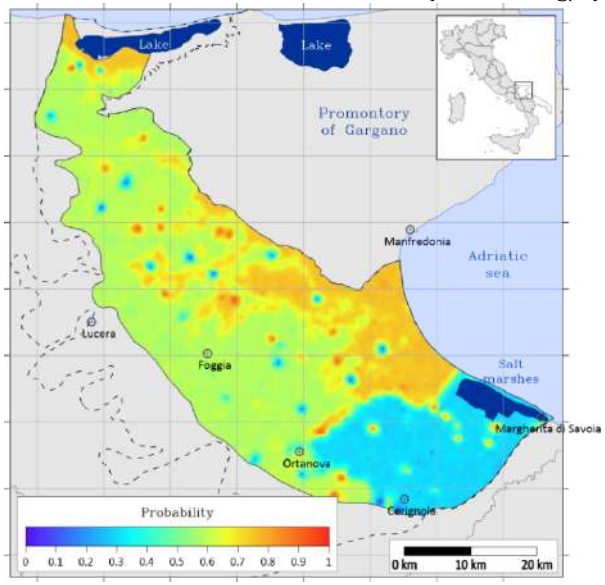
t = 6th month



Class 1 (NO_3 ≤ 10 mg/L)

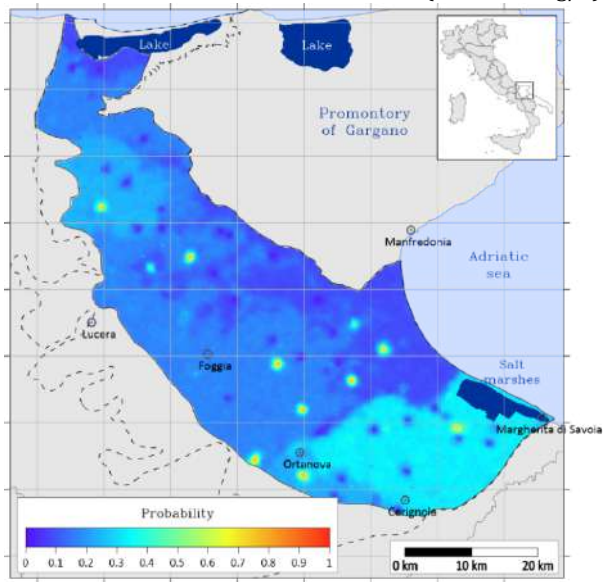


Class 2 (10 < NO_3 ≤ 50 mg/L)

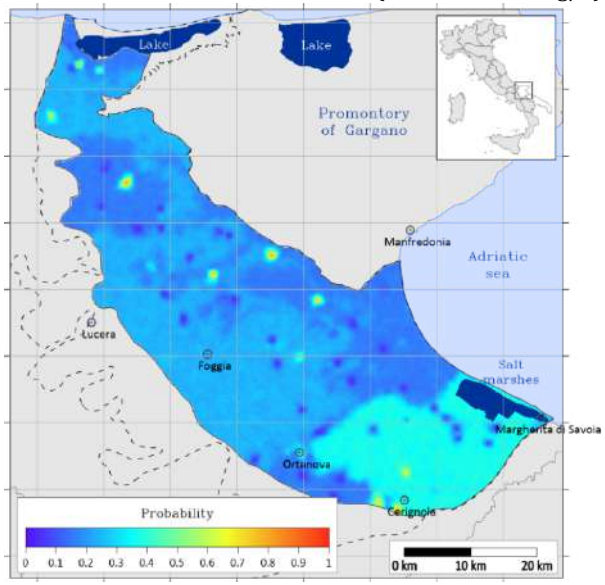


Class 3 (NO_3 ≥ 50 mg/L)

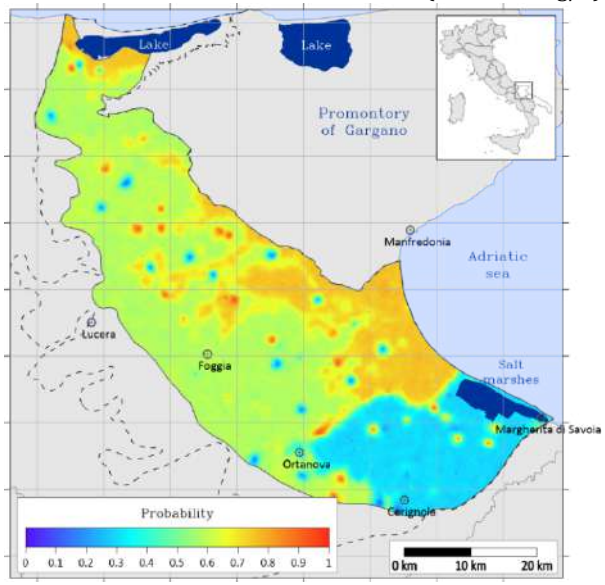
t = 12th month



Class 1 (NO_3 ≤ 10 mg/L)

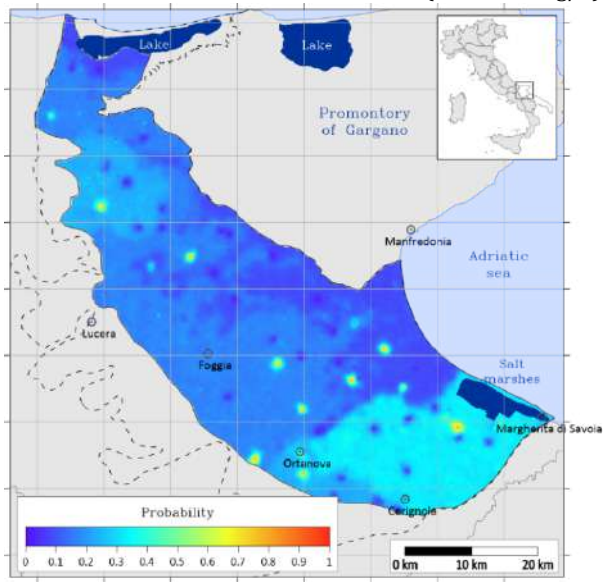


Class 2 (10 < NO_3 ≤ 50 mg/L)

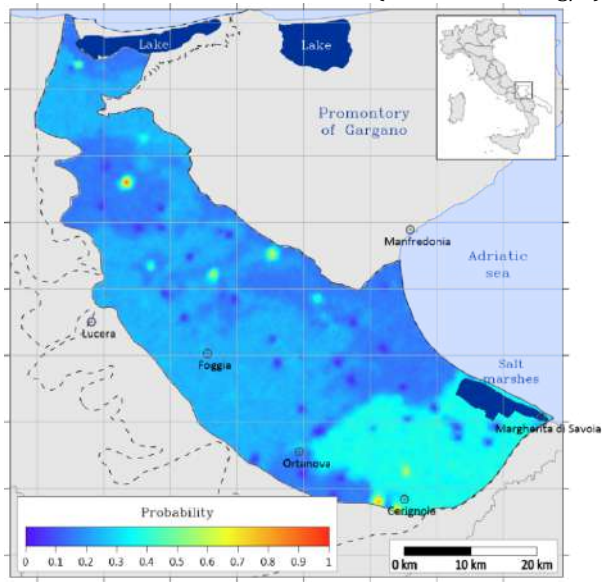


Class 3 (NO_3 ≥ 50 mg/L)

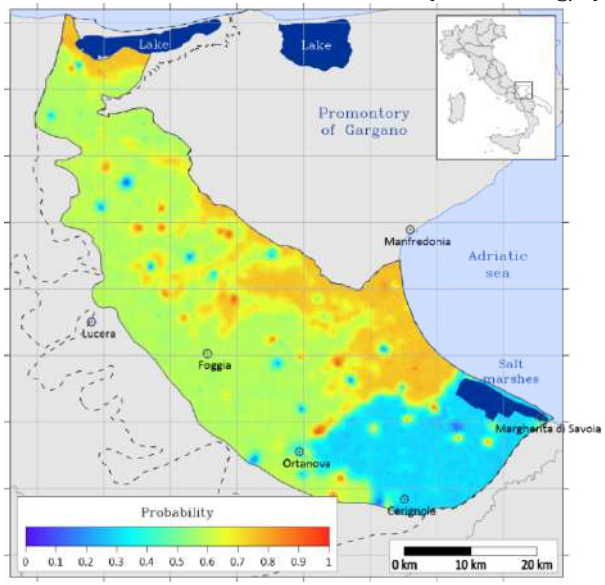
t = 18th month



Class 1 (NO_3 ≤ 10 mg/L)

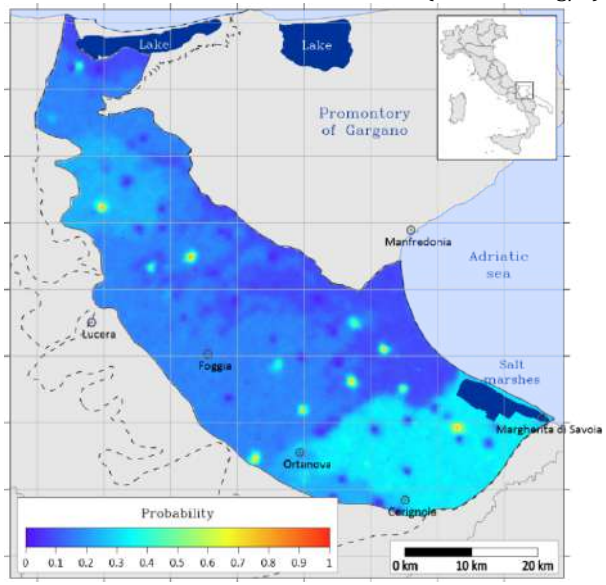


Class 2 (10 < NO_3 ≤ 50 mg/L)

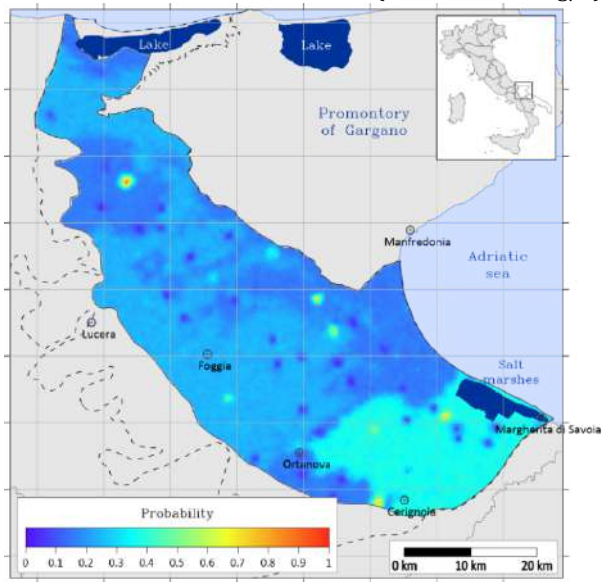


Class 3 (NO_3 ≥ 50 mg/L)

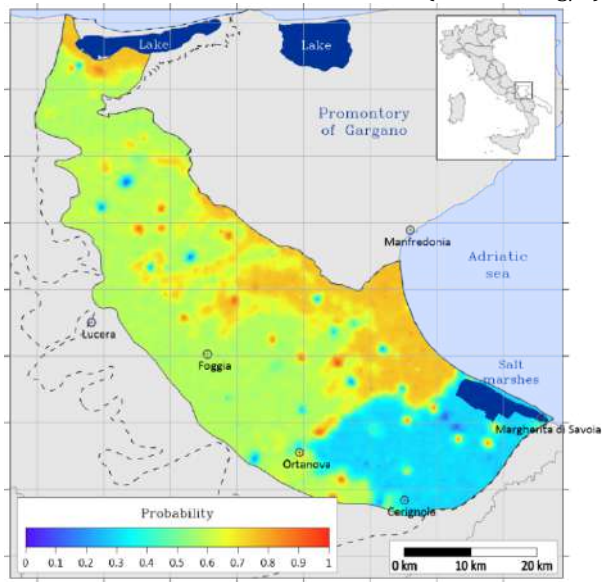
t = 24th month



Class 1 (NO_3 ≤ 10 mg/L)

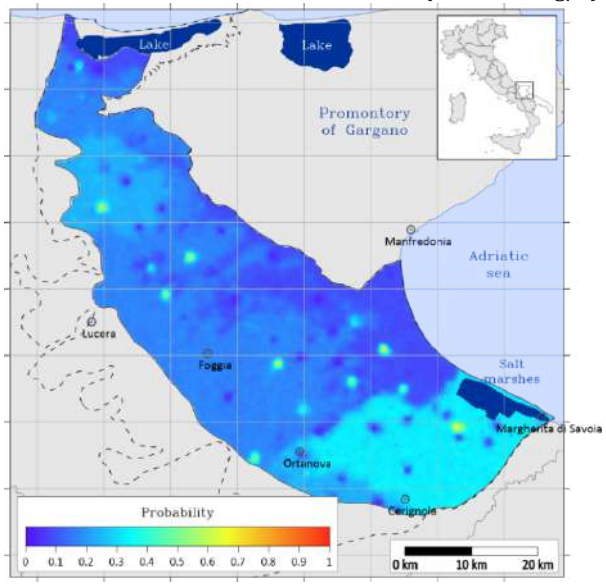


Class 2 (10 < NO_3 ≤ 50 mg/L)

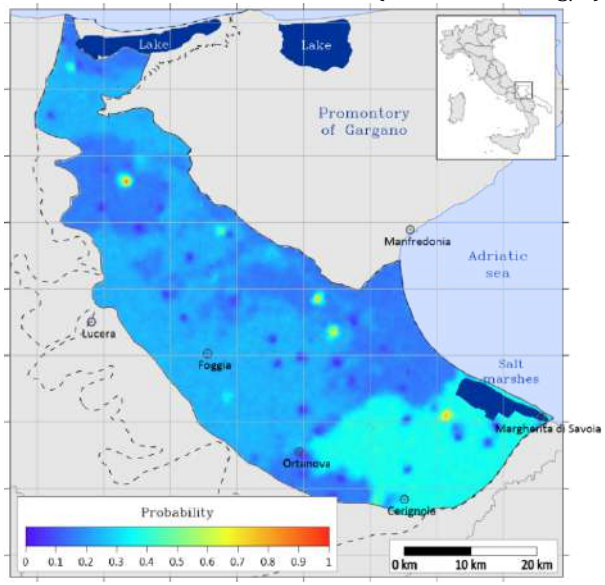


Class 3 (NO_3 ≥ 50 mg/L)

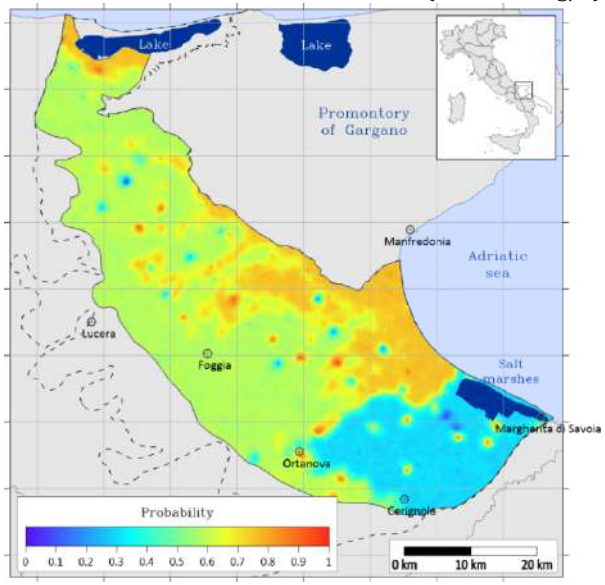
t = 30th month



Class 1 (NO_3 ≤ 10 mg/L)

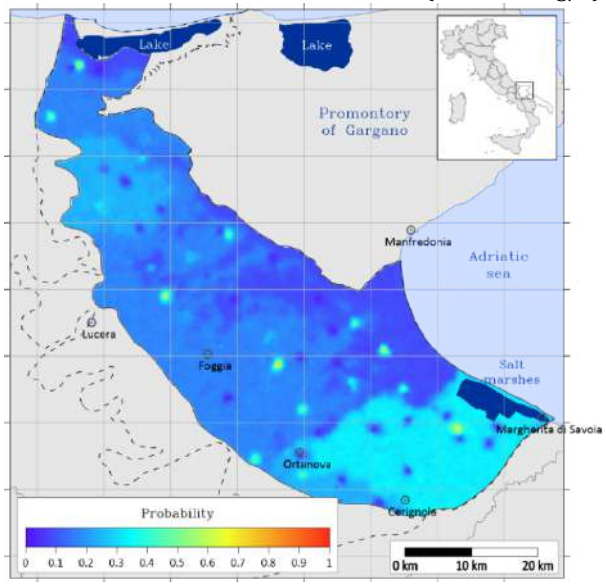


Class 2 (10 < NO_3 ≤ 50 mg/L)

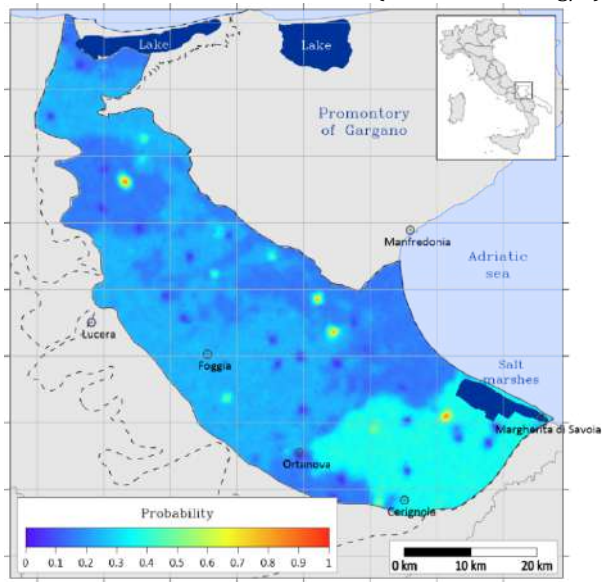


Class 3 (NO_3 ≥ 50 mg/L)

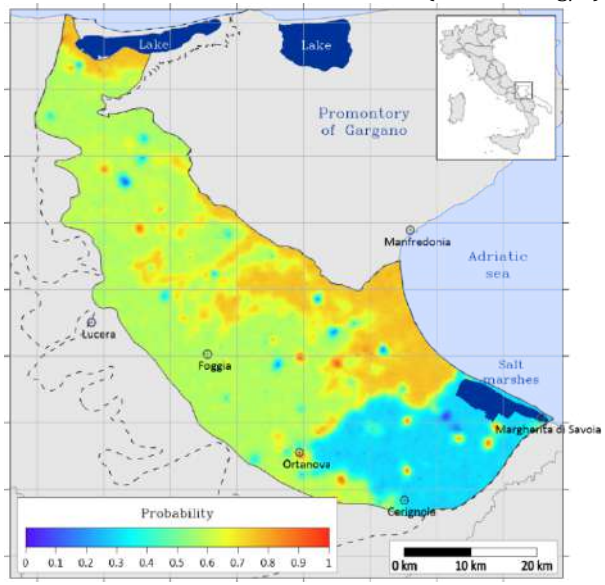
t = 36th month



Class 1 (NO_3 ≤ 10 mg/L)



Class 2 (10 < NO_3 ≤ 50 mg/L)



Class 3 (NO_3 ≥ 50 mg/L)

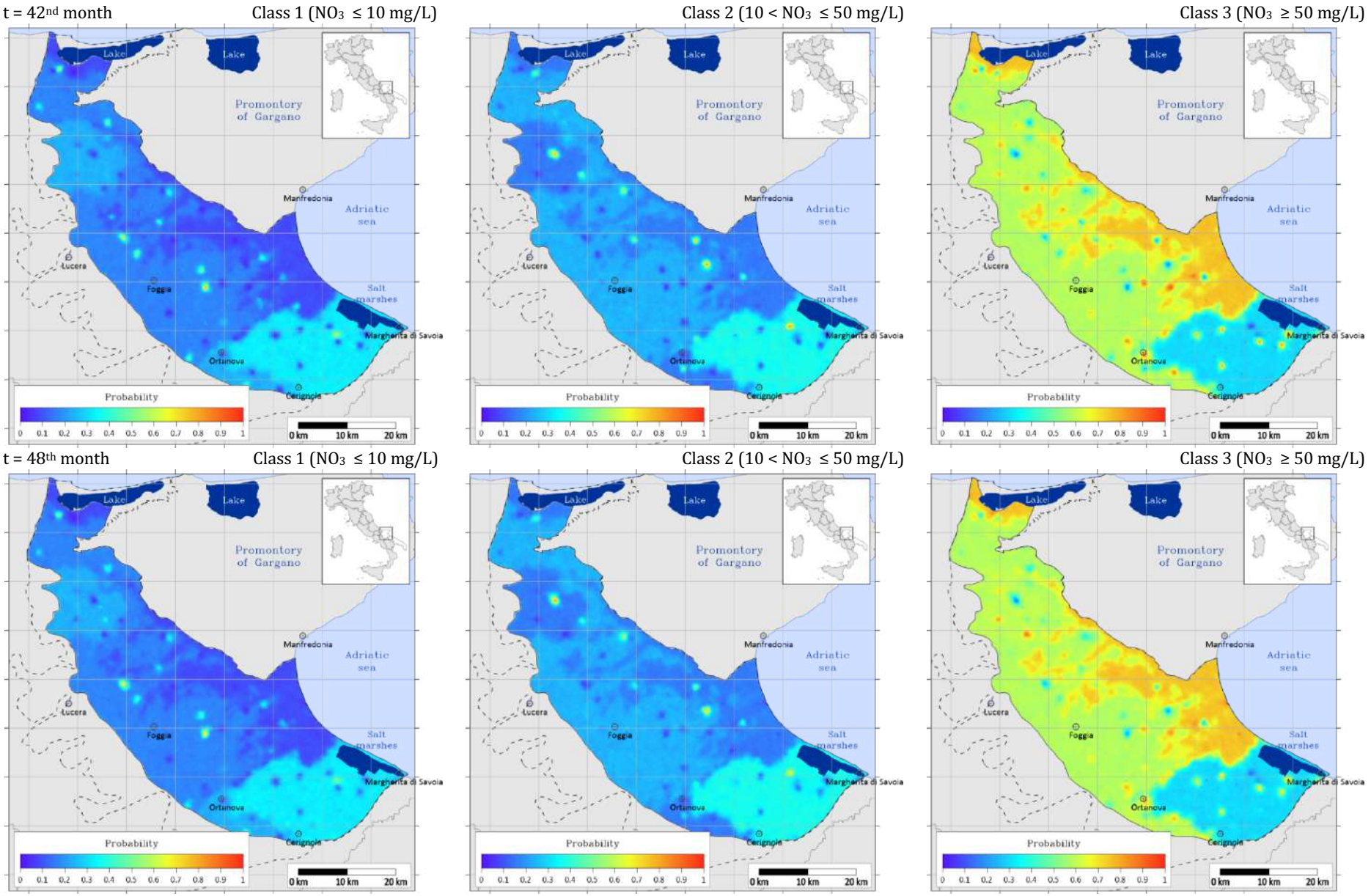


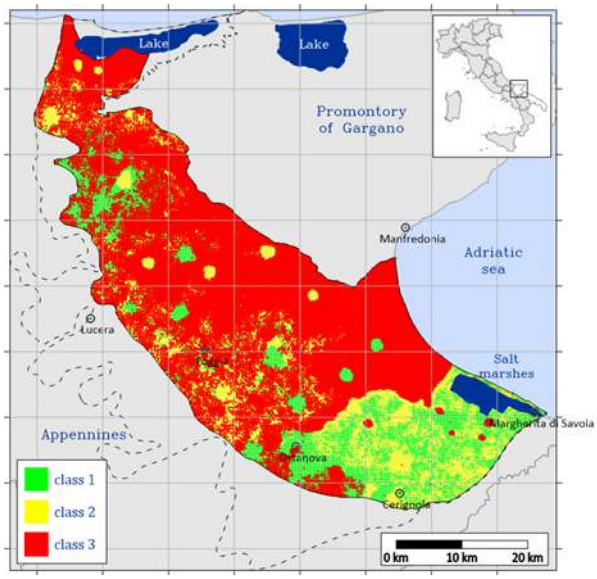
Figure 10: A-posteriori probability maps of the three classes for each monitoring campaigns.

The triple representation of the *a-posteriori* maps, per monitoring campaign, has been summarized into a single map of the most probable class, after the Soares correction (Figure 11). Even in this case no clear seasonal dynamics is evidenced and the spatial location of the probabilities is the same as described above.

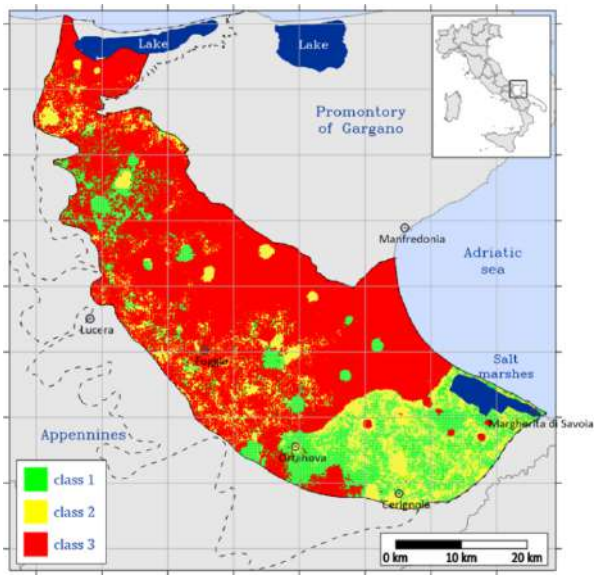
The scene proposed by Figures 11is somewhat worrying, resulting most of the considered area at risk of exceeding the critical nitrate concentration value of 50 mg/L.

Actually, the portions of the study area with permanent crops are mostly characterized by a high probability of being below the critical threshold and at the southern boundary, where the hydraulic conductivity is very low, the probability is high of finding values below the first threshold of 10 mg/L.

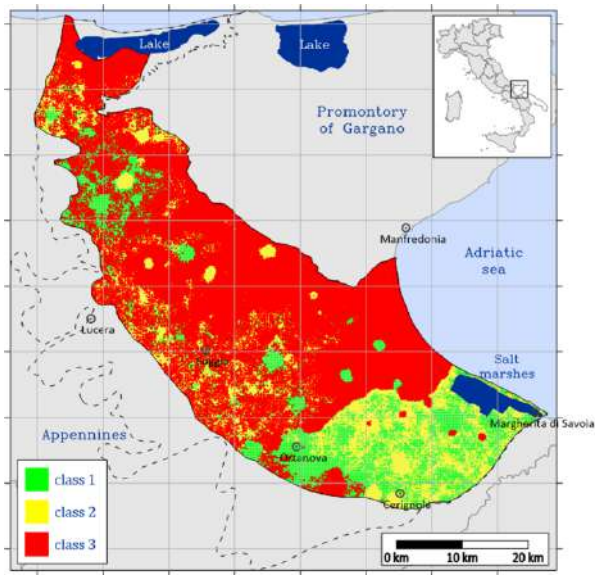
t = 6th month



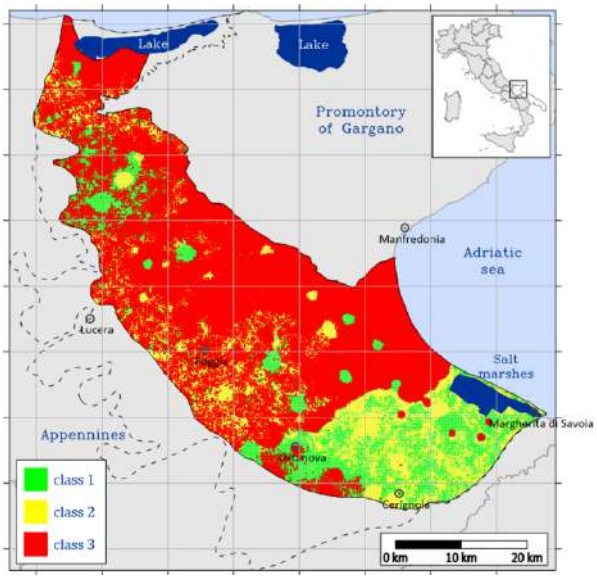
t = 12th month



t = 18th month



t = 24th month



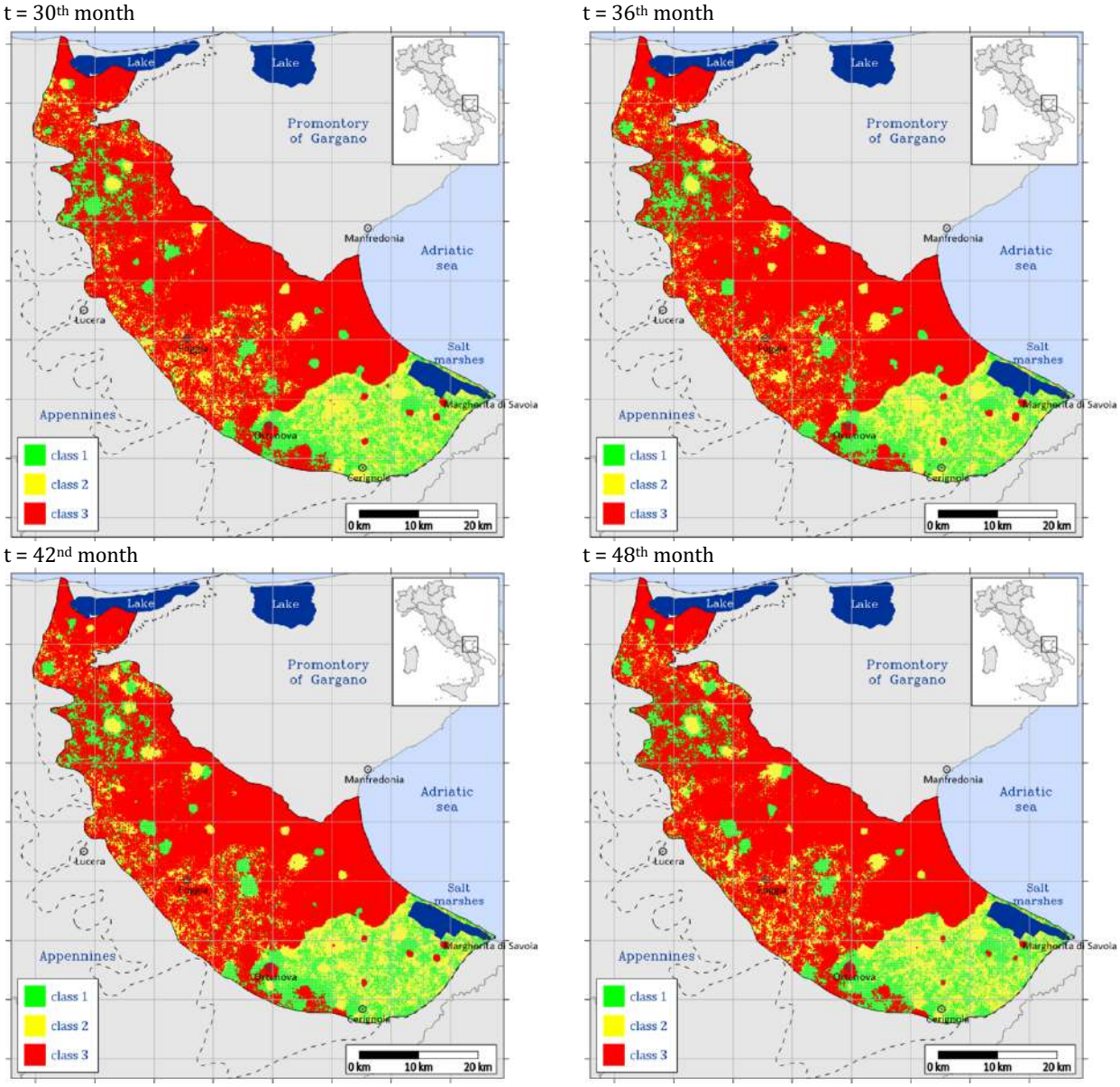
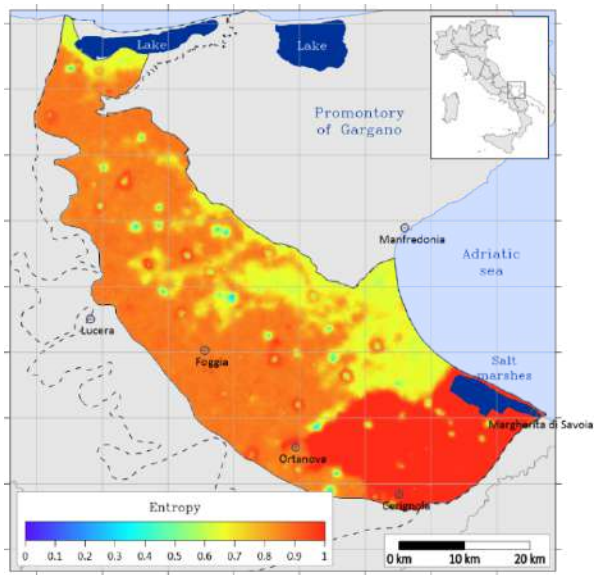


Figure 11: Maps of the most probable class over time, after the Soares correction

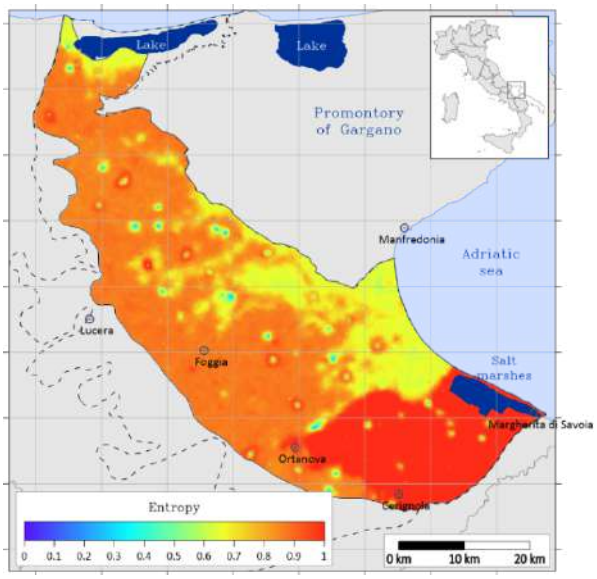
Any risk stochastic modelling is affected by errors. Quantifying it is an important task in order to define and develop reliable plans and actions to restore the environmental status of part or the entire groundwater body. The proposed method provides a suitable tool for measuring the uncertainty associated to the probability estimation. In practice, computing the local standardized entropy (H) at each estimation cell, the uncertainty associated to the risk variable discretized in 3 categories with probabilities p_k (k= 1,2,3) can be univocally assessed in that cell. As described at section 2.2.4, the local standardized entropy varies from 0 to 1, which indicate the minimum and maximum uncertainty of the estimated values, respectively.

Figure 12 shows the maps of the computed entropies at each simulated time. All the maps evidence an entropy value near to 1 in the southeastern part of the study area, characterized by arable land and medium-low hydraulic conductivity. This indicates the three classes have about the same probability of occurring. The minima values of H ≅ 0.65, which means lower uncertainty of the estimated probabilities, always appear at the eastern edge of the study area, which is characterized by arable land and very-low hydraulic conductivity. Finally, Figure 12 shows persistent uncertainty values, H ≅ 0.8, all over the remaining part of the study area entirely characterized by medium-low hydraulic conductivity, even though by different land uses.

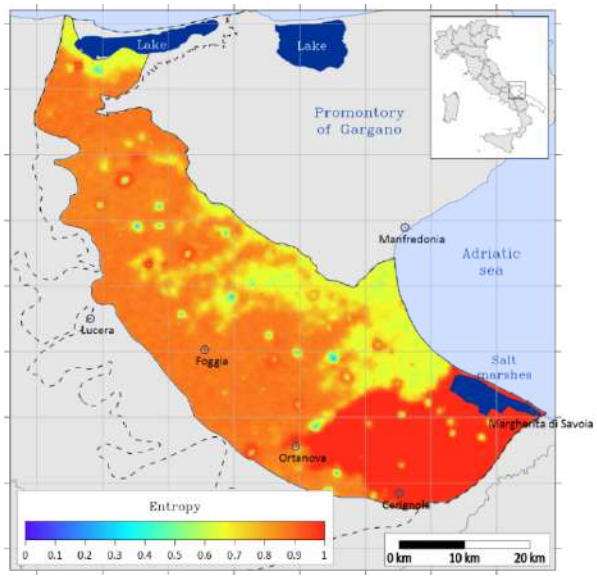
t = 6th month



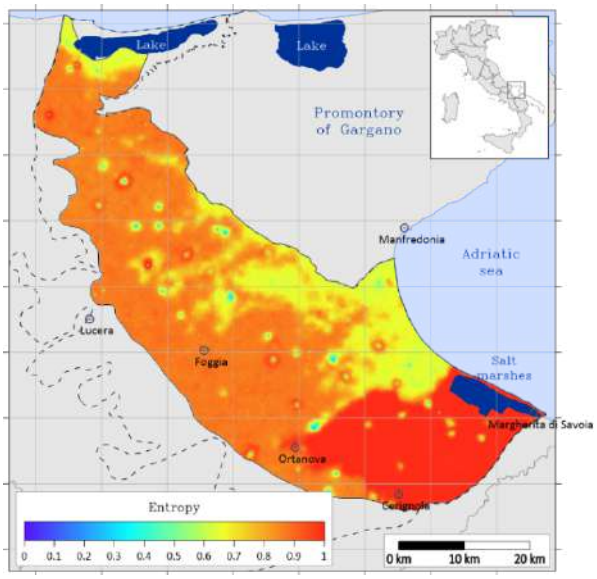
t = 12th month



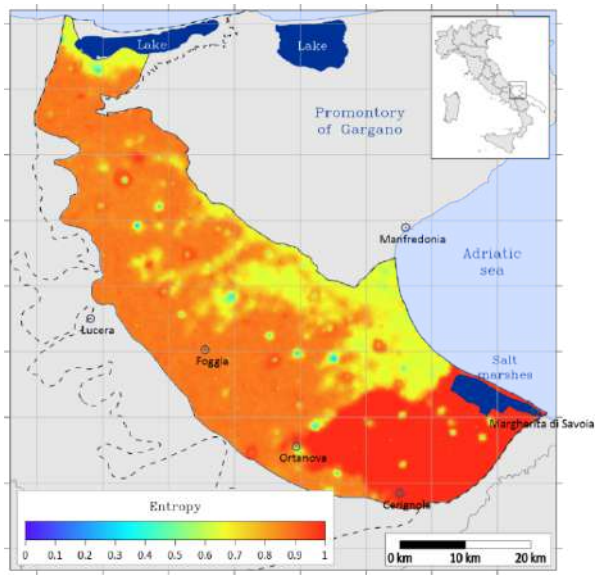
t = 18th month



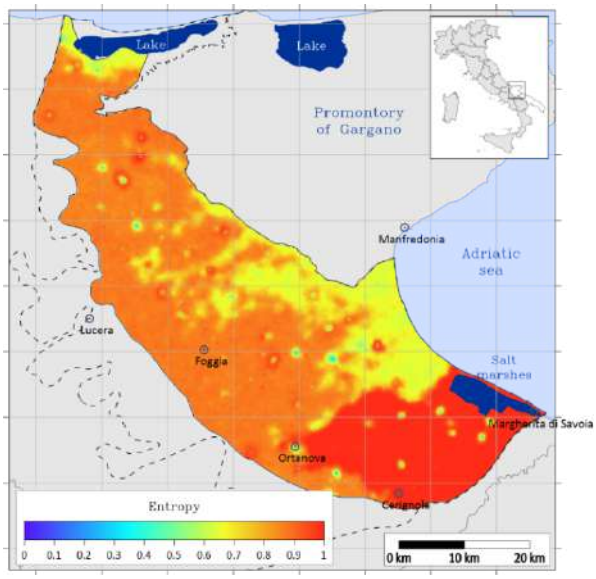
t = 24th month



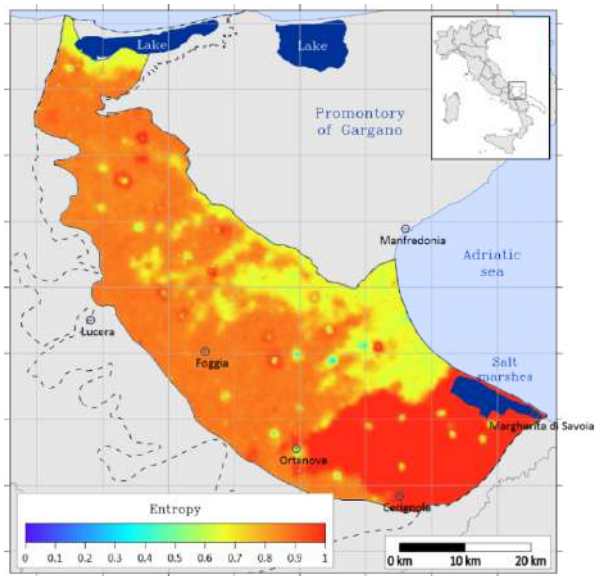
t = 30th month



t = 36th month



t = 42nd month



t = 48th month

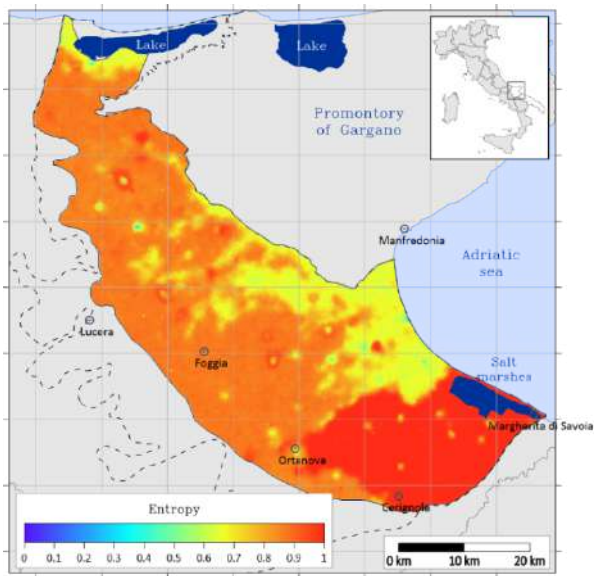


Figure 12: Map of entropy and its evolution over time.

The causes of these high uncertainty values can be attributed to low sampling density and uneven/clustered distribution of the wells under investigation, as well as to intrinsic variability, due to natural (hydrogeological properties) and anthropogenic (land use) factors. The results of these analyses seem to suggest activating a plan of optimization of the monitoring network by intensifying the monitoring locations in areas of higher uncertainty (for example entropy > 0.8) and more densely populated.

The time series of the eight risk maps of Figure 11 has been summarized in time by evaluating the most frequent class in each estimation cell. Figure 13 shows the resulting map of the most frequent classes of risk over the entire simulated period.

In Figure 13, also the four different areas characterized by different land uses and hydraulic conductivities, considered as auxiliary information, have been displayed by different hatchings. It is evident that the areas with the lowest risk, where classes 1 and 2 prevail, are those cultivated with permanent crops (mostly olive groves and, vineyards), while the areas with the highest risk (class 3 prevalence) are those cultivated with arable (mostly cereals and durum wheat), owing to the more intense fertilization.

Fertilizer's use in agriculture is reported to be the highest anthropogenic source of nitrate contamination in groundwater (Shukla & Saxena, 2018). Infact, it is known that nitrogen is one of the major components of fertilizers, whose usage in agriculture has increased in time to escalate the crop yield. This often causes an over-application of fertilizers by farmers, other than an improper timing of applying, in the belief believing that more fertilizer is equivalent to higher crop yield. Fertilizer application and subsequent leaching cause the nitrates to reach the groundwater.

Still concerning the results in Figure 13, it is also possible to establish a relationship between classes of risk and subsoil hydrogeological characteristics. In fact, within the areas with permanent crops, class 3 appears only in the portions characterized by medium-low hydraulic conductivity. This is because, in these portions, the greater hydraulic conductivity of the subsoil facilitates the percolation of nitrates to groundwater.

On the contrary, within the areas characterized by more intensely fertilized arable crops, a higher frequency of class 2 is evident along the whole western strip characterized by medium-low hydraulic conductivity. Otherwise, on the eastern side, the most worrisome class 3 prevails. As detailed at section 3.3, groundwater mainly flow from southwest to northeast and then the main natural recharge area is located just along the western strip.

In this context, even though the western area of the aquifer is the main infiltrating way of nitrates from soils to groundwater, here, the transfer potential, which is the groundwater capability of allowing migration of nitrogen, is higher. This would justify the larger frequency of class 2 in this area.

Instead, the eastern part of the aquifer is characterized by a very low hydraulic conductivity and results to be moderately confined. This, somehow, prevents the direct infiltration of nitrates from soils to groundwater. Nevertheless, here, riverbeds cut the outcropping less permeable sediments and allow surface water to recharge groundwater facilitating the infiltration of nitrates.

Moreover, in this part of the aquifer, which is the most downstream, the groundwater flow velocity decreases and, consequently, the accumulation potential, which is its capability of retaining pollutants, increases allowing nitrates, flowing from the recharge area, to accumulate and increase in concentration.

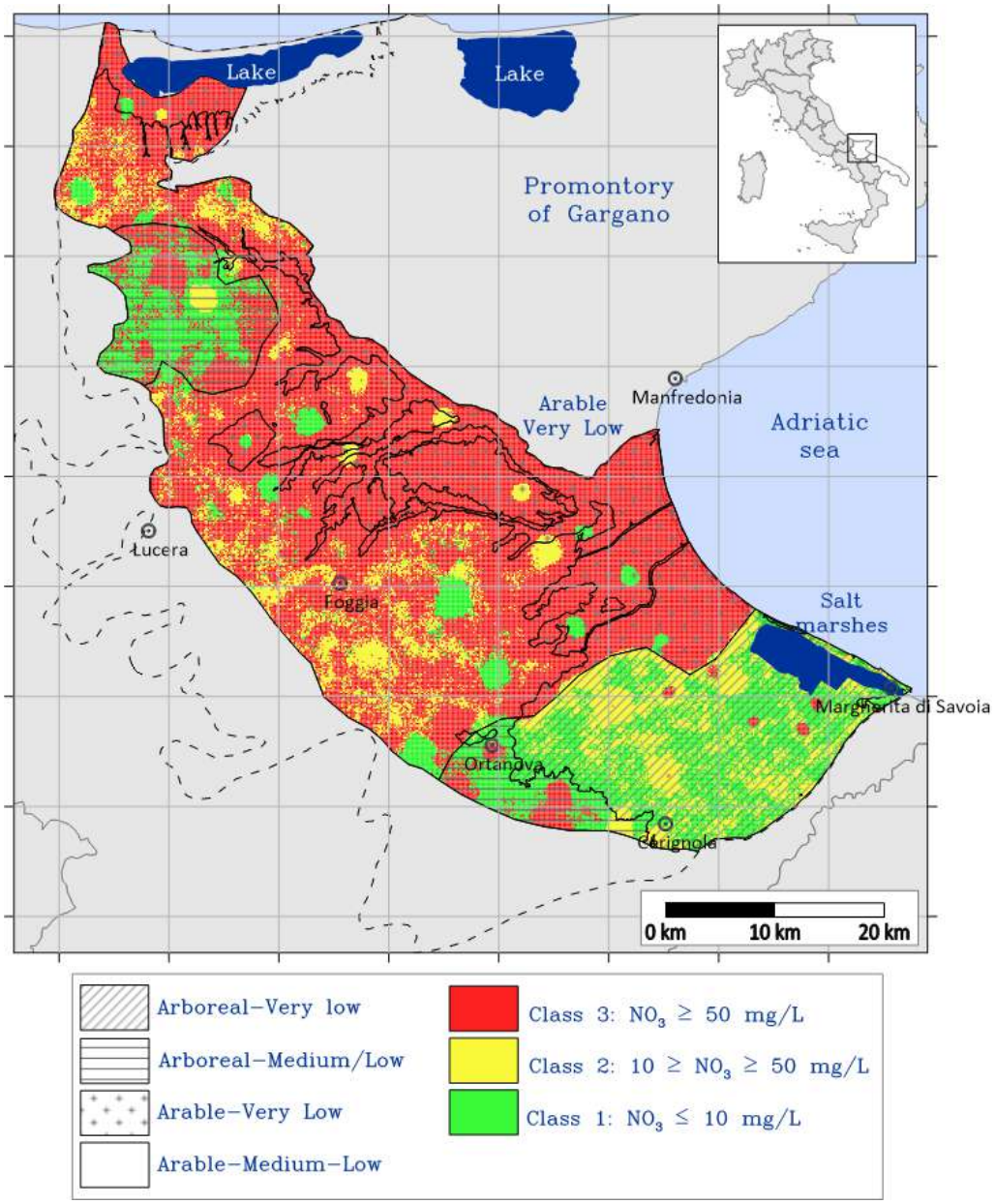


Figure 13: Map of the most frequent classes of risk over the entire simulated period

5. CONCLUSIONS

In arid and semiarid areas, groundwater is often the primary source of freshwater supply. Usually, focus on groundwater quality concerns its use as drinking water. Nevertheless, groundwater should be protected for its environmental value because of its important role

within the hydrological cycle through the maintenance of wetlands and river flows, acting as a buffer through dry periods. From a managerial standpoint, actions are required in order to reduce the risk of groundwater quality degradation in regions such as the study area where the climate is mostly semi-arid (Maggi et al. 2018; Passarella et al., 2020) and land is intensively cultivated. The European legislation (EU, 1991; EU, 2000; EU, 2006) recommends groundwater protection, improvement and restoration, even by promoting good agricultural practices, such as precision farming and irrigation, and rational use of fertilizers.

The goal of this chapter has been to define an approach for performing risk analysis of groundwater quality degradation due to nitrates leaching from soils, in probabilistic terms.

The Indicator Simulation algorithm, a stochastic simulation technique provided by geostatistics, has been applied, which allows to consider together both quantitative (hard) and qualitative (soft) data. The results of the proposed method have been maps showing the probability of exceeding increasing assigned thresholds of nitrate concentration combined to different patterns of land use and hydrogeological features. The more the threshold, the more the risk of groundwater quality degradation increases. The proposed approach, allowed also quantifying the uncertainty associated to any estimated risk class, in terms of entropy.

GIS processing of the probability maps allowed producing summary maps of the most probable risk class per estimation cell, over the whole considered area, at each observed time. Further elaboration produced a final map of the most frequent over time, among the most probable risk classes. All three levels of risk representation should provide land and water resources managers with useful and reliable tools, capable of supporting decisions and define priorities in launching actions. This method could also be decisive to more reliably support the delimitation of nitrate-vulnerable zones.

The proposed computational tools proves to be quite flexible and applicable in different experimental scenarios, due to its capability to treat simultaneously data of different type and quality related to various sources of information. Further, the approach is non-parametric; therefore it can be particularly suitably applied even in the case of highly skewed, multimodal distributions, as often found in nitrate concentrations in groundwater.

However, the proposed technique shows also some limitations: first, it is computationally challenging and the reliability of the results increases with conditioning (sampling data) and absence of spatial clustering in the data. In general, the proposed methodology provides good and reliable results even compared to qualitative, knowledge-based evaluations of the risk of groundwater quality degradation due to nitrate. Improvements could be achieved with spatial

and temporal optimization of monitoring networks and sampling procedures that can provide more detailed information for conditioning the development of the whole proposed methodology.

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