

# Groundwater vulnerability assessment: from overlay methods to statistical methods in the Lombardy Plain area

## *La valutazione della vulnerabilità degli acquiferi: dai metodi a zonazione omogenea ai metodi statistici nell'area di pianura lombarda*

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**Riassunto:** Le acque sotterranee sono tra le più importanti risorse di acqua potabile. A livello mondiale, gli acquiferi sono sottoposti ad una crescente minaccia di inquinamento legato all'urbanizzazione, allo sviluppo industriale, alle attività agricole ed alle imprese minerarie. Quindi sono ampiamente richieste azioni, strategie e soluzioni pratiche per proteggere le acque sotterranee da queste fonti antropiche.

Lo strumento più utile, a supporto della pianificazione territoriale e protezione delle acque sotterranee dalla contaminazione, è rappresentato dalla valutazione della vulnerabilità degli acquiferi. Sono stati sviluppati diversi metodi per la valutazione della vulnerabilità degli acquiferi nel corso degli anni: metodi a zonazione omogenea o a pesi e punteggi, metodi statistici e metodi numerici. Tutti questi strumenti sono utili per sintetizzare informazioni idrogeologiche complesse in un unico documento, come le mappe di vulnerabilità, utilizzabili sia da tecnici, amministratori e politici, che da scienziati e cittadini. Sebbene non sia possibile identificare un approccio che possa essere il migliore in tutte le situazioni, il prodotto finale deve essere sempre scientificamente provato, significativo ed affidabile. Ciò nonostante, diversi metodi possono produrre risultati molto differenti in qualsiasi caso di studio. Perciò è necessario approfondire le ragioni di similitudini e differenze.

**Parole chiave:** vulnerabilità degli acquiferi, metodo statistico, remote sensing, nitrati, Pianura Padana.

**Keywords:** groundwater vulnerability, statistical method, remote sensing, nitrates, Po Plain.

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Questo studio dimostra l'affidabilità e la versatilità di un metodo statistico-spaziale per la valutazione della vulnerabilità degli acquiferi alla contaminazione a scala regionale. Il caso di studio della pianura lombarda è particolarmente interessante per la sua lunga storia di monitoraggio quantitativo e qualitativo delle acque sotterranee, la disponibilità di dati idrogeologici e la combinata presenza di diverse sorgenti antropiche di contaminazione. Aggiornamenti recenti del Piano di Tutela delle Acque hanno sollevato la necessità di realizzare mappe di vulnerabilità degli acquiferi più versatili, affidabili e veritiere. Un confronto tra mappe di vulnerabilità degli acquiferi ottenute da approcci differenti e realizzati in un intervallo di tempo di diversi anni ha dimostrato l'importanza del continuo progresso scientifico, riconoscendo pregi e difetti di ciascuna ricerca.

**Abstract:** *Groundwater is among the most important freshwater resources. Worldwide, aquifers are experiencing an increasing threat of pollution from urbanization, industrial development, agricultural activities and mining enterprise. Thus, practical actions, strategies and solutions to protect groundwater from these anthropogenic sources are widely required.*

*The most efficient tool, which helps supporting land use planning, while protecting groundwater from contamination, is represented by groundwater vulnerability assessment. Over the years, several methods assessing groundwater vulnerability have been developed: overlay and index methods, statistical and process-based methods. All methods are means to synthesize complex hydrogeological information into a unique document, which is a groundwater vulnerability map, useable by planners, decision and policy makers, geoscientists and the public. Although it is not possible to identify an approach which could be the best one for all situations, the final product should always be scientific defensible, meaningful and reliable. Nevertheless, various methods may produce very different results at any given site. Thus, reasons for similarities and differences need to be deeply investigated.*

*This study demonstrates the reliability and flexibility of a spatial statistical method to assess groundwater vulnerability to contamination at a regional scale. The Lombardy Plain case study is particularly interesting for its long history of groundwater monitoring (quality and quantity), availability of hydrogeological data, and combined presence of various anthropogenic sources of contamination. Recent updates of the regional water protection plan have raised the necessity of realizing more flexible, reliable and accurate groundwater vulnerability maps. A comparison of groundwater vulnerability maps obtained through different approaches and developed in a time span of several years has demonstrated the relevance of the continuous scientific progress, recognizing strengths and weaknesses of each research.*

## Introduction

As groundwater resources are becoming more vulnerable due to the increasing number of contamination sources – such as urbanization and agricultural activities – practical actions, strategies and solutions to protect the resources are widely required.

Groundwater vulnerability studies are crucial to understand the cause-effect relationship between groundwater quality and both natural and anthropogenic factors to develop effective groundwater protection plans. Mapping areas where groundwater is most vulnerable to contamination and identifying primary factors influencing the contamination level are imperative to manage and protect groundwater and, thus, human health (Masetti et al. 2008). During the 1990s, aquifer pollution vulnerability assessment and mapping became increasingly utilized as a screening tool for protecting groundwater quality (Foster et al. 2013), and the approach has subsequently been adopted in many countries throughout the world (refer to Wachniew et al. 2016, for a complete review). Although it is not possible to identify an approach which could be the best one for all situations, the final product should always be scientific defensible, meaningful and reliable, to be an effective tool for land use planning and policy makers (Focazio et al. 2002). To this end, the use of statistical methods to assess groundwater vulnerability represents a reasonable compromise among model complexity and costs. Statistical methods represent an effective tool to better determine the role of factors having the highest influence on groundwater vulnerability. Moreover, they allow identifying the likely important sources of contamination (Sorichetta et al. 2013) and assessing the relative probability of contamination occurrence (i.e., groundwater vulnerability), considering the simultaneous presence, or absence, of these factors (e.g., Nolan 2001). In this regard, various authors (Worrall and Besien 2005; Twarakavi and Kaluarachchi 2006; Uhan et al. 2011) showed how the high flexibility of statistical methods allows more reliable groundwater vulnerability assessments over large areas compared to the ones obtained with other methods.

The development of new techniques (i.e., statistical or processed-based methods) to estimate groundwater vulnerability introduced questions as to whether vulnerability or risk is assessed. In some cases, no distinction is made between specific vulnerability and risk assessment, with hazard types, distribution, loading, and transport all included at the risk-assessment stage (e.g., Focazio et al. 2002). Without unambiguous and universally accepted definitions of vulnerability and risk in the assessment methods, this study follows the same terminology used in previous studies on groundwater vulnerability assessment using spatial statistical techniques (e.g., Arthur et al. 2007; Sorichetta et al. 2011). Hence, the term “groundwater vulnerability to nitrate contamination” will be used.

This study presents the implementation of a Bayesian statistical method (Weights of Evidence, Bonham-Carter 1994) to assess groundwater vulnerability to nitrate

contamination in the Po Plain area of Lombardy Region. The obtained vulnerability map is compared to one that has been obtained applying a hydrogeological-pedological integrated approach in the same study area (Beretta et al. 2005).

## Study area

The study area is located within the Po Plain area of Lombardy Region, in northern Italy (Fig. 1a), and covers an area of 13,400 km<sup>2</sup>, where urban, industrial, livestock and agricultural activities are extensively and heterogeneously present.

This area has a complex hydrogeological setting consisting of multiple aquifers with various properties and interactions. The Lombardy plain subsoil is characterized by Plio-Pleistocene sediments, whose upper unit forms the shallow unconfined aquifers. Sediments are mainly gravels and sands, although the presence of finer sediments increases from the north to the south where shallow aquifers are mainly constituted by fine sands and are partially confined. Hydraulic conductivity ranges from 10<sup>-4</sup> to 10<sup>-6</sup> m/s (Regione Lombardia and ENI 2002).

The shallow unconfined aquifer, as Group A all over the plain and Group B in the northern sector of the study area, according to the classification reconstructed by Regione Lombardia and ENI (2002), is the portion of aquifer used in this study to assess groundwater vulnerability to nitrate contamination.

The groundwater flow is generally oriented north-south toward the base level defined by the Po River, with a deviation to east-south-east in the south-east area of Lombardy. The groundwater flow is influenced by the main rivers that surround the plain area, acting mainly as gaining streams (Alberti et al. 2016). The groundwater depth decreases from north to south, ranging from values higher than 70 m to less than 2 m. Locally, groundwater depth reduces to zero in correspondence to typical lowland springs (called “fontanili”), located along the transition zone from the higher to lower plain (De Luca et al. 2014).

Nitrate (NO<sub>3</sub><sup>-</sup>) is the most common non-point-source contaminant found in groundwater in the Po Plain (Cinnirella et al. 2005; Fig. 1b), which is, in addition, classified as a Nitrate Vulnerable Zone by the European Union (Nitrate Directive, 91/676/EEC). Due to its high mobility and widespread presence in shallow groundwater, nitrate can be considered an ideal candidate to be used as environmental indicator of groundwater vulnerability to contamination (e.g., Tesoriero and Voss 1997).

## Method and materials

### ***Weights of Evidence technique and its application in hydrogeological problems***

Among the various statistical methods, the Weights of Evidence (WofE, Bonham-Carter 1994) modelling technique has been chosen for its reliability in performing meaningful and scientific defensible groundwater vulnerability maps, which has been proved by various Authors (e.g., Arthur et

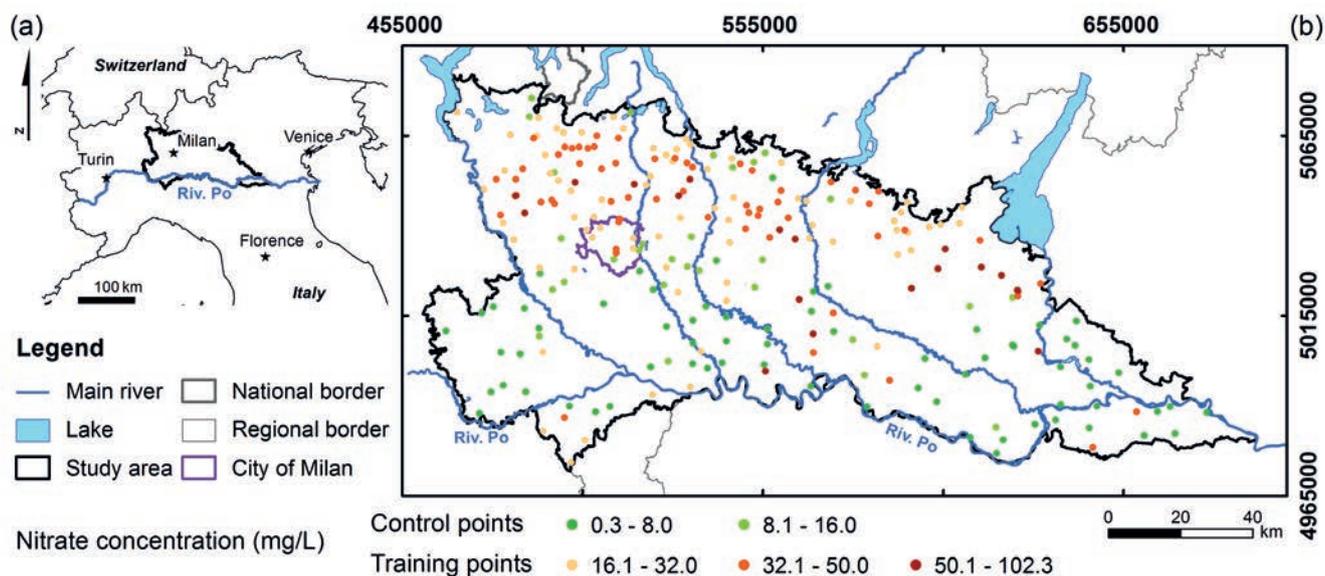


Fig. 1 - (a) Location of the study area; (b) Study area within the Lombardy Region, main rivers and lakes and monitoring-well network. Coordinates refer to WGS 1984 – UTM Zone 32 N projection.

Fig. 1 - (a) Ubicazione dell'area di studio; (b) Area di studio all'interno della Regione Lombardia, principali fiumi e laghi e ubicazione dei pozzi della rete di monitoraggio. Sistema di coordinate: WGS 1984 – UTM Zona 32 N.

al. 2007; Uhan et al. 2011). WofE is a cell-based modeling technique, which combines different spatial datasets in a Geographical Information System (GIS) environment to analyze and describe their interactions and generate predictive patterns (Bonham-Carter 1994; Raines et al. 2000). WofE can be defined as a data-driven Bayesian method in a log-linear form that uses known occurrences, representing the response variable, as training sites (training points). These data are used to obtain predictive probability maps (response themes) from multiple weighted evidences (evidential themes or predictors), which determine the spatial distribution of the occurrences in the study area (Raines 1999).

The main concept in the Bayesian approach is the idea of prior and posterior probability (Bonham-Carter 1994; Raines 1999). Prior probability is simply defined by the ratio between the area containing occurrences (i.e., the number of cells containing a training point  $D$ ) and the total area (i.e., the total number of cells). Thus, the prior probability represents the probability that a cell within the study area contains an occurrence without considering any evidential theme, and it can be expressed as (Bonham-Carter 1994):

$$P\{D\} = \frac{N_D}{N_T} \quad (1)$$

where  $N_D$  and  $N_T$  are respectively the number of cells containing an occurrence (i.e., a training point) and the total number of cells in the study area.

Each evidential theme is generalized and categorized in classes, representing different ranges of values, and for each class of each evidential theme, a positive and a negative weight are computed based on the location of the training points with respect to the study area. For a given class  $B$ ,

the positive weight  $W^+$  and the negative weight  $W^-$  are, respectively, higher and lower than zero or lower and higher than zero. The resulting combination depends on whether  $B$  has more or fewer training points than expected by chance. The weights can be expressed as (Bonham-Carter 1994):

$$W^+ = \log_e \frac{P\{B|D\}}{P\{B|\bar{D}\}} \quad (2)$$

$$W^- = \log_e \frac{P\{\bar{B}|D\}}{P\{\bar{B}|\bar{D}\}} \quad (3)$$

where  $P\{B|D\}$  and  $P\{B|\bar{D}\}$  are respectively the probability of a cell of being in the class  $B$  when the same cell contains or does not contain a training point, and  $P\{\bar{B}|D\}$  and  $P\{\bar{B}|\bar{D}\}$  are respectively the probability of a cell of not being in the class  $B$  when it contains or does not contain a training point.

The contrast (i.e., the difference  $W^+$  minus  $W^-$ ) represents the overall degree of spatial association between each class of a given evidential theme and the training points. Thus, it is a measure of the usefulness of the considered class in predicting the location of the training points (Raines 1999). A positive contrast value means a direct correlation between the class and the training points, and a negative value means an indirect correlation, whereas a value close to zero means low or no correlation. A confidence value for the ratio between the contrast and its standard deviation must be selected to provide a useful measure of the significance of the contrast and, thus, to the respective class (Raines 1999).

The posterior probability represents the relative probability that a cell contains an occurrence based on the evidences provided by the evidential themes (i.e., based on the calculated weights). The posterior probability can be expressed as (Bonham-Carter 1994):

$$\log_e O\{D|B_1^k \cap B_2^k \cap B_3^k \dots \cap B_n^k\} = \sum_{j=1}^n W_j^k + \log_e O\{D\} \quad (4)$$

where  $n$  identifies each single class used to categorize each evidential theme,  $k$  is either + or - depending on whether the prediction spatial class,  $B_n$ , is either present or absent, and  $O\{D\}$  is the odd form of the probability that a cell within the study area contains an occurrence.

The relative probability means that a cell having a higher posterior probability is more likely to contain an occurrence than a cell having a lower probability, and it represents a measure of the relative likelihood of occurrence of an event (Raines 1999).

The WofE technique applied to groundwater vulnerability assessments of a specific region can proceed through the subdivision of the monitoring well network into two subsets: the training and control points. The training points represent the occurrence of an event (e.g., occurrence of contamination), whereas the control points represent the non-occurrence of the event. In this context, the evidential themes are represented by natural and anthropogenic factors, which influence groundwater vulnerability, and the posterior probabilities represent the relative groundwater vulnerability of the area. The WofE technique can be applied in groundwater vulnerability assessments, following the procedure below.

- 1) Identification of the response variable and selection of the level of significance (Raines 1999; Arthur et al. 2005), according to the purposes of the model. The response variable is represented by the concentration of a particular contaminant in groundwater (e.g., Nolan et al. 2002; Sorichetta et al. 2011). The training set is selected basing on a subjective rule (e.g., wells showing a contaminant concentration higher than an established threshold value) and is used to generate and calibrate the predictive probability map. All the other wells represent the control set and are used to validate the obtained probability map (Steps 6 and 8);
- 2) Calculation of the prior probability (Bonham-Carter 1994). It identifies the condition of the study area without considering any evidential theme, that is equivalent to the average combination of all the evidential themes;
- 3) Generalization of the evidential themes and computation of the positive and negative weights, and their derived contrast, which allows determining the influence of each evidential theme on groundwater contamination, following the objective (semi-guided) procedure developed by Sorichetta et al. (2012);
- 4) Evidential themes, significant from a statistical and physical point of view, can be used to generate the model. The first requirement means that the classes obtained

from the generalization process respect the established level of significance, the second that the same classes show a pattern distribution justifiable from a hydrogeological point of view;

- 5) Computation of the response theme (predictive probability map), through the combination of the selected evidential themes (Bonham-Carter 1994; Raines 1999);
- 6) Calibration and validation of the predictive probability map, evaluating the area-under-the-curve value or applying the success rate curve method (Chung and Fabbri 1999);
- 7) Categorization of the predictive probability map in five classes, which represent five degrees of groundwater vulnerability, increasing from 1 to 5. The map is reclassified using the geometrical interval classification method, which ensures that each class has approximately the same number of different posterior probability values (Sorichetta et al. 2011);
- 8) Evaluation of the reliability of the reclassified map by considering its overall performance in classifying the occurrences. Three statistical calibration and validation procedures can be used (Sorichetta et al. 2011): (1) frequency of training set, (2) average nitrate concentration of all wells and (3) density of control set in each vulnerability class. A map can be deemed reliable if it passes these tests.

In this study, the response themes were generated using the Spatial Data Modeler (Sawatzky et al. 2009) for ArcGIS 9.3 (ESRI 2008).

### **Response variable**

Nitrate concentrations are monitored by the Regional Environmental Agency through a network of about 500 wells covering the entire area with a nearly uniform spatial distribution. Data are collected every six months since 2001. From the network, only the wells monitoring the shallow aquifer are selected (Fig. 1b).

The response variable is represented by nitrate concentration in groundwater, as average concentration in each well over the period 2010 – 2012 (Table 1). The WofE modelling technique requires a binary formulation of the response variable. Thus, it is necessary to establish a threshold value to distinguish between training points and control points, obtaining a training and a control set, respectively. The value representing the inflection point of the cumulative probability plot of average nitrate concentrations is selected as an appropriate threshold (Masetti et al. 2009). This value is equal to 16 mg/L.

Groundwater vulnerability maps would represent the vulnerable areas where the combination of natural and anthropogenic factors involves the presence of nitrate contamination in groundwater. Following this purpose, training and control sets have been selected according to the following condition (Fig. 1b): wells showing an average nitrate concentration “higher than 16 mg/L” form the training set, whereas the others constitute the control set.

Tab. 1 – Main statistics of nitrate concentration in the shallow aquifer as average over the period 2010 – 2012.

Tab. 1 - Principali statistiche della concentrazione di nitrati nella falda superficiale quale media sul periodo 2010 – 2012.

| Statistic          | Concentration in mg/L |
|--------------------|-----------------------|
| Minimum            | 0.35                  |
| Maximum            | 102.25                |
| Mean               | 23.5                  |
| Median             | 22.2                  |
| Standard deviation | 18.9                  |

### Explanatory variables

Considering the conceptual hydrogeological model, six explanatory variables are considered as influencing groundwater vulnerability to nitrate contamination in the study area (Masetti et al. 2007). These variables were selected to capture the pathway and the main regional-scale processes that characterize the nitrate contamination pattern in groundwater (Stevenazzi et al. 2017). This includes: potential release from the surface (urban and agricultural sources, as distinct variables) and eventual degradation through superficial soils (soil protective capacity), vertical spreading (hydraulic conductivity of the vadose zone) to the saturated zone (groundwater depth), and transport and dilution in the aquifer (groundwater velocity). The importance of each variable in influencing groundwater vulnerability can differ according to its local spatial relation with the other variables.

Anthropogenic sources of nitrate contamination can be associated with both urban (leakages from the sewage system or septic tanks) and agricultural sources (fertilizers and manures). Since nitrogen loading derived from urban areas cannot be easily or directly estimated quantitatively, other variables need to be selected as proxies: population density for each administrative unit (Nolan et al. 2002; Masetti et al. 2007; Sorichetta et al. 2011; Stevenazzi et al. 2015), land use derived from aerial images (Stevenazzi et al. 2015), or urban areas derived from satellite remote sensing (Stevenazzi et al. 2015; Stevenazzi et al. 2017).

Urban areas derived from radar satellite remote sensing represent an innovative dataset, which allows identifying manmade infrastructures or buildings and zones where different rates of urban growth occurred. Radar backscatter data have been acquired by the SeaWinds scatterometer aboard the QuikSCAT satellite, from 2000 to 2009, and, together with the Dense Sampling Method (QSCAT-DSM; Nghiem et al. 2009), have been used to identify and map urban extent and surface features at a posting scale of about 1 km<sup>2</sup>. The worldwide coverage and the continuous data collection in the decade of 2000s allow the delineation of urban and suburban contours both in metropolitan and rural areas and the identification of urban development both fast and expansive or slow and restrained (Nghiem et al. 2009).

Nitrogen fertilizer loadings are monitored by the Agency

of Services of Agriculture and Forest, which controls the amount of fertilizers and manures sold to the farmers every year, in each district of the Region. Nitrate Directive (91/676/EEC) establishes a maximum limit of 170 kg/ha/year of N from organic manure applied to agricultural lands within Nitrate Vulnerable Zones (NVZs). Actually, Piedmont and Lombardy Regions obtained a derogation, allowing the use of a maximum of 250 kg/ha/year of organic N in a NVZ (2016/1040/UE). In Fig. 2, values exceeding regulatory limits are only indicative, as fertilizer spreading can occur on agricultural fields in adjacent districts.

## Results

### Contrasts of the generalized evidential themes

The contrasts of statistically significant evidential themes (i.e., explanatory variables) enable an assessment of the influence of the variables under consideration on groundwater contamination. A confidence value for the ratio between the contrast and its standard deviation must be selected to provide a useful measure of the significance of the contrast (Raines 1999). For this study, a confidence value of  $|1.282|$ , corresponding approximately to a 90 % level of significance, was chosen as the minimum acceptable value to consider an evidential theme class as statistically significant. The 90% level of significance allows maintaining a good quality of the model respect to the extension of the study area and the number of training and control points.

For each evidential theme, a positive (negative) contrast value indicates a direct (inverse) correlation between the class and high nitrate concentrations in groundwater. Contrast values close to zero indicates a poor influence of the class in the process of distribution of nitrates.

Contrast values of natural and anthropogenic factors are represented in Fig. 2.

### Response theme and vulnerability map

Only the statistically or physically significant evidential themes have been considered to generate the response theme: soil protective capacity, groundwater depth, groundwater velocity, hydraulic conductivity of the vadose zone and extension of urban areas represented by QSCAT-DSM data.

The response theme was categorized in five classes (Fig. 3) with the degree of groundwater vulnerability increasing from 1 (low vulnerability) to 5 (extremely high vulnerability).

### Reliability and validation of the map

The general quality of the response theme (i.e., post probability map) can be evaluated with the area-under-the-curve (AUC) value. AUC is a direct measure of the performance of the statistical approach, and is given by the area under the curve (integral) in a binary plot considering cumulated area/cumulated training points expressed in percentage. The calculated AUC value is equal to 78.4%, indicating a good quality of the map.

Then, the reliability of the classified map is evaluated

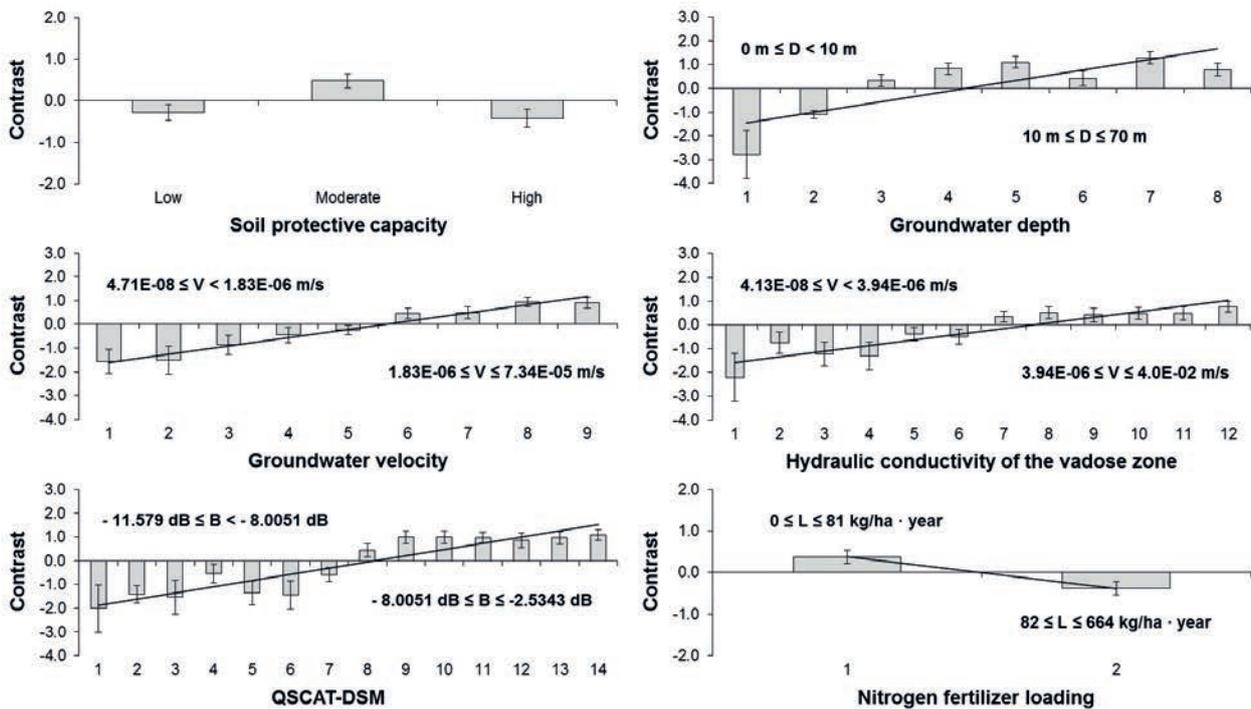


Fig. 2 - Contrasts and error bars of the statistically significant classes of each evidential theme used to generate the vulnerability map in Fig. 3.

Fig. 2 - Istogrammi dei contrasti e barre d'errore delle classi statisticamente significative di ciascun predittore usato per produrre la mappa di vulnerabilità in Fig. 3.

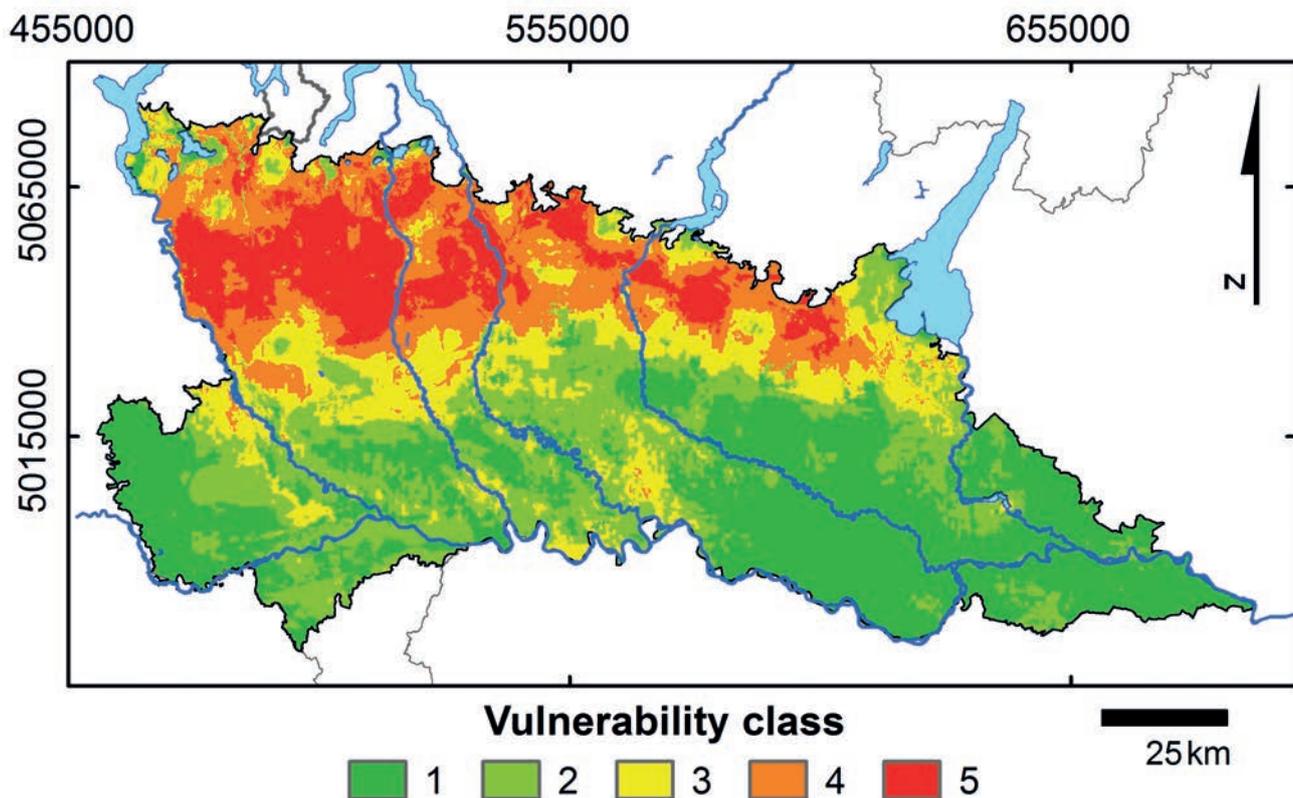


Fig. 3 - Groundwater vulnerability map obtained through WofE technique. Coordinates refer to WGS 1984 – UTM Zone 32 N projection. Fig. 3.

Fig. 3 - Carta di vulnerabilità degli acquiferi ottenuta attraverso il metodo WofE. Sistema di coordinate: WGS 1984 – UTM Zona 32 N.

by considering its overall performance in classifying the occurrences. Three statistical validation procedures were used (Table 2): (1) frequency of training set, (2) average nitrate concentration of all wells, and (3) density of control set in each vulnerability class.

Frequency of the training points is expected to increase monotonically as the degree of vulnerability increases. This technique adds new information to the validation process because it also includes the wells not used in the modeling.

Nitrate concentration should monotonically increase as the degree of vulnerability increases and the central vulnerability class should give a value close to the overall mean value. All wells stored in the database are used to carry out this analysis.

The density of the control points is expected to monotonically decrease as the degree of vulnerability increases. Comparing the density of the central vulnerability class with the prior probability, calculated considering the wells being part of the control set, is expected that the two values should be as close as possible. In fact, the prior probability expresses the probability that a cell contains an occurrence without considering any influencing factor, and it is, ideally, similar to the presence of an average combination of factors, which can be represented by the central vulnerability class.

The obtained vulnerability map significantly passed all the three tests, showing high correlation coefficient values for all the three cases (Fig. 4).

## Discussion

Beretta et al. (2005) have presented a hydrogeological-pedological integrated approach for the evaluation of aquifer vulnerability in the Lombardy Plain area (Fig. 5). Aquifer vulnerability has been assessed combining a hydrogeological approach with the soil protective capacity to nitrate contamination. The hydrogeological approach consists in a modified version of the CNR-GNDCI categorization (Alifracco et al. 1996), which has been developed to better represent the aquifers in Lombardy Region. It considers groundwater depth and thickness of low permeable units to define different degrees of vulnerability (Table 3). The obtained aquifer

| Tab. 2 – Validation procedures.<br>Tab. 2 - Tecniche di validazione. |  |
|--|--|
| Frequency of training set  | $F = \left( N_{wj} / T_{wj} \right)$ $N_{wj} = \text{number of training points in a vulnerability class } j$ $T_{wj} = \text{total number of training and control points in the same class } j$  |
| Average of nitrate concentration                                     | $C_{AVG} = \sum_{i=1}^{T_{wj}} C_{ij} / T_{wj}$ $C_{ij} = \text{nitrate concentration of well } i \text{ in the vulnerability class } j$ $T_{wj} = \text{total number of wells in the same class } j$  |
| Density of control set   | $D = \left( NP_{wj} / TP_j \right)$ $NP_{wj} = \text{number of cells of vulnerability class } j \text{ containing control points}$ $TP_j = \text{total number of cells in the same vulnerability class } j$ <p>The study area must be divided in cells having the same dimension</p> |

vulnerability map has been crossed with the soil protective capacity map, according to the matrix shown in Table 4. Despite of the similarities between the two approaches, the distribution of vulnerability classes obtained by Beretta et al. (2005) is deeply different with respect to the map obtained through the WofE technique. High vulnerable areas in Beretta et al. (2005) are mainly distributed in the central-southern sector, whereas the same area is mainly categorized as low vulnerable through the WofE technique (Fig. 3). By contrast, the northern sector is categorized as a low-medium vulnerable zone in Beretta et al. (2005), whereas as a high vulnerable area through the WofE technique.

The integrated groundwater vulnerability map (Beretta et al. 2005) would be a specific groundwater vulnerability map to nitrate contamination since it takes into account the soil

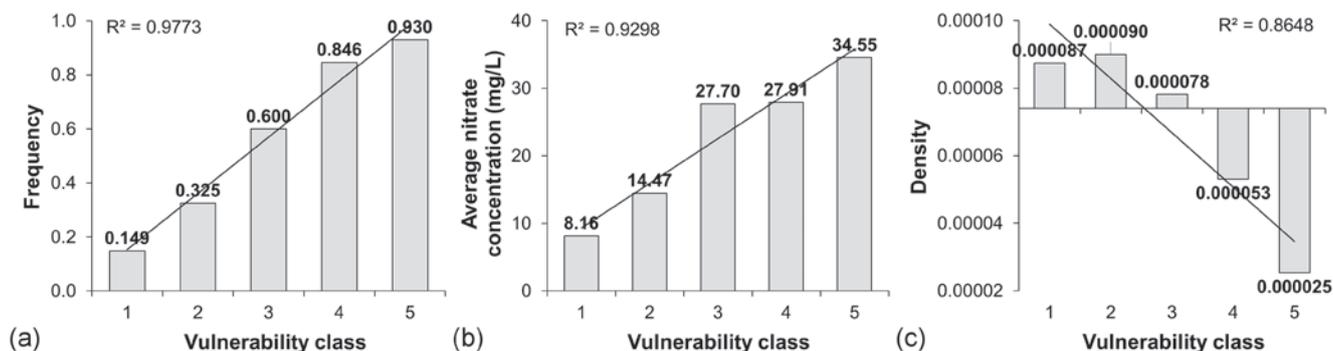


Fig. 4 - Histograms of the frequency of the training points (a), of the average nitrate concentration (b), and of the density of the control points (c) in each vulnerability class of the map in Fig. 3. The degree of vulnerability increases from class 1 to class 5.

Fig. 4 - Istogrammi di frequenza dei training points (a), della concentrazione media di nitrati (b) e della densità dei control points (c) in ciascuna classe di vulnerabilità della carta in Fig. 3. La vulnerabilità cresce dalla classe 1 alla classe 5.

Tab. 3 – Parameter values determining aquifer vulnerability degree (from Beretta et al. 2005).

Tab. 3 - Attribuzione del grado di vulnerabilità degli acquiferi in funzione dei valori dei parametri (da Beretta et al. 2005).

| Groundwater depth (m) | Thickness of low permeable unit (m) | Aquifer vulnerability degree |
|-----------------------|-------------------------------------|------------------------------|
| < 5                   | Clay < 2 or Silt < 4                | Extremely high               |
| < 5                   | Clay > 2 or Silt > 4                | Very high                    |
| 5 – 15                | Clay < 2 or Silt < 4                | Very high                    |
| 5 – 15                | Clay = 2 – 5 or Silt 4 – 10         | High                         |
| 5 – 15                | Clay > 5 or Silt > 10               | Medium                       |
| > 15                  | Clay < 2 or Silt < 4                | High                         |
| > 15                  | Clay = 2 – 5 or Silt 4 – 10         | Medium                       |
| > 15                  | Clay > 5 or Silt > 10               | Low                          |

Tab. 4 – Matrix evaluation of hydrogeological vulnerability VS soil protective capacity (from Beretta et al. 2005).

Tab. 4 - Matrice di incrocio tra vulnerabilità idrogeologica e capacità protettiva dei suoli (da Beretta et al. 2005).

| Aquifer vulnerability degree | Soil protective capacity class |                |                |
|------------------------------|--------------------------------|----------------|----------------|
|                              | LOW                            | MEDIUM         | HIGH           |
| LOW                          | Low                            | Low            | Low            |
| MEDIUM                       | Medium                         | Medium         | Low            |
| HIGH                         | High                           | Medium         | Medium         |
| VERY HIGH                    | Very high                      | High           | High           |
| EXTREMELY HIGH               | Extremely high                 | Extremely high | Extremely high |

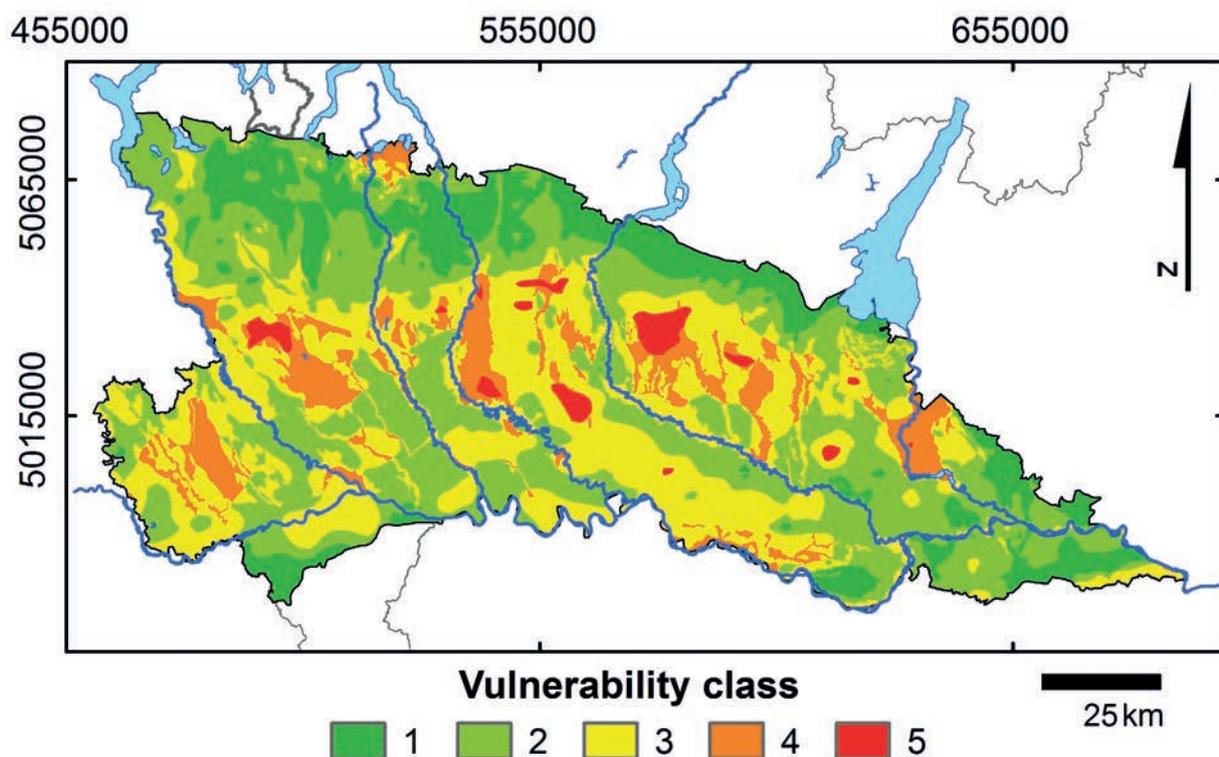


Fig. 5 - Integrated groundwater vulnerability map (from Beretta et al. 2005). Coordinates refer to WGS 1984 – UTM Zone 32 N projection.

Fig. 5 - Carta di vulnerabilità degli acquiferi integrata (da Beretta et al. 2005). Sistema di coordinate: WGS 1984 – UTM Zona 32 N.

protective capacity. However, it cannot adequately represent the distribution of nitrate contamination in groundwater (Tesoriero and Voss 1997; Chowdhury et al. 2003; Fig. 1 versus Fig. 5). Weak points of the integrated groundwater vulnerability map are:

- An approximate evaluation of the effects of the chemical-physical processes within the aquifer as well as in the vadose zone and of the soil protective capacity;
- An evaluation of the effects of hydrogeological parameters according to the assumption on which the subjective rating systems are based; for example, they usually associate a decrease of vulnerability with the increase of groundwater depth.

Thus, the defects of the integrated groundwater vulnerability map have demonstrated the necessity of moving towards new methodologies for groundwater vulnerability assessments (e.g., statistical or process-based methods). In fact, classical methodologies (e.g., overlay and index methods) cannot be applied elsewhere nor represent all contaminants: different contaminants may react in different ways in the same hydrogeological context.

Instead, the WofE technique allows considering several hydrogeological parameters, together with anthropogenic factors influencing the presence of contaminants in groundwater. It allows evaluating both the effects of each parameter and the effects of all parameters at the same time in influencing

WofE technique. Considering the simultaneous presence of these factors together with geological and hydrogeological conditions, useful and unexpected insights can be achieved.

Soil protective capacity can be partially considered as a valuable parameter in preventing the propagation of nitrates. In fact, soil protects groundwater only against pollutants introduced at the land surface. In the case of nitrate sources, fertilizers or manures are spread at the land surface, whereas leakages from the sewer systems occur near the surface, but under the soil layer. Thus, soil can act as a filter only in the first case.

As hydraulic conductivity of the vadose zone influences the movements of contaminants from surface to aquifers, groundwater velocity controls the movements within aquifers, in terms of transport and dilution processes. In the Lombardy Plain case study, the transport process is generally prevalent over the dilution one, confirming the impacts of these hydrogeological factors on the distribution of contaminants.

An increase of nitrate concentrations correlated to the increase of groundwater depth has been observed at different scales, from the field dimension (Best et al. 2015), to sub-basins (e.g., Masetti et al. 2008), to regional (Sacchi et al. 2013) and country scales (e.g., Nolan et al. 2002). In particular, occurrence of denitrification in the southern sector of the Lombardy Plain area has been identified and confirmed by Sacchi et al. (2013). The explanation can be found in bio-geochemical conditions of the vadose zone. In fact, very shallow water table leads to waterlogged conditions conducive to denitrification processes, in which denitrification rates tend to decrease as water-table depth increases. In conditions of high hydraulic conductivity of the vadose zone, mainly related to coarse-grained sediments, high concentrations could persist at depth and in oxidizing conditions, where the transport process prevails on dilution and denitrification is not facilitated. Moreover, there could be preferential flow paths, created by interconnected higher permeable units, which accelerate the percolation of contaminants in the subsurface (Masetti et al. 2016). This outcome disagrees with the assumption on which the subjective rating systems are based.

Combining all factors influencing groundwater vulnerability reveals that the northern sector of the Lombardy Plain is the most vulnerable to nitrate contamination. This is due to the combined presence of (a) extensive urban and industrial areas with high population density, as nitrate sources, (b) high permeability of both the unsaturated and the aquifer zones and (c) the great depth of the water table. Such conditions do not favor denitrification processes (Sacchi et al. 2013). Extensive agricultural fields, where fertilizers and manures are intensively adopted, and point sources of pollution such as septic tanks or sewage characterize the southern sector. Despite these nitrate sources, the combined presence of low permeable sediments and shallow water table (Sacchi et al. 2013) or redox conditions (Pilla et al. 2006) creates the favorable conditions to denitrification. Thus, contrary to Beretta et al. (2005), the southern sector of the Lombardy Plain is less vulnerable to nitrate contamination.

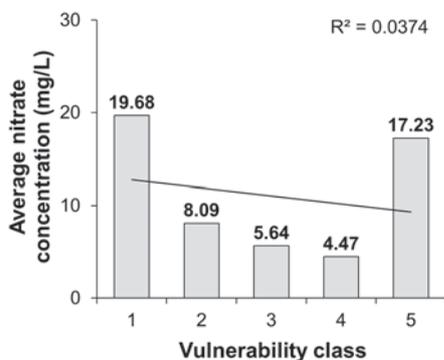


Fig. 6 - Histogram of the average nitrate concentration (in 2003) in each vulnerability class of the integrated groundwater vulnerability map (Beretta et al. 2005; Fig. 5). The degree of vulnerability increases from class 1 to class 5.

Fig. 6 - Istogramma della concentrazione media di nitrati (del 2003) in ciascuna classe di vulnerabilità della carta di vulnerabilità degli acquiferi integrata (Beretta et al. 2005; Fig. 5). La vulnerabilità cresce dalla classe 1 alla classe 5.

groundwater contamination of a particular contaminant. The obtained groundwater vulnerability map represents vulnerable areas to nitrate contamination, since it has been developed starting from the distribution of nitrate contamination.

Despite the weak points of the integrated groundwater vulnerability map by Beretta et al. (2005), it was already demonstrated by the Authors that urban nitrate sources are prevalent on agricultural sources in the Lombardy Plain area. This result is confirmed and deeply investigated applying the

## Conclusions

Characterizing the vulnerability of shallow aquifers to nitrate contamination should help decision makers evaluating current land use practices and make recommendations for regulation changes, with the aim of minimizing impacts on groundwater quality. The main results of this work are the following:

- The application of different methods to assess groundwater vulnerability to nitrate contamination in the Lombardy Plain area lead to conflicting results;
- Statistical methods, such as the WofE technique, contribute to groundwater vulnerability assessments in the evaluation of the influence of natural and anthropogenic factors on vulnerability by considering the presence or absence of contamination in groundwater, thus representing the conceptual model in a more realistic perspective;
- Advantages of the method include a more detailed, consistent and quantitative evaluation of both natural and anthropogenic factors influencing groundwater vulnerability avoiding the use of preassigned weight to each variable;
- Limiting factors of statistical methods are the necessity of spatially distributed datasets regarding natural and anthropogenic factors and the presence of a well distributed monitoring well network with sufficient water quality data in relation to the contaminant in question in the given study area.

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