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Application of Indicator kriging to Evaluate the Probability of Exceeding Nitrate Contamination Thresholds

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ABSTRACT: Nitrate contamination is one of the main risks for groundwater in agricultural areas. The evaluation of the effect of agricultural practices on groundwater nitrate concentration, especially in highly sensitive areas, is crucial for a correct land planning, and a good agronomic intervention scheduling. Aim of this paper is to map the probability to exceed nitrate regulatory threshold applying a non-parametric geostatistical approach, the Indicator Kriging (IK). A study in the Fucino Plain (Abruzzo, Central Italy), characterized by highly profitable intensive agriculture with mainly irrigated horticultural and short rotation crops, was carried out. The Plain has a shallow and controlled groundwater table, and channels draining the surplus water during winter. Water samples were collected monthly from piezometers and analysed for nitrate. IK provided a model of spatial uncertainty, representing the probability that the threshold of 50 mg/L fixed by the European Nitrate Directive is exceeded, and results were transferred into a GIS. Maps obtained for each month showed how the probability to exceed the threshold changes during an average year. The methodology can provide an effective operative tool to support decision-makers for the identification and the designation of nitrate vulnerable zones.

Key words: Nitrate, Indicator kriging, Contamination, Groundwater, Central Italy

INTRODUCTION

Water resources for agriculture and other activities are considered as poorly renewable, and their conservation has become crucial, worldwide. Among the parameters used for water quality definition, nitrate content is of primary importance (Coetzee et al., 2011; Tabesh et al., 2011; Uemura et al., 2011; Llopis-Gonzalez et al., 2011; Hudak, 2012; Li et al., 2012). Nitrate is the most frequently introduced pollutant into groundwater systems (Spalding and Exner, 1993). Contamination by nitrate of surface and groundwater usually originates from diffuse sources, such as intensive agriculture (Jarvis, 1999), and can pose risks to human health and the environment (Harrison, 1992; Addiscott, 1999). Hence, agriculture stands as the most commonly correlated land use with nitrate contamination of groundwater, and severe nitrate contamination is found to be mainly associated with vegetable cultivation, due to the high rate of application of chemical and organic fertilizers (McLay et al., 2001). Moreover, irrigated agricultural areas have considerable potential for contaminating groundwater because irrigated crops, in addition to an abundant fertilization, are occasionally over-watered (Ghaderi et al., 2012). As a response to this threat the EU has adopted the Nitrate Directive

(91/976/EC) which imposed to Member States to take measures to protect water against pollution caused by nitrate from agricultural sources, and to implement these measures within the identified nitrate vulnerable zones. As a consequence, where groundwater characteristics may change irreversibly due to anthropic disturbance, it is of primary importance to identify the areas with an intrinsic sensitivity to pollution. This allows a correct land planning, and a good agronomic intervention scheduling through the implementation of Best Agricultural Management Practices. The maximum allowable concentration (or critical level) conforming to Italian and European legislation is 50 mg NO_3/L . Since the criteria for the designation of nitrate vulnerable zones (that undergo limitations in agricultural practice) cannot be univocally established, testing rapid and cheap methodologies for decision support is crucial (Bragato, 2001).

Point data may be inadequate to define and delimit vulnerable areas, and traditional mapping is of little help when the uncertainty associated with the estimated values at unsampled locations is required to support decision making. Geostatistical methods can be used to generate maps and to assess the uncertainty of the predicted values as an alternative

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to a detailed survey (Caridad-Cancela et al., 2005). In particular, Indicator Kriging (IK) methodology provides information on the spatial distribution of specific classes of values, estimating the probability to exceed threshold values (Goovaerts, 1997; Cullmann and Saborowski, 2005; Grunwald et al., 2006; Zhang and Yao, 2008). IK has been widely used for probabilistic analysis, spatial prediction and risk assessment in many fields of investigation, where a probability map allows a better knowledge of the studied phenomena (Alli et al., 1990; Tarboton et al., 1995; Demir et al., 2009; Odeh and Onus, 2008). Many authors adopted this non-parametric geostatistical approach to assess the risk of soil and groundwater pollution (Lin et al., 2002; Diodato and Ceccarelli, 2005; Reis et al., 2005; Adhikary et al., 2010; Zhang et al., 2009).

In this work IK is applied for mapping the nitrate vulnerability at a sub-regional scale in the area of the Fucino Plain (Abruzzo, Central Italy), which is characterised by a profitable intensive agriculture, mainly irrigated horticultural and short rotation crops. These crops are widespread, thanks to favourable conditions allowing 2-3 growing cycles on the same field, provided that adequate water resources are available (Petitta *et al.*, 2005). The intrinsic vulnerability of the area is due to factors such as geomorphologic structure (endorheic basin), soil origin (from reclamation) and the many efforts of artificial drainage since the Roman age. In order to assess the suitability of the IK application to evaluate the probability to

exceed the nitrate content limit in groundwater in a highly intensive agricultural area, data from piezometers in the Fucino area were processed, and results were transferred into a GIS. The maps obtained represent the probability that groundwater exceeds the threshold of 50 mg/L of nitrate.

MATERIALS & METHODS

The Fucino Plain is an endorheic basin surrounded by mountains, without natural effluents, situated at 650-700 m above mean sea level. Despite the many efforts of artificial drainage, until 1865 it was a lake with an area of about 200 km² and a maximum depth of 18 m. The reclamation of Lake Fucino was successfully carried out through the construction of an artificial underground canal that led to the complete and irreversible disappearance of the lake. Climate is temperate semi-continental, with mean annual rainfall and temperature 637 mm and 9.9°C respectively (average 1987-2004). Monthly data are reported in Fig. 1, where PET is the Potential Evapotranspiration. From April through October rainfall does not contribute to the water balance of the basin. Consequently, in summer large amounts of water are used to irrigate farm crops (Petitta et al., 2005).

Soils have generally a little evidence of the development of pedogenic horizons due to the short time since the reclamation, the carbonate parent material and the continuous mixing caused by agricultural activities practiced for a long time. They are young, mineral soils, with a prevalent silty-loam texture, alkaline





reaction and high bases saturation, classified as Entisols according to the Soil Taxonomy (SSS, 1999). In some more clayey units the development of a Bw horizon weakly coloured and structured can be observed (Chiuchiarelli *et al.*, 2006). Chemical analyses were performed on soil samples collected from 20 profiles according to the standard methods (SSSA, 1986; 1996; MIPA, 1997; MIPAF, 2000). Mean values of the main physical, chemical and hydrological parameters of topsoil horizons (~40 cm depth) are summarized in Table 1.

These soils have a shallow depth, limited either by a water table or by an impervious hard pan, and are often further limited by a thick plough pan. The groundwater table is present across the whole area, and its levels are controlled by a channel network draining water surplus during fall and winter. In spring and summer these levels show large fluctuations due to the abstraction for irrigation. Initially, in the Fucino Plain the growing of three main crops (wheat, potatoes and sugar beets) on the basis of a three-year rotation was encouraged. This system remained practically unaltered until 1962. These crops required minimal amounts of water and the demand was satisfied by the natural flows in the canals. However, in the past few years, farmers gradually switched to much more profitable vegetable crops, such as carrots, salad greens, fennel, celery, etc. This tendency was accompanied by high water requirements, exacerbated by the practice of two/three harvests per year (Petitta et al., 2005). In Fig. 2 the evolution of crops from 1958 to 2008 is showed.

At present, the most widespread crops are carrots, potatoes, fennels and chicory: carrots are available from January to December, potatoes from August to March, fennels, chicory and other horticultural crops from June to December (Peruzzi *et al.*, 2005). Nitrogen fertilization for these crops ranges from 150 to 200 kg ha⁻¹, while gross irrigation supplies can reach a total of 500 mm for each cultivation cycle. The frequent and large use of fertilisers, and the intensive irrigation combined with the shallow water table create a favourable environment for the leaching of nutrients to subsoil layers and groundwater. A piezometric network in the area intercepts groundwater at 2 m depth. Locations of the 19 piezometers are reported in Fig. 3.

During a 4 year period (2001-2004), chemical characteristics of water were determined in each piezometer, and particularly nitrate concentration as N-NO₃. Chemical routine analyses were performed on water samples according to the standard methods (APHA, 1995; MIPAF, 2001), using colorimetric method for N-NO₃ determination.

Geostatistics is used to estimate the values of target variable in non sampled locations from point type data, and for their spatialization and mapping. Geostatistical analysis is based on the assumption that the higher the closeness of points, the higher is their similarity (i.e. spatial autocorrelation exists), and offers a set of tools and methods aimed at understanding and modelling the spatial variability of the data. With the term "kriging" are indicated several types of interpolation algorithms which can be used to quantify

Parameter	Unit	Mean	St. Dev.	Parameter	Unit	Mean	St. Dev.
Sand	g/kg	113	61	CEC	cmol ₍₊₎ /kg	7.31	2.68
Silt	g/kg	721	84	Na^+	cmol(+)/kg	0.12	0.05
Clay	g/kg	166	49	\mathbf{K}^+	cmol ₍₊₎ /kg	0.40	0.15
Water retention	% dry weight			Ca ²⁺	cmol(+)/kg	4.61	2.57
-10 kPa		41.6	3.4	Mg^{2+}	cmol ₍₊₎ /kg	2.18	0.58
-33 kPa		35.1	4.1	ESP	%	2	1
-100 kPa		30.3	4.4	Organic carbon	g/kg	17.8	3.7
-1500 kPa		15.6	3.1	Organic matter	g/kg	30.7	6.3
$EC_{1:2}$	dS/m	0.31	0.07	Available P	mg/kg	50	23
pH _{12.5}		8.2	0.2	Total N	g/kg	2.4	0.4
Total carbonate	%	74.5	11.0	Inorganic N	mg/kg	25	5
Active carbonate	%	15.6	1.6				

Table 1. Mean values of selected topsoil parameters in the Fucino Plain

CEC: Cation Exchange Capacity; ESP: Exchangeable Sodium Percentage







Fig. 3. Location of water sampling points

the spatial structure of the data and produce predictions. The method chosen depends on the assumptions made about the data structure and the model.

Although geostatistics have been successfully used in the past decades to model and display the spatial variability of the most different environmental variables, kriging variance as a measure of uncertainty for kriging estimates have been misused in most cases due to the limiting assumptions of normality of errors distribution and of homoscedasticity, i.e., that error variance is independent of data values (Van Meirvenne and Goovaerts, 2001). Such conditions are rarely met in practice, as environmental variables are characterized in most cases by skewed distributions. In this work data frequencies distribution, even after a logarithmic or power transformation, was not normal, so common geostatistical parametric techniques (i.e. Ordinary Kriging) were not applicable to the dataset (Monti, 2005). Thus, a non parametric geostatistical approach, the Indicator Kriging, was used. This type of kriging produces a spatial distribution of the probability of exceeding a threshold, allowing to generate maps representing lines with the same probability of exceeding 50 mg/L of nitrate. Indicator Kriging is based on a binary code 0 (Z_{nitrate} \geq 50 mg L⁻¹) and $1(Z_{nitrate} > 50 \text{ mg/L})$ (Journel 1983; Castrignanò and Martinelli, 2000; Goovaerts, 2001), and provides not only an estimation of the values in non sampled locations, but a probabilistic model of the uncertainty over the whole area.

When modelling the uncertainty of an attribute z at an unsampled location **u** (**u** representing a vector of coordinates), the available observations are considered as the realization of one set of *n* spatially correlated random variables $Z(\mathbf{u})$. The model is given by the conditional cumulative distribution function of a continuous random variable $Z(\mathbf{u})$ (Goovaerts, 1997): $F\{\mathbf{u}; z\} = \operatorname{Prob}\{Z(\mathbf{u}) \le z\}$

that fully describes the uncertainty in **u** since it provides the probability that the unknown value is greater than any given threshold value z. Detailed descriptions of the indicator kriging and its formalisms are given by Journel (1983) and Goovaerts (1997).

The semivariogram is a statistical tool used to measure the between-sample autocorrelation. Indicator semivariograms provide information on the spatial distribution of specific classes of values, allowing the assessment of the probability to exceed threshold values (Goovaerts, 1997). The indicator semivariogram value measures how often two points located a distance apart belong to different categories, above or below a given threshold. Spatial analysis was performed assuming that in the considered period (2001-2004) the value $z_{\text{nitrate}}(x_0)$ in the point with position x_0 into the study area is a particular realization of the random variable $Z_{\text{nitrate}}(x_0)$ defined in that point. Extending this assumption to all the points in the area, a set of random variables is defined, forming a random function. Since the random variables have a spatial character, the random function is characterized by a spatial law that explains the variability in the measured points. The spatial structural analysis was performed on the monthly average values of nitrate water concentration for every year, obtaining a final mean dataset of 12 months. Averaging the experimental data by month was possible provided that they did not show substantial differences among different years in the considered period, thus allowing reducing the occurrence of missing data. Variogram modelling was performed by the software VarioWIN 2.2 (Pannatier, 1995), and map elaboration was performed by ArcGISTM 9.2 with the Geostatistical AnalystTM extension.

RESULTS & DISCUSSION

Indicator variograms were built adopting a lag of 1300 m. Fitting of the variogram models was performed by minimizing an "Indicative Goodness of Fit" criterion (IGF), which is a standardized measure of difference between observed and model values (Pannatier, 1996). An IGF value close to zero indicates a good fit of the model. The analysis of the 12 variograms obtained (Fig. 4) showed generally two isotropic patterns of spatial dependence, with short and long range respectively. Only in January, May and June there was only one pattern.

Parameters of the spatial structures are reported in Table 2, together with the IGF and the Root Mean Squared Normalized Error of the estimation (RMNSE). This last value should be close to one to have a good estimation: it ranges between 0.949 and 1.078, which is fully acceptable.

The monthly maps showing the probability of exceeding the threshold, together with standard error maps are reported in Fig. 5a-5b-5c. The distribution of the probability shows higher values at the western and south-western border of the Plain.

Maps show that the area with the higher probability of exceeding the threshold is wider during the period from January to April: this could be ascribed to the common agricultural systems, i.e. intensive horticultural systems such as carrots, potatoes, fennels and salads crops (Peruzzi *et al.*, 2005). Usual agricultural practices, such as sowing and transplanting from February to April, and harvesting Piccini, C. et al.



Fig. 4. Indicator variograms of monthly averages in 2001-2004

from June to November, leave the soil bare or scarcely covered during winter with null or reduced nitrate uptake. The effect of low evapotranspiration and high rainfall coupled with a high soil nitrate surplus due to organic matter mineralization and previous fertilization causes a nitrate leaching to groundwater.

In some areas the probability of exceeding the threshold was always high regardless of the month, probably due to an excess of nitrogen fertilisation, to a peculiar hydro-pedological situation leading to a nitrate accumulation and leaching, or both. Here the risk of water contamination is higher due to the mobility in soil and persistence in groundwater of the NO^{3"}.

Standard error maps can be used to predict where the uncertainty is higher. Obviously close to sampling points the estimation error was minimum, while in non sampled locations it increased differently. However, the overall reliability of the maps is suitable for the present purposes, since the error values are mostly below the standard deviation of the probability levels.

Month	1° model	C ₀ [nugget]	C [sill]	A (m) [range]	2° model	C [sill]	A (m) [range]	IGF	RMNSE
January	Spherical	0.003	0.297	7096	-	-	-	0.014	0.997
February	Gaussian	0.021	0.174	2368	Gaussian	0.118	9200	0.084	1.016
March	Gaussian	0.03	0.212	2668	Gaussian	0.056	9200	0.054	0.960
April	Spherical	0.018	0.186	2834	Gaussian	0.109	9200	0.030	0.949
May	Spherical	0	0.255	2813	-	-	-	0.163	0.965
June	Spherical	0.027	0.226	2837	-	-	-	0.166	0.967
July	Spherical	0	0.184	2819	Spherical	0.108	9200	0.301	0.993
Augu st	Spherical	0.003	0.126	2621	Gaussian	0.156	9100	0.071	1.041
September	Spherical	0.044	0.055	1985	Gaussian	0.147	9200	0.103	1.049
October	Spherical	0.036	0.062	1858	Gaussian	0.152	9200	0.161	1.078
November	Spherical	0	0.08	1318	Gaussian	0.18	9100	0.108	0.971
December	Spherical	0.012	0.201	2819	Gaussian	0.042	9200	0.061	0.977

Table 2. Variographic parameters of the selected models

IGF: Indicative goodness of Fit - RMNSE: Root Mean Squared Normalized Error

PROBABILITY

STANDARD ERROR

PROBABILITY

STANDARD ERROR





Fig. 5b. Probability and standard error maps of monthly averages from May to August



Fig. 5c. Probability and standard error maps of monthly averages from September to December

CONCLUSION

Monitoring of groundwater quality for decision making and environmental policies evaluation requires a least number of samples and a proper level of accuracy and information. From these preliminary results, Indicator Kriging seems to be accurate and significant in the identification of nitrate vulnerable zones, allowing the assessment of the probability to exceed a critical threshold in a cost-effective way.

The monthly maps derived from the proposed model, representing the probability to exceed the threshold of 50 mg/L fixed by the European Nitrate Directive, showed that during the period ranging from January to April the probability was high in a wide area, due among other to the reduced nitrate uptake of crops at the starting stage of growth in this period. Despite the general trends, in some areas the probability was always high: this could be attributed to an excess of nitrogen from fertilisation or a particular hydropedological situation. Anyhow these areas should be targeted by best management practices to reduce nitrogen loads, and attention has to be given to any land use activity performed within these high risk areas. The spatial probability maps could be used to determine the natural or anthropogenic factors that best explain the occurrence and distribution of elevated concentrations of nitrate (or other constituents) in shallow groundwater. This information, relatively cheap and easy to update, can be used by local landuse planners, ecologists, and managers to protect water supplies and identify land use planning solutions and monitoring programs in vulnerable areas (LaMotte and Greene, 2007). The proposed methodology is suitable as a preliminary screening, rather than as a model to study nitrate dynamic and loss from agricultural lands. Nevertheless, adding secondary information such as crops, climate and soil data could improve the accuracy of the methodology reducing the prediction errors (Grunwald *et al.*, 2006) and allowing nitrate studies in soils and waters.

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