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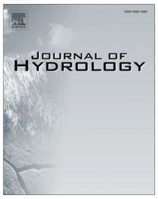

Groundwater vulnerability and pollution risk assessment of porous aquifers to nitrate: Modifying the DRASTIC method using quantitative parameters

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SUMMARY

In the present study the DRASTIC method was modified to estimate vulnerability and pollution risk of porous aquifers to nitrate. The qualitative parameters of aquifer type, soil and impact of the vadose zone were replaced with the quantitative parameters of aquifer thickness, nitrogen losses from soil and hydraulic resistance. Nitrogen losses from soil were estimated based on climatic, soil and topographic data using indices produced by the GLEAMS model. Additionally, the class range of each parameter and the final index were modified using nitrate concentration correlation with four grading methods (natural breaks, equal interval, quantile and geometrical intervals). For this reason, seventy-seven (77) groundwater samples were collected and analyzed for nitrate. Land uses were added to estimate the pollution risk to nitrates. The two new methods, DRASTIC-PA and DRASTIC-PAN, were then applied in the porous aquifer of Anthemountas basin together with the initial versions of DRASTIC and the LOSN-PN index. The two modified methods displayed the highest correlations with nitrate concentrations. The two new methods provided higher discretisation of the vulnerability and pollution risk, whereas the high variance of the (ANOVA) F statistic confirmed the increase of the average concentrations of NO_3^-, increasing from low to high between the vulnerability and pollution risk classes. The importance of the parameters of hydraulic resistance of the vadose zone, aquifer thickness and land use was confirmed by single-parameter sensitivity analysis.

1. Introduction

Groundwater resources are under intense anthropogenic pressures and constant threat of pollution. Human activities such as agriculture, urbanization and industry have caused irreversible degradation of groundwater quality, therefore prevention is the most appropriate strategy in the fight against groundwater pollution. In many Mediterranean regions, the majority of water demands are met by porous aquifers because of their substantial water quantities and the low exploitation cost. However, the coexistence of porous aquifers with agricultural land and the simultaneous overuse of fertilizers in farming have led to the increased contamination of groundwater by nitrates. The concentration of nitrate in groundwater is considered an indicator of groundwater quality degradation (US Environmental Protection Agency, 1996) and confrontation of nitrate pollution demands an interdisciplinary approach. On this basis, this study focused on combining a vulnerability method with model describing nitrogen cycle processes.

Vulnerability and pollution risk maps of groundwater constitute important tools for groundwater management and protection (Patrikaki et al., 2012). Groundwater vulnerability is divided into specific vulnerability and intrinsic vulnerability (National Research Council, 1993). Intrinsic vulnerability of an aquifer can be defined as the ease with which a contaminant introduced onto the ground surface can reach and diffuse in groundwater (Vrba and Zaporozec, 1994). Specific vulnerability is used to define the vulnerability of groundwater to particular contaminants or a group of contaminants by taking into account the contaminants' physico-chemical properties and their relationships (Gogu and Dassargues, 2000). Groundwater pollution risk can be defined as the process of estimating the possibility that a particular event may occur under a given set of circumstances (Voudouris, 2009) and the assessment is achieved by overlaying hazard and vulnerability (Gogu and Dassargues, 2000; Uricchio et al., 2004).

A variety of index methods have been proposed for the assessment of intrinsic vulnerability. The GOD index estimates

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groundwater vulnerability using three parameters: Groundwater occurrence, Overlying lithology and Depth to groundwater (Foster, 1987). Van Stempoort et al. (1993), proposed an aquifer vulnerability index (AVI) which is based on the material of the vadose zone and a flexible multi-parameter method (SINTACS) for the assessment of groundwater vulnerability developed by Civita and De Maio (1997). Additionally, Petelte-Giraude et al. (2000) developed a methodology, named RISKE, to evaluate groundwater vulnerability in karst aquifers.

The most established method worldwide is DRASTIC (Aller et al., 1987), although some significant disadvantages have been indicated in its application. These drawbacks include mainly the use of qualitative parameters, the overestimation of vulnerability in porous aquifers compared to fractured media, and the limited vulnerability discretisation observed in specific aquifer types. Various research groups have validated and modified the original intrinsic vulnerability methods (mainly the DRASTIC method) in order to estimate the specific vulnerability and risk of nitrate pollution (Rupert, 2001; McLay et al., 2001; Panagopoulos et al., 2006; Antonakos and Lambrakis, 2007; Patrikaki et al., 2012; Huan et al., 2012). However, the aforementioned methods do not consider various climatological conditions which tend to alter nitrogen cycle processes, and accordingly these methods are limited in use and may lead to ambiguous results (Salemi et al., 2014). Additionally, models that describe water movement and the transport and transformation of nitrogen from agricultural land and soil profiles, such as GLEAMS (Knisel and Davis, 2000) and HYDRUS (Šimunek et al., 2008), or indices such as LOS (Aschonitis et al., 2012), underestimate hydrogeological factors (e.g. vadose zone) which could prevent the contamination of groundwater by nitrogen.

The combination of a hydrogeological vulnerability index method with a nitrogen loss method would increase the reliability of the prediction of specific groundwater vulnerability to nitrates. Furthermore, the modification of a vulnerability method for porous aquifers could increase the discretisation of the vulnerability zones and thus help produce a sustainable management plan for the protection of porous aquifers. Combining the above index and models with a statistical process could produce reliable hybrid groundwater vulnerability and risk methods.

The objective of this study was the modification and validation of the DRASTIC method to the specific characteristics of a porous aquifer and the pollutant nitrate in order to achieve higher reliability and vulnerability discretisation than the original method. The modification was based on the replacement of qualitative with quantitative parameters, whereas the validation of the weightings, ratings and classes of the parameters were performed with statistical and grading methods in a GIS environment. A variety of data were collected for the integration of this study including lithological profiles, climate data (temperature, rainfall), hydraulic parameters of the aquifer and the vadose zone, soil characteristics and hydrochemical data.

2. Study area

The study area is located in the eastern part of Thermaikos Gulf in northern Greece and includes the porous aquifer of Anthemountas river basin (Fig. 1). The region's major river is Anthemountas that flows from east to west. The mean altitude of the basin is 259 m and the mean slope is 20%. A typical Mediterranean climate characterizes the area with an average annual temperature of 15.1 °C. The annual precipitation amount is 522.1 mm and 70–80% of this occurs in the wet period (October–May), while summers are usually dry (June–September). Neogene and Quaternary sediments are located in the lowlands and represent 65% of the formations. The sediments have varying thicknesses ranging from 150 m in the eastern part to over 1000 m in the coastal area. The Neogene sediments are situated in the south and consist of three series: (1) sandstone-marl with sandstones, marls, sands and gravels, (2) red-clay, composed of clay with lenses of sands, and (3) the conglomerate series with conglomerates, gravels and sands. Alluvial deposits (gravels, sands and clays) and terrace systems (pebbles, sands, gravels and clays) comprise the basin's Quaternary sediments. In the mountainous part of the basin Mesozoic schist, gneiss, ophiolite and carbonate rocks are located.

The porous aquifer is approximately 181.5 km^2 in area and can be divided into an eastern and a western part. The porous aquifer is developed in the Quaternary and Neogene sediments, and the highest part is covered by agricultural land. A fissured rock aquifer and a karst aquifer are developed in the crystalline and carbonate rocks of the basin, respectively (Fig. 1). The degradation of water quality in the karst aquifer and the limited available water in the fault zones of the fissured rock aquifer prevents their exploitation. Therefore, the water demands of the basin are mainly met by the porous aquifer through a large number of boreholes.

Increased human activities of the last decades have contributed to the deterioration of groundwater quality in the porous aquifer. Intense agriculture, the absence of aquifer protection zones and the overuse of fertilizers have caused the groundwater to become polluted by nitrate. The protection of the porous aquifer is of utmost importance to sustain the water supply in the study area, whereas a nitrate pollution vulnerability and risk map may constitute the initiation of an integrated protection and management plan.

3. Methodology

3.1. Groundwater vulnerability

The DRASTIC method (Aller et al., 1987) is based on the following seven morphological, hydrological and hydrogeological parameters: Depth to groundwater (D), net Recharge (R), Aquifer media (A), Soil media (S), Topography (T), Impact of the vadose zone (I), and Hydraulic Conductivity (C). Each parameter is divided into classes with a rating value and has a weight based on their importance. The method estimates vertical groundwater vulnerability with the following assumptions: (a) the contaminant is introduced at the ground surface, (b) the contaminant reaches the groundwater table by precipitation/infiltration, (c) the contaminant has the same mobility (velocity) as water and, (d) the study area is greater than 0.4 km^2. The DRASTIC method has two versions; one for intrinsic vulnerability (DRASTIC-typical) and one for specific vulnerability of pesticides (DRASTIC-Pesticide). The difference between these versions is the redefinition of their parameter weights. The Eq. (1) for the DRASTIC Index (DI) is:

$$DI = Dr \cdot Dw + Rr \cdot Rw + Ar \cdot Aw + Sr \cdot Sw + Tr \cdot Tw + Ir \cdot Iw + Cr \cdot Cw \tag{1}$$

where D, R, A, S, T, I, C were defined earlier, r is the rating for the study area, and w is the weight of each parameter. Each parameter, including the index, must have a numeric value between 1 and 10.

A quantitative description of the vadose zone characteristics can be described as the relative transit time from the surface to the saturated zone. The relative transit time can be roughly estimated from the hydraulic resistance of the vadose zone and is computed from two parameters: the thickness of each sedimentary unit above the uppermost aquifer (d), and the estimated hydraulic conductivity of each of these layers (k) (Eq. (2)).

$$c = \sum d_i/k_i \tag{2}$$

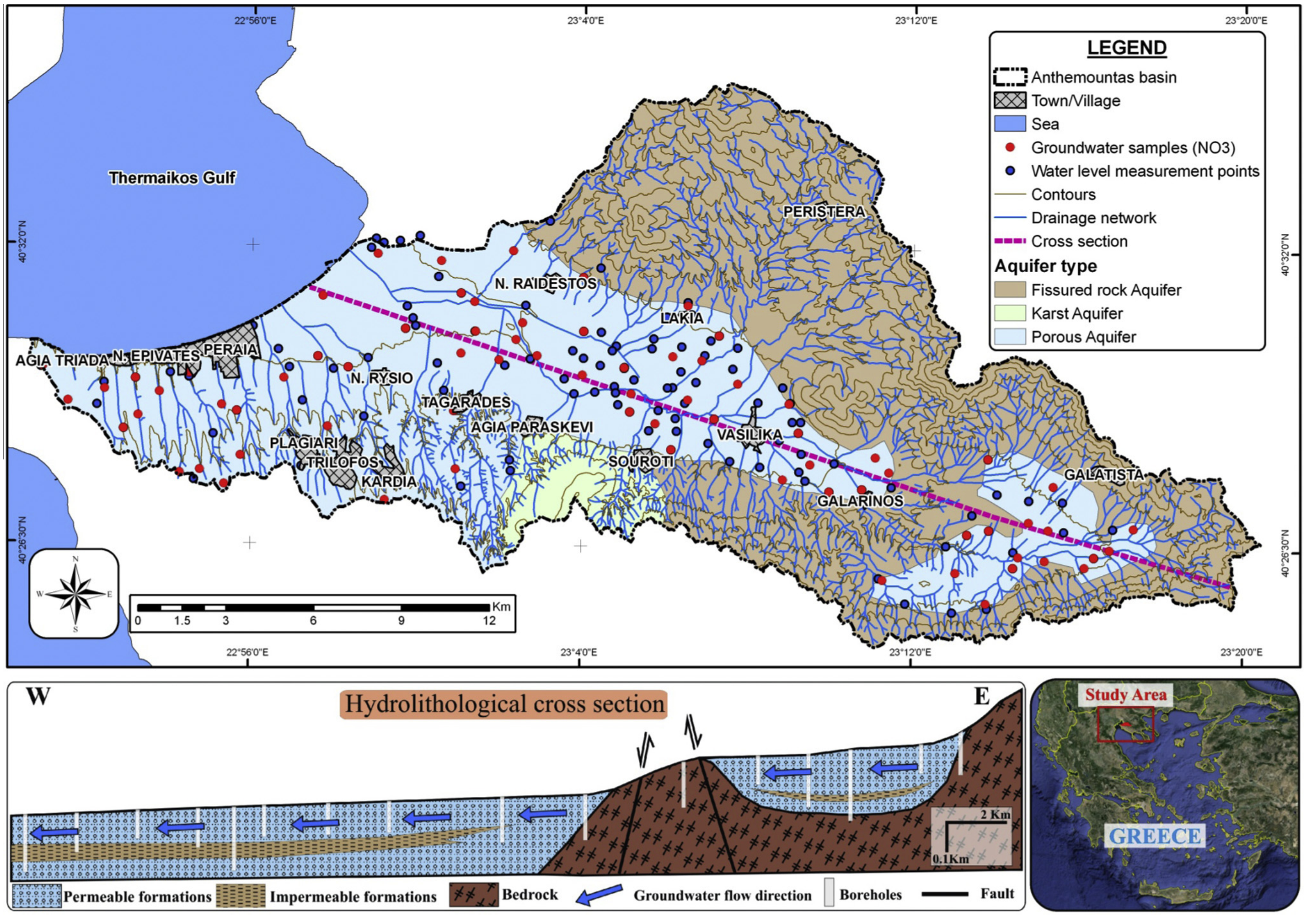

Fig. 1. Hydrogeological map, cross section, sampling points and aquifer types of the Anthemountas River basin.

Although the DRASTIC-Pesticide and DRASTIC-typical methods have been previously applied in the porous aquifer of the study area (Kazakis, 2013), the reliability of the resulting maps were not examined. Therefore, the method was revised by changing the data set of groundwater depth to the mean value of two hydrological years and the groundwater recharge by using the LOSW-PW index which estimates the water losses from soil. In this study the hydraulic resistance is considered a significant factor because it is a quantitative parameter of the vadose zone and can describe the difficulty of a pollutant to reach groundwater from the surface through the vadose zone. The thickness of each sedimentary unit (*d*) can be calculated from lithological profiles, whereas the hydraulic conductivity of each unit can be roughly estimated from pumping tests or literature references.

3.2. Pollution risk assessment

The groundwater pollution risk map was evaluated by combining the vulnerability and hazard maps with the following equation (Uricchio et al., 2004; Voudouris, 2009).

$$\text{Risk} = \text{Vulnerability} \times \text{Hazard} \qquad (3)$$

Hazard corresponds to the probability that a detrimental event will occur in a period of time in a given area (Passarella et al., 2002). The hazard map resulted from the pollution source records and the Corine land cover map (Bossard et al., 2000) (Table 1). The Corine land cover map was updated and the specific crop types were determined according to data for a 20-year period from the National Statistical Service of Greece and verified in the field. Crop type is fundamental as it determines the amount of the fertilizers applied and thus determines the concentration of nitrates in the groundwater. The risk map illustrates the areas with high probability of groundwater to be contaminated by human activities, as the highest risk of contamination exists when a hazard is located in zones with high vulnerability (Werz and Hötzl, 2007).

Table 1
Land use ratings for the DRASTIC-L pollution risk assessment.

L – Land uses (DRASTIC-L)	Rating
Complex irrigated cultivations	10
Urban area	10
Agricultural area	9
Industrial-Commercial area	8
Airport-Military area	8
Farms	7
Olive groves	5
Pastures	5
Non-irrigated arable land	4

3.3. Nitrogen and water losses from topsoil – LOS indices method

The water and nitrogen losses caused by percolation from the topsoil were estimated with LOS indices which are based on climatic, soil and topographic data with emphasis on the topsoil (unsaturated zone) (Aschonitis et al., 2012). The LOS indices were developed from simulations made with the GLEAMS V3.0 model (Knisel and Davis, 2000) and multiple regression analysis. The simulation scenarios included the parameters of soil organic matter content *OM*%, surface slope inclination *S*%, various climatic variables (temperature *T*, precipitation *PCP*, potential evapotranspiration *PE*), saturated hydraulic conductivity K_s, and irrigation *IR* (non-irrigated and irrigated cases), and were performed with various combinations of these. The nitrogen losses caused by percolation beneath the 30 cm deep root zone (kg N $\text{ha}^{-1}\,\text{yr}^{-1}$) were estimated using the LOSN-PN index (Eq. (4)) and the water losses from the LOSW-PW index (Eq. (5)) that describes the annual water losses through percolation beneath the 30 cm root zone (mm yr^{-1}) and is actually the recharge of the porous aquifer.

$$\mathrm{LOSN}-\mathrm{PN}=\left\{\begin{array}{c}-0.1536\sqrt{\mathrm{OM}}+2.6981\sqrt{T}+0.0439\sqrt{\mathrm{Ks}}\\-0.2046\sqrt{\mathrm{S}}+0.0471\sqrt{\mathrm{PCP}}-0.2515\sqrt{\mathrm{PE}}\\-0.0116\sqrt{\mathrm{IR}}\end{array}\right\}^2 \qquad (4)$$

$$\mathrm{LOSW}-\mathrm{PW}=\left\{\begin{array}{c}0.0941\sqrt{\mathrm{Ks}}-0.761\sqrt{\mathrm{S}}+0.4185\sqrt{\mathrm{PCP}}\\-0.0487\sqrt{\mathrm{PE}}+0.0903\sqrt{IR}\end{array}\right\}^2 \qquad (5)$$

where OM: organic matter content (%), *T*: temperature (°C), K_s: saturated hydraulic conductivity (mm day^{-1}), *S*: surface slope inclination (%), PCP: precipitation (mm yr^{-1}), PE: potential evapotranspiration and IR: irrigation (mm yr^{-1}).

3.4. Data sampling and analysis

A detailed hydrogeological survey should precede a vulnerability assessment in order to determine the groundwater occurrence, piezometric conditions, hydraulic and geometrical characteristics of the aquifers, the water balance and the hydrochemical regime. Aquifer type and geometry (thickness, anatomy, boundaries, etc.) can be determined from geological maps and lithological profiles of boreholes. Furthermore, the thickness and the material of the vadose zone can also be defined from lithological profiles and/or geoelectrical vertical soundings in combination with water level measurements. The hydraulic conductivity and transmissivity of the aquifer can be estimated by pumping tests. Aquifer porosity is necessary to estimate groundwater velocity and its calculation can be performed by laboratory tests on core samples. Soil characteristics such as soil texture, hydraulic conductivity and organic matter content are also important and can be determined by particle-size analysis, falling-head tests and chemical analysis, respectively. The climatic variables of rainfall, temperature and evapotranspiration are used to estimate recharge, in combination with the slope and elevation of the study site. Additionally, spatial distribution of the above variables is required for the application of the vulnerability models. The majority of the above data were obtained from previous studies, whereas chemical analysis of groundwater and water level measurements were performed in the framework of this research.

A total of seventy-seven (77) groundwater samples were collected in the dry period of the 2011 hydrological year. Plastic 500 ml bottles were used to store the samples which were filtered through Millipore filters (0.45 μm), and analyzed for NO_3^- using the cadmium reduction method and a DR/2000 Hach spectrophotometer.

Water level measurements were taken in 120 wells in the wet and dry periods of the hydrological years 2010 and 2011, and the water table map was generated from the mean value of the four periods. The required climatic data such as distribution of temperature, potential evapotranspiration, precipitation (Kazakis, 2014), the soil texture, and hydraulic conductivity (Kazakis et al., 2014), organic matter content (Kazakis, 2013), hydraulic conductivity, thickness of the porous aquifer (Kazakis et al., 2013), and groundwater velocity (Kazakis et al., 2015) were obtained from previous hydrogeological studies. Groundwater velocity was estimated using ArcGIS software with the Groundwater-Darcy's velocity model package. The calculation was performed using the groundwater head elevation, effective porosity, thickness of the saturated zone and transmissivity. The mean irrigation of the agricultural land was estimated as 340 mm by using the water balance approach of Burri and Petitta (2004), whereas irrigation was considered as zero in the basin's non-agricultural land. The topographical data was calculated from the digital elevation model (20 × 20 m) of the study area and the use of GIS. Finally, 200 lithological profiles were used to determine the vadose zone characteristics.

3.5. Optimization and validation of groundwater vulnerability and pollution risk to nitrate

The applied methodology of this paper aimed for a representative groundwater vulnerability-risk index for porous aquifers and nitrate pollution by removing the subjectivity of the weightings, rating and classification of the parameters. The DRASTIC method was chosen as the base index and the validation of the modifications and the produced indices was verified with statistical methods. The modifications performed were: (1) replacement of the qualitative with quantitative parameters, (2) selection of the appropriate grading method of the parameters and the final index, (3) revision of the rating scale and the weightings, and (4) removal of parameters with low correlations.

The parameter modifications were: (1) The aquifer media (A) was replaced with the thickness of the porous aquifer, (2) the soil type (S) was replaced with the nitrogen losses obtained by the LOSN-PN index and (3) the hydraulic conductivity (C) was replaced with groundwater velocity (according to Darcy's law). Finally, the classes of vadose zone impact (I) where replaced with the values of the hydraulic resistance of the vadose zone layers. The replacement of the parameters was verified by their correlation with nitrate concentration (Table 2), while the rationale of the aforementioned replacements is:

- The aquifer media (A) of the DRASTIC method is a qualitative parameter which mainly distinguishes the aquifer types according to their geological framework (sandstone, limestone, sand and gravel, etc.). Consequently, in porous aquifers the rating of this parameter is uniform throughout the aquifer. The thickness of the porous aquifer was selected instead of the aquifer media, because it can be calculated easily from the lithological profiles and indicates spatial distribution in porous aquifers. Furthermore, aquifer thickness is considered a critical parameter to determine the nitrate dilution ability of groundwater (Zhong, 2005) and it has been used previously in DRASTIC modifications (Huan et al., 2012).

Table 2
The weight and grading method for each parameter of the DRASTIC and DRASTIC-PA specific vulnerability method and the correlation factor of each grading method.

Parameter	Grading method	DRASTIC		DRASTIC-PA	
		Weight	Correlation n rank	Weight	Correlation n rank
D	Equal interval	5	0.035	0.5	0.059
R	Geometrical interval	4	0.115	1.1	0.128
A	Natural breaks	3	0.000	1.8	0.207
S	Quantile classification	2	0.008	0.7	0.079
T	Equal interval	1	0.085	0.8	0.091
I	Quantile classification	5	0.255	4.5	0.528
C	Equal interval	3	−0.152	0.6	0.072

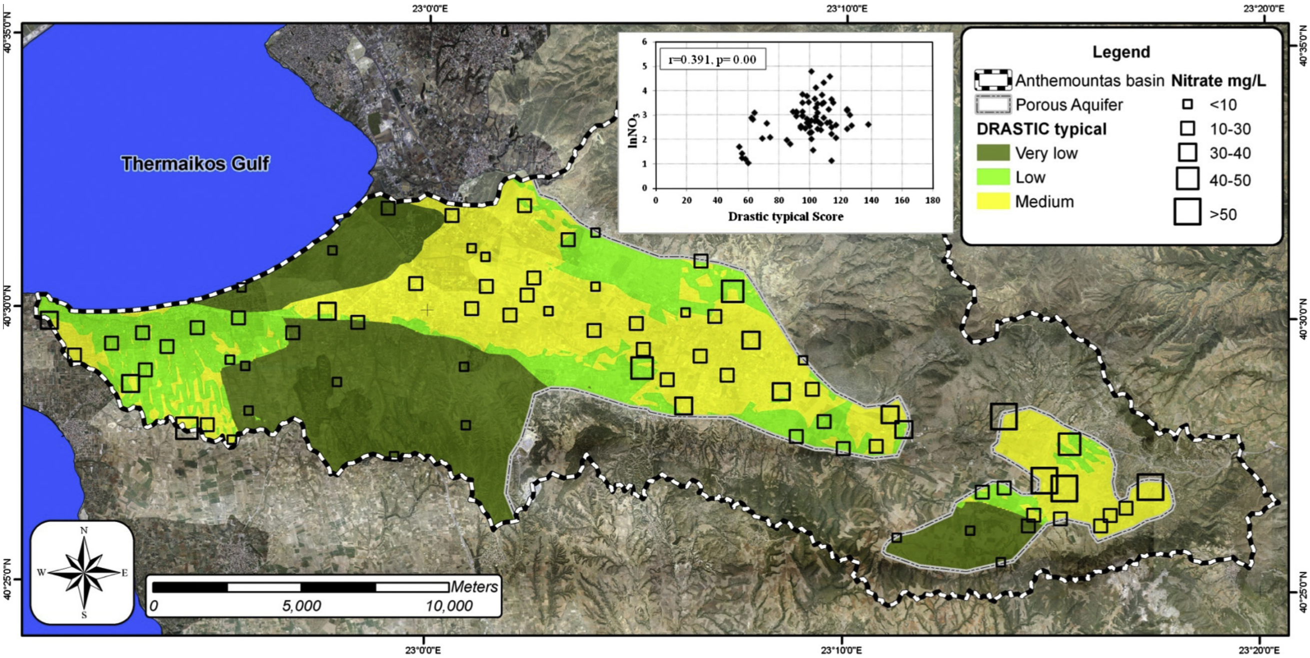

Fig. 2. Distribution and relationship of typical DRASTIC intrinsic vulnerability and nitrate concentrations in the study area.

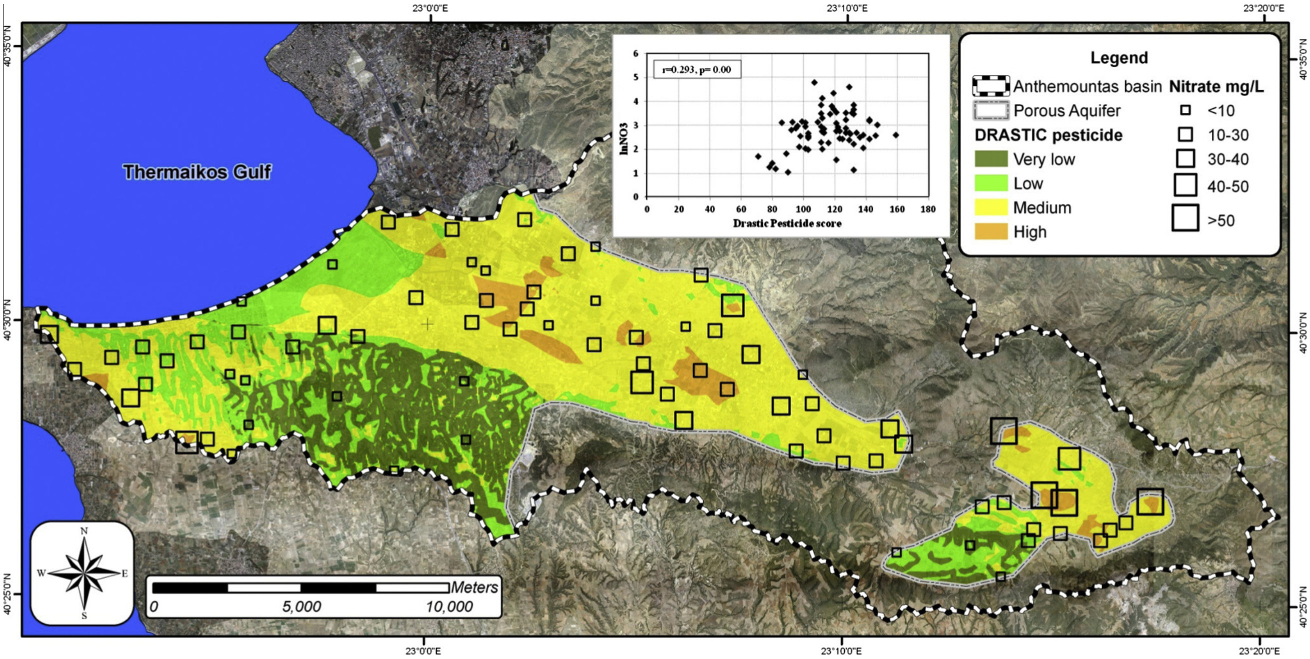

Fig. 3. Distribution and relationship of pesticide DRASTIC intrinsic vulnerability and nitrate concentrations in the study area.

- The highest denitrification rates occur in the upper soil horizon (Clement et al., 2002; Cosandey et al., 2003; Kustermann et al., 2010; Jahangir et al., 2010, 2012) thus the soil characteristics parameter is important when estimating specific vulnerability to nitrates. In DRASTIC, the soil parameter considers mainly the soil texture and assumes that nitrates are a conservative substance. The model does not take into account that nitrates can also originate from the nitrification of ammonia species in fertilizers and organic matter mineralization, the denitrification process occurring in anaerobic environments, or nitrogen immobilization when soil C/N ratios are high (Aschonitis et al., 2012). Therefore, the quantitative LOSN-PN index was used as a general consideration of soil cover.
- The vadose zone is the most important parameter for the protection of groundwater. The DRASTIC method provides small discretisation of the vadose zone characteristics in porous

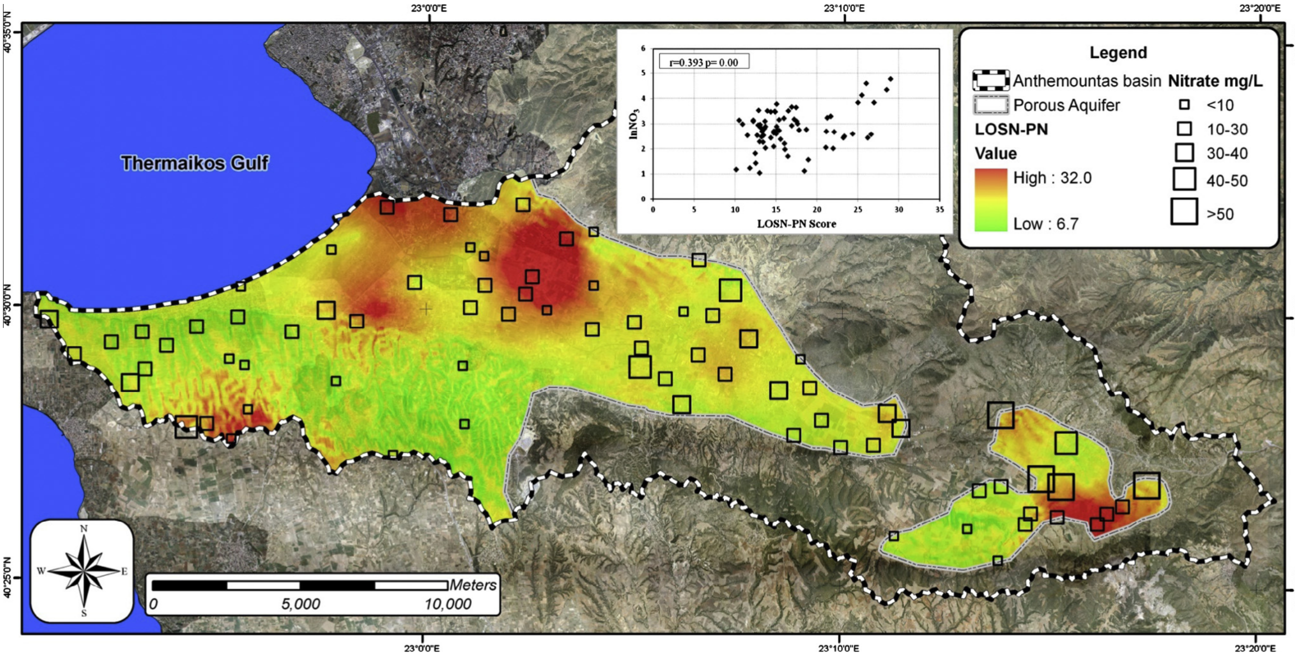

Fig. 4. Distribution and relationship of nitrogen losses (LOSN-PN index in kg N ha^{-1} yr^{-1}) and nitrate concentrations in the study area.

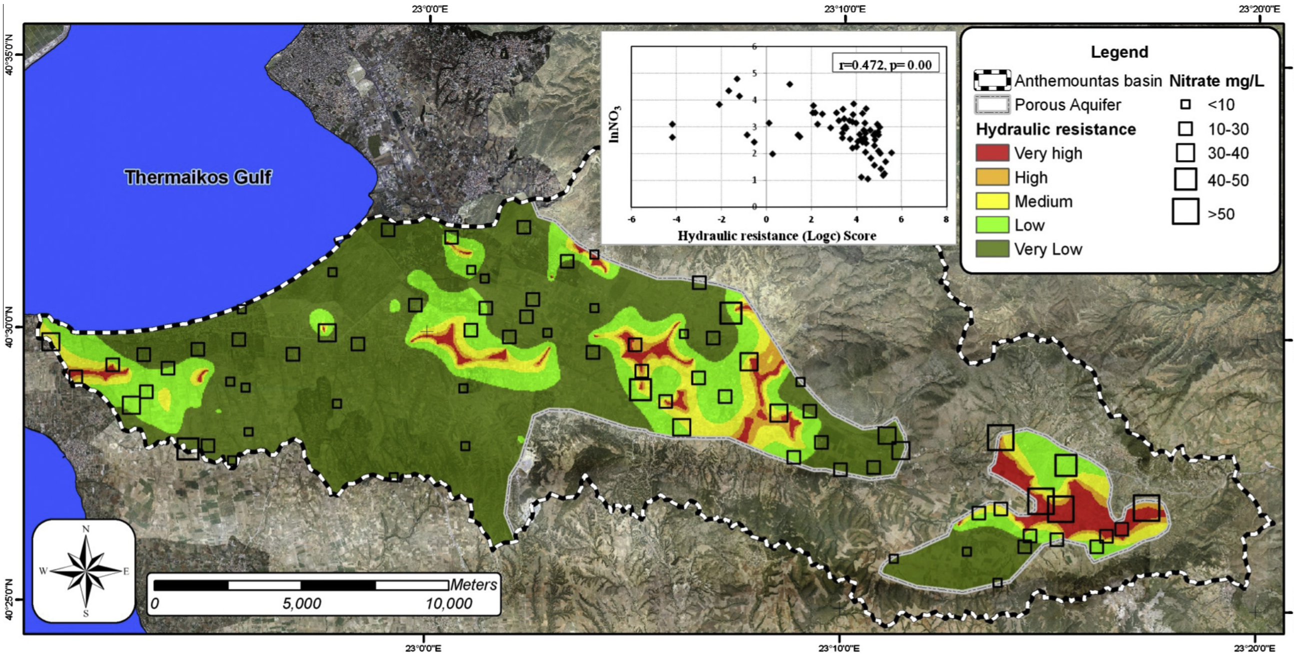

Fig. 5. Distribution and relationship of hydraulic resistance and nitrate concentrations in the study area.

aquifers because the clay-sand-gravel material is determined as qualitative. The thickness of the clay-sand-gravel layers of the vadose zone in combination with their vertical hydraulic conductivity can determine the relative transit time of the nitrates from the surface to the groundwater, which is well described by the hydraulic resistance factor. Accordingly, hydraulic resistance replaced the qualitative approach of the original DRASTIC index.

- The negative relationship of hydraulic conductivity with nitrates has been referred in previous studies (Panagopoulos et al., 2006; Masetti et al., 2008) and verified in this research ($r = -0.082$). Conversely, a positive correlation was observed between nitrate concentrations and groundwater velocity. When using the groundwater velocity, the hydraulic gradient is simultaneously included in the final estimation of this factor. Furthermore, groundwater velocity has also been used in similar methodologies (Mohamed and Moumtaz, 2009; Huan et al., 2012).

The grading methods of natural breaks, equal interval, quantile and geometrical intervals have been used to define the class ranges of the final vulnerability to nitrate index (Huan et al., 2012). Here,

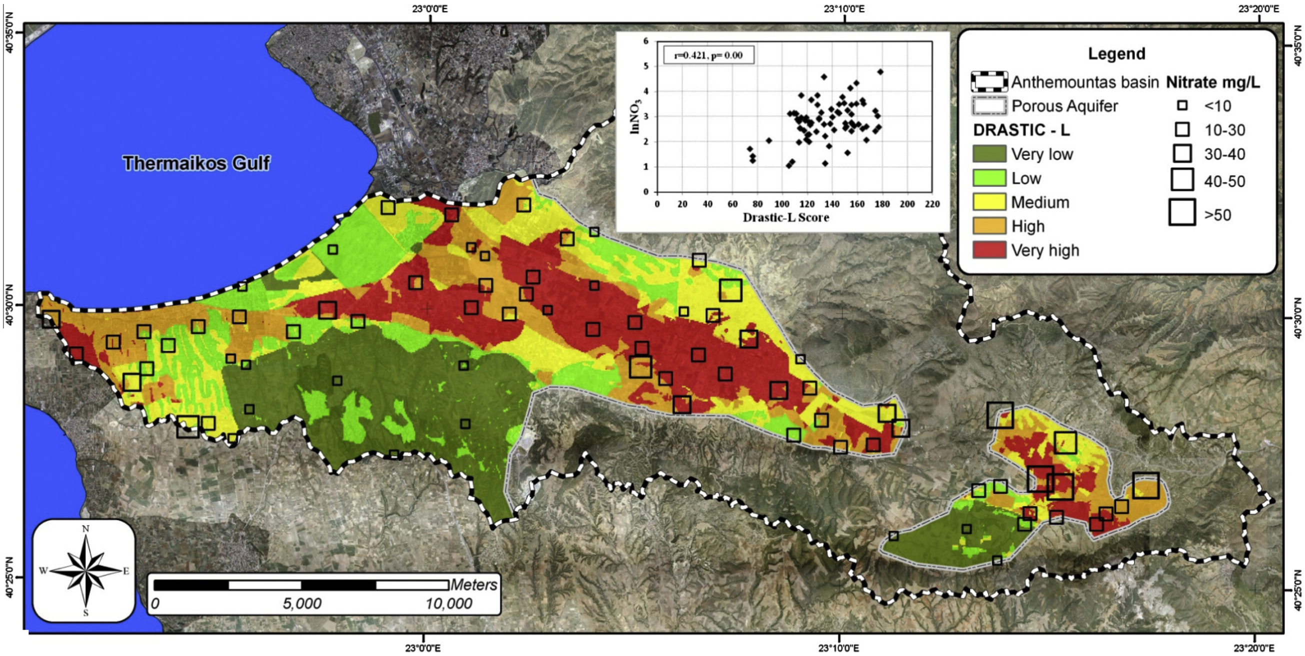

Fig. 6. Distribution and relationship of DRASTIC-L intrinsic risk and nitrate concentrations in the study area.

this technique was used to select the most appropriate class range of the final parameters as well as the final index class range in combination with the highest correlation with nitrate concentrations. Each parameter comprised 10 classes with a rating score from 1 to 10, whereas the final indices comprised 5 classes.

3.6. Statistical methods

The correlation between nitrate concentration and the vulnerability-risk degree of groundwater was used as an indicator of the reliability and accuracy of the applied methods (McLay et al., 2001; Rupert, 2001). The reliability of the correlation between a point measurement (nitrate concentrations) and spatial distribution data (the vulnerability-risk degree) is based on the representativeness of the point measurements (groundwater samples) according to the specific characteristics of the area (land use, aquifer type, depth of groundwater, etc). The stratified sampling method (Chase and Bown, 1997; Fink, 2003) was used for the collection of groundwater samples and the distance between the samples ranged from 500 to 1000 m.

Validation of the weighting, rating and parameter class range of the vulnerability and pollution risk was performed with Pearson's (r) correlation factor (Pearson, 1896). The application of Pearson's (r) correlation factor presupposes a normal distribution of nitrate concentrations which is not satisfied from the available data as shown by the statistical significance of the Shapiro–Wilk's test ($p = 0$) (Shapiro et al., 1968). Therefore, a logarithmic transformation of the nitrate concentrations was performed (Panagopoulos et al., 2006) and used to modify the weightings and ratings and select the grading method of each parameter of the vulnerability and pollution risk methods.

The weighting of each parameter was recalculated using Eq. (6) on a scale of 10. The grading method of each parameter was selected according to the highest correlation with nitrate concentration.

$$W = \frac{r}{\sum_{i=7}^{7}(r_i)} \times 10 \tag{6}$$

where W: the modified weighting of each parameter and r: the correlation value of each parameter with nitrate concentration.

The rating of each crop and land use type of the hazard map was performed according to previous studies (Panagopoulos et al., 2006; Antonakos and Lambrakis, 2007; Huan et al., 2012) and Eq. (7):

$$r = \frac{L(\mathrm{NO_3^-})}{L_{\max}(\mathrm{NO_3^-})} \times 10 \tag{7}$$

where r is the value of the rating, $L(\mathrm{NO_3^-})$ is the mean nitrate concentration in the corresponding land use and crop type, and $L_{\max}(\mathrm{NO_3^-})$ is the highest mean nitrate concentration in the corresponding land use and crop type.

Analysis of variance of F statistic (Eq. (8)) variances, which is the ratio of between to within sample (Bryman and Cramer, 1997), was used to verify the overlap between the vulnerability parameters and the nitrate concentrations. The larger the ANOVA F statistic, the less overlap between the nitrate concentrations in the different vulnerability classes (Lake, 2003).

$$F = \frac{\mathrm{MST}}{\mathrm{MSE}} = \frac{\mathrm{SST}/K-1}{\mathrm{SSE}/N-K} \tag{8}$$

where MST is the mean square, MSE is the mean square for error, SST is the sum of squares for treatment, SSE is the sum of squares for error, K–1 is the freedom degree for treatment, and N–K is the freedom degree for error.

The single-parameter sensitivity analysis (Napolitano and Fabbri, 1996) was used to evaluate the impact of each factor on the final proposed pollution risk to nitrates index (DRASTIC-PAN). Sensitivity analysis has been used widely in groundwater vulnerability analysis as it aids the analyst to judge the significance of subjectivity elements and provides useful information on the influence of rating and weighting values assigned to each parameter (Gogu et al., 2003; Huan et al., 2012).

The effective weighting was calculated as follows:

$$W = (P_r P_w / V) \times 100 \tag{9}$$

where W is the effective weighting of each parameter, P_r is the rating value, P_w is the weighting value of each parameter, and V is the overall value of the applied index.

Table 3
Original and modified ranges and ratings of the seven DRASTIC and DRASTIC-PA methods parameters.

D – Depth of groundwater			*R* – Recharge			*A* – Aquifer type/Thickness			*S* – Soil media/Nitrogen losses		
DRASTIC	DRASTIC-PA	Rating	DRASTIC	DRASTIC-PA	Rating	DRASTIC	DRASTIC-PA	Rating	DRASTIC	DRASTIC-PA	Rating
Range (m)	Range (m)		Range (mm)	Range (mm)		Type	Range (m)		Type	Range (kg N ha^{-1} yr^{-1})	
0–1.5	<20	10		>131	10	Karst limestone	<29	10	Thin or absent/Gravel	>20.5	10
1.5–4.5	20-36	9	>254	106–131	9	Basalt	29-44	9	Sand	18–20.5	9
	36-53	8	178–254	91–106	8	Sand and gravel	44–58	8	Peat	16.6–18.0	8
4.5–9	53-69	7		83–91	7	–	58–72	7	Shrinking/Aggregated clay	15.6–16.6	7
	69-85	6	102–178	77–83	6	Massive limestone/Sandstone	72–85	6	Sandy loam	14.9–15.6	6
9–15	85–102	5		74–77	5	Glacial till	85–96	5	Loam	14.4–14.9	5
	102–118	4		69–74	4	Weathered metamorphic/Igneous	96–109	4	Silty loam	13.6–14.4	4
15–23	118–134	3	51–102	60–69	3	Metamorphic/Igneous	109–123	3	Clay loam	12.6–13.6	3
23–30.5	134–151	2		46–60	2	Massive shale	123–140	2	Muck	11.2–12.6	2
>30.5	>151	1	0–51	<46	1	–	>140	1	No shrinking/Aggregated clay	<11.2	1

T – Topography			*I* – Impact of the Vadose zone/Hydraulic Resistance (c)			*C* – Conductivity/Velocity		
DRASTIC	DRASTIC-PA	Rating	DRASTIC	DRASTIC-PA	Rating	DRASTIC	DRASTIC-PA	Rating
Range (%)	Range (%)		Type	Range (Logc)		Range (m/d)	Range (m/d)	
0–2	<5	10	Karst limestone	<2.33	10	>81.6	>64	10
2–6	5–10	9	Basalt	2.33–3.28	9		57–64	9
	10–15	8	Sand and gravel	3.28–3.77	8	40.8–81.6	49–57	8
	15–19	7	–	3.77–4.15	7		42–49	7
	19–24	6	Limestone. Sandstone. Sand and Gravel with significant silt and clay	4.15–4.38	6	28.56–40.8	35–42	6
6–12	24–29	5	–	4.38–4.57	5		28–35	5
	29–34	4	Metamorphic/Igneous	4.57–4.76	4	12.24–28.56	21–28	4
12–18	34–39	3	Silt/clay. Shale	4.76–5.03	3		14–21	3
	39–44	2	–	5.03–5.29	2	4.08–12.24	7–14	2
>18	>44	1	Confining layer	>5.29	1	0.04–4.08	<7	1

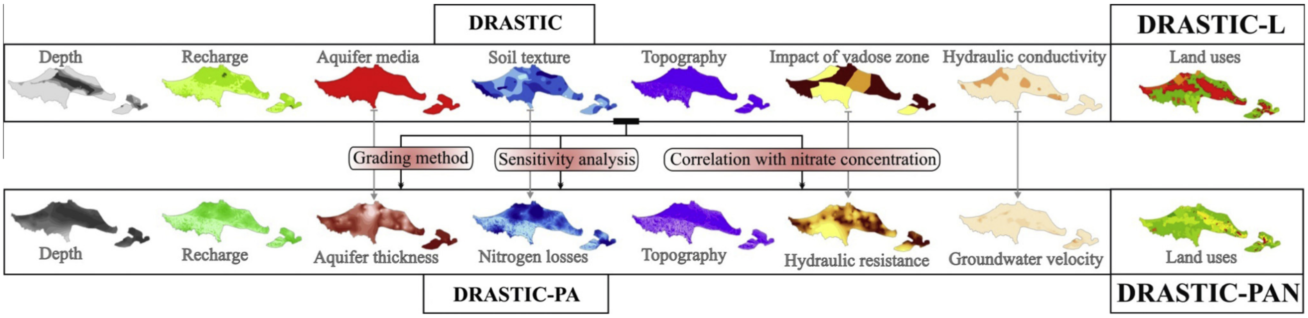

Fig. 7. Schematic representation of the processes used to modify the DRASTIC method and the thematic maps of each parameter.

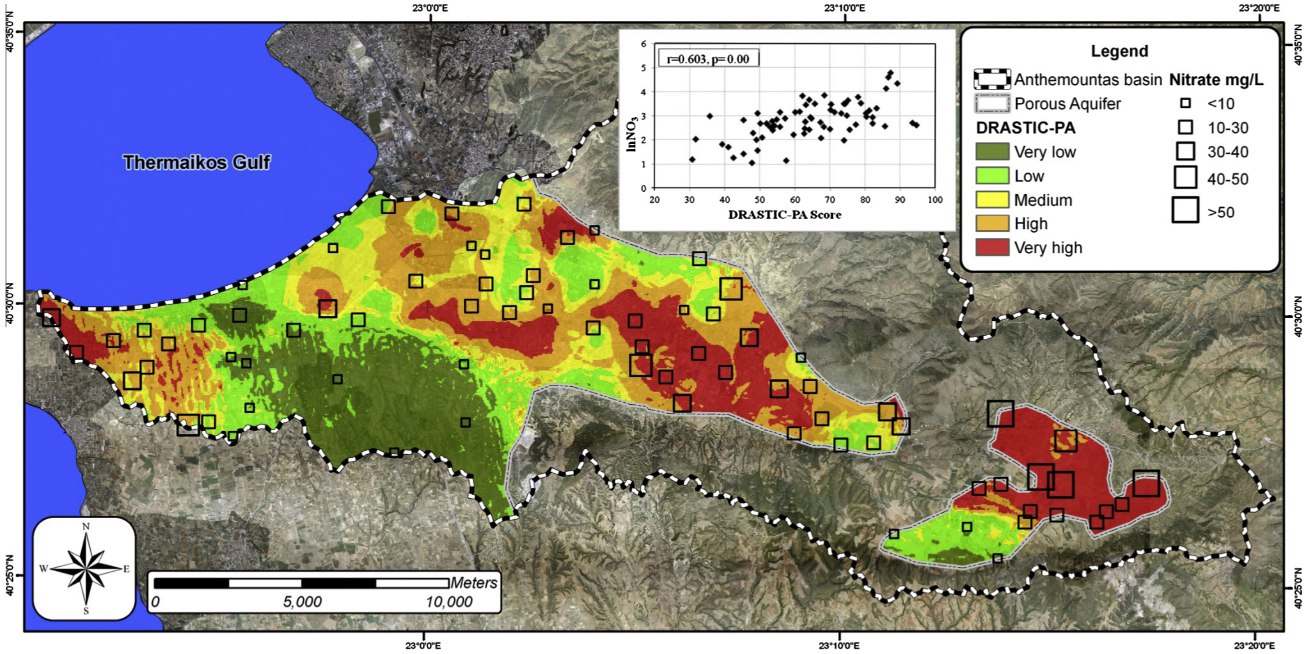

Fig. 8. Distribution and relationship of DRASTIC-PA specific vulnerability and nitrate concentrations in the study area.

4. Results

4.1. Results of the original vulnerability methods

The typical and pesticide DRASTIC methods were both applied in the porous aquifer of Anthemountas basin and the distribution of the intrinsic vulnerability values are shown in Figs. 2 and 3 together with the correlation with nitrate concentrations. The typical DRASTIC method underestimates vulnerability to nitrates because the largest class is that of medium vulnerability and the correlation with nitrate concentrations is low ($r = 0.391$). The pesticide version presents a remarkable improvement in vulnerability discretisation but the correlation with nitrate concentration is lower than that of the typical method ($r = 0.293$). These results confirm the known disadvantages of the DRASTIC method which are also apparent in the pesticide version and highlight a low degree of reliability for use in porous aquifers. The nitrogen losses estimated with the LOSN-PN index vary from 6.7 to 32 kg ha^{-1} yr^{-1}, whereas the correlation with nitrate concentrations is predictably low ($r = 0.393$) (Fig. 4) because this is not a groundwater vulnerability method and disregards the vadose zone characteristics and the hydraulic characteristics of the aquifer. Nevertheless, this method provides a general view of the nitrogen cycle processes in soils and consequently constitutes an important parameter when estimating vulnerability to nitrates. The highest correlation ($r = 0.472$) with nitrate concentration was observed with the hydraulic resistance of the vadose zone (Fig. 5) and this highlights the importance of the vadose zone in groundwater vulnerability assessments. Finally, the groundwater pollution risk was estimated with the DRASTIC-L method and the result is shown in Fig. 6. Although land uses were included in the risk assessment a low correlation with nitrate concentrations was observed ($r = 0.421$).

The use of qualitative parameters and the disregard of the specific characteristics of porous aquifers explain the low correlation with nitrate concentrations observed with the DRASTIC method. For this reason, a quantitative modification of the rating, weightings and class ranges was considered necessary to increase the reliability of the vulnerability and pollution risk to nitrates assessment.

4.2. The DRASTIC-PA and DRASTIC-PAN methods

The methods of DRASTIC-PA and DRASTIC-PAN were formulated to increase reliability and representativeness of vulnerability and pollution risk maps of porous aquifers to nitrate, respectively.

Table 4
Revised land use ratings for the DRASTIC-PAN specific pollution risk assessment.

Land Use – Ln (DRASTIC-PAN)	NO_3^- (mg/L)	Rating
Corn (L_{max})	86.6	10.0
Farms	47.0	5.4
Vines	39.6	4.6
Greenhouses	32.0	3.7
Cotton	28.1	3.2
Vegetables	23.1	2.7
Complex cultivations	18.4	2.1
Urban-Industrial-Military-Commercial-Pasture area	16.0	1.8
Olive groves	15.8	1.8
Wheat	13.1	1.5
Clover	10.6	1.2

Table 5
Vulnerability and pollution risk classes of the DRASTIC-PA and DRASTIC-PAN methods.

Classes	DRASTIC-PA	DRASTIC-PAN
Very low	<41.7	<44
Low	42–54	44–58
Medium	54–60	58–77
High	60–72	77–103
Very high	>72	>103

The grading methods used for the seven parameters and their revised weightings are shown in Table 2. The ranges of the original and revised classes are shown in Table 3, whereas the reshape and replacement procedure results of the thematic maps are shown in Fig. 7. The geometrical interval was the grading method of the final vulnerability classes with the highest correlation to nitrate concentration. The DRASTIC-PA method can be used to assess specific vulnerability of porous aquifers to nitrates with the following equation:

$$\text{DRASTIC} - \text{PA} = 0.5 \cdot D + 1.1 \cdot R + 1.8 \cdot A + 0.7 \cdot S + 0.8 \cdot T + 4.5 \cdot I + 0.6 \cdot C \quad (10)$$

Table 6
Statistics of the single-parameter sensitivity analysis.

Index	Effective weighting (%)			
	Min.	Max.	Average	Standard deviation
Depth of groundwater (D)	0.89	14.01	6.11	1.51
Net Recharge (R)	1.41	21.63	8.85	3.76
Thickness of the aquifer (A)	1.70	46.08	17.85	7.86
Nitrogen losses from soil (S)	0.57	14.10	5.69	2.85
Topography (T)	2.76	23.22	11.73	2.86
Hydraulic resistance of the vadose zone (I)	5.19	57.66	24.89	9.70
Groundwater velocity (C)	0.44	14.55	6.52	1.62
Land uses (Ln)	5.39	55.97	13.90	5.46

where D = Depth of groundwater (m), R = Recharge (estimated with LOSW-PW), A = Thickness of the aquifer, S = Nitrogen losses (estimated with LOSN-PN), T = Topography (Slope), I = Hydraulic resistance of the vadose zone, and C = Groundwater velocity. PA indicates the applicability of the method to porous aquifers.

Application of the DRASTIC-PA method produced a significantly increased correlation coefficient with nitrate concentration ($r = 0.603$). Additionally, discretisation of the vulnerability classes in the porous aquifer was improved as shown in Fig. 8. A further increase in the correlation coefficient ($r = 0.696$) with nitrate concentration was achieved when the DRASTIC-PAN method was applied. (PAN: indicates that the method is used to estimate the risk of nitrate pollution in porous aquifers). The revised land use (Ln) ratings were used (Table 4) with weight equal to 4.5. The higher mean concentrations of nitrates in groundwater are associated with crop types with high fertilizer demands such as corn, grapes and cotton. In contrast, the lowest concentrations were observed in olive groves and wheat crops. The correspondence between nitrate concentrations and crop type highlights the importance of fertilizers in the groundwater pollution risk assessment to nitrates. The nitrate pollution risk classes were defined with the geometrical interval grading method and are shown in Table 5 with a minimum range of 14.5–145, whereas the resulting map is presented in Fig. 9. Based on the statistics of the single-parameter sensitivity analysis (Table 6), the average effective

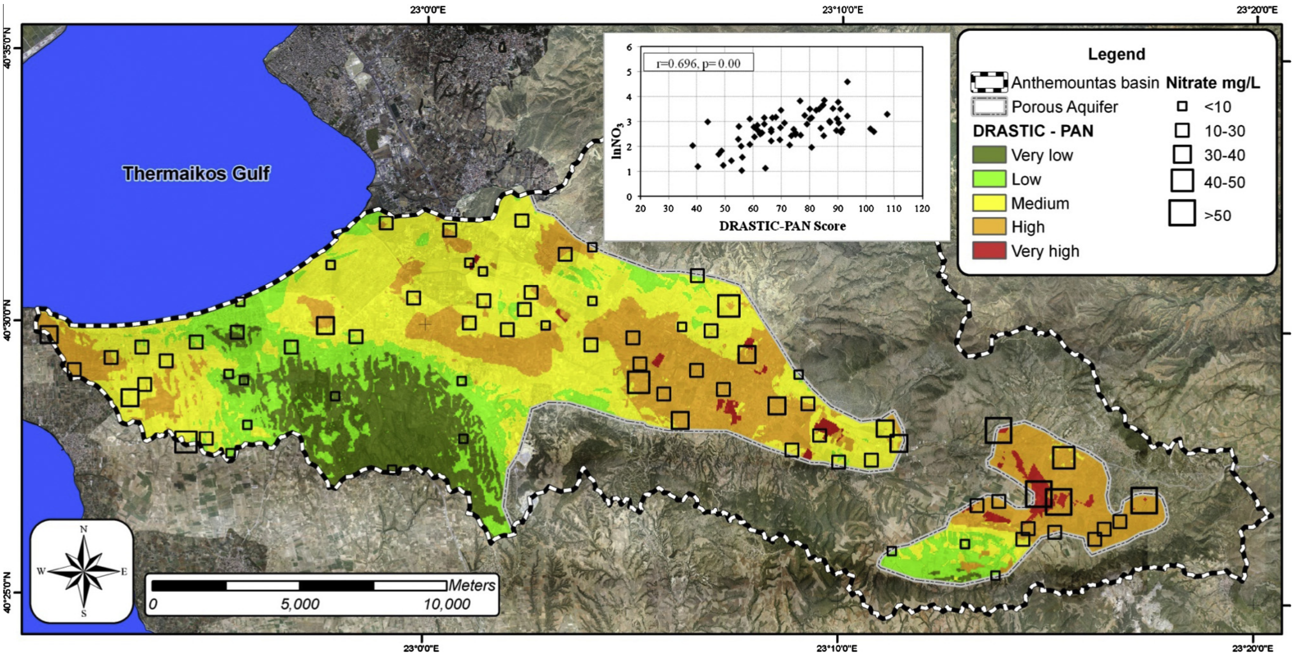

Fig. 9. Distribution and relationship of DRASTIC-PAN specific risk and nitrate concentrations in the study area.

Table 7
Correlation coefficients of the various methods.

Method	Pearson rank correlation	ANOVA F statistic
DRASTIC typical	0.391	7.85
DRASTIC pesticide	0.293	2.11
Hydraulic resistance	0.472	7.92
DRASTIC-L	0.421	4.11
DRASTIC-PA	0.603	9.43
DRASTIC-PAN	0.696	18.87

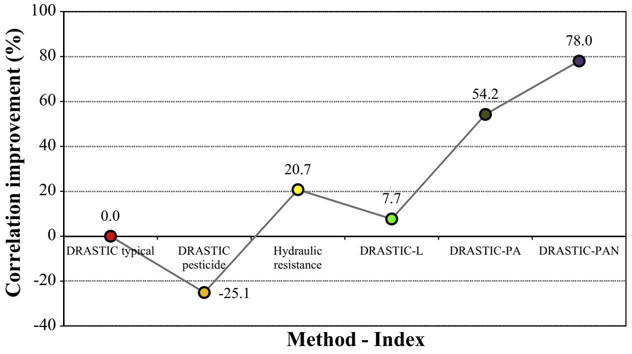

Fig. 10. Correlation improvement from the initial DRASTIC method.

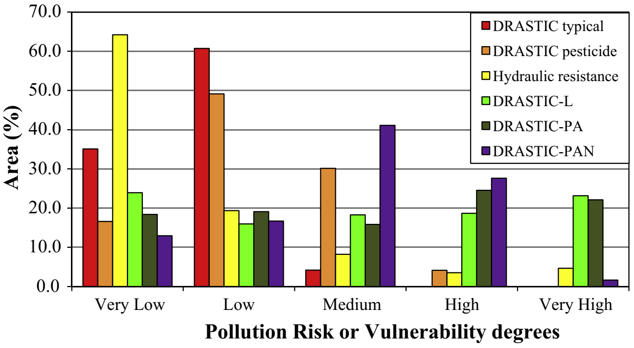

Fig. 11. Distribution of the class areas (%) according to each applied method.

weightings varied from 5.69% to 24.89% indicating that the eight parameters do not differ greatly. The value of each effective weighting is in accordance with the nitrate correlation as groundwater depth exhibited the lowest value and hydraulic resistance of the vadose zone the highest.

The resulting variance of the ANOVA-F statistic test was greater when the modified DRASTIC methods were applied than with the original methods and indicates the lower overlap between the mean values of nitrates in the different vulnerability classes and pollution risk to nitrate classes. The higher the ANOVA F statistic of the method, the higher the Pearson's rank (Table 7). Furthermore, the correlation (Pearson's rank) of nitrate concentrations and the applied methods improved by up to 78% compared to the original DRASTIC method (Fig. 10). A further improvement was attempted by excluding the parameters which had low correlations with nitrate concentrations (i.e., depth of groundwater, topography and groundwater velocity). However, in this case an insignificant increase was observed ($r = 0.707$). The removal of these parameters may be beneficial to the results of this specific study area but reduces the advantage of multi-parameter use (Evans and Myers, 1990) a method that decreases the probability that some important parameters will be ignored (Rosen, 1994).

The distribution of the vulnerability and pollution risk classes produced by each applied method is shown in Fig. 11. The original DRASTIC indices (typical and pesticide) underestimate the vulnerability of the porous aquifer since the majority of the study area is characterized with very low to low vulnerability. The vulnerability degrees produced by DRASTIC-PA are uniformly distributed as is the pollution risk to nitrates produced by DRASTIC-L and DRASTIC-PAN. The majority of the porous aquifer is characterized with high vulnerability to nitrates by DRASTIC-PA and medium nitrate pollution risk by DRASTIC-PAN.

5. Discussion

The assessment of groundwater vulnerability and pollution risk is essential to protect and manage the groundwater in a watershed, however the large amounts of required data and their accuracy are the disadvantages in any assessment method applied. The use of quantitative parameters in DRASTIC-PA and DRASTIC-PAN eliminates the subjectivity of the methods and reliable comparisons can be made between different areas. However, it is advisable to first apply the initial DRASTIC-typical method as it requires less data and covers all aquifer types. The methods proposed here are specified for porous aquifers and are inappropriate for karst and fissured rock aquifers. Zwahlen (2003) proposed the COP method for the pollution risk assessment of karst aquifers, whereas Denny et al. (2007) modified the DRASTIC method for application in fissured rock aquifers. Validation of the DRASTIC method and the improvement achieved in the correlation rank with nitrates increases its reliability (Panagopoulos et al., 2006).

The validation of these methods can be also achieved with logistic regression, correspondence analysis and sensitivity analysis (Pacheco et al., 2015). However, sensitivity analysis has also been used to evaluate the impact of each factor on the final index (Napolitano and Fabbri, 1996) or for weights revision (Dixon, 2005). In addition, the application of the ANOVA-F statistic test can verify the overlap between the nitrate concentrations and the vulnerability parameters (Huan et al., 2012). Aveline et al. (2009) estimated the risk of nitrate leaching groundwater after validating the applied indicators. The main disadvantage of the proposed methods is the large quantity of data required for their application. However, the large amounts of data can ensure reliability as the accurate assessment of aquifer vulnerability and pollution rsk requires the integration of very diverse variables. Additionally, the estimation of nitrogen losses from soil and their combination with hydrogeological factors has increased the reliability of the prediction of specific groundwater vulnerability to nitrates.

Overall, the application of DRASTIC-PA and other vulnerability methods should be preceded by connecting crop or land use types with detrimental groundwater pollutants. It should be noted that pollution risk assessment is the most suitable method for crop re-planning and re-allocation as it takes existing land uses into account. The method should provide reliability and a high degree of discretisation of the risk classes in an aquifer without to distinguish the pollution risk generally between different geological formations.

All the methods applied in this research estimated low vulnerability or pollution risk in the southern central section of the porous aquifer, whereas the highest vulnerability and risk values are observed in the north eastern part. The advantage of DRASTIC-PAN compared to the other methods is the higher discretisation in the classes and renders it suitable for application in areas with small-scale agriculture and dispersed crops. Furthermore, the quantitative approach and the use of the nitrogen losses parameter make DRASTIC-PAN the most appropriate method to assess the pollution risk of porous aquifers to nitrates. In combination with a decision support system (DSS), this method could facilitate the definition of groundwater protection zones and land allocation (Voudouris et al., 2010).

On balance, DRASTIC-PA and DRASTIC-PAN applications can be extended to assess groundwater pollution risk of porous aquifers to nitrates in various regions. The method is flexible as parameters can be added or removed according to the hydrogeological and hydrological status of specific areas.

6. Conclusions

This study verifies the unsuitability of the original DRASTIC methods (typical and pesticide) for the accurate assessment of the vulnerability of groundwater in porous aquifers to nitrates. Similarly, DRASTIC-L is not suitable for the assessment of pollution risk to nitrates, whereas the LOSN-PN index showed poor correlation with nitrate concentration in groundwater. A modification was made to the DRASTIC method by replacing the qualitative (aquifer type, soil, impact of the vadose zone) with quantitative parameters (nitrogen losses, aquifer thickness, hydraulic resistance). Additionally, the class range of each parameter and the final index were modified using nitrate concentration correlation with four grading methods (natural breaks, equal interval, quantile and geometrical intervals). The DRASTIC-PA and DRASTIC-PAN methods were developed to estimate specific vulnerability and pollution risk of nitrates in porous aquifers. The DRASTIC-PAN includes land use as an extra parameter. The correlation (Pearson's rank) of nitrate concentrations improved by 54% and 78% compared to the original DRASTIC method when using DRASTIC-PA and DRASTIC-PAN respectively, whereas the two methods were graded by the geometrical interval method. Their use improved the discretisation of the vulnerability and pollution risk maps, whereas the average concentrations of NO_3^- increased from low to high between the vulnerability and pollution risk classes and was confirmed by the high variance of the (ANOVA) F statistic. According to the single-parameter sensitivity analysis the parameters of hydraulic resistance of the vadose zone, aquifer thickness and land use play a more important role than the other parameters. The single-parameter sensitivity analysis also confirmed the revision of the parameter's weight of the two methods. The two new methods provide a complete approach for the estimation of specific vulnerability and pollution risk of nitrates in porous aquifers, whereas the high discretisation can be used to create a sustainable water management plan, flexible land use allocation, and define groundwater quality protection zones in porous aquifers. The ability of the proposed methods to include additional criteria facilitate similar applications in different regions and environments.

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