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Article

Preventing Groundwater Pollution Using Vulnerability and Risk Mapping: The Case of the Florina Basin, NW Greece

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Abstract: The alluvial aquifer system of the Florina basin (320 km^2) in North Greece is a representative area where irrigated agriculture is applied. Groundwater is the main source of water. The highest and mean nitrate concentrations in groundwater are 67.9 mg/L and 25 mg/L, respectively. High values could be associated with the use of nitrogen fertilizers from agricultural activities. This study deals with the evaluation of the groundwater quality. For this reason, hydrochemical analyses from 29 groundwater samples and water level measurements were performed for the wet and dry periods of 2016. The suitability of groundwater quality for irrigation purposes is examined by using different indices (Chlorinity Index, SAR, Sodium Percentage, Potential Salinity and Kelly's index). In addition, the DRASTIC method was modified by using statistical methods, land use map and nitrate concentrations and applied in order to assess the groundwater vulnerability to external pollution. Notably, there was no correlation between the standard DRASTIC method and nitrate concentrations. However, the modified version and the obtained risk map showed high correlation with nitrate concentrations (ρ = 0.55) and the Groundwater Quality; hence, it is suggested as the base for a protection plan of the alluvial aquifer.

Keywords: alluvial aquifer; groundwater quality; DRASTIC index; nitrate pollution; vulnerability mapping

1. Introduction

Groundwater constitutes a valuable source of fresh water for sustainable water supply for humanity. Greece and other Mediterranean countries are groundwater dependent, while this invaluable source is under constant stress. In these regions, groundwater constitutes the main source to meet the irrigation and domestic use demands. Furthermore, degradation of groundwater quality is a limiting factor for the socio-economic development of a region. Direct and indirect human activities such as application of fertilizers, disposal of untreated household wastewater and leachate from landfills in rivers constitute the main causes of groundwater quality degradation [1]. Elevated concentrations of nitrate in groundwater are observed due to extensive agricultural activities and intensive application of nitrogen fertilizers, which is one of the most widespread non-point pollution sources [2]. After 1930, agricultural development led to the use of mineral nitrogen fertilizers [3]. Additionally, nitrification of low land aquifers notably increased starting from 1970 due to nitrogen fertilizer leaching [4]. Hence, elevated concentrations of nitrate occur all over Europe. According to the European Environment Agency [5], groundwater bodies with mean nitrate concentration 25 mg/L cover 80% in Spain, 36% in Germany, 50% in the United Kingdom, 32% in Italy and 34% in France [6].

The EU Water Framework Directive (Directive 2000/60/EC) has aimed to improve the quality of water bodies; however, degradation of groundwater quality is continuous. Prevention might constitute the optimal strategy in the fight against groundwater pollution. Vulnerability is a measure of how easy it is for a pollutant at the land surface to reach to groundwater level [7]. Thus, a groundwater vulnerability map constitutes a useful tool for groundwater protection and land use management [8]. The most widely used method for groundwater vulnerability assessment is DRASTIC, developed by the US EPA [9].

DRASTIC is an internationally recognized method that uses seven parameters including soil, depth to groundwater, vadose zone, infiltration, topography, aquifer material, and hydraulic conductivity to assess groundwater vulnerability by external pollutants such as nitrate ions [10]. Hazard is defined as the probability that a pollution event resulting from human activities will occur in a given area in a period of time [11]. The conjunction of vulnerability and hazard represents the risk [12]. It is obvious that vulnerability and pollution risk assessment stimulates scientific interest, especially in areas with extensive agriculture. The Florina basin is an interest example in North Greece, where agricultural activities are the main stressors of groundwater quality. Hence, a pollution risk map of groundwater would contribute to the optimal and sustainable management of the valuable alluvial aquifer.

Hence, the aim of this study is to determine the hydrochemical regime of the alluvial aquifer of the Florina basin. Water quality indices (Chlorinity Index, SAR, Sodium Percentage, Potential Salinity and Kelly's index) were used to determine the groundwater quality status and the suitability for irrigation use. Then, the DRASTIC method was adapted and modified according to the specific characteristics of the basin in order to establish the pollution risk map. The Florina basin is considered a representative basin of intensive agriculture and land use changes, while groundwater constitutes the main source for drinking and irrigation purposes in the basin.

2. Methodology

2.1. Study Area

The Florina basin is located in the West Macedonia region, Greece, covering an area of 320 km^2, with mean altitude and slope of 620 m and 1.5%, respectively. This study was focused on the alluvial aquifer in the lowlands of the basin. The climate of the region is characterized as continental with a mean annual rainfall of 472 mm and a mean annual temperature of 12.6 °C. The rainfall occurs mainly in the wet period, which extends from early October to April.

From a geological point of view, the Florina basin is part of the Pelagonian geotectonic zone of Greece. The lowlands of the study area consist of Neogene and Quaternary sediments [13] (Figure 1). Within these sediments, a multiple aquifer system is developed. The alluvial aquifer covers an area of 180 km^2 and consists of alternations of sands, gravels, conglomerates and clays. The hydraulic conductivity ranges between 3×10^{-3} m/s and 4×10^{-6} m/s. The groundwater level ranges from less than 1 m to more than 45 m below the ground surface, while the main groundwater flow direction is from south to north. The water demands of this area are mainly covered by the exploitation of groundwater via numerous boreholes in the alluvial aquifer.

2.2. Data Collection and Analysis

Groundwater level measurements were performed in 59 boreholes and piezometers for two periods (wet and dry periods of 2016), in order to create piezometric maps. In total, 79 lithological profiles were analyzed to determine the thickness and lithology of the aquifer. In June of the same year, 29 groundwater samples were collected from accessible boreholes and were analyzed for the main ions at the Laboratory of Engineering Geology & Hydrogeology of Aristotle University of Thessaloniki. In particular, nitrate ions (NO_3^-), chloride (Cl^-), sulphate ions (SO_4^{2-}), bicarbonate (HCO_3^-), calcium (Ca^{2+}), magnesium ions (Mg^{2+}), Sodium (Na^+) and Potassium (K^+) were measured in the laboratory using Standard Methods for the Examination of Water and Wastewater [14]. The physicochemical parameters of water, like pH, Electrical Conductivity (EC) and Temperature (T), were measured in the field. The hydrochemical water type was determined by the Piper diagram [15]. In addition, various water quality indices have been applied in order to check groundwater suitability for irrigation as this is the main groundwater use in the alluvial Florina basin. The determination of the hydrochemical regime of the alluvial aquifer is critically important with respect to the vulnerability assessment, as described in the next paragraph.

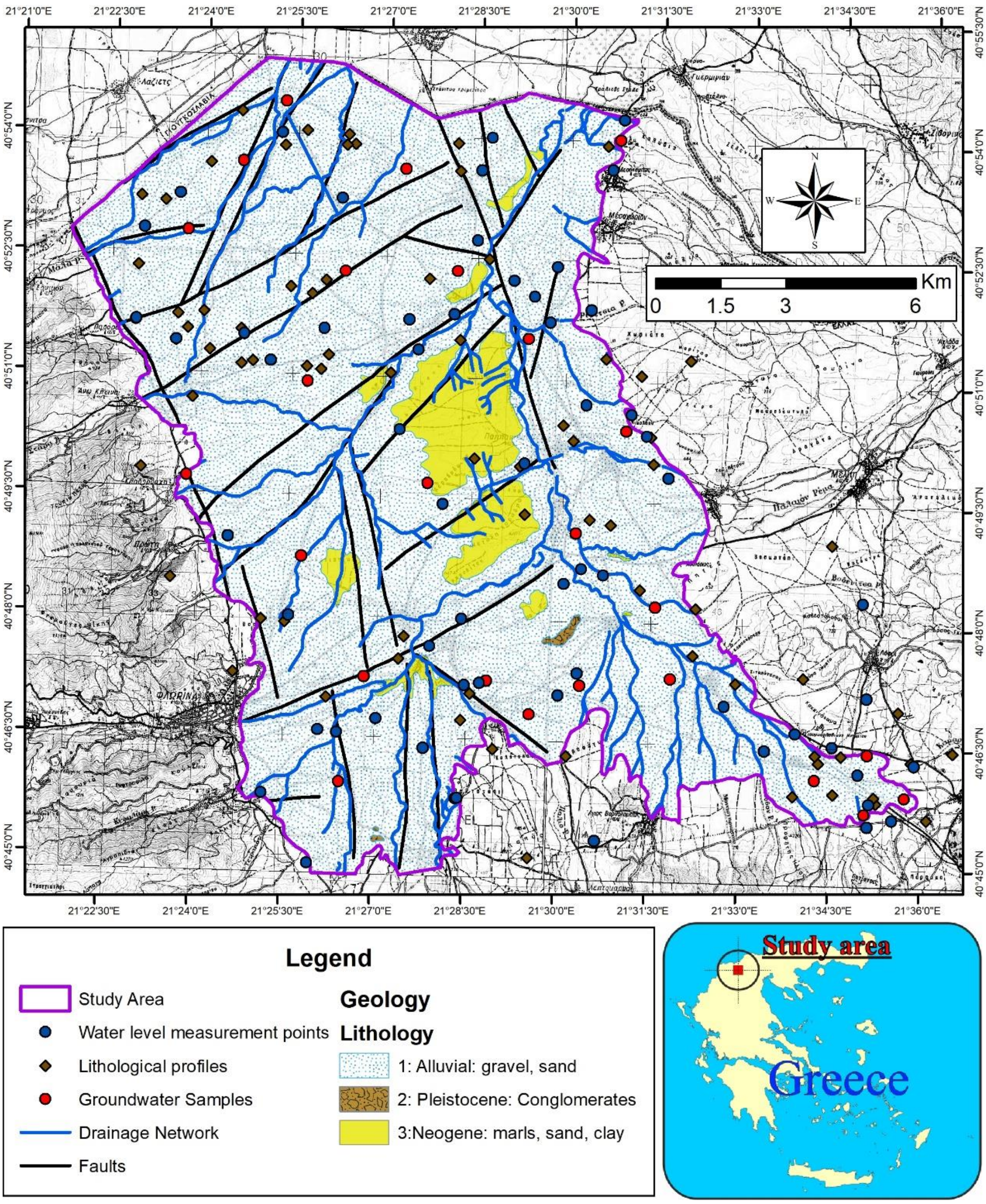

Figure 1. Geological map and measurement points of the Florina basin.

2.3. Vulnerability Assessment

Groundwater vulnerability was assessed based on the DRASTIC method. The DRASTIC method [9] considers seven morphological, hydrological and hydrogeological parameters. The name of the method originates from the acronyms of the parameters, which are Depth to groundwater (D), Recharge (R), Aquifer media (A), Soil media (S), Topography (T), Impact of the vadose zone (I), and Hydraulic Conductivity of the aquifer (C). The seven parameters have a weight based on their importance and are divided into classes with a rating value.

The two versions of the DRASTIC method refer to the assessment of the intrinsic (typical) and specific vulnerability of pesticides (pesticide). The main difference between the two versions is the weights of the parameters. The estimation of the DRASTIC Index (DI) is based on the following equation:

$$\text{DRASTIC} = D_i \times D_n + R_i \times R_n + A_i \times A_n + S_i \times S_n + T_i \times T_n + I_i \times I_n + C_i \times C_n \quad (1)$$

where i is the rating for the study area, and n is the weight of each parameter. The rating of each parameter ranges between 1 and 10.

In this study the following data were used for the assessment of the vulnerability map: Hydrogeological data (groundwater level measurements) and geological data (lithological profiles from boreholes) were used to determine the aquifer material and the thickness of the vadose zone in order to apply DRASTIC method. The digital elevation model (DEM) of the study area was used to extract the morphological data. Soil data, meteorological data and pumping tests data were also used for the determination of soil material, aquifer supply and hydraulic conductivity, from previous research [16]. The standard DRASTIC method was validated based on the nitrate concentration in groundwater following similar approaches from previous studies [7,17]. The produced indexed named DRASTIC-N was used for the estimation of the pollution risk map in the basin.

2.4. Pollution Risk

The assessment of groundwater pollution risk is based on the conjunction of the vulnerability and hazard maps with the following equation [11,12]:

$$\text{Risk} = \text{Vulnerability} + \text{Hazard} \quad (2)$$

Hazard corresponds to the probability that a pollution event will occur in a period of time in a given area [18]. In the alluvial aquifer of the Florina basin, the hazard map resulted from the conjunction of field work records, digitization of crop areas from satellite images and the Corine land cover map [19].

3. Results and Discussion

3.1. Aquifer System

The main aquifer is developed within quaternary deposits of the basin. The aquifer is recharged by the direct infiltration of rainfall with a mean annual value of 50 mm/year, the infiltration of surface water through torrent beds during the wet period, the lateral supply from the neighboring aquifers and the return flow of irrigated water. The piezometric data obtained from this study during the periods of May and September 2016 verified the direction of the groundwater flow, which is from south to north. The groundwater depth in most boreholes is less than 10 m from the ground surface, while the highest depth was measured in the south-eastern part of the basin and was greater than 60 m below ground surface. Groundwater level decline ranged from 0 to 7.6 m between the wet and dry periods of 2016.

3.2. Groundwater Quality

The general statistical characteristics (maximum, minimum, mean, median and standard deviation values) of the major ions calculated by chemical analyses are shown in Table 1. The pH values range from 5.5 to 7.6. The lowest values are recorded in the central part of the alluvial aquifer due to the natural presence of carbonate dioxide in groundwater originating from deeper layers and mixing with shallow aquifers through faults. Temperature values of groundwater range from 15.6 to 22.7 °C. The EC values of the samples collected range from 320 to 1960 µS/cm. Calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations range from 27.4 to 251.6 mg/L and 0.73 to 74.23 mg/L, respectively. Chloride concentrations for all water samples were measured between 1.8–46.4 mg/L, while sodium ions concentration range from 6.94 to 209 mg/L. Based on Piper and Durov diagrams (Figure 2A,B) it is concluded that the main hydrochemical type of groundwater in the research area is calcium-bicarbonate (Ca-HCO_3).

Table 1. Statistical analysis of the hydrochemical data.

Parameters	Units	Min	Max	Mean	Median	Standard Deviation
pH	-	5.6	7.7	6.4	6.9	6.2
T	°C	15.6	22.7	18.6	18.8	1.8
EC	µS/cm	320	1960	770	620	408
TDS	mg/L	160	990	388	310	222.9
Ca^{2+}	mg/L	27	252	89	77	53.7
Mg^{2+}	mg/L	1	74	17	15	15.1
Na^{+}	mg/L	7	209	39	20	49.6
K^{+}	mg/L	1	21	2.7	1.7	3.7
Cl^{-}	mg/L	2	46	11	8	10.4
NO_3^{-}	mg/L	2	68	25	26	21.8
$SO4^{2-}$	mg/L	13	1020	130	95	129.7
HCO_3^{-}	mg/L	88	840	235	198	153.6
Ionic Ratios						
Na^{+}/K^{+}		3.8	393.8	44.6	21.1	77.6
Mg^{2+}/Ca^{2+}		0.01	1.1	0.43	0.37	0.3
Na^{+}/Cl^{-}		1.5	179.7	12.1	3.9	32.9
$(Ca^{2+} + Mg^{2+})/(Na^{+} + K^{+})$		0.7	22.8	5.6	3.8	5.1
$(Ca^{2+} + Mg^{2+})/HCO_3^{-}$		0.9	7.0	1.7	1.5	1.1
SO_4^{2-}/Cl^{-}		1.0	419.9	22.4	6.0	76.8
Water Quality Index						
SAR		0.2	4.4	1.1	1.1	1.1
(Na%)		4.2	59.2	21.7	19.8	12.4
Potential Salinity		0.3	10.7	1.7	1.8	2.0
Kelly Index		0.04	1.5	0.3	0.3	0.3
Chlorinity Index		1.8	46.4	11.2	11.4	10.4

The concentrations of nitrate (NO_3^{-}) and sulphate ions (SO_4^{2-}) are worth noting as they are elevated and, in some samples, exceed the upper limit of 50 mg/L for nitrates and 250 mg/L for sulphate ions set by the European Union. The range of values measured is from 1.7 to 67.9 mg/L for nitrate ions and 13 to 1020 mg/L for sulphate ions. Increased values of nitrates concentration are attributed to the use of fertilizers. The water suitability for irrigation purposes was determined using various water quality indices (Table 1). Those indices are the Chlorinity Index, SAR, Sodium Percentage (Na%), ionic ratio Mg^{2+}/Ca^{2+}, Potential Salinity (PS) and Kelly's index. Richards diagram (Figure 2C) based on the SAR (Sodium Absorption Rate) indicator shows that most water samples are in the C2-S1 category. This means that water quality is good to moderate and should be used with caution in soils that do not drain well [20]. The remaining samples belong to the C3-S1 category with moderate to very modest quality. The water that these samples represent should be used with precautionary measures.

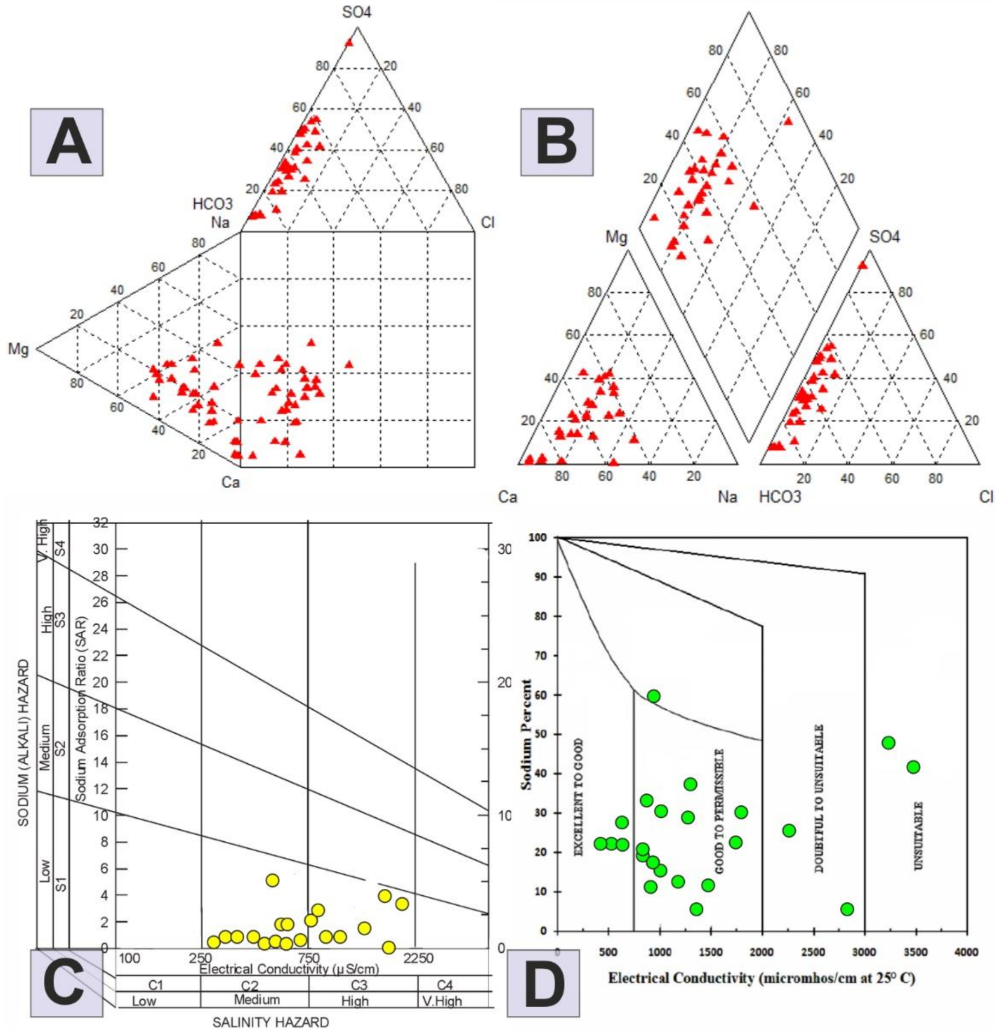

Figure 2. Piper (**A**); Durov (**B**); Richards (**C**) and Wilcox (**D**) diagrams of ion concentrations.

According to the Wilcox diagram (Figure 2D), two samples are unsuitable for irrigation, two other samples range from dubious quality to unsuitable, while the suitability of the remaining water samples for irrigation ranges from excellent to good, and good to acceptable. The PS (Potential Salinity) values in most of the samples is lower than 3, indicating water suitable for irrigation. Another simplified index that was used is the Kelly index. From its values, it can be observed that all samples were suitable for irrigation, since all of them were less than 1. From the chlorine indicator, which is a simple indicator of water suitability for irrigation, all samples were found to be suitable for irrigation, since the chloride concentrations are less than 350 mg/L. Water is absolutely suitable for irrigation when the concentration of Cl^- is less than 70 mg/L. For concentration values between 70–350 mg/L, irrigation must be done carefully, depending on the sensitivity of the crop [11]. In this study, all values are less than 70 mg/L. Finally, the ionic ratio of Mg^{2+}/Ca^{2+} (in meq/L) was also used as the irrigation index. The results of its application for all samples were less than 1.5, suggesting that groundwater is safe for irrigation use.

Water quality indices can be categorized by a number of parameters and may vary in time and space [21]. Hence, it is critically important to update the hydrochemical status of groundwater by applying a detailed monitoring plan. In the Florina basin, nitrate pollution has an increasing trend that is attributed to agricultural activities. However, a sustainable groundwater management plan requires the comparison of different groundwater quality indices [22]. In literature, there are more than thirty water quality indices based on different parameters and generation methods [23]. Giri et al. [24] suggested a Metal Pollution Index (MPI), which could be applied in a future work in the Florina basin.

In some cases, water quality indices have been coupled with GIS in order to produce a holistic quality map [25].

3.3. Groundwater Vulnerability and Risk Mapping

The typical DRASTIC method was applied in the alluvial aquifer of the Florina basin. The DRASTIC method has been also applied in previous studies conducted in the Florina basin [16]; however, in this article, the vulnerability map was updated using recent data. In the central and northeastern part of the study area the vulnerability is characterized as low, while vulnerability of the southwestern part seems to be very high (Figure 3). Vulnerability increases from the center to the northwestern and southeastern ends of the basin. High vulnerability is associated with areas with low groundwater depth, aquifer material that consists of pebbles and gravels, which are highly permeable low surface ground slope (0–2%) and sludge-clayey or clayey soil materials. Lower vulnerability refers to sandy and sandy-clay soil, higher groundwater depth, fine-grained aquifer and the vadose zone. Notably, there was no correlation between the standard DRASTIC method and nitrate concentrations. The risk map takes into account the land uses and is considered more suitable in an agricultural region. Initially the DRASTIC methods weights were validated, and the DRASTIC-N index was developed (Table 2). Continuously, the hazard map was created illustrating the crop types that dominated in the Florina basin (Figure 4A). The lowlands were distinguished into five zones according to the crop types. Mixed crops occur in each zone such as corn, wheat, vegetable, trees and sunflower. Hence, the risk map was created by combining the DRASTIC-N map with the land use map using overlay techniques in a GIS environment (Figure 4B).

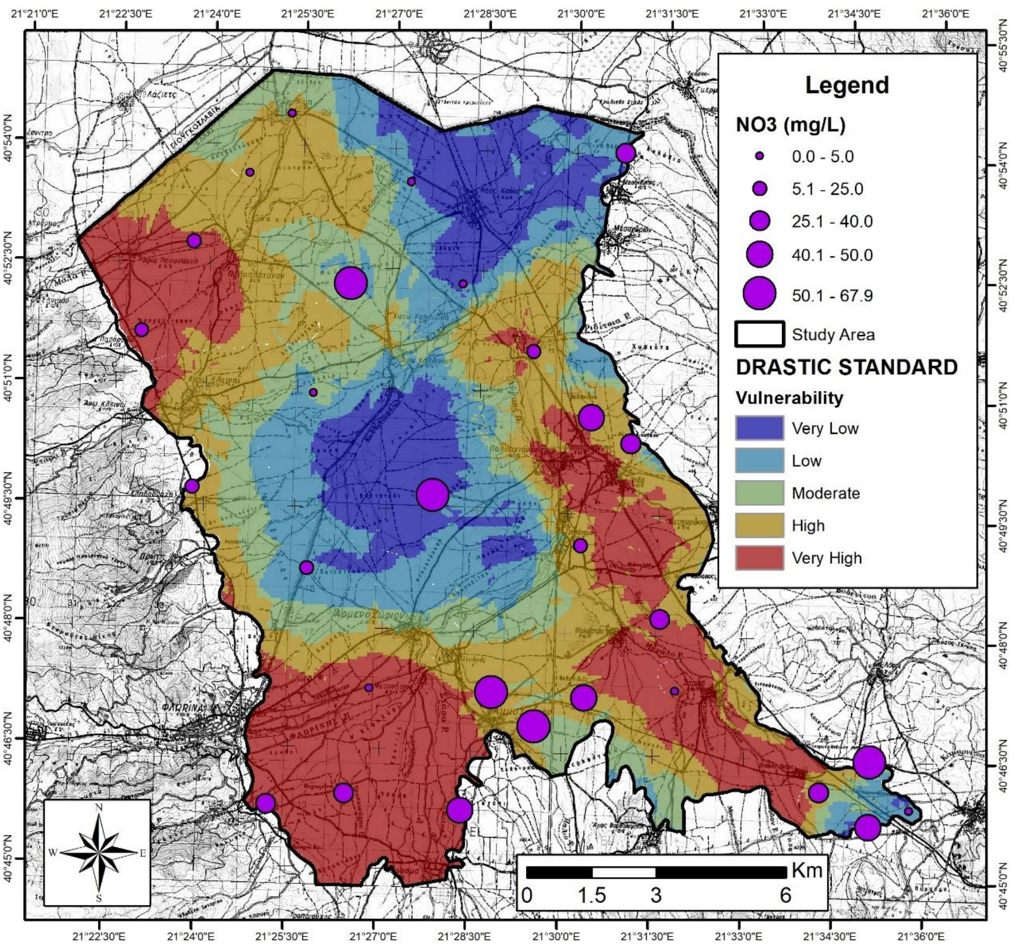

Figure 3. Vulnerability map of the study area based on the DRASTIC index.

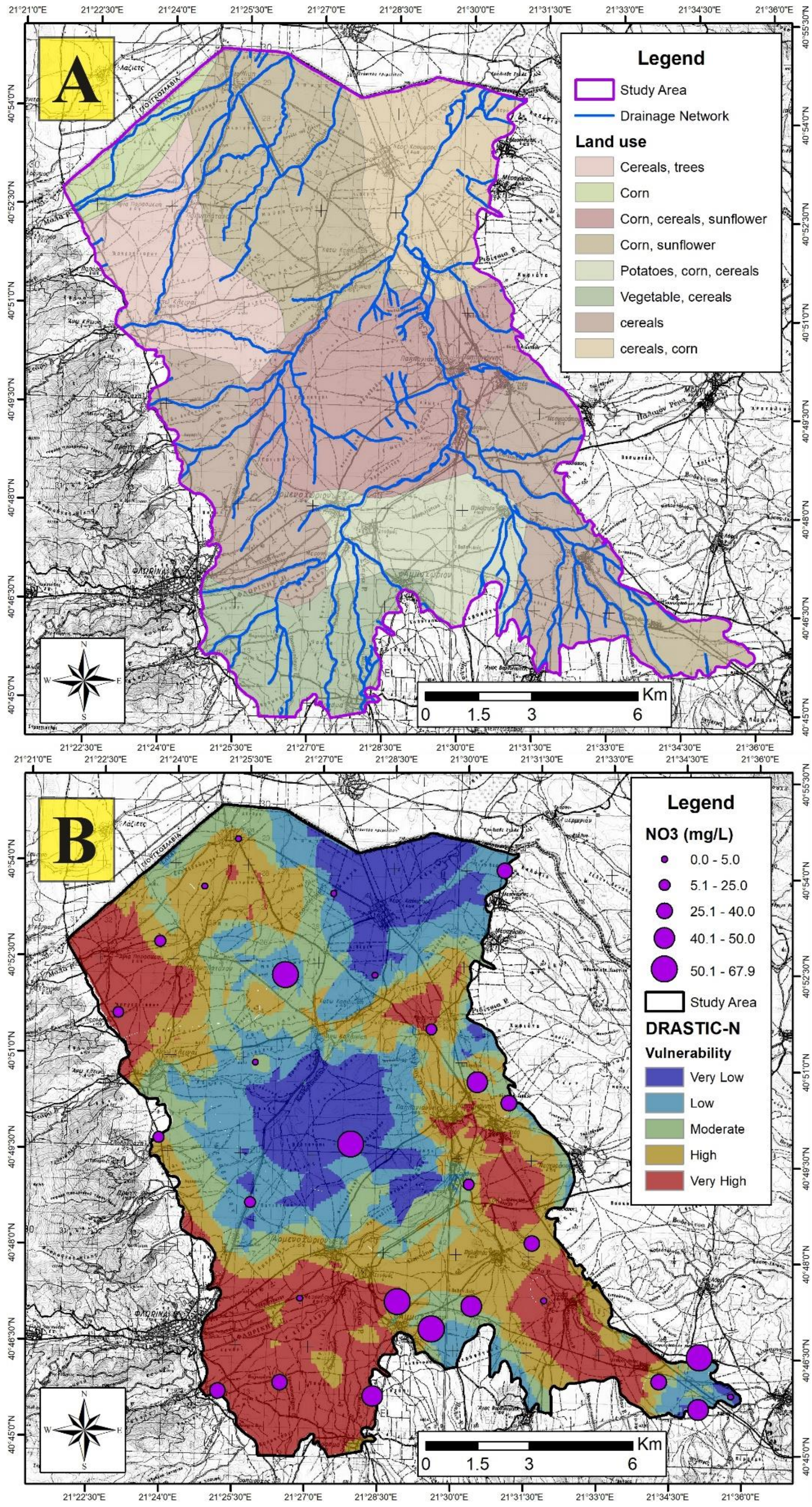

Figure 4. Hazard map of the study area showing land uses (**A**) and vulnerability map based on the DRASTIC-N index (**B**).

Table 2. Standard and Modified weights of the applied indices.

Parameter	Standard Weights	Modified Weights
D—Depth of groundwater	5	2.08
R—Recharge	4	1.33
A—Aquifer type	3	2.65
S—Soil media	2	2.41
T—Topography	1	0.03
I—Impact of the Vadose zone	5	1.32
C—Conductivity	3	0.16
L—Land use	-	2.66

The final DRASTIC-LN indices were divided into five categories from very low to very high using the geometrical interval method (Figure 5) [7]. The highest pollution risk was observed in the central and the two southern edges of the basin. In these areas, the main crop is maize, where $(NH_4)_2SO_4$ and phosphate fertilizers are being used, increasing the groundwater pollution risk. This figure also presents concentrations of nitrate ions. The correlation coefficient of the DRASTIC-LN values with the nitrate ion concentration values was calculated to be 0.54. The correlation is positive and shows that land use is an important factor in calculating the risk of external pollution. In particular, when nitrate fertilizers are the specific pollutant, the amount that is used depends on the type of the crop. The areas of the vulnerability and pollution risk classes are shown in Table 3.

The concept of groundwater vulnerability, first introduced by Margat [26], is based on the assumption that the natural environment can protect one aquifer system. Several methods have been developed, while DRASTIC is the most applied method worldwide. Comparisons between different methods highlighted that standard DRASTIC can be used as an initial and general guide for vulnerability assessment [27]. Rupert [28] was the first to introduce a hybrid approach using a calibration procedure for modifying the groundwater vulnerability map. This approach was initially developed using the DRASTIC method, according to its correlation with nitrate concentrations in the Snake River Basin in USA. Thereafter, numerous modifications of the DRASTIC method have been applied [29,30].

In the Florina basin, the low correlation of the DRASTIC method is notable, even after the modification based on nitrate concentration. It is worth mentioning that the permeability of the vadose zone has been obtained by lithological profiles in this study. In the literature, it is clear that the permeability influences the nitrate and ammonium transport [31–33] as well as the organic matter [34], which is not considered in DRASTIC method. Nevertheless, the pollution risk map overcomes this drawback, increasing the correlation with nitrate concentrations and hence the reliability of the map. A future modification might include the application of the Analytic Hierarchy Process [35], fuzzy logic [36], multivariable statistical analysis [37] and sensitivity analysis [38]. Finally, it is worth mentioning the necessity of monitoring and data updating [39].

Table 3. Distribution of groundwater vulnerability and pollution risk according to the different indices in the Florina basin.

Vulnerability Pollution Risk	DRASTIC	DRASTIC-N	DRASTIC-LN
	Area (km^2)		
Very Low	23.7	26.0	21.6
Low	31.0	34.7	31.1
Moderate	29.2	30.9	24.0
High	51.4	48.5	63.1
Very High	50.0	45.4	45.1

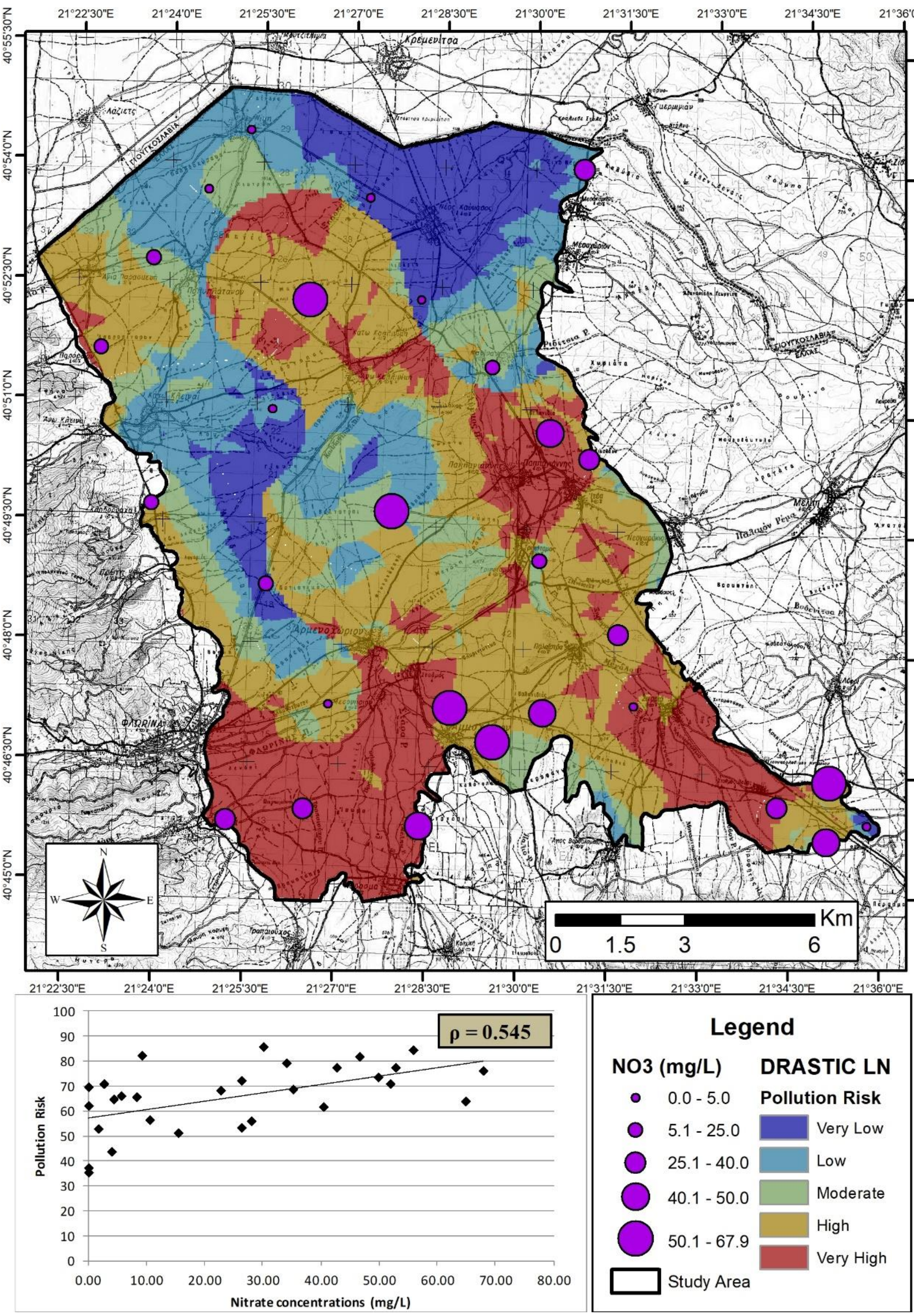

Figure 5. Pollution risk map of the study area based on the DRASTIC-LN index.

4. Conclusions

The intense agriculture and the use of fertilizers result in groundwater quality degradation in the alluvial aquifer of the Florina basin. For this reason, elevated values of nitrate (NO_3^-) concentration were recorded. The highest and mean values of NO_3^- are 67.9 mg/L and 25 mg/L, respectively. Based on the values of various water quality indices, the quality of groundwater was found to be good to moderate for irrigation, while in two cases, groundwater samples were unsuitable according to the Wilcox diagram.

Highest vulnerability occurs at the southwestern edge of the basin. Average to high vulnerability occurs at the northwestern and southeastern ends, while lower vulnerability occurs in the northeastern and central parts of the study area. Nitrate concentrations and land uses were used to optimize the DRASTIC index as additional parameters for more reliable results. Furthermore, DRASTIC-N and DRASTIC-LN indicators were created as well as the corresponding thematic maps. The DRASTIC-LN method evaluates the risk of the aquifer's external pollution. The correlation coefficient of its values with the nitrate concentration showed a higher value. Specifically, it was equal to 0.55, indicating the existence of a positive correlation. Therefore, the risk map that was created from the DRASTIC-LN index constitutes a useful tool to obtain a protection plan for groundwater in the Florina basin.

Generally, vulnerability maps, especially when they are combined with risk maps, are essential tools for water resource management, land use planning, or protection of buffer zones. However, the field of research for collecting data of high quality and density is irreplaceable. In addition, the rational use of fertilizers, changes in land use and systematic monitoring of groundwater quality are some of the strategies proposed in order to limit further degradation in the Florina basin.

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Author Contributions: Konstantinos Voudouris conceived the project idea and coordinated and conducted the data collection. Paschalia Mandrali conducted the field and laboratory measurements, contributed to the application of the method and supported the GIS analysis. Nerantzis Kazakis contributed to the application of the method, including the preparation of the maps.

Conflicts of Interest: The authors declare no conflict of interest.

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