



RIVA: a new proposed method for assessing intrinsic groundwater vulnerability

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Abstract

A novel index-based method (RIVA) for the assessment of intrinsic groundwater vulnerability is proposed, based on the successful concept of the European approach (Zwahlen 2003) and by incorporating additional elements that provide more realistic and representative results. Its concept includes four main factors: accounting for the recharge to the system (R), the infiltration conditions (I), the protection offered by the vadose zone (V), and the aquifer characteristics (A). Several sub-factors and parameters are involved in calculation of the final intrinsic vulnerability index. However, even though RIVA is a comprehensive method that produces reliable results, it is not data intensive, does not require advanced skills in data preparation and processing, and may safely be applied regardless of aquifer type, prevalent porosity, geometric and geo-tectonic setup, and site-specific conditions. Its development has incorporated careful consideration of all key existing groundwater vulnerability methods and their critical aspects (factors, parameters, rating, etc.). It has studied and endorsed their virtues while avoiding or modifying factors and approaches that are either difficult to quantify, ambiguous to assess, or non-uniformly applicable to every hydrogeological setup. RIVA has been successfully demonstrated in the intensively cultivated area of Kopaida plain, Central Greece, which is characterized by a complex and heterogeneous geological background. Its validation was performed by a joint compilation of ground-truth monitoring-based data, in-depth knowledge of the geological structure, hydrogeological setup, regional hydrodynamic evolution mechanisms, and also by the dominant driving pressures. Results of the performed validation clearly demonstrated the validity of the proposed methodology to capture the spatially distributed zones of different vulnerability classes accurately and reliably, as these are shaped by the considered factors. RIVA method proved that it may be safely considered to be a fair trade-off between succeeded accuracy, and data intensity and investment to reach highly accurate results. As such, it is envisaged to become an efficient method of performing reliable groundwater vulnerability assessments of complex environments when neither resources occur nor time to generate intensive data is available, and ultimately be valorized for further risk assessment and decision-making processes related to groundwater resource management.

Keywords Groundwater, Intrinsic vulnerability, Index-overlay methods, Aquifer contamination, Kopaida plain

Introduction

Groundwater resources are widely used in the national economies for various key purposes: domestic water

supply, industrial uses, irrigation, medicinal uses (balneotherapy), and energy applications (low and high enthalpy geothermal energy). Hence, considering that groundwater is the only source of water supply for some countries (Denmark, Malta, Saudi Arabia, etc.) or the dominant for others, their quantitative sufficiency and good quality status is of paramount importance in order to secure the environmental sustainability and socio-economic prosperity. Nevertheless, groundwater systems are subject to variable factors that deteriorate or tend to deteriorate their quality characteristics. Those factors could be both geogenic and anthropogenic; the latter are

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mainly related to agricultural practices, industrial activities, urbanization, landfills, domestic effluents, and aquifer over-exploitation (Appelo and Postma 2005). Another critical aspect related to groundwater management is that once contaminated, groundwater is difficult to be managed (Travis and Doty 1990), while environmental monitoring projects which are meant to provide critical feedback of ground-truth values for groundwater quality, are not always feasible, due to lack of personnel, funding, and time.

In this respect, scientists and decision makers seek for alternative strategic tools to spatially identify threats, and subsequently to design and implement groundwater protection measures towards sustainable groundwater management. To this goal, Margat (1968) envisaged and introduced the concept of groundwater vulnerability to contamination, as an approach for assessing and spatially delineating the potential susceptibility of aquifer systems to surface contamination. The task of assessing groundwater vulnerability is essentially equivalent to predicting contaminant concentrations within the groundwater body or at the groundwater receptors (Wachniew et al. 2016). Assessment of groundwater vulnerability is a cost-effective, yet robust proactive tool, despite the criticism received for the subjectivity of the different methods used and the limited factors considered per case (Rupert 2001). Groundwater vulnerability constitutes a specific characteristic of the groundwater system which cannot be directly measured (Machiwal et al. 2018). Instead, groundwater vulnerability indicators are defined, quantified, and mapped to reflect the actual or to predict the potential severity of human-induced deterioration in groundwater quality (Wachniew et al. 2016).

The overall concept of groundwater vulnerability assumes that the physical environment may provide some degree of protection to groundwater against contamination; hence, some areas are more susceptible than others due to the intrinsic system properties. Based on the definition proposed initially by Vrba and Zaporozec (1994), groundwater vulnerability is distinguished into two separate parts: (a) the intrinsic vulnerability, which takes into account the inherent properties of the system (e.g., geological, hydrological, and hydrogeological characteristics) and (b) the specific vulnerability, which takes into account the properties of a particular contaminant or group of contaminants, in addition to the intrinsic vulnerability of the area. This research is focused on the intrinsic vulnerability; hence, the proposed method (RIVA) is independent of the properties of the contaminants and the contamination scenario. Visualization of groundwater vulnerability on a map shows various areas which have different levels of vulnerability. However, vulnerability maps only show relative vulnerability of certain areas to others, and do not represent absolute

values. Therefore, groundwater vulnerability is a relative and non-measurable, dimensionless property.

There are mainly three categories of techniques used in the compilation of vulnerability maps, viz., statistical techniques (e.g., Burkart et al. 1999; National Research Council 1993; Teso et al. 1996; Troiano et al. 1997; Erwin and Tesoriero 1997; Li et al. 2016), process-based simulation techniques (e.g., Jury and Ghodrati 1987; Piñeros Garcet et al. 2006; Rao et al. 1985; Tiktak et al. 2006; Sinkevich et al. 2005; Milnes 2011), and index-based techniques (e.g., Aller et al. 1987; Civita 1994; Antonakos and Lambrakis 2007; Daly et al. 2002; Doerfliger et al. 1999; Margane 2003; Pacheco et al. 2015; Goldscheider 2005). An overview of the abovementioned techniques is given in Zaporozec et al. (2002) and recently in Kumar et al. (2015). Index-based techniques have significant advantages over the others, as they are easy to use and resolve limitations regarding data availability and complex computational tasks. They focus on key factors controlling the potential contaminant transport, and they are relatively inexpensive, straightforward, and adaptable to on-site specific conditions (e.g., Guo et al. 2007; Lin et al. 2016); in addition, they have a minimum demand of data and produce outcomes which may be directly embraced into the decision-making processes (Focazio et al. 2002). They usually include the aggregation of key vulnerability attributes to one vulnerability class (index). This process involves the various steps of selection, scaling (transforming attributes into dimensionless measures), rating, and weighting. The final groundwater vulnerability class is a mathematical aggregation of individual attributes across different measurement units, so that the final vulnerability output is dimensionless.

Due to their significant advantages and their ability to be easily used as strategic tools, the scientific community has shown an increasing interest on the index-based techniques; hence, variable methods have been developed, including DRASTIC (Aller et al. 1987), GOD (Foster 1987), AVI (Van Stempvoort et al. 1992), SINTACS (Civita 1994), GLA (Hörling et al. 1995), ISIS (Civita and De Regibus 1995), KARSTIC (Davis et al. 2002), DRISTPI (Jimenez-Madrid et al. 2013), PI (Goldscheider et al. 2000), EPIK (Doerfliger and Zwahlen 1997), SI (Ribeiro 2000), VULK (Jeannin et al. 2001), TIME-INPUT (Kralik 2001), COP (Vías et al. 2002), PaPRIKa (Kavouri et al. 2011), PRESK (Koutsis and Stournaras 2011), and global risk approach (Allouche et al. 2017). Most of these methods were principally focused on a specific aquifer medium (mainly karst) and only few, e.g., the DRASTIC method (e.g., Mimi et al. 2012) can be applied in both media (porous and karstic). This constitutes a critical drawback of these methods which questions their uniform efficiency and applicability. To this aim, the proposed RIVA method aims to bridge this gap of efficient dual media applicability. A detailed overview and comparison of the previously developed methods may be found in relevant literature

(e.g., Zaporozec et al. 2002; Zwahlen 2003; Kumar et al. 2015).

Make a step further, several of the initial methods have been evolved and/or additional components/tools have been added to optimize the results. Thereby, groundwater vulnerability assessment was performed by the modification of the initial methods, e.g., DRASTIC (Denny et al. 2007), PI (Tziritis and Lombardo 2017), SINTACS (Busico et al. 2017), by using K-means cluster analysis (Javadi et al. 2017), by integrating the results from different methods with risk assessment (Shrestha et al. 2017), by coupling intrinsic vulnerability with numerical modelling (Yu et al. 2010; Sophocleous and Ma 1998; Connell and Van Den Daele 2003), by coupling vulnerability with hazard and risk intensity (Sullivan and Gao 2017), and by applying state-of-the-art techniques of artificial intelligence (Rodriguez-Galiano et al. 2014; Barzegar et al. 2018). However, the more complex the approach is, the hardest it is to be applied by personnel of limited skills in computation or advanced modeling; in addition, the applied vulnerability methods should secure the reliability of the results, and if possible, be successfully applicable in different conditions (e.g., aquifer media).

Towards this approach, we propose a novel index-based method (RIVA) for the assessment of intrinsic groundwater vulnerability. RIVA is designed to provide a qualitative, yet accurate approach. It does not require advanced skills in data preparation and processing and is envisaged to be applied regardless of aquifer type, prevalent porosity, geometric and geotectonic setup, and site-specific conditions. Its development has incorporated all the successful critical aspects (factors, parameters, rating, etc.) of the previously developed methods and attempts to tackle with their identified drawbacks or flaws. Furthermore, RIVA includes additional sub-factors and parameters to assess the influencing process (e.g., recharge, infiltration) in a more detailed and accurate way, and finally provide representative and reliable results. Therefore, the aim of the present paper is to introduce, apply, and evaluate the effectiveness of a novel methodological approach for intrinsic groundwater vulnerability assessment and deliver a robust tool for further risk assessment and decision-making processes related to groundwater resource management.

Description of RIVA method

The RIVA method (R-recharge, I-infiltration, V-vadose zone, A-aquifer system) constitutes a novel approach for the assessment of intrinsic groundwater vulnerability. It is based on the concept of the European approach (Zwahlen 2003); however, it incorporates additional elements that provide more realistic and representative results. RIVA can be applied independently of area specifics, and regardless of the targeted aquifer media; hence, it can be successfully applied to assess the

vulnerability of karstic, porous, and hard fissured aquifers. This is a significant advantage compared to the previous methods, as direct comparisons between different aquifer media are now feasible and may provide reliable and robust results, through a unified assessment procedure. The RIVA method considers 4 main factors which have independent impact to groundwater vulnerability (Fig. 1) as the potential contaminant is flushed by the precipitation recharge and travels through vadose media to the saturated zone:

- a) The total recharge (R factor)
- b) The conditions of infiltration (I factor)
- c) The protection of the vadose zone (V factor)
- d) The hydrogeological setting of the uppermost aquifer system (A factor)

The four selected main factors of RIVA method encompass all critical aspects and processes related to the intrinsic vulnerability of the aquifer system, from recharge to the saturated zone. Their selection has been carefully designed to include all significant parameters addressed by the previous methods, following the classic origin-pathway-target model of the European approach (Zwahlen 2003).

Each of the 4 factors affects groundwater vulnerability individually and independently of the potential interactions between them. The final assessment of each factor is related to 5 classes of vulnerability (Fig. 1), from very low (VL) to very high (VH), respectively. The aggregation of the individual results constitutes the final assessment of groundwater vulnerability, as their cumulative impact (Eq. 1).

$$i = R + I + V + A \tag{1}$$

where

- i* the final value of intrinsic groundwater vulnerability
- R the value of recharge factor
- I the value of infiltration factor
- V the value of vadose zone factors
- A the value of aquifer factor

The results for the intrinsic vulnerability (*i*) of groundwater according to RIVA method are calculated by the classification shown in Table 1.

The factors do not contribute equally to the final equation (Eq. 1), but each one is multiplied by a weighting factor (*a*, *b*, *c*, *d*) which reflects its significance to the result. The weighting factors ($a + b + c + d = 1$) were calculated with the use of analytical hierarchy process (AHP) (Saaty 1970), based on expert judgment and literature (e.g., United States Department of Agriculture 1986; Norris 1993; Civita and De Maio 1997; Goldscheider et al. 2000; Petelet-Giraud et al. 2000; Vías et al. 2002; Andreo et al. 2006; Lewis et al. 2006;

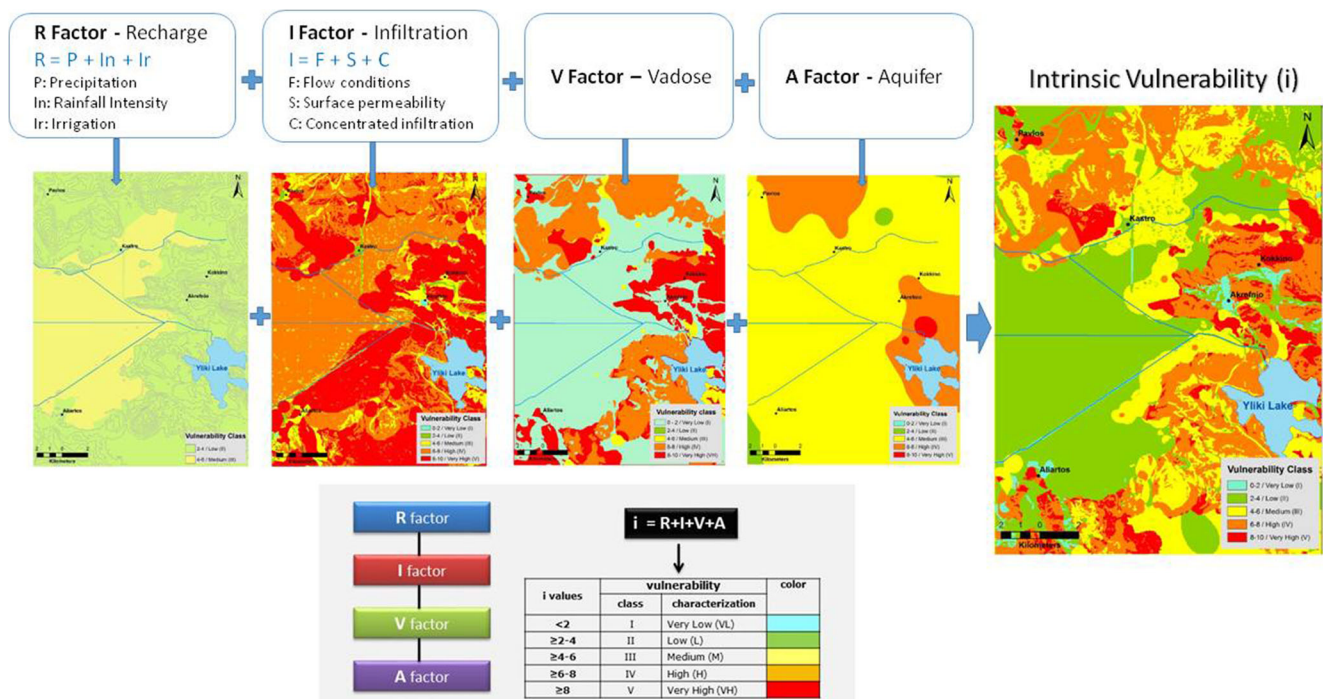


Fig. 1 Schematic presentation of RIVA method

Vías et al. 2006; Ravbar and Goldscheider 2007; Ravbar and Goldscheider 2009; Owor et al. 2009; Koutsi and Stournaras 2011; Mirus and Loague 2013; Pavlis and Cummins 2014;). Based on that, we formulated RIVA’s approach, in which the V factor is the most important with a weighting factor of $a = 0.40$, followed by the I factor with $b = 0.30$ and the R and A factors with equal weights $c = d = 0.15$. These weight factors are independent of the aquifer media (porous, karstic, and fractured) and they do not appear in the final equation (Eq. 1). They are incorporated in the intermediate steps for the calculation of the individual sub-factors and parameters (see below).

Accordingly, calculations of sub-factors and parameters follow a weighting system, in which the initial values of the five classes are 0, 2, 5, 7, and 10, corresponding to I, II, III, IV, and V vulnerability class, respectively. These values are multiplied each time by the weighting factors (0.4, 0.3, 0.15) to deliver the final (weighted) values of each sub-factor and/or factor. More details are described in individual sections.

Description and calculation of R factor

The R factor refers to the estimation of the overall recharge conditions; it considers all possible sources of recharge,

Table 1 Classification, characterization, and visualization of intrinsic vulnerability of groundwater (i values) and according to the calculated i and R, I, V, A factors’ values

<2	I	Very Low (VL)	Cyan
2-4	II	Low (L)	Green
>4-6	III	Medium (M)	Yellow
>6-8	IV	High (H)	Orange
>8-10	V	Very High (VH)	Red

including natural (e.g., precipitation) and man-induced (e.g., irrigation returns), which under conditions may reach the uppermost aquifer system through infiltration. The R factor does not constitute an internal (intrinsic) factor of the system (e.g., infiltration or vadose zone cover); however, it affects the system as an external critical condition because it regulates the available quantity of the transport media (water) of a potential contaminant (e.g., nitrates). It includes three sub-factors, which are linked through Eq. 2:

$$R = P + In + Ir \tag{2}$$

where

- R the recharge factor
- P the precipitation sub-factor
- In the rainfall intensity sub-factor
- Ir the irrigation recharge sub-factor

Each sub-factor contributes to Eq. 2 with a different weight; the weights were extracted with the use of AHP (Saaty 1970) with significant reliability (CR = 1%) and are embedded to the intermediate calculations of each factor as 0.5, 0.3, and 0.2 for P, Ir, and In, respectively. The aggregation of values of the above factors through Eq. 2 constitutes the result for R factor. Classification is shown on Table 1.

Description and calculation of P sub-factor

The P sub-factor refers to the total available quantity of water (mm), as a function of the annual median precipitation (mm/year); hence, it expresses the total amount of recharge water received naturally, which depending on the additional conditions (e.g., infiltration capacity) may potentially runoff in the (sub)surface and/or infiltrate vertically and reach the saturated zone (uppermost aquifer). The values of the P sub-factor are calculated according to Table 2, which is based on the initial conceptualization of Civita and De Maio (1997) and Vias et al. (2006), as well as the threshold values of precipitation addressed below.

The concept of classification and accordingly the attributed P values assumes that a potential increase in precipitation is

Table 2 Calculation of P sub-factor and correlation with the vulnerability class

P (mm/year)	P value *	Vulnerability class	Characterization
< 200 or > 1600	0	I	Very low (VL)
200–400 or 1400–1600	1	II	Low (L)
400–600 or 1200–1400	2.5	III	Medium (M)
600–800 or 1000–1200	3.5	IV	High (H)
800–1000	5	V	Very high (VH)

* Weighted with $w = 0.5$

not straightforward related to an increase in vulnerability, as similarly described in previous methods (e.g., Goldscheider et al. 2000). The followed approach considers that for small volumes of precipitation, vulnerability is reasonably low and progressively increases up to a specific limit of precipitation which maximizes its effect (e.g., 800–1000 mm/year); beyond this point, larger volumes of precipitation favor the process of dilution, hence groundwater vulnerability is progressively decreasing (Vias et al. 2006).

It should be noted that the overall recharge (volume of water finally leached to deeper vadose zone horizons) of an area depends on the actual evapotranspiration too. However, although critical, this parameter is intentionally omitted by the calculations of R factor. This is since calculation of ETo will increase the uncertainty, due to different results given by the application of different methods. In addition, it would require more detailed data to be applied (including time-series), and this could be a limiting factor for RIVA application. Instead, we chose to follow a more generic approach, based on the widely accepted fact that the initial water volume that reaches surface as precipitation or irrigation returns, is the dominant factor which controls recharge (available water volume) and could be regarded as a reliable factor for R estimation.

Finally, RIVA considers that P values lower than 200 mm/year or higher than 1600 mm/year have practically negligible impact to groundwater quality through actual aquifer recharge (for different reasons) and thereby do not affect vulnerability. Indeed, very low rates can hardly recharge an aquifer even if its depth is small (near surface). Most of the water volume received, increases soil moisture and does not reach the saturated zone or saturated zone receives minor quantities. On the contrary, very high recharge rates significantly favor dilution, and practically, the concentration of a potential contaminant will be of negligible importance in the saturated zone. Both cases are regarded as having the same minor impact in vulnerability, according to RIVA approach.

Description and calculation of In sub-factor

The recharge of an aquifer system is dependent, among others, on the intensity of the rainfall, which is reflected on the total quantity of water (mm) that an area receives in a certain time span. The exact impact of water intensity is difficult to be assessed, due to the complexity and the interactions of the engaged parameters (e.g., soil texture, rooting system, soil moisture, fissures of bedrock). However, it is widely accepted (Owor et al. 2009; Zuo et al. 2010; Pavlis and Cummins 2014) that in general, (i) an increase of rainfall intensity eventually increases the recharge of the system in case of karstic or fractured bedrocks, and oppositely, (ii) an increase in rainfall intensity (beyond a capacity threshold) eventually decreases the recharge, in case of porous media due to clogging of pores. Both processes are affecting groundwater vulnerability since

they impact on groundwater recharge. Theoretically, the In sub-factor is closely related to the infiltration conditions and could potentially be incorporated in I factor. Nevertheless, it does constitute an external stress to the overall system; hence, it was selected to be included in the R factor to highlight better the external conditions. Besides, this factor does account for the temporal unevenness of the precipitation, an event which as a factor is inherently related to the precipitation and the fraction of it that percolates to the saturated zone.

In respect to its calculation, the approach of RIVA method is a compilation of the approaches followed in other methods (Owor et al. 2009; Zuo et al. 2010; Pavlis and Cummins 2014). The In values are calculated through Eq. 3:

$$In = \Sigma P / \Sigma d \quad (3)$$

where

- In the value of rainfall intensity (In sub-factor)
 ΣP the total precipitation (mm) at a given time span (e.g., annually)
 Σd the total number of rainfall days in the same time span (e.g., annually)

Based on Eq. 3 results and depending on the type of substrate, the final In values are delivered through Table 3. The calculation process initially includes the spatial identification of the substrate into two categories: (a) karst or fissured/fractured solid formations (bedrock) and (b) primary porosity media, medium-heavy textured soils, organic soils, or in general formations of low permeability. Accordingly, following

the calculation of Eq. 3 and depending on its combination with Table 3, the final values of In are derived. The ranges of the classification were selected by compiling previous methods (Vías et al. 2006; Andreo et al. 2006; Ravbar and Goldscheider 2009); however, a finer classification (5 instead of 3 classes) was followed in order to achieve finer discrepancies and thus increased representativeness of the results.

It should be noted that the substrate formations of “b” category may yield only low to medium values of vulnerability, caused by rainfall intensity. This is reasonable considering that clogging effects in high-intensity rainfall events protect the system from the vertical movement of potential surface contaminants. In these cases, the surface runoff is the decisive factor of contaminant transport; however, this concept is not related to index-overlay approaches (just like RIVA method) and should be tackled with physically based approaches.

Description and calculation of Ir sub-factor

The Ir sub-factor accounts for the effect of irrigation in groundwater vulnerability. So far, irrigation effect has not been related to vulnerability as an individual factor. Few attempts made in previous methods incorporated the irrigation water volume to the total recharge (e.g., by summing it up with precipitation as total recharge). However, the estimation of exact irrigation recharge in catchment scale is difficult and includes several interacting parameters (e.g., crop type, soil moisture, agricultural practices including irrigation doses, available water quantity, efficiency of irrigation method, soil

Table 3 Calculation of In sub-factor values and correlation with the vulnerability class

In (mm/d)	In value ^{1*}	Vulnerability class ¹	Characterization	In value ^{2*}	Vulnerability class	Characterization
<5	0	I	Very Low (VL)	0	I	Very Low (VL)
5-10	0.4	II	Low (L)	0.4	II	Low (L)
>10-15	1	III	Medium (M)	1	III	Medium (M)
>15-20	1.4	IV	High (H)	0.4	II	Low (L)
>20	2	V	Very High (VH)	0	I	Very Low (VL)

* Weighted with $w = 0.2$

¹ Substrate: karst or fractured solid formations

² Substrate: primary porosity media, soil of medium or heavy soil texture (Al content), soil of high organic content, solid formations without significant fracturing or karstification, or in general formations of low permeability

wetting pattern of irrigation method, losses of irrigation network) which significantly increase uncertainty and finally jeopardize the reliability of the results. Nonetheless, acknowledging the importance of the irrigation effect in groundwater vulnerability, RIVA method has included the irrigation impact through a qualitative approach based on the general conditions of the applied irrigation doses, shown in Table 4. The benefit of this approach is that RIVA considers irrigation as a stand-alone sub-factor, without increasing the uncertainties that will be anticipated by e.g. a quantitative approach that would require accurate data and finer analysis. The term “suggested” irrigation dose accounts for the general rationale followed at catchment scale. If no specific information exists about deficient or excessive irrigation in an area, then, if the area is irrigated by default is classified to the “nominal irrigation” value, in order to incorporate the effect or irrigation recharge and distinguish this area from a non-irrigated land parcel.

Description and calculation of I factor

The I factor refers to the assessment of intrinsic vulnerability as a function of surface infiltration, which accordingly, affects deep percolation to the saturated zone. Its calculation is based on Eq. 4, and its classification is shown on Table 1.

$$I = F + S + C \tag{4}$$

where

- I the infiltration factor
- F the flow conditions sub-factor
- S the permeability of the Surface medium
- C the concentrated infiltration sub-factor

The F and S sub-factors have equal weights (0.5) of contribution to Eq. 4 (weighting is incorporated in the individual sub-factors calculations). On the contrary, the C sub-factor does not contribute equally; it is considered as a critical aspect (additional adverse condition), which if existing, may individually cause maximum vulnerability to groundwater (V class).

Table 5 Calculation of “s” values according to topographic slope and correlation with the vulnerability class

Topographic slope	Vulnerability class	s values
≤ 3°	V	10
> 3°–6°	IV	7
> 6°–12°	III	5
> 12°–25°	II	2
> 25°	I	0

Description and calculation of F sub-factor

The F sub-factor expresses the flow conditions of surface water (diffuse surface runoff) which in turn may increase infiltration to the saturated zone. Its calculation is dependent on two parameters, namely the topographic slope (s) and vegetation (v). The classification of “s” values was made according to the approaches of Petelet-Giraud et al. (2000), Koutsi and Stournaras (2011), and Mirus and Loague (2013) and is shown in Table 5.

The vegetation (v) parameter is used regulatory to slope; denser vegetation decreases diffuse surface runoff and vice versa. Vegetation is classified into three main groups: (a) forest vegetation (high vegetation), (b) cultivated and grassland areas (low vegetation), and (c) bare land or sparse vegetation. Classification into groups may be achieved by different methods (e.g., databases, references, macroscopic investigations). However, the authors suggest a generic and easy way of classification according to widely acceptable CORINE categorization (EEA 2020) shown in Table 6. Through this approach, only two categories of CORINE (which include vegetation) should be considered, namely category 2 (agricultural areas) and category 3 (forest and semi-natural areas); in all other cases (categories), the F sub-factor is considered zero.

The impact of “v” parameter was assessed according to the approach of Descroix et al. (2001), in which high vegetation areas may cause a decrease of surface runoff up to 88% and 44% for high and low vegetation areas, respectively. The final calculation of the F sub-factor values is performed through the compilation of “s” and “v” parameters, as shown in Table 7.

Table 4 Calculation of Ir sub-factor values and correlation with the vulnerability class

Irrigation dose	Ir values	Vulnerability class	Characterization
Non-irrigated areas or deficiently irrigated (lower than suggested)	0	I-II	Very low (VL)–low (L)
Nominal Irrigation (suggested**)	1	III	Medium (M)
excessive irrigation (greater than suggested)	3	IV–V	High (H)–very high (VH)

* Weighted with w = 0.3

** Suggested according to local agronomists or experts

Table 6 Classification of vegetation according to CORINE Nomenclature (EEA 2020)

Vegetation	CORINE category
Low vegetation	2.1 Arable land
	2.2 Permanent crops
	2.3 Pastures
	2.4 Heterogeneous agricultural areas
	3.2 Scrub and/or herbaceous vegetation associations
High vegetation	3.1 Forests
Bare land or sparse vegetation	3.3 Open spaces with little or no vegetation

Description and calculation of S sub-factor

The S sub-factor refers to the permeability of the surface formations which in turn may affect percolation to deeper horizons and groundwater vulnerability. RIVA regards as surface formations those occurring up to 1.5 m below surface (topsoil) and control surface/sub-surface flow; thus, affecting the potential percolation to deeper horizons of the vadose zone and subsequently aquifer recharge. The threshold of 1.5 m is indicative and could deviate depending on the case. However, the 1.5 m is a good approximation for a mean subsoil depth (O, A, and B horizons) and a mean depth of the active rooting system.

The surface formations are classified to (a) soils and (b) consolidated geological formations. In respect to soils, these include the upper soil horizons (topsoil and subsoil) which are developed over non-consolidated (non-lithified) geological formations (e.g., Quaternary). In respect to consolidated geological formations, RIVA method considers those who are lithified and constitute the underlying bedrock. RIVA assumes that the soil horizons that may have developed over the consolidated geological formations have negligible impact (e.g., due to their small thickness), since practically the underlying bedrock drives the flow conditions. It should be noted that RIVA incorporates the concept of permeability twice in its calculations. Even though it seems an overlap because

typically the considered upper 1.5 m zone (as defined by RIVA) are included in the vadose zone, their impact is assessed individually, acknowledging their paramount importance in the surface hydrological conditions. In addition, their concept is differentiated to RIVA approach; the S sub-factor considers the permeability at the surface controlling the surface vs sub-surface runoff, while the V factor (see below vadose zone parameter) considers the permeability below it and controls the sub-surface runoff vs aquifer recharge.

The calculation of the S sub-factor is achieved through the construction of the S map, which includes the compilation of the S values derived by soils and the consolidated geological formations. The S values of soils (Table 8) are based on their texture according to the relative classification of the US Department of Agriculture (United States Department of Agriculture 1999). The S values of the consolidated formations are based on their permeability (according to the classification of the British Geological Survey (Lewis et al. 2006)). Based on that, qualitative characterization of permeability is not always straightforward due to various factors (e.g., degree of fracturing, karstification, tectonic stress, intercalations) and a more generic assessment framework is suggested which is flexible and provides a range of values (Lewis et al. 2006), which in RIVA approach are directly related to vulnerability classes. The lower values correspond to solid (unaffected) formations, while the higher ones reflect the effect of the aforementioned factors that eventually increase their permeability and thus their vulnerability class. In this context, a basic classification is provided, but the final evaluation should be performed by coupling them with expert judgment, thus leading to a more realistic and representative approach (Table 9).

Description and calculation of C sub-factor

The C sub-factor refers to the spatially concentrated flow due to specific surface features which results to increased infiltration and thus maximum aquifer vulnerability. The C sub-factor derives from the relevant C map, which spatially delineates the zones characterized by increased infiltration potential around critical surface features. These may include (but are not limited to and may be expanded following in accordance

Table 7 Calculation of F values according to “s” and “v” parameters and link with vulnerability classes (I to V)

		Slope* (s)				
		≤ 3°	3°–6°	> 6°–12	> 12°–25°	> 25°
Vegetation (v)	High vegetation	5 (V)	5 (V)	5 (V)	3.5 (IV)	2.5 (III)
	Low vegetation	5 (V)	5 (V)	3.5 (IV)	2.5 (III)	1 (II)
	Bare land or sparse vegetation	5 (V)	3.5 (IV)	2.5 (III)	1 (II)	0 (I)

* Weighted with $w = 0.5$

Table 8 Calculation of S values for soils and correlation with the vulnerability class. The classification of soils is based on the relative nomenclature of the US Department of Agriculture (USDA 1999)

Soil type	Texture	Permeability	Vulnerability class	S value*
A1	Sand	Very high	V	5
A2	Loamy sand, sandy loam	High	IV	3.5
B	Silt loam, loam, silt	Medium	III	2,5
C	Sandy clay loam	Low	II	1
D	Clay loam, silty clay loam, sandy clay, silty clay, clay	Very low	I	0

* Weighted with $w = 0.5$

to expert judgment): (a) epikarst (C_k), (b) drainage pattern or surface reservoirs (e.g., lakes) which are documented to recharge aquifer (C_s), (c) sink holes, and (d) tectonic structures (C_t), e.g., faults, overthrusts, etc. Within the influence zone of the above features, infiltration is significantly favored, and a potential surface contaminant is regarded as totally by-passing vadose zone protection (worst-case scenario); thus, causing eventually very high (VH) vulnerability to aquifer. It is obvious that the exact delineation of the influence zones is not possible due to variable influencing factors (e.g., slope, vegetation, surface runoff, etc.) and would require modelling approaches which are out of scope within the framework of the qualitative concept of this method. Nevertheless, based on previous research efforts (Norris 1993; Goldscheider et al. 2000; Vias et al. 2002; Pavlis and Cummins 2014) and following an indicative framework, RIVA proposes to use an approximate influence zone of 100m around the aforementioned structures, in which is attributed a maximum score of

10 (VH vulnerability). However, this limit can be modified based on site-specific conditions and expert judgment; thus, clearly promoting a more flexible and objective evaluation. In case no such structures occur (therefore no influence zones), C value is by definition 0. Hence, C sub-factor constitutes an on-off (0–10) approach.

Description and calculation of V factor

The V factor refers to the protection provided by the vadose zone, depending on the permeability of its formations and their total thickness. As mentioned, it differentiates from the I factor, because it regards the part below 1.5 m from surface (practically below a typical topsoil horizon). In this context, V factor may include (a) the soil’s underlying non-lithified geological formations and/or strongly weathered (or mylonized) zones of bedrock, and (b) the bedrock (lithified geological

Table 9 Calculation of S values for consolidated geological formations and correlation with permeability and the vulnerability class. The classification is based on the relative nomenclature of the British Geological Survey (Lewis et al. 2006). The affecting factors (indicative

but not limited to) are (a) karstification, (b) fracturing (tectonic, hydrothermal dissolution, etc.), weathering, (c) intercalations with lower permeability horizons

Geological formation	Affecting ¹ factor	Intensity of affecting factor	Permeability	S value*	Vulnerability class
Limestone	a–b	(VL-L, M, H-VH)	(L, M, H)	(2.5, 3.5, 5)	(III, IV, V)
Sandstone	b	(VL-L, M, H-VH)	(L, M, H)	(1, 2.5, 3.5)	(II, III, IV)
Mudstone/shale	b	(VL-L-M, H-VH)	(L-M, H)	(0, 1)	(I, II)
Granite	b	(VL-L-M, H-VH)	(L-M, H)	(1, 2.5)	(II, III)
Gneiss	B	(VL-L-M, H-VH)	(L-M, H)	(1, 2.5)	(II, III)
Dolostone	a–b	(VL-L, M, H-VH)	(L, M, H)	(2.5, 3.5, 5)	(III, IV, V)
Schist	B	(VL-L-M, H-VH)	(L-M, H)	(1, 2.5)	(II, III)
Marble	a–b	(VL-L, M, H, VH)	(VL, L, M, H)	(1, 2.5, 3.5, 5)	(II, III, IV, V)
Basalt	b	(VL-L, M, H-VH)	(L, M, H)	(1, 2.5, 3.5)	(II, III, IV)
Ophiolite	b	(VL-L, M, H-VH)	(L, M, H)	(1, 2.5, 3.5)	(II, III, IV)
Marl	b	(VL-L-M, H-VH)	(L-M, H)	(1, 2.5)	(II, III)
All	c	(VL-L, M, H-VH)	(– 1, – 2, – 3) vulnerability classes from the initial		

¹ Indicative but not limited to (a) karstification, (b) fracturing (tectonic, hydrothermal dissolution, etc.), (c) intercalations with low permeability horizons
 VL very low, L low, M medium, H high, VH very high, L low, M medium, H high

* Weighted with $w = 0.5$

Table 10 Classification of layer reference (*ly*) values for representative geological formations (modified from: Bear 1972; Goldscheider et al. 2000; Vias et al. 2002, Lewis et al. 2006; Ravbar and Goldscheider 2007)

Layer reference value (<i>ly</i>)	Geological formation
5000	Claystone, siltstone, mudstone, shale, slate
1000	Marl, granite, gneiss, schist, basalt, ophiolite, flysch, sandstone, marble, quartzite
500	Alluvial deposits with high clayey content, marly limestones
100	Limestone, dolostone, conglomerates, breccias, turf and other organic rich formations, alluvial deposits with average (variable) clayey content, volcanic tuffs
10	Sand
1	Gravel, colluvium, debris, weathered zones, crust, mylonitized formations

formations). The characterization of V factor and its link to vulnerability class is shown on Table 1.

Calculation of the V factor is performed through the modification and compilation of previous approaches (Goldscheider 2002; Vias et al. 2002; Lewis et al. 2006; Ravbar and Goldscheider 2007), as follows: initially, each geological formation of the vadose zone is classified according to its dominant lithological type, prior to any secondary effects (e.g., karstification), and is attributed a “reference layer (*ly*) value” based on its permeability range, as shown on Table 10. It should be noted that Table 10 can be modified (by adding or adjusting formations) according to case study specifics, based on the proposed (1–5000) classification.

Accordingly, the “*ly*” values are multiplied by the fracturing or karstification factor (*f*), corresponding to an internal modification of the initial value “*ly*” due to secondary effects that impact permeability. The “*f*” factor derives from the assessment of the fracturing/karstification degree of the considered geological formation (only for the lithified) based on the values of Table 11.

The derived product (*ly* × *f*) will eventually be multiplied by the total thickness of the formation (*m*) in meters and will give the final value of the protective cover (*pc*), which

Table 11 Values of the “*f*” factor according to the assessed fracturing/karstification degree of the geological formations

Fracturing or karstification degree	<i>f</i>
Negligible/none/na*	1
Low	0.5
Medium	0.1
High	0.01

* Not applicable (e.g., in case of porous formations)

corresponds to a class of V factor (Table 12). It should be noted that in the case of relatively high water level aquifers (e.g., piezometric level depth at less than 1.5 m from surface), the V factor value is by default 10, leading to maximum vulnerability class (V). If more than one layer exists in the vertical dimension (e.g., alluvia and marbles) from surface to the saturated zone, then each formation is calculated individually as described, and then they are summed up to derive the final “*pc*” value (e.g., $pc = pc_1 + pc_2 + \dots + pc_n$).

Description and calculation of A factor

The A factor (aquifer) refers to the easiness with which a potential contaminant will travel within the saturated zone of an aquifer, as a function of its hydraulic conductivity. The concept of A factor refers to source, rather than resource vulnerability, according to the definitions provided by the European methodological approach (Zwahlen 2003). However, considering that the saturated zone constitutes an active part of the system, it has been incorporated by RIVA method in the assessment of intrinsic vulnerability, as an integral extension of the resource protection approach. The concept behind this is mainly attributed to the significant role of the contaminant transport process when a potential contaminant reaches the saturated zone, which clearly affects the overall vulnerability of the aquifer system. In this context, the resource vulnerability approach is not limited in the interface between saturated and unsaturated zone but includes the key hydrogeological characteristic of the aquifer which is the hydraulic conductivity. The values of A factor are calculated according to the hydraulic conductivity of the aquifer, as shown in Table 1.

The estimation of A factor values can be performed either through quantified (measured) values or through a qualitative (estimated) approach. In case of measured values, the link between hydraulic conductivity and class vulnerability (A factor values) is shown on Table 13, based on a modified generic, yet widely accepted, classification of conductivity according to Bear (1972).

Table 12 Protective cover (*pc*) values and corresponding vulnerability characterization and V factor values

<i>pc</i> value	V factor	Vulnerability class	Vulnerability characterization
< 250	10	I	Very high (VH)
250–1000	7	II	High (H)
1000–5000	5	III	Medium (M)
5000–15000	2	IV	Low (L)
> 15,000	0	V	Very low (VL)

Table 13 Main geological formations and suggested link between hydraulic conductivity and A values, corresponding to specific vulnerability classes

Hydraulic conductivity (cm/s)	A values	Vulnerability class
$< 10^{-7}$	0	I
$10^{-7} - 10^{-5}$	2	II
$> 10^{-5} - 10^{-3}$	5	III
$> 10^{-3} - 10^{-1}$	7	IV
$> 10^{-1}$	10	V

Alternatively, if no measured hydraulic conductivity values exist, the A factor values can be estimated by accepted classifications in the hydrogeological science (e.g., Schwartz and Zhang 2003) but always following the five-class approach of Table 13 or as indicatively shown in Table 9, which shows the permeability of main geological formations. Based on that, the vulnerability classes may be derived and subsequently correspond to specific A factor values (according to Table 1).

Application of RIVA method

Case study area description

Kopaida basin is a fertile plain area with intensive agricultural activities, considered among the most productive basins of Greece with profound financial significance due to its high product supply (mainly onions, potatoes, and carrots). It is located in Boeotia, central Greece, covering an area of approximately 2000 km², and constitutes the downstream-end part of the Viotikos Kifissos River (VKR) basin (Fig. 2), consisting of at least three sequential heterogeneous karstic aquifer systems (Pagounis et al. 1994). The eastern part of Kopaida basin (red-shaded in Fig. 2) has been chosen as the test site for the application of the proposed RIVA method. The importance of this part for the hydrogeological regime of the area is significant, as it includes nearly 80% of the boreholes situated in the entire Kopaida plain (Tziritis 2008). Additionally, Kopaida plain in its central parts is characterized by great thickness (> 500 m) of Quaternary deposits (Allen 1986); on the contrary, at the eastern part the alluvial thickness is significantly reduced and the underlying karstic aquifer systems are susceptible to contamination from surface sources (Tziritis 2010). The latter is enhanced by the great number of katavothraes and sinkholes which further increase the vulnerability potential of the aquifer system (Tziritis 2009).

In respect to the geological regime of the area (Pagounis et al. 1994), it includes at the bottom of the sequence Triassic to lower Jurassic limestones often containing intercalations of dolostones and dolomitic limestones; accordingly, it follows a

stratigraphic sequence of a tectonically driven metamorphic complex (melange) of schists which includes serpentized ophiolites in blocks and intercalations of limestones. Stratigraphy continues with a series of upper Jurassic bituminous limestones; at their top, it develops a paleo-karst surface filled by chemically weathered material of the surrounding ultrabasic formations (ophiolites) that has been progressively altered into an Fe–Ni-rich lateritic horizon; finally, the upper bedrock sequence is completed with a highly karstified Cretaceous limestone and the typical flysch. Post-Alpine formations have variable thickness and consist of recent fluvial, lacustrine, and terrestrial deposits.

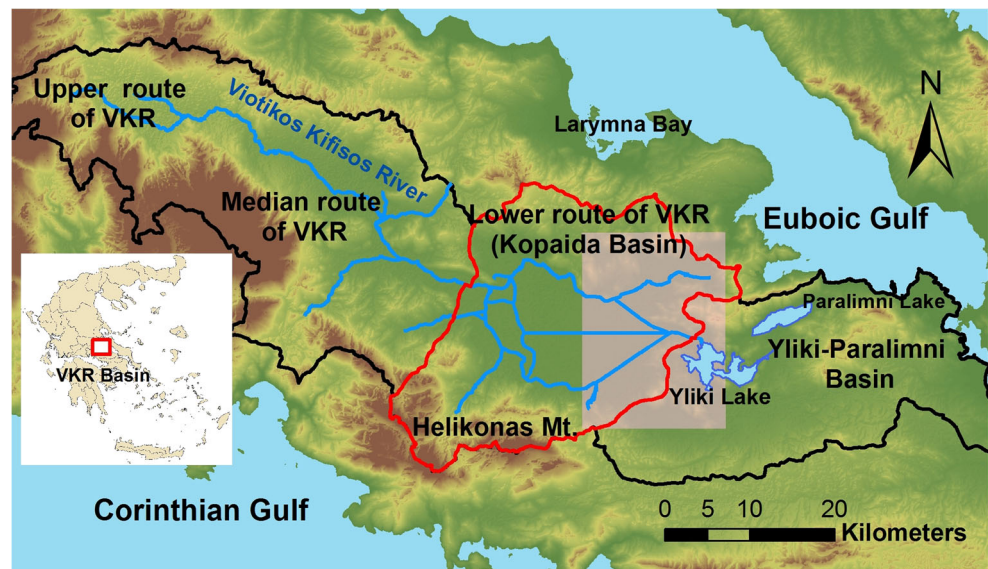
The hydrogeological regime is controlled by the karstic network which drives the general groundwater flow from west to east; water depth from surface varies locally from a few meters to 150 m, depending on substrate permeability (Tziritis 2008). The main aquifer bodies in terms of water storage and yield are developed within the variable karstic formations but are often interconnected and may be considered as a unified heterogeneous system. Based on previously recorded data (Pagounis et al. 1994; Tziritis 2008), hydraulic conductivity (K) in productive aquifers ranges between 10⁻¹ and 10⁻⁴ cm/s and specific storage (S) between 0.08 and 0.039. Discharge rates (Q) range from 50 to 120 m³/h and reach up to 170 m³/h for most of the productive boreholes. Pumped volumes are used mainly for irrigation (about 90–95%) and the remaining as drinking water reserved for local communities.

Calculation of R factor

The calculation of the abovementioned factor, sub-factors, and parameters was performed by the described equations and tables, based on variable sources and datasets (described above). The calculation of factor values and their spatial distribution was performed with the aid of ArcGIS 10.1 software. Ultimately, all data were transformed to raster grids (38 m × 38 m) which covered the entire case study area of eastern Kopaida plain. Specific details for the calculations are described below.

The meteorological data, accounting for a time period of 30 years (1967–1997), was obtained from the nearest meteorological station, located within the Kopaida plain (100 m above sea level). Based on that, the P value was calculated by the mean annual precipitation as 583 mm/year which according to Table 2 corresponds to P = 2.5 (vulnerability class III). The total days of precipitation were 91.8 corresponding (Eq. 3) to 6.4 mm/day and ln = 0.4 (Table 3, vulnerability class II). The calculation of the Ir sub-factor was performed with the aid of CORINE classification system and the input data from variable sources (personal contacts, macroscopic investigations, field works, statistical datasets, etc.). Accordingly, based on the above sources, local agronomists

Fig. 2 Geographical setting of Viotikos Kifissos River (VKR) basin and its lower route (Kopaïda basin). The red-shaded rectangle delineates the area where RIVA method has been applied



and data from the Government Gazette (Government Gazette 16/6631 1989) which defined the optimum irrigation doses for the cultivations of the area, the permanently irrigated land (CORINE sub-division 2.1.2) was characterized as “normally irrigated” and attributed a value of 1 for Ir (Table 4), which corresponds to vulnerability class III. Finally, based on Eq. 2, the R factor was calculated as function of R, In, and Ir. The derived values were classified to vulnerability classes II and III, and spatially distributed as shown in Fig. 3.

Calculation of I factor

The I factor was calculated as a function of F, S, and C sub-factors following Eq. 4. Its spatial distribution is shown in Fig. 4.

The F sub-factor was assessed through slope (s) and vegetation (v) parameters. The s parameter is derived from the digital elevation model (DEM) of the area, according to the classification of Table 5. The v parameter is derived from the classification of vegetation according to Table 6. In succeeding this, CORINE classification (EEA 2020) provided the generic land-use categories which were linked to the vegetation. Finally, according to their combination and Table 7, the derived F values were classified between vulnerability classes I and V. The calculation of the S sub-factor was performed in two stages. Initially, based on the local geological maps (1:50,000 scale), the formations were classified to consolidated and non-consolidated (lithified). In respect to the non-consolidated ones, two categories (Alluvial deposits and Neogene formations) were identified and further classified according to their uppermost soil horizon, based on previous soil studies (Theocharopoulos 1992). Three different soil texture classes were identified in the study area (A2, B, and C), and the corresponding S values (S_s) were assigned according

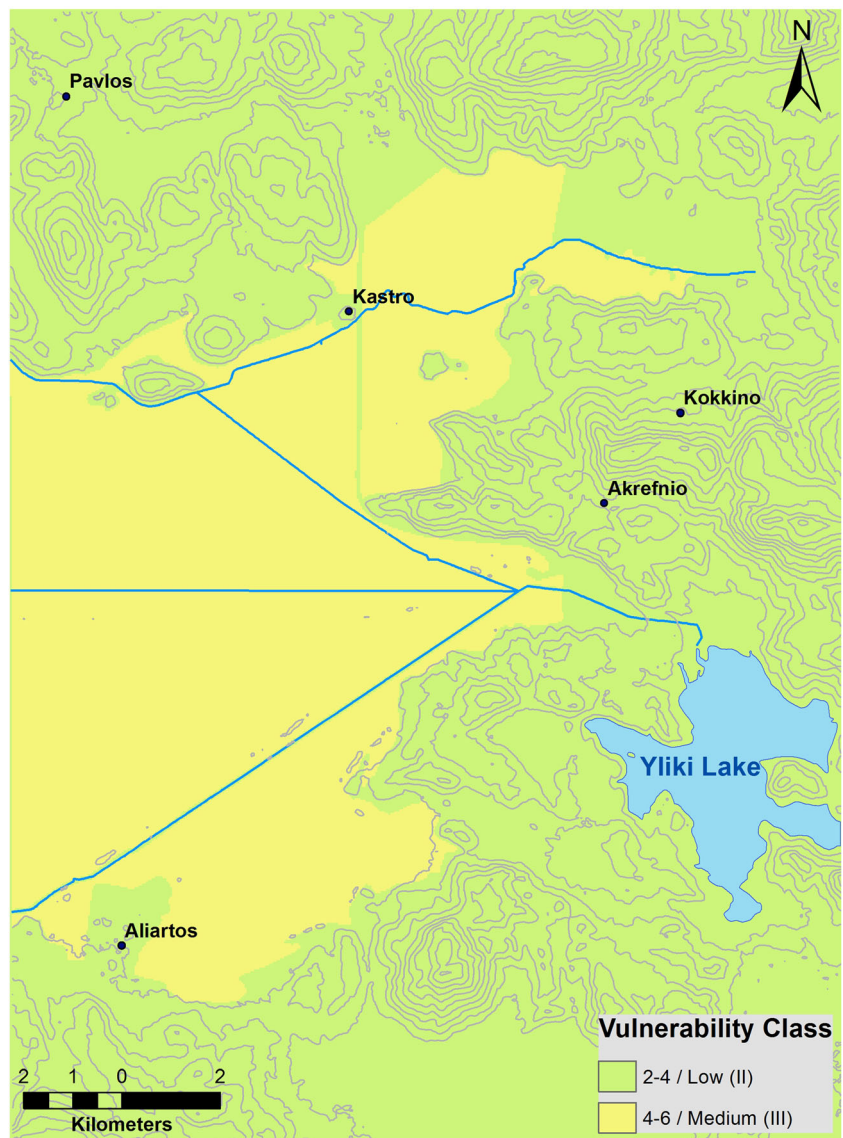
to Table 8. With regard to the consolidated formations, the S values (S_g) were calculated according to the hydrogeological classification based on available data from Pagounis et al. (1994) and Tziritis (2008). Five different geological formations were identified ranging from very low (Pyrites, Flysch (undivided)) to very high permeability (Cretaceous limestones). The compilation and spatial integration of S_s and S_g produced the final S map and the corresponding S values (Fig. 5).

The C sub-factor was calculated according to previous records of karstic (katavothraes) and tectonic features in the area (Papadopoulou and Gournellos 1993; Tziritis 2008). Each of the above features was attributed a buffer zone of impact (100 m) which is directly connected to very high (VH) vulnerability risk. The spatial delineation of C sub-factor is shown in Fig. 6.

Calculation of V factor

The V factor, accounting for the protection of the vadose zone, was calculated according to data obtained from (i) local geological maps (Hellenic Institute of Geology and Mineral Exploration, sheets Thiva, Vayia, Livanates Larimna, Elatia, Livadia in scale 1:50,000), (ii) 72 boreholes (Pagounis et al. 1994), and (iii) field work (Tziritis 2008) through the following procedure: initially, the thickness (m_s) of the non-lithified formations was calculated, based on borehole data and its spatial interpolation with IDW method. Each of the non-lithified formation was attributed a “ly” value according to the classification of Table 9; subsequently, m_s was multiplied by ly to calculate the pc_s values for subsoil. Consequently, the piezometric level (wl) was estimated based on borehole data. That was regarded as the level of the saturated zone. The thickness of the bedrock (lithified formations— m_b) was

Fig. 3 Spatial distribution of vulnerability classes according to the R factor in the study area



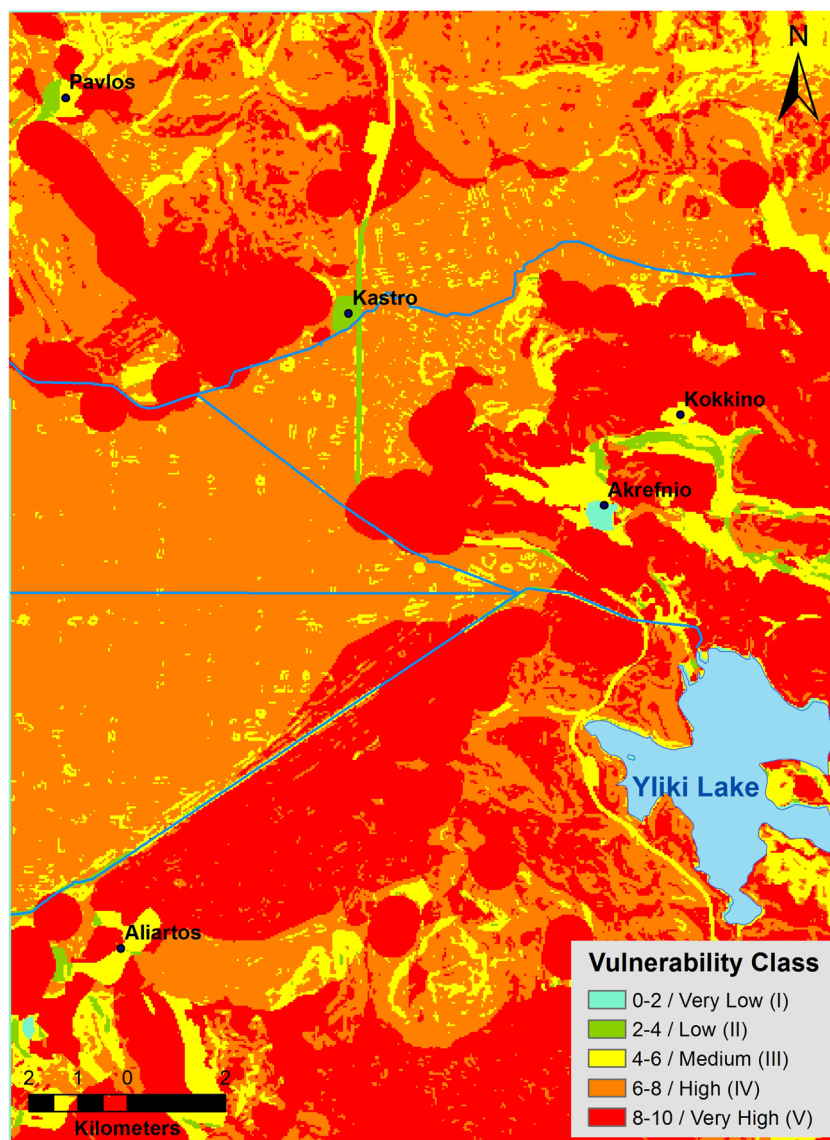
calculated by subtracting w_l from m_s . Then, each one of the lithified formations was attributed an “ l_y ” value according to Table 13. The l_y values have been multiplied by the karstification/fracturing degree (f) for each formation (if existing) according to Table 10. The pc_b value for the bedrock was then calculated by multiplying the bedrock thickness (m_b) by the product of l_y and f ($l_y \times f$). Accordingly, pc_s and pc_b values were added to extract the final pc value for the protective cover of the vadose zone. Finally, based on Table 12, the pc values were attributed to a vulnerability class/characterization, corresponding to a V factor value, the spatial distribution of which (V map) is illustrated in Fig. 7.

Calculation of A factor

The A factor values were calculated qualitatively, due to lack of sufficient ground-truth data (e.g., values of hydraulic

conductivity). To this aim, the following were used: (i) discharge rates from the 72 boreholes (m^3/h), (ii) data of hydraulic conductivity (m/s) for 5 boreholes, and (iii) empirical correlations of discharge rates–hydraulic conductivity from literature (Schwartz and Zhang 2003). Following this approach, each of the 72 boreholes was assigned a value for hydraulic conductivity, which according to Table 13, correlated to a vulnerability class and ultimately a value of A factor. Subsequently, the individual 72 values of the boreholes were spatially interpolated with IDW method, to distribute the A values at the entire area coverage. The specific interpolation method was carefully chosen as it presented the best results (minimum root mean square error (RMSE)) compared to other tested (e.g., kriging, natural neighbor, etc.). The ground-truth values of the 5 boreholes were used to validate the derived (simulated) results. The spatial distribution of A factor (A map) is shown at Fig. 8.

Fig. 4 Spatial distribution of vulnerability classes according to the I factor in the study area

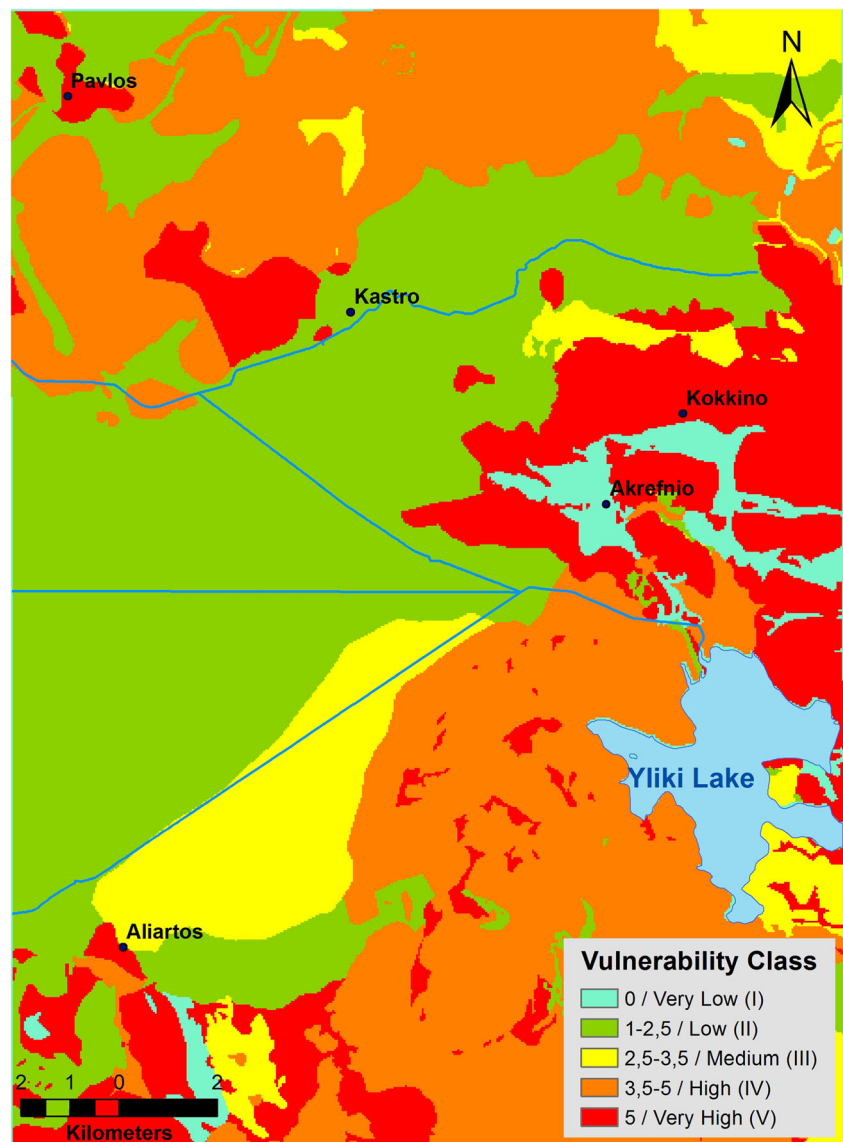


Calculation of groundwater intrinsic vulnerability (*i*)

Groundwater intrinsic vulnerability has been estimated according to the described RIVA approach. The final calculation of the individual factors (R, I, V, A) has been performed following a normal grid of 38 m × 38 m cells (total 271,450 cells), with the aid of Arc GIS 10 software. The intrinsic vulnerability (*i*) value of each cell is derived by summing up the individual scores of all factors for this specific cell, according to Eq. 1. Finally, each cell was attributed a vulnerability value and their combination produced the final intrinsic vulnerability map of Fig. 9. According to it, the plain parts of the area are characterized by low vulnerability (II), occupying 36.4% of the study area which is the highest percentage among other vulnerability classes. This is probably ought to the protection of the vadose zone, which in these areas is highly effective. On the contrary, the hilly and

mountainous areas show high (IV) and sometimes very high (V) vulnerability, probably reflecting the bedrock geology, which is mostly karst, occupying 26.9% and 7.2%, respectively. The boundaries of the plain areas appear to have medium vulnerability (III), which is reasonable because they contribute the transition zones of topography and geology, occupying 27.8% of the study area. The elevated vulnerability values are probably attributed to the decreased thickness of the protection cover (alluvium) and the outcrop of karstic features (katavothraes). It should be noted the linear and then curved area crossing Kastro town (N-S direction) is not an artifact and shows the motorway, which of course exhibits very low vulnerability values due to its proactively impermeable character. It should be noted that the areas of very low (I) vulnerability occupy a very low percentage (1.7%) of the study area, mainly attributed to the existence of low permeability bedrock (flysch, schists).

Fig. 5 Spatial distribution of vulnerability classes according to the S sub-factor in the study area



Validation of intrinsic vulnerability map

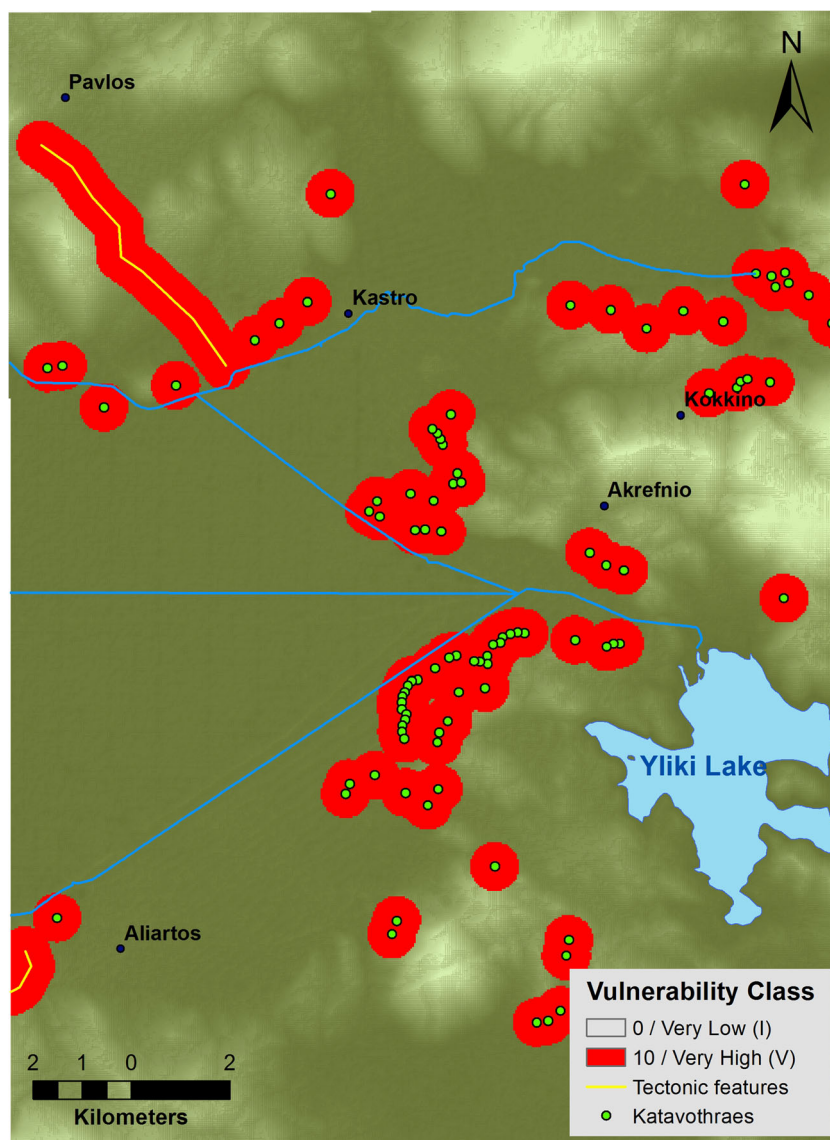
Validation of results is a critical and integral part of the entire modeling process for the soundness and the validity of outcomes and should be considered as an indispensable procedure in groundwater vulnerability assessment (Machiwal et al. 2018). Having in mind the initial vulnerability concept (susceptibility of groundwater to contamination due to a surface released contaminant), validation was performed by comparing the ground-truth values of nitrates with the modelled vulnerability, as defined by spatial distribution of the “*i* map” (Fig. 9). Nevertheless, this comparison is not always straightforward and should be performed with caution due to the following restrictions:

1 Vulnerability as concept has a vertical dimension. It assesses the susceptibility of a surface released

contaminant and its potential transport through a vertical axe, before reaching groundwater. This is practically not the case in nature, as horizontal dimension is frequently dominant.

2 The concentration of nitrates in groundwater is a dynamic process which is highly influenced by many factors including contamination sources (intensity, locality, other characteristics, etc.), hydrodynamic processes (e.g., flow paths, infiltration zones, recharge, lateral crossflows, interaction with other water bodies, etc.) and hydrogeochemical implications (e.g., redox conditions, biodegradation, etc.). Several of the processes and factors are not covered by this paper as they either refer to specific groundwater vulnerability, and/or relate to saturated zone hydrodynamics. In this context, nitrate values may change along their pathway, due to many factors which cannot be quantified by a vulnerability method.

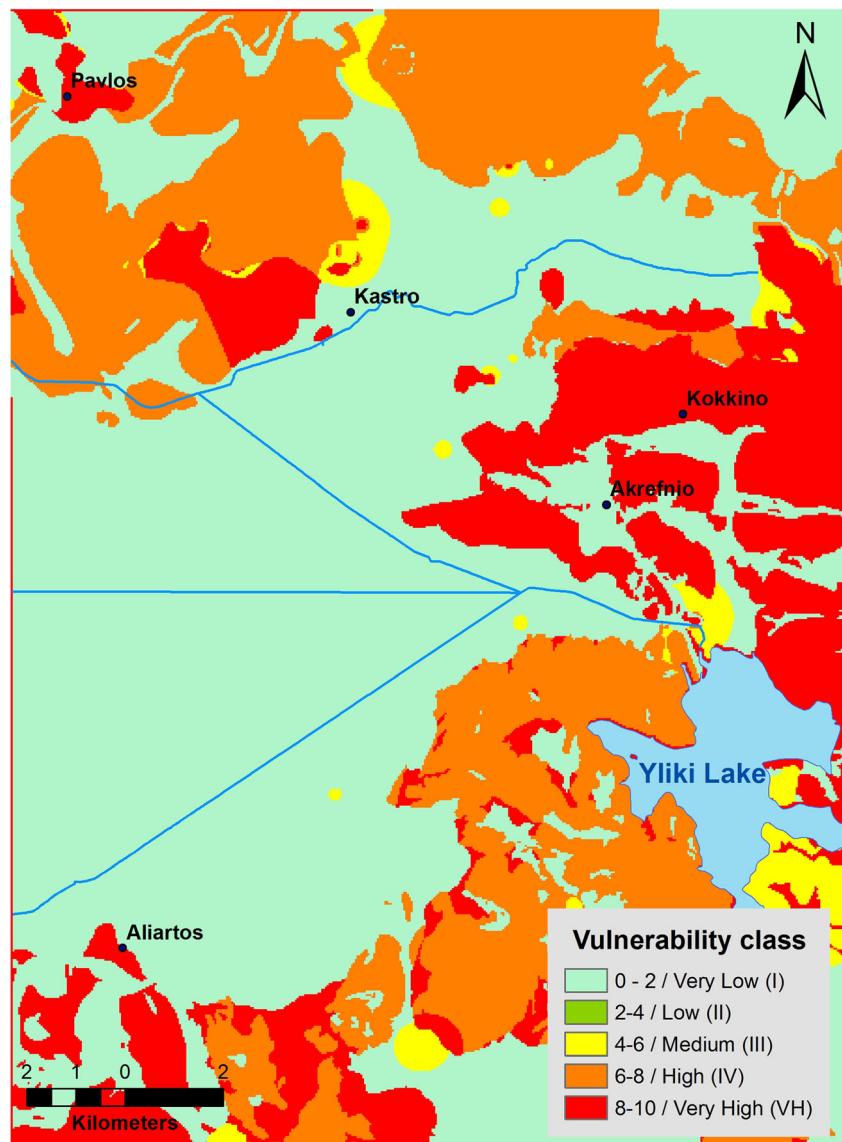
Fig. 6 Spatial distribution of vulnerability classes according to the C sub-factor in the study area



For the above reasons, nitrate concentrations distribution should be regarded with caution when considered for validation of vulnerability. Potential deviations between the derived vulnerability map and the ground-truth values, does not always mean failure of the assessment procedure or the soundness of the modelling process (intrinsic vulnerability assessment), but rather require a more in depth and joint consideration of the local conditions (geology, hydrogeology, hydrodynamics, hydrogeochemistry). In this context, the validation of vulnerability map was performed by having in mind the above considerations and by constructing the validation map of Fig. 10, which was subsequently compared to the *i* map (Fig. 9). The validation process was performed as described below:

- 1 Ground-truth values of nitrates (72 boreholes) were used to construct the spatial distribution of nitrates in the study area through interpolation technique (IDW method). At the compiled map, a nitrate concentration value was attributed to each cell of the grid.
- 2 The derived nitrate values were classified into ranges of nitrate concentrations as follows: < 10 mg/L very low (I), 10–20 mg/L low (II), 20–30 mg/L medium (III), 30–40 mg/L high (IV), > 40 mg/L very high (VH). The above classes by no means imply directly the environmental status of groundwater. They are used conventionally, as a relative measure of contamination, to facilitate the validation process. Their classification is based on a modified version of the classification used in the Nitrates Directive (91/676/EC), adjusted to provide a finer resolution in the lower concentrations.
- 3 Based on the above classification of nitrate concentration, a relevant map is constructed with the spatial distribution of nitrates contamination classes (I–V).

Fig. 7 Spatial distribution of vulnerability classes according to the V factor in the study area



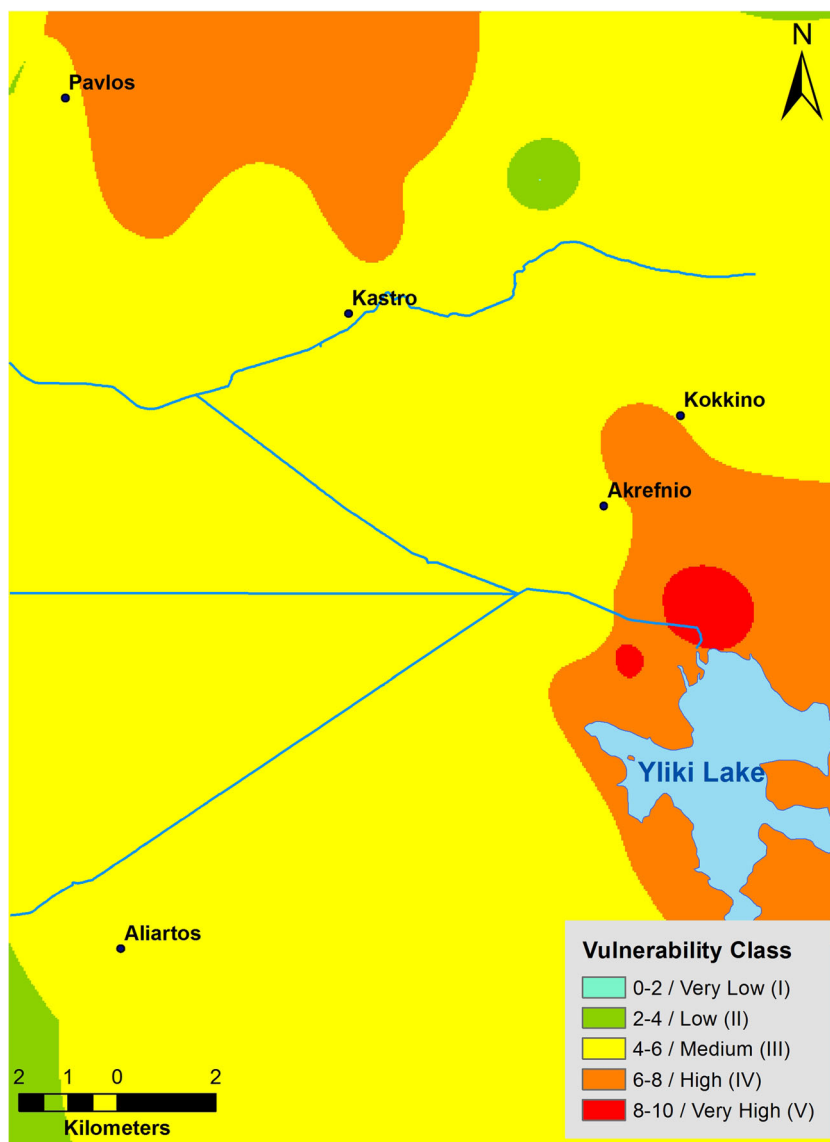
4 The above map (classified ground-truth nitrate values) is compared to the vulnerability map (*i* map, Fig. 9). The outcome is the validation map (Fig. 10) which shows the result of the subtraction (for each cell of the grid) of the classified ground-truth nitrates from the *i* map (modelled vulnerability).

Based on the validation map of Fig. 10, 38% of the study area exhibits a perfect match (same vulnerability class) between modelled and real values, while 87% exhibits very good match by a difference of one class (− 1, + 1). The latter is regarded as a rather satisfactory outcome which demonstrates successfully the reliability of the results. The analytical results of the validation are summarized in Table 14.

Analyzing further the results of, only 13% exhibits difference of more than two classes, thus showing inaccuracy to the

modelled vulnerability values. About 2.8% exhibits lower RIVA values than the monitoring-based ones, while 10.2% exhibits higher. The lower values (− 2, − 3) are mainly observed at specific parts of the plain area, as well as locally at hot spots. Regarding the parts of the plain area which exhibit deviation in vulnerability classes, these are well related to zones of lateral crossflows through which groundwater is being transported from adjacent hydrological units or even hydrological basins (Tziritis and Lombardo 2017). Therefore, nitrate contamination in these areas does not reflect the local vulnerability conditions (vertical concept), but the horizontally migrated contamination plume. Hence, deviations between modelled and monitoring-based values are well explained. Furthermore, local hotspots, which exhibit large monitoring-based values, are spatially correlated with point contamination sources (e.g., livestock farms) which have been identified in the area (Tziritis 2008). In these cases, preferential flow paths

Fig. 8 Spatial distribution of vulnerability classes according to the A factor in the study area



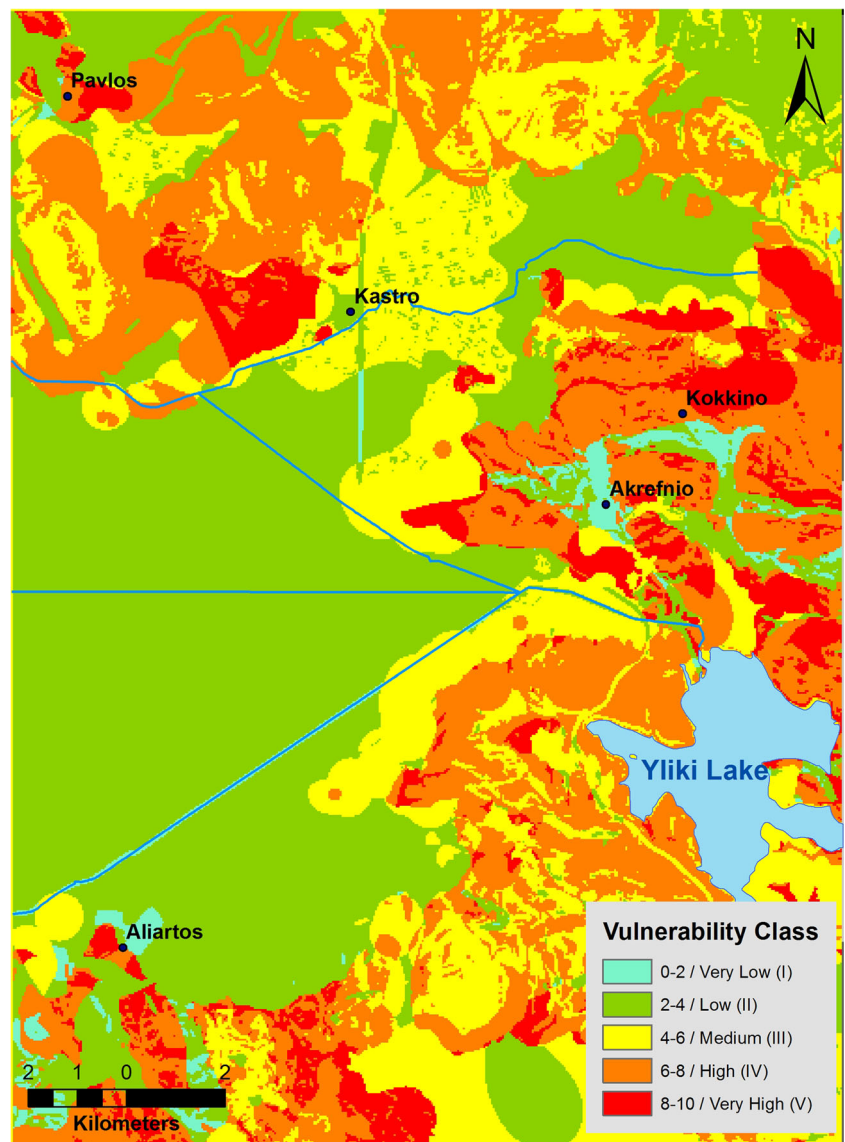
in smaller scale (plot scale) combined with the heterogeneous karstic bedrock and the larger scale that RIVA regards may possibly create difference in vulnerability classes. However, good knowledge of local conditions may provide sound explanations about them, without creating an ambiguity on the results. Regarding the areas of higher modelled compared to monitoring-based values (+ 2, + 3, + 4), these are mainly related to hilly/mountainous areas of elevated topography where no agricultural activities occur (and thus elevated nitrate concentrations and corresponding monitoring-based vulnerability values are not expected to occur). Nevertheless, the overall susceptibility of the system in these areas is probably elevated (e.g., high vulnerability) but cannot be justified by the selected ground-truth values. However, this assessment is rather important to identify the vulnerable areas, regardless of the existence of any contamination source at the time RIVA was

assessed. Finally, both positive and negative deviations between the modelled and monitoring-based values may occur due the heterogeneity of the aquifer system (different types of aquifer, different depths of sampling).

Discussion

RIVA can be utilized as a relatively quick overview methodology to assess the protection zoning of groundwater systems and assist land-use planning. Bearing in mind the lack of resources (financial, human, etc.) and the need for an initial estimation of groundwater susceptibility to contamination, it may serve as a rather reliable tool for decision makers, stakeholders, and scientists. More specifically, RIVA may significantly contribute to:

Fig. 9 Spatial distribution of vulnerability classes according to RIVA method



- Delineate protection zones for groundwater bodies and/or water abstraction points
- Support local, regional, and even national (wide scale) planning of rational groundwater resource management
- Prioritize areas of groundwater monitoring of special consideration
- Act as a global proxy for the evaluation of changes in groundwater risk assessment, over different periods
- Assess under a uniform context and approach intrinsic vulnerability of aquifers of different characteristics, at regions of diverse setups with regards to land and water use, on the basis of a minimum set of data that are normally readily available or may be easily deduced from standard geological knowledge

Nevertheless, it is important to note that intrinsic vulnerability maps are only one of the tools and considerations that

need to be accounted for when making the above assessments and decisions. The maps do not consider the potential hazards which are present at the land surface, and therefore do not present a complete assessment of the risk to groundwater contamination, which includes the vulnerability, hazard, and consequence of losing the resource. The intrinsic vulnerability maps are also not meant to replace site-specific investigations as they are compiled—mostly—at a regional scale. However, they do provide useful synoptic information for many purposes, including those listed above. As stated by Machiwal et al. (2018), all vulnerability assessments are subject to uncertainties. Therefore, uncertainties are inevitably incorporated into RIVA concept, ranging from inherent uncertainties induced by the representation and conceptualization of the whole system, to uncertainties related to errors in input data or spatial interpolation. Sensitivity analysis constitutes one of the most efficient techniques for the incorporation of

Fig. 10 Validation map of the RIVA method, showing the class difference between modeled and monitoring-based (real) values

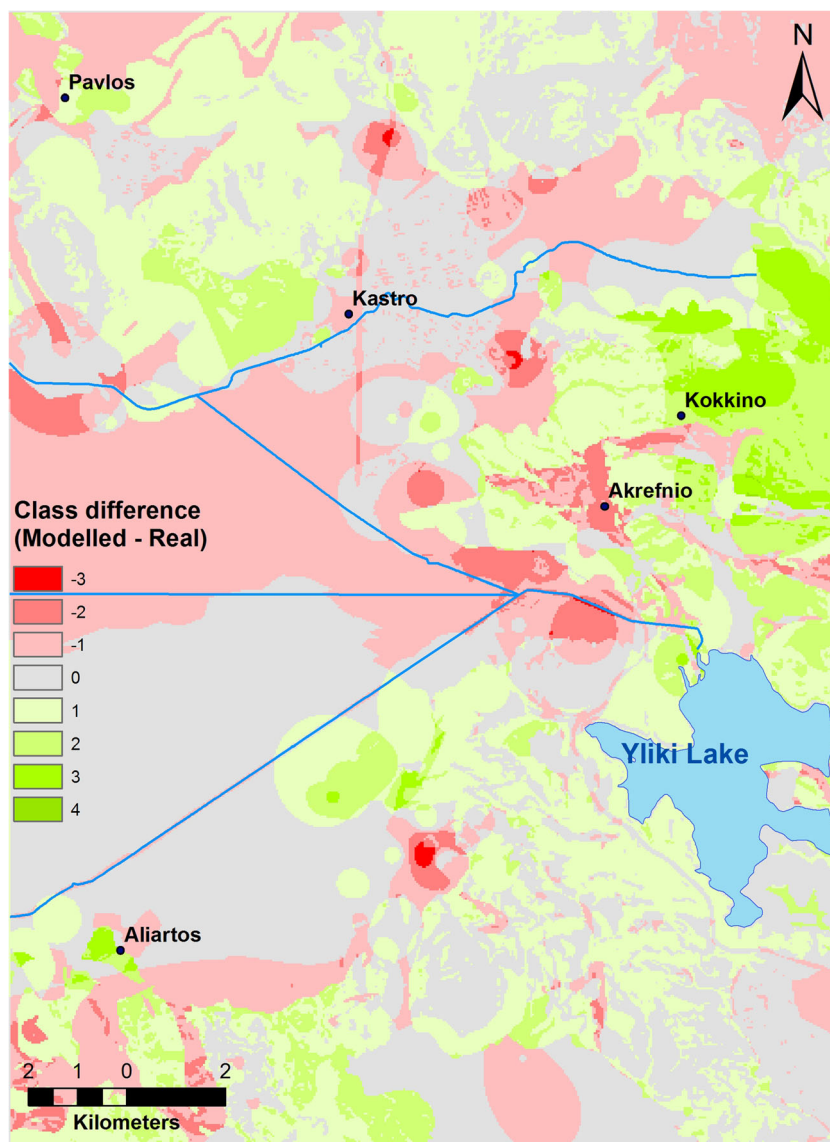


Table 14 Difference of vulnerability class between modelled and real values

Modelled ¹ —monitoring-based ² vulnerability class	Percentage (%)
-3	0.1
-2	2.7
-1	23.1
0	38
+1	25.9
+2	8
+3	2.1
+4	0.1

¹ Based on RIVA method

² Based on ground-truth values of NO₃ concentrations

uncertainty into vulnerability assessment studies (Machiwal et al. 2018).

An important potential application of RIVA concept could apply in the designation and delineation of nitrate vulnerable zones (NVZs), considered as a highly ranked environmental issue related to water resources in the European Union. In the context of the Nitrates Directive 91/676/EEC (Council of the European Communities 1991), NVZ delineation encompasses a multi-criteria analysis of several factors, among which the characterization of groundwater vulnerability is an essential one. One of the difficulties faced in the implementation of the EU environmental policies for nitrate pollution control is the lack of a consensus on the criteria for designating the NVZs (Pisciotta et al. 2015), which in turn may limit the success of APs in poorly defined vulnerable areas (Arauzo and Martínez– Bastida 2015; Worrall et al. 2009). In this regard, it is clear that additional work is required to improve

accuracy in NVZ designation and the efficiency of APs. To this end, RIVA method may be proved an efficient and robust global tool for the preliminary characterization of areas susceptible to surface contaminants (like nitrates) and could serve as basic method for directing and/or further focusing on more detailed investigations. This is rather important in countries like Greece, where the development financial model is strongly related to the agricultural sector and its activities, which in turn, if not rationally managed may cause adverse impacts to environmental sustainability of groundwater resources. As a result, it is imperative need to adopt common strategies and policies towards the integrated sustainable agriculture, as dictated by the new European Common Agricultural Policy (CAP).

As the method was presented and in accordance with what commonly applies to all relevant methodological approaches, the outcome is a spatially distributed index based on long-term or annual average values of considered parametric values. In this way, vulnerability assessment yields the spatial distribution of calculated indices averaged over the considered time span. Interestingly enough, it has been demonstrated in previous studies that vulnerability assessments on a narrow time scale may yield considerably different results. Seasonal variations of vulnerability after DRASTIC applied on part of the same region used for the validation of RIVA suggests that calculated differences may be significant and vary up to two classes (Panagopoulos et al. 2015). This in turn reveals the sensitivity of such methods in specific parameters that present considerable temporal variability. Such parameters are the annual precipitation, the depth to the saturated zone, the rainfall intensity, and the vegetation cover (at agricultural land where irrigated annual crops are cultivated and the considered timespan is winter). Obviously, each approach provides a different characterization, and both are equally correct but correspond to different viewpoints and therefore dominant purpose of use. In some occasions, the seasonal approach may lead to vulnerability indices that are comparable in values to the annually averaged values simply because differences cancel out (e.g., precipitation to depth to groundwater). However, as already mentioned, there are cases where considerable differences may be found in the seasonal compared to the mean annual approach, or even the long-term averaged approach. It is suggested that the mean annual approach is more suitable for strategic planning at regional scale, whereas the seasonal approach can pinpoint vulnerability issues that are critical for local or even regional scale risk assessment uses. Through the seasonal or even smaller time span approach, it is considered that one may detect the worst-case scenario in potential contamination of an aquifer system due to its high vulnerability over the given period. Therefore, based on

this approach, one may design special protection-management measures applicable under the given sensitive period.

Specifically, rainfall intensity in RIVA is considered an important external to the water system parameter in shaping up the final vulnerability index of a region. It is therefore easy to understand that the calculated intensity may vary considerably, and consequently so will vulnerability index, depending on the timespan selected to perform the calculations. The following example demonstrates the significance of the time scale selected to perform the vulnerability assessment exercise under the proposed method. For a specific region, the 30-year average, the 15-year average of the first and the second half of afore-considered period of time and the peak 2-day rainfall event, along with the corresponding wet days is given: 600 mm–39.8 days, 620 mm–55.1 days, 570 mm–21.3 days, 180 mm–2 days. Based on these figures, the rainfall intensity calculated after Eq. 3 is 15.790 mm/day, 11.990 mm/day, 21.390 mm/day, and 90 mm/day, respectively. It therefore follows that consideration should always be given when selecting the appropriate timescale over which parametric values of considered parameters are averaged. Of course, rainfall intensity is only one of the sub-factors that shape the final vulnerability index, and still, careless selection of reference time period may result to misleading calculations for each of the time-dependent sub-factors that altogether may have a cumulative effect.

In absence of detailed climate change forecasting modeling, seasonal values of the involved parameters may be providing a very rough approximation of the expected evolution of groundwater vulnerability under the changing conditions. By no means of course, this statement may suggest that climate change forecasts can be substituted or omitted in future planning of adaptation and mitigation measures, part of which is obviously the assessment of groundwater vulnerability.

Two interesting parameters, the effects of which are not considered in RIVA, are the snow cover and the water-holding capacity of the topsoil zone. The former one is considered of minor importance especially in the Mediterranean zone where the method has been developed; moreover, the exact mechanisms and effects expected are still not well studied. Consequently, although the authors acknowledge the potential importance of the mechanism, they have not incorporated it in the method as it is a data-intensive and ambiguous to quantify parameter, thus not within the scope and philosophy of RIVA. As for the second mentioned parameter, this is indeed an important one that however is being indirectly considered in the methodology for ease of application, in line with the philosophy that drove the development of RIVA. Hence, a more detailed address of the water-holding capacity would again require a data-intensive approach and the quantification of the parameter would probably had to shift the index-based method to one of the other two categories discussed in the

introduction of the paper, therefore again out of the scope of the developed method.

As with all index-based methods, subjectivity is a major concern and requires careful consideration and assessment of each parameter involved, following clear and uniformly applied rules. Special attention is required, among others, with regard to assessing the soil-related parameters. For example, terraced soils will have to be handled as low or zero slope soils, if terraces are well developed and maintained. Likewise, careful consideration is required when assessing the class to heavy textured soils, is the dominant percolation mechanism flow through the primary porosity, or for some reason deep cracks have developed rendering the particular soil equivalent to a fractured formation rather than a typical soil layer.

Conclusions

RIVA is a novel index-based method proposed for the assessment of intrinsic groundwater vulnerability. It is designed to provide a qualitative, yet accurate approach. Among its assets in comparison to other methods, it does not require advanced skills in data preparation and processing and is envisaged to be applied regardless of aquifer type, prevalent porosity type, geometric and geo-tectonic setup, and site-specific conditions. Its development has incorporated all the successful critical aspects (factors, parameters, rating, etc.) of the previously developed methods and attempts to tackle with their identified drawbacks or flaws. Furthermore, RIVA includes additional sub-factors and parameters to assess the influencing processes (e.g., recharge, infiltration, etc.) in a more detailed and accurate way, and finally provide representative and reliable results. It has been demonstrated that the proposed novel methodology is not only versatile and easy to apply but is also able to reliably reach vulnerability characterizations that are meaningful and trustworthy. Being based on well-defined parameters and sub-factors' classifications, the methodology is also believed to be largely repeatable, by either the same or different group of scientists, as the margin for erroneous assessments and classifications of the involved parameters is minimal. Intrinsic groundwater vulnerability assessments may thus be delivered through a robust tool for further risk assessment and decision-making processes related to groundwater resource management. Having in mind the afore discussed merit of the proposed method, it is possible to apply it globally employing numerous groups of scientists, either within a single territory or even transboundary, thus easily reaching uniformly assessed conditions, hence obtaining comparable results.

RIVA was tried on different hydrogeological setups to prove its versatility and reliability to implement regardless of the type of aquifer involved. Indeed, especially in

hydrogeological environments, the evolution of which are controlled by alpine tectonics, as is typically the case in the Mediterranean region; it is more often than never needed to assess the vulnerability of formations of various lithologies, tectonic status, and prevailing porosity. Hence, employing a methodology that by default is not applicable across all types of porosities and lithological setups render it problematic and call for characterization of different media using different methodologies. This by default leads to inability to produce comparable results.

As already discussed, and demonstrated, a key asset of the method is it does not require either large or sophisticated datasets to be reliably applied. As a result, it may produce characterizations that are reliable and accurate, being based on well-classified table of parametric values of considered parameters, which are easily selected correctly even without deep knowledge of the scientific background of groundwater vulnerability. This having been stated does not imply that no relevant scientific background is required at all, but only stresses the fact that no in-depth knowledge of each involved factor is required, at least as a primary approach.

Validation of the method is performed on the basis of real high-frequency spatio-temporal monitoring data, in-depth knowledge of the geological structure, hydrogeological setup and regional hydrodynamic evolution mechanisms, and also the driving pressures. Results of the performed validation clearly demonstrate the validity of the proposed methodology to accurately and reliably capture the spatially distributed zones of different vulnerability classes, as these are shaped by the considered factors. Despite the fact our methodology is index-based, it proves to yield results of high resolution that are meaningful, fully substantiated, and well-interpreted, even though the tested hydrogeological environment is characterized by a high degree of complexity in terms of geology, tectonics, hydrodynamics, and land and water use. Hence, it is thought that RIVA would be capable of accurately and reliably delineating vulnerability zones across any given exercise, regardless its complexity, provided minimal knowledge of the considered region is offered. Nonetheless, it should be stressed that this is a groundwater vulnerability assessment method and its validity and usage should be restrained to this scope. Hence, we do expect to receive highly accurate results in vulnerability assessment at regional scale, which is critical for strategic planning; However, detailed data demanding field work may not be skipped when passing from regional to local or even site-specific scale focusing on the resolution of critical issues such as the assessment of point source pollution potential or prevention of pollution.

Overall, RIVA is a brand new, reliable, easy to apply, and data-efficient method that can be accurately, reliably, and easily applied across any hydrogeological environment. Being the deliberation of careful consideration of all key existing groundwater vulnerability methods, it has studied and

endorsed their virtues while avoiding or modifying factors and approaches that are either difficult to quantify, ambiguous to assess, or non-uniformly applicable to every hydrogeological setup. RIVA may be safely considered to be a fair trade-off between succeeded accuracy and data intensity and investment to reach highly accurate results. As such, it may prove to become the key between performing and not performing a reliable groundwater vulnerability assessment of a complex environment when neither resources occur nor time to generate intensive data is available.

Author contributions E.T. conceived the methodological approach, developed the basic theory, and performed the assessments/validations. A.P., G.A., and V.P. verified and optimized the methodology, contributed to the discussion parts, and revised the text.

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Compliance with ethical standards

Ethical approval All authors declare that there is no ethical violation in this manuscript. Also, this manuscript does not contain data belonging to others.

Consent to participate All authors have confirmed that this has not been published elsewhere and is currently not considered to be published elsewhere.

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References

- Allen HD (1986) Late Quaternary of the Kopais basin, Greece: sedimentary and environmental history. Ph.D. thesis, University of Cambridge, p 282
- Aller L, Bennet T, et al (1987) DRASTIC: A standardized system for evaluating ground water pollution potential using hydrogeologic settings. National Water Well Association Dublin
- Allouche N, Maanan M, Gontara M, Rollo N, Jmal I, Bour IS (2017) A global risk approach to assessing groundwater vulnerability. *Environ Model Softw* 88:168–182. <https://doi.org/10.1016/j.envsoft.2016.11.023>
- Andreo B, Goldscheider N, Vadillo I, Vias JM, Neukum C, Sinreich M, Jimenez P, Brechenmacher J, Carrasco F, Hötzl H, Perles MJ, Zwahlen F (2006) Karst groundwater protection: First application of a Pan-European Approach to vulnerability, hazard and risk mapping in Sierra de Libar (Southern Spain). *Sci Total Environ* 357:54–73. <https://doi.org/10.1016/j.scitotenv.2005.05.019>
- Antonakos AK, Lambrakis NJ (2007) Development and testing of three hybrid methods for the assessment of aquifer vulnerability to nitrates, based on the drastic model, an example from NE Korinthia, Greece. *J Hydrol* 333:288–304. <https://doi.org/10.1016/j.jhydrol.2006.08.014>
- Appelo CAJ, Postma D (2005) *Geochemistry, groundwater and pollution*, 2nd edn. A.A. Balkema, Rotterdam
- Arauzo M, Martínez-Bastida JJ (2015) Environmental Factors Affecting Diffuse Nitrate Pollution in the Major Aquifers of Central Spain: Groundwater Vulnerability vs. Groundwater Pollution. *Environmental Earth Sciences* 1–16
- Barzegar R, Moghaddam AA, Deo R, Fijani E, Tziritis E (2018) Mapping groundwater contamination risk of multiple aquifers using multi-model ensemble of machine learning algorithms. *Sci Total Environ* 621:697–712. <https://doi.org/10.1016/j.scitotenv.2017.11.185>
- Bear J (1972) *Dynamics of Fluids in Porous Media*. Dover Publications
- Burkart MR, Kolpin DW, Jaquis RJ, Cole KJ (1999) Agrichemicals in ground water of the Midwestern USA: relations to soil characteristics. *J Environ Qual* 28(6):1908–1915
- Busico G, Kazakis N, Colombani N, Mastrocicco M, Voudouris K, Tadesco D (2017) A modified SINTACS method for groundwater vulnerability and pollution risk assessment in highly anthropized regions based on NO₃⁻ and SO₄²⁻ concentrations. *Sci Total Environ* 609:1512–1523. <https://doi.org/10.1016/j.scitotenv.2017.07.257>
- Civita MV (1994) *Le carte della vulnerabilità degli acquiferi all'inquinamento: teoria & pratica (Groundwater Vulnerability Maps to Contamination: Theory and Practice)*. Ed. Pitagora, Bologna, 325 pp
- Civita M, De Maio M (1997) SINTACS. Un sistema parametrico per la valutazione e la cartografia della vulnerabilità degli acquiferi all'inquinamento: Metodologia e automatizzazione [SINTACS]: a parametric system for the assessment and mapping of the groundwater vulnerability to contamination: methodology and automation]. Ed. Pitagora, Bologna, 191 pp
- Civita M, De Regibus C (1995) *Sperimentazione di alcune metodologie per la valutazione della vulnerabilità degli acquiferi (in Italian). Quaderni di Geologia Applicata*, Ed. Pitagora, Bologna, 3rd edn, pp 63–71
- Connell LD, Van Den Daele G (2003) A quantitative approach to aquifer vulnerability mapping. *J Hydrol* 276(1–4):71–88. [https://doi.org/10.1016/S0022-1694\(03\)00038-6](https://doi.org/10.1016/S0022-1694(03)00038-6)
- Council Directive 91/676/EEC of 12 December 1991 concerning the protection of waters against pollution caused by nitrates from agricultural sources
- Daly D, Dassargues A et al (2002) Main concepts of the “European approach” to karst- groundwater-vulnerability assessment and mapping. *Hydrogeol J* 10(2):340–345. <https://doi.org/10.1007/s10040-001-0185-1>
- Davis A, Long A, Wireman M (2002) KARSTIC: a sensitivity method for carbonate aquifers in karst terrain. *Environ Geol* 42:65–72. <https://doi.org/10.1007/s00254-002-0531-1>
- Denny SC, Allen DM, Journeay JM (2007) DRASTIC-Fm: a modified vulnerability mapping method for structurally controlled aquifers in the southern Gulf Islands, British Columbia, Canada. *Hydrogeol J* 15:483–493. <https://doi.org/10.1007/s10040-006-0102-8>
- Descroix L, Viramontes D, Vauclin M, Gonzalez Barrios JL, Esteves M (2001) Influence of soil surface features and vegetation on runoff and erosion in the Western Sierra Madre (Durango, Northwest Mexico). *Catena* 43(2):115–135. [https://doi.org/10.1016/S0341-8162\(00\)00124-7](https://doi.org/10.1016/S0341-8162(00)00124-7)
- Doerflinger N, and Zwahlen F (1997) *Practical guide: Groundwater vulnerability mapping in karstic regions (EPIK)*. Swiss Agency for the Environment, Forests and Landscape (SAEFL), Bern, p. 56
- Doerflinger N, Jeannin PY et al (1999) Water vulnerability assessment in karst environments: a new method of defining protection areas using a multi-attribute approach and GIS tools (EPIK method). *Environ Geol* 39(2):165–176

- European Environment Agency (2020) CORINE Land Cover, Methodology and Nomenclature, <https://www.eea.europa.eu/publications/COR0-landcover>. Accessed 2020
- Erwin ML, Tesoriero AJ (1997) Predicting ground-water vulnerability to nitrate in the Puget Sound Basin. USGS Fact Sheet 061-97:1–4. <https://doi.org/10.3133/fs06197>
- Focazio M, Reilly TE, Rupert MG, Helsel DR (2002) Assessing ground-water vulnerability to contamination: providing scientifically defensible information for decision makers. USGS Circ 1224
- Foster SSD (1987) Fundamental concepts in aquifer vulnerability, pollution risk and protection strategy. *Vulnerability Soil Groundw Pollut* 38:69–86
- Goldscheider N (2002) Hydrogeology and vulnerability of Karst systems – examples from the Northern Alps and Swabian Alb. *Schr. Angew. PhD thesis. Geol. Karlsruhe, Vol.68, p.236*
- Goldscheider N (2005) Karst groundwater vulnerability mapping: application of a new method in the Swabian Alb, Germany. *Hydrogeol J* 13(4):555–564. <https://doi.org/10.1007/s10040-003-0291-3>
- Goldscheider N, Klute M, Sturm S, Hötzl H (2000) The PI method: a GIS based approach to mapping groundwater vulnerability with special consideration of karst aquifers. *Z Angew Geol Band 46, Heft 3:157–166*
- Government Gazzete 16/6631 (1989) Definition of the upper and lower limits of the required water quantities for the rational use of water in irrigation
- Guo Q, Wang Y, Gao X, Ma T (2007) A new model (DRARCH) for assessing groundwater vulnerability to arsenic contamination at basin scale: a case study in Taiyuan basin, northern China. *Environ Geol* 52:923–932. <https://doi.org/10.1007/s00254-006-0534-4>
- Höiting B, Haertle T, Hohberger KH, Nachtigall KH, Villinger E, Weinzierl W, and Wrobel JP (1995) Konzept zur Ermittlung der Schutzfunktion der Grundwasserüberdeckung. *Geologisches Jahrbuch, Reihe C, Heft 63, Hannover*
- Javadi S, Hashemy SM, Mohammadi K, Howard KWF, Neshat A (2017) Classification of aquifer vulnerability using K-means cluster analysis. *J Hydrol* 549:27–37. <https://doi.org/10.1016/j.jhydrol.2017.03.060>
- Jeannin PY, Cornaton F, Zwahlen F, Perrochet P (2001) VULK: a tool for intrinsic vulnerability assessment and validation. 7th Conference on Limestone Hydrology and Fissured Media, Besançon 20-22 Sept. 2001, *Sci Tech Environ Mem. H. S., 13: 185-190*
- Jimenez-Madrid A, Carrasco F, Martinez C, Gogu RC (2013) DRISTPI, a new groundwater vulnerability mapping method for use in karstic and non-karstic aquifers. *Q J Eng Geol Hydrogeol* 46:245–255. <https://doi.org/10.1144/qjegh2012-038>
- Jury WA, Ghodrati M (1987) Overview of organic chemical environmental fate and transport modeling approaches. Reactions and movement of organic chemicals in soils. Proceedings of a Symposium of the Soil Science Society of America and the American Society of Agronomy. Soil Science Society of America, Atlanta, Georgia
- Kavouri K, Plagnes V, Tremoulet J, Dörfliger N, Reijbba F, Marchet P (2011) PaPRIKA: a method for estimating karst resource and source vulnerability—application to the Ouyse karst system (southwest France). *Hydrogeol J* 19(2):339–353
- Koutsis R, Stournaras G (2011) Groundwater vulnerability assessment in the Loussi polje area. *N Peloponessus:335–342*. https://doi.org/10.1007/978-3-642-24076-8_39
- Kralik M (2001) A strategy for protecting karst groundwater in Austria. Report BE-189, pp.99, Environmental Agency, Vienna
- Kumar P, Bansod BKS, Debnath SK, Thakur PK, Ghanshyam C (2015) Index-based groundwater vulnerability mapping models using hydrogeological settings: a critical evaluation. *Environ Impact Asses* 51:38–49. <https://doi.org/10.1016/j.eiar.2015.02.001>
- Lewis MA, Cheney CS, Ódochartaigh BÉ (2006) Guideline to permeability indices. British Geological Survey, Information products programme, open report CR/06/160N, p.29
- Li X, Philp J, Cremades R, Roberts A, He L, Li L, Yu Q (2016) Agricultural vulnerability over the Chinese Loess Plateau in response to climate change: Exposure, sensitivity, and adaptive capacity. *Ambio* 45(3):350–360
- Lin M, Ji D, Cui C, Sun Y, Su J, Xi B, Nixdorf E (2016) Groundwater Vulnerability Partition in Ashi River Basin. *Res Environ Sci* 29: 1773–1781
- Machiwal D, Jha MK, Singh VP, Mohan C (2018) Assessment and mapping of groundwater vulnerability to pollution: current status and challenges. *Earth Sci Rev* 185:901–927. <https://doi.org/10.1016/j.earscirev.2018.08.009>
- Margane A (2003) Guideline for groundwater vulnerability mapping and risk assessment for the susceptibility of groundwater resources to contamination. BGR and ACSAD, Damascus, 4, p. 177
- Margat TJ (1968) Vulnérabilité des nappes d'eau souterraine à la pollution. BRGM Publication, Orléans, France (68 SGL 198 HYD)
- Milnes E (2011) Process-based groundwater salinisation risk assessment methodology: Application to the Akrotiri aquifer (Southern Cyprus). *J Hydrol* 399:29–47. <https://doi.org/10.1016/j.jhydrol.2010.12.032>
- Mimi Z, Mahmoud N, Abu-Madi M (2012) A modified DRASTIC model for intrinsic vulnerability mapping for karst aquifers: A case study. *Environ Earth Sci* 66(2):447–456. <https://doi.org/10.1007/s12665-011-1252-0>
- Mirus BB, Loague K (2013) How runoff begins (and ends): characterizing hydrologic response at the catchment scale. *Water Resour Res* 49:1–20. <https://doi.org/10.1002/wrcr.20218>
- National Research Council (1993) Ground water vulnerability assessment: contamination potential under conditions of uncertainty. National Academy Press, Washington, DC
- Norris V (1993) The use of buffer zones to protect water quality: a review. *Water Resour Manag* 7:257–272. <https://doi.org/10.1007/BF00872284>
- Owor M, Taylor RG, Tindimugaya C, Mwesigwa D (2009) Rainfall intensity and groundwater recharge: empirical evidence from the Upper Nile Basin. *Environ Res Lett* 4(3):035009 (6pp. <https://doi.org/10.1088/1748-9326/4/3/035009>
- Pacheco FAL, Pires LMGR, Santos RMB, Sanches Fernandes LF (2015) Factor weighting in DRASTIC modeling. *Sci Total Environ* 505: 474–486. <https://doi.org/10.1016/j.scitotenv.2014.09.092>
- Pagounis M, Gkertzos T, Gkatzogiannis A (1994) Hydrogeological research of Viotikos Kifissos River basin. Technical report, Institute of Geological and Mineral Research (IGME), Greece, p 94 (in Greek)
- Panagopoulos A, Domakinis C, Arampatzis G, Charoulis A, Vrouhakis I, Panoras A (2015) Seasonal variations of aquifer intrinsic vulnerability in an intensively cultivated vulnerable basin in Greece, In: Innovative strategies and policies for soil conservation—advances in geocology, (Eds) Fullen, M., Famadimu, J., Karyotis, Th., Noulas, Ch., Panagopoulos, A., Rubio, J., Gabriels, D. *Catena* 44:118–134
- Papadopoulou K and Gournellos T (1993) Quantitative analysis of katavothraes at the ex-Lake Kopaida. Proceedings of 3rd Pan-Hellenic Geographic Conference, p.34-39 (in Greek)
- Pavlis M, Cummins E (2014) Assessing the vulnerability of groundwater to pollution in Ireland based on the COST-620 Pan-European approach. *J Environ Manag* 133:162–173. <https://doi.org/10.1016/j.jenvman.2013.11.044>
- Petelet-Giraud E, Dörfliger N, Crochet P (2000) RISKE: méthode d'évaluation multicritère de la cartographie de la vulnérabilité des aquifères karstiques. Application aux systèmes des Fontanilles et Cent-Fonts (Herault, Sud de la France). *Hydrogéologie* 4:71–88
- Piñeros Garcet JD, Ordoñez A et al (2006) Metamodeling: theory, concepts and application to nitrate leaching modelling. *Ecol Model* 193(3–4):629–644. <https://doi.org/10.1016/j.ecolmodel.2005.08.045>
- Pisciotta A, Cusimano G, Favara R (2015) Groundwater nitrate risk assessment using intrinsic vulnerability methods: A comparative study

- of environmental impact by intensive farming in the Mediterranean region of Sicily. Italy, *Journal of Geochemical Exploration* 156:89–100. <https://doi.org/10.1016/j.gexplo.2015.05.002>
- Rao PSC, Hornsby AG, et al (1985) Indices for ranking the potential for pesticide contamination in groundwater. *Proceedings of Soil Crop Science Society, Florida*
- Ravbar N, Goldscheider N (2007) Proposed methodology of vulnerability and contamination risk mapping for the protection of karst aquifers in Slovenia. *Acta Carsologica* 36(3):397–411. <https://doi.org/10.3986/ac.v36i3.174>
- Ravbar N, Goldscheider N (2009) Comparative application of four methods of groundwater vulnerability mapping in a Slovene karst catchment. *Hydrogeol J* 17(3):725–733. <https://doi.org/10.1007/s10040-008-0368-0>
- Ribeiro L (2000) SI: a new index of aquifer susceptibility to agricultural pollution. ERSHA/CVRM, Instituto Superior Técnico, Lisboa, Portugal
- Rodriguez-Galiano V, Mendes MP, Garcia-Soldado MJ, Chica-Olmo M, Ribeiro L (2014) Predictive modeling of groundwater nitrate pollution using random forest and multisource variables related to intrinsic and specific vulnerability: a case study in an agricultural setting (Southern Spain). *Sci Total Environ* 477:189–206. <https://doi.org/10.1016/j.scitotenv.2014.01.001>
- Rupert MG (2001) Calibration of the DRASTIC ground water vulnerability mapping method. *Groundwater* 39(4):625–630. <https://doi.org/10.1111/j.1745-6584.2001.tb02350.x>
- Saaty TL (1970) How to make a decision: the analytic hierarchy process. *Eur J Oper Res* 4:9–26. [https://doi.org/10.1016/0377-2217\(90\)90057-1](https://doi.org/10.1016/0377-2217(90)90057-1)
- Schwartz FW, Zhang H (2003) *Fundamentals of groundwater*. Wiley, New York
- Shrestha S, Kafle R, Pandey VP (2017) Evaluation of index-overlay methods for groundwater vulnerability and risk assessment in Kathmandu Valley, Nepal. *Sci Total Environ* 575:79–90. <https://doi.org/10.1016/j.scitotenv.2016.09.141>
- Sinkevich MG, Walter MT, Lembo AJ, Richards BK, Peranganing N, Aburime SA, Steenhuis TS (2005) A GIS-based ground water contamination risk assessment tool for pesticides. *Ground Water Monit R* 25:82–91
- Sophocleous M, Ma T (1998) A decision support model to assess vulnerability to salt water intrusion in the great bend prairie aquifer of Kansas. *Groundwater* 36:476–483. <https://doi.org/10.1111/j.1745-6584.1998.tb02819.x>
- Sullivan TP, Gao Y (2017) Development of a new P3 (probability, protection, and precipitation) method for vulnerability, hazard, and risk intensity index assessments in karst watersheds. *J Hydrol* 549:428–451. <https://doi.org/10.1016/j.jhydrol.2017.04.007>
- Teso RR, Poe MP et al (1996) Use of logistic regression and GIS modeling to predict groundwater vulnerability to pesticides. *J Environ Qual* 25(3):425–432. <https://doi.org/10.2134/jeq1996.00472425002500030007x>
- Theocharopoulos SP (1992) Soil survey report of Viotia district. Soil Science Institute. Scale 1:100,000. Acreage 141,974 Ha, (in Greek)
- Tiktak A, Boesten JJTI et al (2006) Mapping ground water vulnerability to pesticide leaching with a process-based metamodel of EuroPEARL. *J Environ Qual* 35(4):1213–1226. <https://doi.org/10.2134/jeq2005.0377>
- Travis CC, Doty CB (1990) Can contaminated aquifers at Superfund sites be remediated? *Environ Sci Technol* 24(10):1464–1466
- Troiano J, Nordmark C et al (1997) Profiling areas of ground water contamination by pesticides in California: phase ii—evaluation and modification of a statistical model. *Environ Monit Assess* 45(3):301–319. <https://doi.org/10.1023/A:1005778719859>
- Tziritis EP (2008) Hydrogeochemical—environmental study of eastern Kopaida—Yliki karstic system and assessment of vulnerability with the use of geoinformatics. 3333, National and Kapodistrian University of Athens, p 512
- Tziritis EP (2009) Groundwater and soil geochemistry of Eastern Kopaida region, (Beotia, central Greece). *Cent Eur J Geosci* 1(2): 219–226. <https://doi.org/10.2478/v10085-009-0011-x>
- Tziritis EP (2010) Assessment of NO₃-contamination in a karstic aquifer, with the use of geochemical data and spatial analysis. *Environ Earth Sci* 60(7):1381–1390. <https://doi.org/10.1007/s12665-009-0274-3>
- Tziritis EP, Lombardo L (2017) Estimation of intrinsic aquifer vulnerability with index-overlay and statistical methods: The case of eastern Kopaida, central Greece. *Appl Water Sci* 7:2215–2229. <https://doi.org/10.1007/s13201-016-0397-0>
- United States Department of Agriculture (1986) *Urban hydrology for small watersheds*. Technical Release 55 (TR-55) (Second Edition ed.). Natural Resources Conservation Service, Conservation Engineering Division
- United States Department of Agriculture (1999) *Soil Taxonomy A Basic System of Soil Classification for Making and Interpreting Soil Surveys*, 2nd edn. Agriculture Handbook, Number, p 436
- Van Stempvoort D, Ewert L and Wassenaar L (1992) AVI: a method for groundwater protection mapping in the Prairie Provinces of Canada. Regina, Saskatchewan: Prairie Provinces Water Board
- Vías JM, Andreo B, Perles MJ, Carrasco F, Vadillo I, Jiménez P (2002) Preliminary proposal of a method for vulnerability mapping in carbonate aquifers. In: Carrasco F, Durán JJ, Andreo B (eds) *Karst and Environment*. Patronato de la Cueva de Nerja, Málaga, pp 75–83
- Vías JM, Andreo B, Perles MJ, Carrasco F, Vadillo I, Jiménez P (2006) Proposed method for groundwater vulnerability mapping in carbonate (karstic) aquifers: the COP method. Application in two pilot sites in Southern Spain. *Hydrogeol J* 14(6):912–925. <https://doi.org/10.1007/s10040-006-0023-6>
- Vrba J, and Zaporozec A (1994) *Guidebook on mapping groundwater vulnerability*. IAH International Contributions to Hydrogeology, 16. FRG, Heise Verlag, Hannover
- Wachniew P, Zurek AJ, Stumpp C, Gemtzi A, Gargini A, Filippini M, Rozanski K, Meeks J, Kvaerner J, Witzczak S (2016) Toward operational methods for the assessment of intrinsic groundwater vulnerability: a review. *Crit Rev Environ Sci Technol* 46(9):827–884. <https://doi.org/10.1080/10643389.2016.1160816>
- Worrall F, Spencer E, Burt TP (2009) The effectiveness of nitrate vulnerable zones for limiting surface water nitrate concentrations. *J Hydrol* 370:21–28
- Yu C, Yao Y, Hayes G, Zhang B, Zheng C (2010) Quantitative assessment of groundwater vulnerability using index system and transport simulation, Huangshuihe catchment, China. *Sci Total Environ* 408(24):6108–6116. <https://doi.org/10.1016/j.scitotenv.2010.09.002>
- Zaporozec A, Aureli A, Conrad JE, Hirata R, Johansson P-O, Nonner JC, Romijn E, Weaver JMC (2002) *Groundwater Contamination Inventory: a methodological guide*. UNESCO IHP-VI Series Groundw 2:17–21
- Zwahlen F (ed) (2003) *Vulnerability and risk mapping for the protection of Carbonate (karst) Aquifers*. European Approach, COST Action 620, Final Report