CrossMark

A combined methodology to assess the intrinsic vulnerability of aquifers to pollution from agrochemicals

Vassilis G. Aschonitis[1] · Giuseppe Castaldelli[1] · Nicolò Colombani[2] · Micòl Mastrocicco[3]

Abstract The groundwater vulnerability indices are valuable tools for the development of agrochemicals management strategies based on environmental/agricultural policies. The groundwater vulnerability methods of LOS, SINTACS, DRASTIC, Pesticide DRASTIC, GOD and AVI were applied for the agricultural fields of Sarigkiol basin (Northern Greece). The results of the aforementioned methods were examined and discussed in order to show how the dissimilarities in the vulnerability assessment approaches may become an advantage. The results of the methods were used to propose a combined conceptual approach which adds another two dimensions (depth and time) in the current two-dimensional vulnerability mapping (longitude, latitude) procedures. The LOS method provided information about the intrinsic vulnerability of the topsoil (30 cm) to water (+conservative pollutants) and nitrogen losses, and the AVI method described the vulnerability of the unsaturated zone to allow pollutants to reach the aquifer while the aquifer vulnerability was analysed using SINTACS, DRASTIC, Pesticide DRASTIC and GOD. In this study, the results of the SINTACS method were found more accurate to describe the local aquifer conditions. The final conceptual approach provided a stratified vulnerability (dimension of depth) of the overall hydrogeologic system using LOS for the topsoil, AVI for unsaturated zone and SINTACS for the aquifer. The dimension of time was introduced by the LOS and AVI methods, which provide quantitative results in time. The use of LOS method also highlighted the basic limitation of the other methods to describe the potential contribution to pollution of areas (especially upland areas) which are out of the aquifer boundaries.

Keywords Vulnerability classifications · GIS · Groundwater · Nitrate · Non-point source pollution

✉ Nicolò Colombani
  nicolo.colombani@uniroma1.it

1 Department of Life Sciences and Biotechnology, University of Ferrara, Via L. Borsari 46, 44121 Ferrara, Italy

2 Department of Earth Sciences, "Sapienza" University of Rome, P.le A. Moro 5, 00185 Rome, Italy

3 Department of Environmental, Biological and Pharmaceutical Sciences and Technologies, Second University of Naples, Via Vivaldi 43, 81100 Caserta, Italy

Introduction

Groundwater as a source of water supply, ecological asset and geological agent is of great importance and has drawn a growing attention in order to meet the increasing demand of water resources due to fast demographic growth, accelerated urbanization, economic and agricultural activity diversification/intensification and increase of per capita consumption (Bouwer 1997; de Marsily 2003; Salemi et al. 2011; Winter et al. 2013). However, groundwater quality is affected by serious factors mostly associated to pollution due to human activities (Morris et al. 2003). Treatment of groundwater pollution is expensive and time consuming, so groundwater vulnerability assessment is a useful tool for building best management practices for groundwater pollution prevention. Groundwater vulnerability is classified into intrinsic vulnerability and specific vulnerability: the former is defined as the ease with which a contaminant introduced into the ground surface can reach and diffuse into groundwater taking into account the inherent geological, hydrological and hydrogeological characteristics

Springer

but being independent of the nature of contaminants; the latter is used to define the vulnerability of groundwater to particular contaminants (Gogu and Dassargues 2000). The use of nitrogen (N) fertilizers in agricultural fields represents one of the most important non-point sources of pollutants (Puckett et al. 2011; Tesoriero et al. 2013). Excess of N from agricultural soils is a function of the physico-chemical soil properties, topography, water supply from irrigation and precipitation, climate and agronomic practices and represents a serious threat for shallow aquifers due to the leaching of nitrates (NO_3^-) trough the unsaturated zone. A large part of farmed areas is affected by NO_3^- pollution since decades (Galloway et al. 2008) and alluvial plains are usually the most impacted zones by agricultural pollution and especially by NO_3^- contamination (Castaldelli et al. 2013; Mastrocicco et al. 2011; Voudouris 2006). Existing methods to assess groundwater vulnerability include the following: (i) process-based mathematical models dealing with the water movement and the transport and transformations of dissolved compounds through the soil profile, such as GLEAMS (Knisel and Davis 2000) and HYDRUS (Šimůnek et al. 2008); (ii) process-based models combined with GIS, such as NLEAP (Shaffer et al. 1991), NITS-SHETRAN (Birkinshaw and Ewen 2000), AgriFlux-IDRISI GIS (Lasserre et al. 1999), DAISY-MIKE SHE (Refsgaard et al. 1999) and GIS NIT-1 (De Paz et al. 2009), which are used to predict the spatial and temporal distribution of NO_3^- leaching and to assess NO_3^- contamination in groundwater at regional scale but are limited by the large number of data required to describe the groundwater properties; (iii) overlay indices methods based on ratings and weights, such as DRASTIC (Aller et al. 1987; Neshat et al. 2014), GOD (Foster 1987), AVI (Van Stempvoort et al. 1992), SINTACS (Civita and De Maio 1997), COP (Zwahlen 2003) and MERLIN (Aveline et al. 2009) that can be easily applied at regional scale via GIS because they require few and more accessible climatic, topographical, soil and geological data; (iv) probabilistic-stochastic methods (Neshat and Pradhan 2015a, b; Neshat et al. 2015) that recently have introduced analysis on the uncertainty in vulnerability and risk mapping and (v) combined methods, such as LOS indices (Aschonitis et al. 2012, 2013, 2014), which have been calibrated via regression analysis based on the results of the deterministic GLEAMS model. Some of the most popular vulnerability indices and their general characteristics are given in Table 1.

In view of the above-mentioned literature, there is still a need of easy to use (not requiring extensive model calibration) and flexible methodologies to assess the intrinsic vulnerability of groundwater resources. The aim of the study is to propose an integrated approach for vulnerability assessment combining indices of low data requirements which can describe separately the vulnerability of the topsoil, of the unsaturated zone and of the aquifer system. The separate analysis and combination of the three aforementioned compartments can provide a more robust and detailed description of the response of hydrogeological systems to pollution. This attempt aims to change the current perspective of the vulnerability maps from two-dimensional visualization (latitude, longitude) to four-dimensional by adding the dimensions of depth and time.

Study site

Sarigkiol basin (Western Macedonia, GR) covers an area of 469 km² characterized by a semi-arid Mediterranean climate. The mean annual temperature in the region is 11.3 °C while the monthly variation of precipitation presents a bimodal pattern (two peaks, one in autumn and one in spring) with a total annual value of 640 mm.

The min, max and mean altitude of the basin are 640, 1796 and 952 m a.s.l. (Fig. 1a) and the min, max and mean slope are 0, 116.5 and 18 %, respectively. The alluvial deposits in the centre of the basin host an unconfined aquifer superimposed on confined or semi-confined aquifers, covering an area of approximately 60 km². The depth of the water table ranges from 7 to 75 m b.g.l. Despite the documented heterogeneities, the aquifer can be considered uniform at the watershed scale (Voudouris 2006). The most important activities in the basin are lignite mining, agricultural exploitation of the lowland region and livestock-farming on the fringes of the mountains. The basin is covered by agricultural land (32.7 %), forests and semi natural areas (56.9 % km²) and urban or artificial surfaces (10.4 %) (Fig. 1b). Agricultural fields exhibit three main domains: non-irrigated arable land (9318.7 ha), permanently irrigated land (5207.0 ha) and pastures (804.9 ha) (Fig. 1c). Irrigation takes place mainly through private drillings and in some cases by pumping from the Soulou stream and the draining channels. The crop distribution is the following: 61.45 % hard wheat, 6.56 % soft wheat, 6.28 % barley, 9.89 % sugar beet, 8.96 % maize, 1.25 % potatoes, 0.38 % oat and 5.25 % pastures.

Methods

LOS method

The LOS approach (Aschonitis et al. 2012) is based on two different indices, LOSW-P and LOSN-PN, that estimate the annual water and N losses beneath the top 30 cm of the soil profile, respectively. The LOSW-P also describes the vulnerability of conservative pollutant losses. The methodology was calibrated for temperate climates using climatic data observed at four stations located in Sindos (Greece-Thessaloniki province), Mirabello (Italy-Emilia Romagna province), Allardt (USA-Tennessee state) and Oakland (USA-Iowa state). The general form for LOSW-P and LOSN-PN was developed

**Table 1** General attributes of the most popular vulnerability indices

Vulnerability index	Unit	Climate	Aquifer media	Topography	Pollutant type	Time	Human interventions	Result
DRASTIC	R	AR	Yes	Yes	C	No	No	QL
Pesticide DRASTIC	R	AR	Yes	Yes	Non-C	No	Irrigation and pesticides	QL
LOSW	V	PCP, PE, T	No	Yes	C	Yes	Irrigation	QL-QN
LOSN	V	PCP, PE, T	No	Yes	Non-C	Yes	Irrigation and nitrogen	QL-QN
COP	R	PCP	Yes	Slope of sink	C	No	No	QL
GOD	R	No	No	No	C	No	No	QL
EPIK	R	Water storage	No	Slope of sink	C	No	No	QL
SINTACS	R	AR	Yes	Yes	C	No	No	QL
AVI	V	no	No	No	C	Yes	No	QN

R ratings, *V* values, *QL* qualitative, *QN* quantitative, *C* conservative, *AR* aquifer recharge, *PCP* precipitation, *PE* potential evapotranspiration, *T* temperature

using multiple regression analysis based on the results of various scenarios implemented with the GLEAMS model. Results from 384 simulation scenarios, combining different soil properties, topography and climatic conditions of a reference field-crop, were used as "observed values" for the calibration of the LOS method for water and N losses. Simulations were performed under a uniform reference square area of 1 ha with homogeneous soil profile cropped with perennial grass, the same N fertilization (including specific rates of ammonia and nitrate nitrogen from industrial fertilizers and

Fig. 1 **a** Altitude, **b** main land uses and **c** sub-categories of agricultural areas of Sarigkiol basin
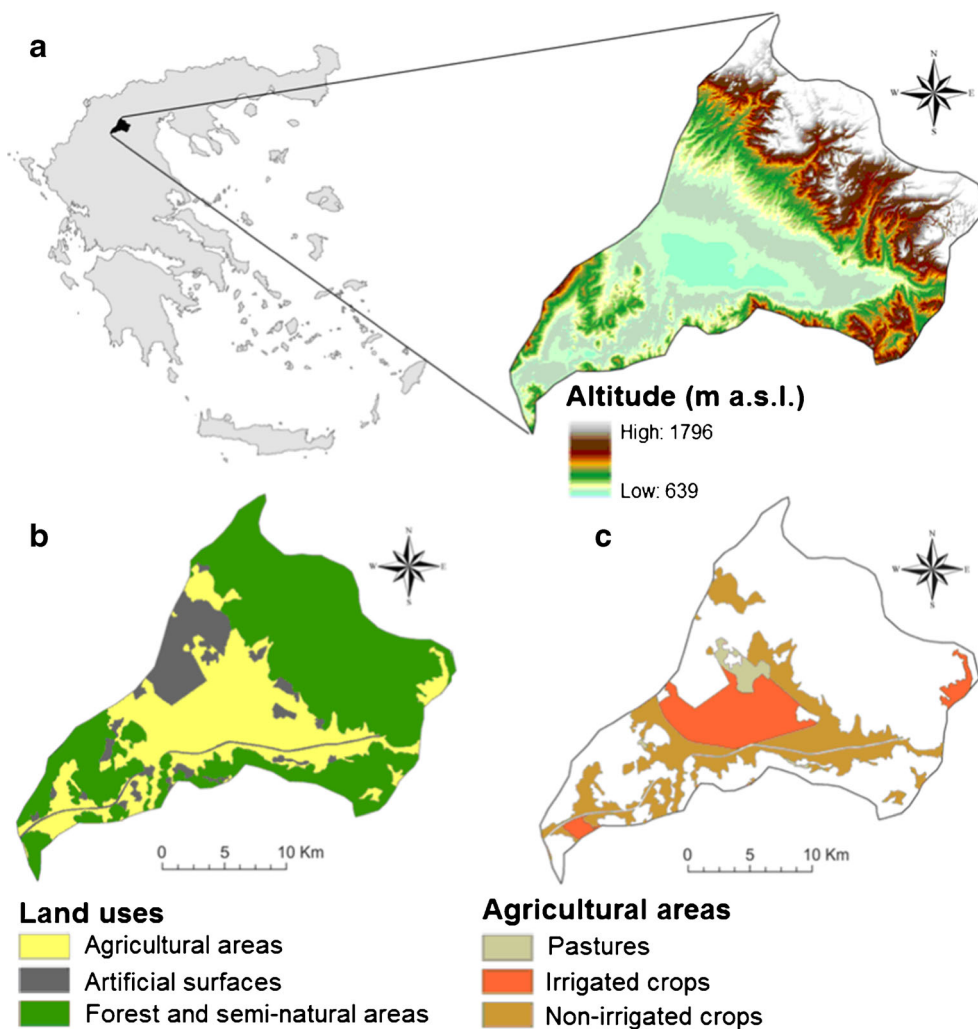
manure) and two cases of irrigation conditions: (a) no irrigation and (b) automatic irrigation keeping soil moisture at field capacity (Aschonitis et al. 2012). The equations for estimating the LOSW-P and LOSN-PN indices are the following:

$$
LOSW\text{-}P = \left\{ \begin{array}{l} 0.0941\sqrt{Ks} - 0.761\sqrt{S} + 0.4185\sqrt{PCP} \\ -0.0487\sqrt{PE} + 0.0903\sqrt{IR} \end{array} \right\}^2
$$

$$
\text{if } (LOSW\text{-}P)^{1/2} < 0 \quad \text{then}(LOSW\text{-}P) = 0
$$

(1)

$$
LOSN\text{-}PN = \left\{ \begin{array}{l} -0.1536\sqrt{OM} + 2.6981\sqrt{T} + 0.0439\sqrt{Ks} \\ -0.2046\sqrt{S} + 0.0471\sqrt{PCP} - 0.2515\sqrt{PE} \\ -0.0116\sqrt{IR} \end{array} \right\}^2
$$

$$
\text{if}(LOSN\text{-}PN)^{1/2} < 0 \quad \text{then}(LOSN\text{-}PN) = 0
$$

(2)

where LOSW-P is the amount of water losses beneath the top 30 cm of the soil profile (mm year^{-1}), LOSN-PN is the amount of nitrogen losses beneath the top 30 cm of the soil profile (kg ha^{-1} year^{-1}), Ks is hydraulic conductivity (mm day^{-1}), S is the surface slope (%), PCP is the total annual precipitation (mm year^{-1}), PE is the total annual potential evapotranspiration (mm year^{-1}), IR is the total annual irrigation amount (mm year^{-1}), OM is the organic matter (%) and T is the mean annual temperature (°C),

In Eqs. 1 and 2, the positive values of regression coefficients indicate an increase in water and nitrate percolation, while negative values of regression coefficients indicate a decrease in water and nitrate percolation. For instance, the positive values of the Ks and PCP regression coefficients for LOSW-P and LOSN-PN indicate an increase in both water and nitrate percolation due to higher water and N leaching with increasing Ks and PCP; the negative coefficient of S in both LOSW-P and LOSN-PN indicates that higher slope reduces the available water for percolation due to runoff increase; the negative coefficient of PE in both LOSW-P and LOSN-PN indicates that higher potential evapotranspiration reduces the available water for percolation and consequently N leaching; the IR coefficient is positive in LOSW-P because irrigation increases water percolation while it is negative in LOSN-PN because it reduces nitrification and consequently the available nitrates for leaching; the negative value of the OM regression coefficient for LOSN-PN indicates a decrease in nitrate leaching due to nitrate reduction via heterotrophic denitrification processes, while the positive coefficient of T indicates the increase of available nitrates for leaching due to the increase of nitrification due to temperature increase. The results of the method are comparable among different regions while the set of LOS indices has been expanded to describe also the water and N losses from runoff and other intrinsic rates of N cycle

components such as denitrification, ammonia volatilization, nitrification and mineralization (Aschonitis et al. 2012, 2013).

SINTACS method

SINTACS was established for hydrogeological, climatic and impacts settings typical of the Mediterranean countries (Civita and De Maio 2004). The acronym SINTACS stands for the seven parameters included in the method: Soggiacenza (depth to water), Infiltrazione efficace (recharge), Non-saturo (vadose zone), Tipologia della copertura (soil cover), Acquifero (aquifer), Conducibilità idraulica (hydraulic conductivity) and Supeficie topografica (slope of topographic surface). The rating assigned to each parameter must be multiplied by a weight (Table 2) to describe the environmental impact or the particular hydrogeological conditions. The form of the Eq. 3 is the following:

$$
I_{\text{SINTACS}} = \sum_{J=1}^{7} P_J W_J
$$

(3)

where P_J is the rating of each parameter and W_J is the corresponding weight. The ratings P_J are obtained from nomographs provided by Civita and De Maio (2004) (see Supplementary Material Fig. S.1).

DRASTIC and Pesticide DRASTIC methods

DRASTIC is an empirical method developed by US EPA to evaluate the potential pollution of groundwater systems on a regional scale (Aller et al. 1987). The acronym DRASTIC stands for the parameters included in the method: Depth to water (D), net Recharge (R), Aquifer media (A), Soil media (S), Topography (T), Impact of vadose zone (I) and hydraulic Conductivity of the aquifer (C). This method includes two versions: the generic DRASTIC for inorganic pollutants and the Pesticide DRASTIC. Each parameter is assigned a weight based upon its relative significance in the potential pollution.

Table 2   Strings of multiplier weights given for SINTACS R5 (from Civita and De Maio 2004)

Parameter	Normal impact	Severe impact	Seepage	Karst	Fissured	Nitrate
S	5	5	4	2	3	5
I	4	5	4	5	3	5
N	5	4	4	1	3	4
T	3	5	5	3	4	5
A	3	3	2	5	4	2
C	3	2	2	5	5	2
S	3	2	5	5	4	3

Each parameter is further assigned a rating for different ranges of the values. The typical ratings range from 1 to 10 and the weights from 1 to 5. Two sets of weights, one for general vulnerability and another for vulnerability to pesticides, can be used (Table 3). Pesticide DRASTIC weights were specifically designed to address the important processes offsetting the fate and transport of herbicides and pesticides in the soil (Wang et al. 2007). The DRASTIC index values measuring the aquifer vulnerability vary from 23 to 226 in the generic version and from 26 to 247 in the pesticide version. Both versions indicate four different relative classes of groundwater vulnerability: very low, low, moderate and high. DRASTIC index is computed implying linear combinations of the products of rating and weights for each factor:

$$
\begin{aligned}
\text{DRASTIC index} = & (DrDw) + (RrRw) + (ArAw) \\
& + (SrSw) + (TrTw) + (IrIw) \\
& + (CrCw)
\end{aligned}
\tag{4}
$$

where the capital letter indicates the corresponding parameter and the subscript 'r' and 'w' refer to the variable rating and weight, respectively (Aller et al. 1987). The ratings 'r' for each parameter in DRASTIC are provided in Table S.1 of the supplementary material.

GOD method

GOD is an empirical method for the assessment of aquifer vulnerability to pollution (Foster, 1987). GOD uses three parameters: (i) G—groundwater occurrence, (ii) O—overlying lithology and (iii) D—depth to groundwater with specific ratings and no additional weights as in the case of DRASTIC and SINTACS. GOD parameters are estimated based on the graphical nomograph given in Fig. S.2 of the supplementary material. The final GOD index is computed by:

$$
I = G \times O \times D
\tag{5}
$$

Table 3   Weights for DRASTIC and Pesticide DRASTIC methods

Parameter	DRASTIC	Pesticide DRASTIC
Depth to water (D)	5	5
Net recharge (R)	4	4
Aquifer media (A)	3	3
Soil media (S)	2	5
Topography (T)	1	3
Impact of vadose zone (I)	5	4
Hydraulic conductivity (C)	3	2

AVI method

AVI is a measure of groundwater vulnerability based on two physical parameters (Van Stempvoort et al. 1992): thickness of each sedimentary layer above the uppermost saturated aquifer surface (d) and estimated hydraulic conductivity (K) of each sedimentary layer. Based on d and K, the hydraulic resistance (c) is calculated. c is a theoretical factor describing the resistance of an aquitard to vertical flow (Kruseman and Ridder 1990) and has the dimension of time, indicating the estimated travel time for water to move downward through the porous media above the uppermost saturated aquifer surface. Thus, the weighting of d and K for each sedimentary layer above the uppermost saturated aquifer surface is not arbitrary but based on physical theory. The equation for c is:

$$
c = \sum_{i=1}^{n} \frac{d_i}{K_i}
\tag{6}
$$

where n is the number of the sedimentary units above the aquifer.

Single-parameter effect of weight-rating factors on DRASTIC and SINTACS methods

For the case of indices which use both weights and ratings (such as SINTACS, DRASTIC and Pesticide DRASTIC), a single-parameter analysis was performed, calculating the percentage contribution of each factor (Napolitano and Fabbri 1996) to better understand the differences between the methods. The mean effective contribution of each parameter was calculated in ArcGIS environment, using the following equation for each subarea i:

$$
Wpi = \frac{P_{ri}P_{wi}}{vuln_i} \times 100
\tag{7}
$$

where Wpi is the effective contribution expressed in percent for each parameter, P_{ri} and P_{wi} are the ratings and the weights of the parameter P assigned to the subarea i and $vuln_i$ is the vulnerability index.

General concept of method combination

The LOS method was selected in order to assess the vulnerability of the water (+conservative substances) and nitrogen losses beneath the top 30 cm of the soil profile while the AVI method was used to assess the vulnerability of the unsaturated zone. In both methods, the calculations are based on deterministic concepts and thus their results

are not related to subjective expert judgement. For the case of aquifer vulnerability, SINTACS, DRASTIC and Pesticide DRASTIC were analysed using Eq. 7 in order to examine empirically the validity of the contribution of their parameters effects taking into account (a) existing knowledge about the regional characteristics of the aquifer and (b) the results of LOS and AVI which describe similar attributes of some parameters incorporated in SINTACS, DRASTIC and Pesticide DRASTIC. The GOD method is a very simple and more conservative method with much lower uncertainty and for this reason its results played a supportive role for further comparisons with SINTACS, DRASTIC and Pesticide DRASTIC. For the case of SINTACS method, the weights of 'Normal Impact' (Table 2) were selected based on expert judgement and after comparing its final values with GOD. The vulnerability assessment procedure, for each method, was performed using ArcGIS 9.3. All the parameters used in the vulnerability indices were arranged in raster format with a regular grid of 30 × 30 m resolution. At the end, the LOS and AVI methods were combined with the final selected method for aquifer vulnerability in order to provide a more robust and detailed description of the response of the specific hydrogeological system to pollution, which creates a four-dimensional perspective of vulnerability by adding the dimensions of depth and time.

Results and discussion

Figure 2a, b shows the vulnerability of the topsoil to water and nitrogen losses estimated by the LOSW-P and LOSN-PN, respectively. LOSW-P map (Fig. 1a) shows that water and conservative pollutants' losses are lower in the centre of the basin and increase moving to the outskirts especially in the north-eastern region due to the following: (i) the transition from fine textured soils with low Ks values to coarser soils with higher Ks values and (ii) the transition to areas with higher rainfall and lower evapotranspiration. The LOSN-PN map (Fig. 2b) shows an analogous distribution but some dissimilarities are observed between the moderate and high vulnerable zones, indicating a different behaviour between the conservative and non-conservative (N) pollutants. This difference occurs because in the high vulnerable zone (the north-eastern region, according to LOSW-P), temperature is lower so N processes take place at lower rates in comparison to the moderate vulnerable zones. The lower temperature inhibits the transformation of inorganic ammonia into NO_3^-, so even if the infiltration rates are higher than in the rest of the basin (due to presence of more permeable soils), NO_3^- concentration is lower than in the flat western zones, where higher temperatures allow ammonia transformation. The SINTACS map (Fig. 2c) shows that the northern and western zones of the
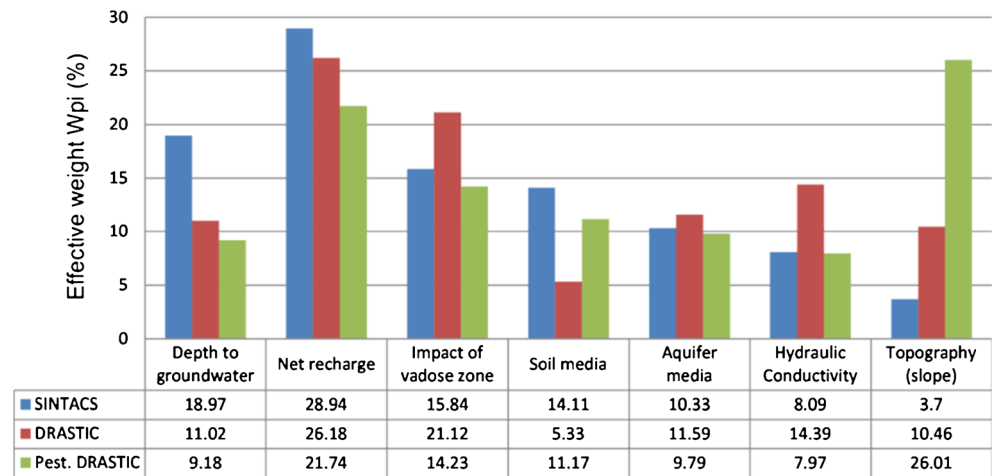
aquifer are in the high vulnerable class because of the presence of old talus stones giving high values of infiltration rate. In the southern part, a high vulnerable stripe is present in correspondence with fractured limestones and dolomites outcrops. The central part of the aquifer (50 % of the total surface examined) is classified as low vulnerable because of the presence of fine lacustrine and alluvial deposits with low Ks. In the GOD map (Fig. 2d) the high vulnerable class is not present. All the aquifer ranges from low to moderate vulnerability because of the high depth of the water table (14 to 113 m). This method is recommended only in absence of adequate datasets and for expeditious preliminary investigation, which needs to be followed by more accurate examination via other methods. DRASTIC and Pesticide DRASTIC (Fig. 2e, f) show similar results except for the eastern part which is classified as high vulnerable according to DRASTIC and moderately vulnerable for Pesticide DRASTIC, since in the latter method the impact of the vadose zone and of the hydraulic conductivity have a lower weight compared to DRASTIC. The two DRASTIC maps show a good agreement with the SINTACS map concerning the high vulnerable zones, while there is an inversion of the low and moderate classes in the central part of the basin. The single-parameter analysis (Fig. 3) shows how in these three maps the net recharge and the impact of the vadose zone are the most influent parameters for the vulnerability assessment. SINTACS map shows remarkable differences regarding the influence of groundwater depth and topsoil media parameters. These parameters are very important in the specific case study because the fine alluvial soils of the plain play an important role to slow down the percolation of water and pollutants towards the aquifer. The single-parameter sensitivity analysis suggests that SINTACS explains in a more realistic way the vulnerability of the Sarigkiol basin while the results of GOD method are more in agreement with SINTACS rather with the results of DRASTIC and Pesticide DRASTIC.

The AVI map (Fig. 2g) indicates the approximate travel time for water to move downward through the porous media above the uppermost saturated aquifer surface. However, it should be noted that, c is not a travel time for water or contaminants, since factors such as hydraulic gradient, diffusion and sorption are not considered (Van Stempvoort et al. 1992). In the Sarigkiol basin, the output c ranges from 21 to 829 days. The most vulnerable areas are the northern and eastern zones and a strip in the southernmost zone, where more permeable sediments are present. In the central part, even if the aquifer is located at shallower depth the presence of fine sediments reduce Ks. Despite the AVI method has some important limitations (lateral discontinuity of aquifer, climate, hydraulic gradient, porosity, water content of the porous media and sorptive or reactive properties of the layers are ignored), it uses the definition of hydraulic resistance (c) to assign the relative contribution of K and d parameters in vulnerability assessment.
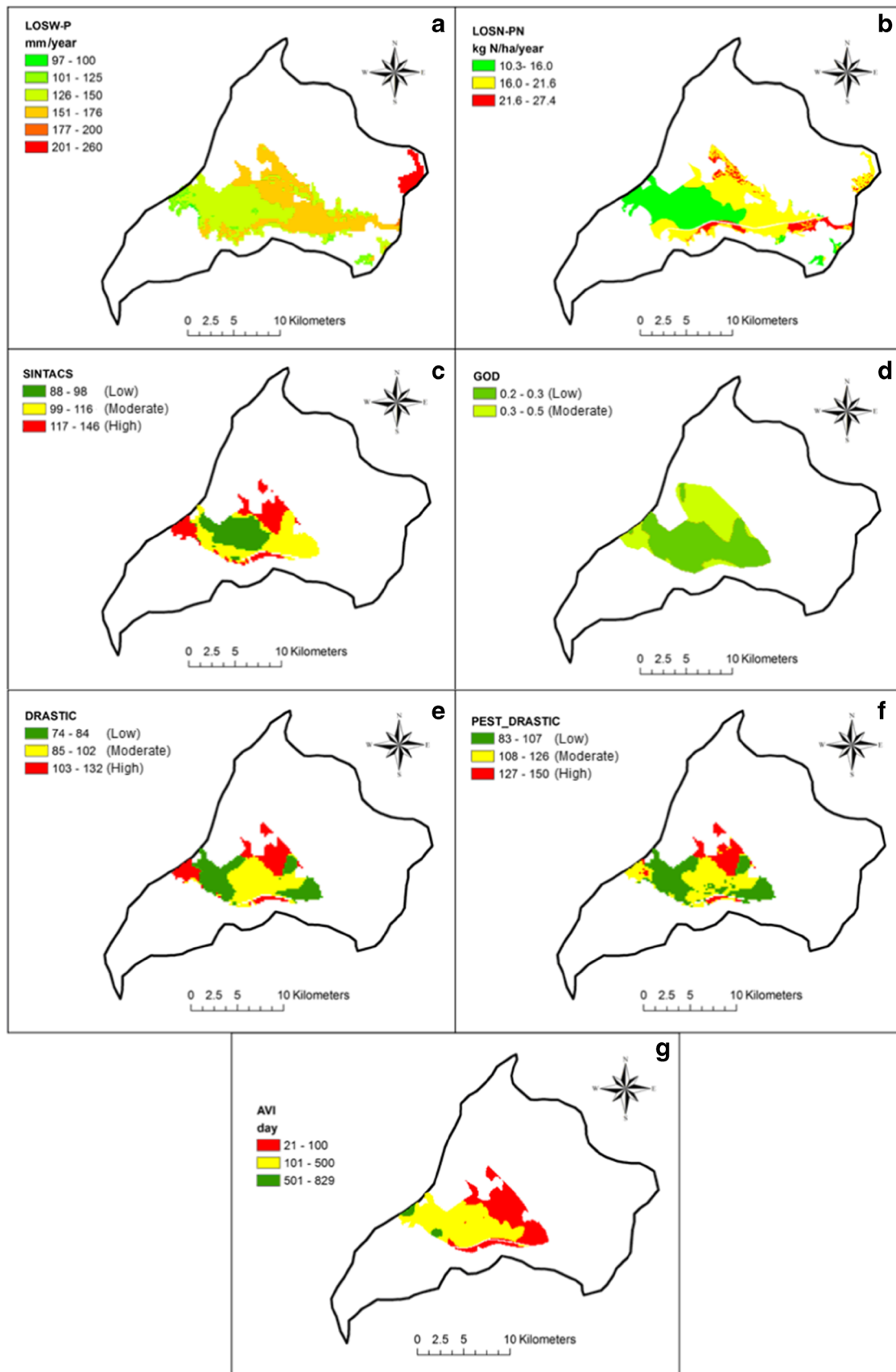
Fig. 2 Vulnerability maps obtained with **a** LOSW-P; **b** LOSN-PN; **c** SINTACS; **d** GOD; **e** DRASTIC; **f** Pesticide DRASTIC and **g** AVI

Fig. 3 Single-parameter effect of weight-rating factors of SINTACS, DRASTIC and Pesticide DRASTIC maps

	Depth to groundwater	Net recharge	Impact of vadose zone	Soil media	Aquifer media	Hydraulic Conductivity	Topography (slope)
■ SINTACS	18.97	28.94	15.84	14.11	10.33	8.09	3.7
■ DRASTIC	11.02	26.18	21.12	5.33	11.59	14.39	10.46
■ Pest. DRASTIC	9.18	21.74	14.23	11.17	9.79	7.97	26.01

Combining LOS, AVI and SINTACS methods, it is possible to provide a more comprehensive assessment of vulnerability, identifying the vulnerability of the topsoil to water (+conservative pollutants) and nitrogen losses using LOS, the vulnerability of the unsaturated zone to allow pollutants to reach the aquifer using AVI and the level of aquifer vulnerability using SINTACS (in other cases DRASTIC or other method can be used instead of SINTACS). In the case of Sarigkiol basin, the combination of the three methods becomes essential creating a three-dimensional perspective of vulnerability by adding the dimension of depth as it is visualized in Fig. 4. The use of LOS and AVI, which also include the unit of time, also add the dimension of time providing a final four-dimensional perspective. SINTACS and AVI maps highlight that the northern part of the aquifer is the most vulnerable. LOS, conversely, identified the upland north-eastern part of the basin as the most vulnerable area, where the aquifer boundaries do not reach, indicating that the possible pollutants which are infiltrated there could reach and threaten the aquifer in the alluvial plain following a non-vertical pathway. This observation is very important because methods such as SINTACS, AVI, DRASTIC, etc. are analysed only for the area, which is defined by the aquifer boundaries while LOS is not restricted by this attribute. Furthermore, the knowledge of the relative transit time of the infiltrated water to reach groundwater completes the vulnerability analysis, linking the LOS method with the SINTACS one, thus linking the source-area of the potential pollution with the receiving aquifer, as shown in the conceptual model of Fig. 4.

Other important differences, between the various methods applied, are the following: (i) SINTACS, DRASTIC, Pesticide DRASTIC and GOD do not take into account climatologic conditions such as temperature that tend to change the N cycle in comparison to the LOS index, which can be adapted to different climatic environments. The application in Sarigkiol basin showed that temperature is a driving factor for non-conservative pollutants, such as N; (ii) the single-parameter analysis showed that SINTACS is more appropriate in comparison to DRASTIC and Pesticide DRASTIC, to describe the aquifer vulnerability of the Sarigkiol basin; (iii) LOS provides quantitative results of water and nitrogen losses while the other methods give only a qualitative result in a range of vulnerability classes. The quantification of water and N losses is one of the LOS strengths because it allows a comparison between different regions with different characteristics; (iv) uncertainty is increased in the calibration of weights and ratings in SINTACS, DRASTIC, Pesticide DRASTIC and GOD because they are based on subjective criteria. On the other hand, LOS estimation is straightforward reducing significantly the subjectivity, which is introduced by the use of ratings in other methods. Moreover, the LOS method shows improved performance because it was developed using a process-based model, and for this reason, it better described the differences between the lower and higher altitude areas mostly associated to different climatic conditions; (v) the contribution of AVI in combination with LOS is very important because both of them add also the dimension of time and (vi) GOD is recommended only for preliminary investigations and comparisons because it considers a limited number of parameters.

Conclusions

The application of different indices to assess the intrinsic vulnerability of the Sarigkiol basin (Greece) highlighted the strengths and weaknesses of each method and at the same time showed that their combination can provide an overall view linked to the fate and transport of pollutants from the topsoil to the aquifer. The LOS method provided information about

Fig. 4 Conceptual model of integrated approach for vulnerability assessment (use of LOS for the 30 cm of the topsoil, use of AVI for the unsaturated zone and use of SINTACS for the aquifer)
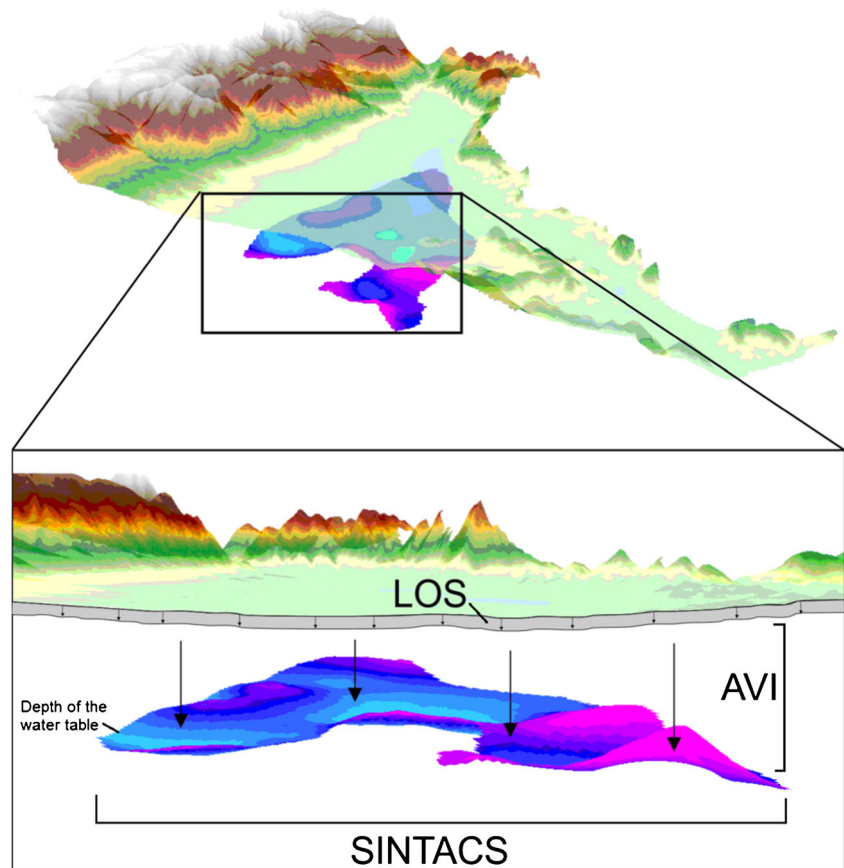
the intrinsic vulnerability of the topsoil (30 cm) to water (+conservative pollutants) and nitrogen losses, and the AVI method described the vulnerability of the unsaturated zone to allow pollutants to reach the aquifer while the aquifer vulnerability was analysed using SINTACS, DRASTIC, Pesticide DRASTIC and GOD. In the context of this study, the aquifer vulnerability was better described by SINTACS method and for this reason; the final conceptual approach for the description of a stratified vulnerability (toposoil, unsaturated zone and aquifer) of the overall hydrogeologic system was build combining LOS-AVI-SINTACS. The conceptual approach of combining the three indices led to a four-dimensional description of vulnerability by adding the dimensions of depth and time. The dimension of depth was described by the three layers of LOS-AVI-SINTACS, while the dimension of time was introduced by the LOS and AVI methods which provide quantitative results in time. The use of LOS method also highlighted the basic limitation of the other methods to describe the potential contribution to pollution of areas (especially upland areas) which are out of the aquifer boundaries. The combination of the aforementioned methods can be used as a more robust tool for establishing detailed monitoring programmes and measures to achieve the Water Framework Directive objectives of good groundwater status.

References

Aller L, Bennett T, Lehr JH, Petty RJ, Hackett G (1987) DRASTIC: a standardized system for evaluating ground water pollution potential using hydrogeologic settings: NWWA/EPA Series, EPA-600/2–87-035

Aschonitis VG, Mastrocicco M, Colombani N, Salemi E, Kazakis N, Voudouris K, Castaldelli G (2012) Assessment of the intrinsic vulnerability of agricultural land to water and nitrogen losses, via deterministic approach and regression analysis. Water Air Soil Pollut 223(4):1605–1614. doi:10.1007/s11270-011-0968-5

Aschonitis VG, Salemi E, Colombani N, Castaldelli G, Mastrocicco M (2013) Formulation of indices to describe intrinsic nitrogen transformation rates for the implementation of best management practices in agricultural lands. Water Air Soil Pollut 224:1489. doi:10.1007/s11270-013-1489-1

Aschonitis VG, Mastrocicco M, Colombani N, Salemi E, Castaldelli G (2014) Assessment of the intrinsic vulnerability of agricultural land

to water and nitrogen losses: case studies in Italy and Greece. Proc Int Assoc Hydrol Sci 364:14–19

Aveline A, Rousseau ML, Guichard L, Laurent M, Bockstaller C (2009) Evaluating an environmental indicator: case study of MERLIN, a method for assessing the risk of nitrate leaching. Agric Syst 100:22–30. doi:10.1016/j.agsy.2008.12.001

Birkinshaw SJ, Ewen J (2000) Nitrogen transformation component for SHETRAN catchment nitrate transport modelling. J Hydrol 230(1):1–17. doi:10.1016/S0022-1694(00)00174-8

Bouwer H (1997) Role of groundwater recharge and water reuse in integrated water management. Arab J Sci Eng 22(1):123–131

Castaldelli G, Soana E, Racchetti E, Pierobon E, Mastrocicco M, Tesini E, Fano EA, Bartoli M (2013) Nitrogen budget in a lowland coastal area within the Po river basin (northern Italy): multiple evidences of equilibrium between sources and internal sinks. Environ Manag 52(3):567–580. doi:10.1007/s00267-013-0052-6

Civita M, De Maio M (2004) Assessing and mapping groundwater vulnerability to contamination: the Italian "combined" approach. Geofis Int 43(4):513–532

Civita M, De Maio M (1997) SINTACS – Un sistema parametrico per la valutazione e la cartografia della vulnerabilità degli acquiferi all'nquinamento. Quaderni di tecniche di protezione ambientale, n. 60. Pitagora Editrice, Bologna

de Marsily G (2003) Importance of the maintenance of temporary ponds in arid climates for the recharge of groundwater. Compt Rendus Geosci 335(13):933–934. doi:10.1016/j.crte.2003.10.001

De Paz JM, Delgado JA, Ramos C, Shaffer MJ, Barbarick KK (2009) Use of a new GIS nitrogen index assessment tool for evaluation of nitrate leaching across a Mediterranean region. J Hydrol 365:183–194. doi:10.1016/j.jhydrol.2008.11.022

Foster SDD (1987) Vulnerability of soil and groundwater to pollutants. In: Van Duijvenbooden W, Waegeningh HD (eds) Proc TNO Comm Hydrogeol Res 38:69–86.

Galloway JN, Townsend AR, Erisman JW, Bekunda M, Cai Z, Freney JR, Martinelli LA, Seitzinger SP, Sutton MA (2008) Transformation of the nitrogen cycle: recent trends, questions, and potential solutions. Science 320(5878):889–892. doi:10.1126/science.1136674

Gogu R, Dassargues A (2000) Current trends and future challenges in groundwater vulnerability assessment using overlay and index methods. Environ Geol 39(6):549–559. doi:10.1007/s002540050466

Knisel WG, Davis FM (2000) GLEAMS, groundwater loading effects from agricultural management systems V3.0. Publ. No. SEWRL-WGK/FMD-050199. USDA, Tifton

Kruseman GP, Ridder NA (1990) Analysis and evaluation of pumping test data. ILRI publication, 47

Lasserre F, Razack M, Banton O (1999) A GIS-linked model for the assessment of nitrate contamination in groundwater. J Hydrol 224(3–4):81–90. doi:10.1016/S0022-1694(99)00130-4

Mastrocicco M, Colombani N, Castaldelli G, Jovanovic N (2011) Monitoring and modelling nitrate persistence in a shallow aquifer. Water Air Soil Pollut 217(1–4):83–93. doi:10.1007/s11270-010-0569-8

Morris BL, Lawrence ARL, Chilton PJC, Adams B, Calow RC, Klinck BA (2003) Groundwater and its susceptibility to degradation: a global assessment of the problem and options for management. Early warning and assessment report series, 03–3, United Nations Environment Programme, 126 pp

Neshat A, Pradhan B, Pirasteh S, Shafri HZM (2014) Estimating groundwater vulnerability to pollution using modified DRASTIC model in the Kerman agricultural area, Iran. Environ Earth Sci 71(7):3119–3131. doi:10.1007/s12665-013-2690-7

Neshat A, Pradhan B (2015a) An integrated DRASTIC model using probabilistic based frequency ratio and two new hybrid methods for groundwater vulnerability assessment. Nat Hazards 76(1):543–563. doi:10.1007/s11069-014-1503-y

Neshat A, Pradhan B (2015b) Risk assessment of groundwater pollution with a new methodological framework: application of Dempster-Shafer theory and GIS. Nat Hazards 78(3):1565–1585. doi:10.1007/s11069-015-1788-5

Neshat A, Pradhan B, Javadi S (2015) Risk assessment of groundwater pollution using Monte Carlo approach in an agricultural region: an example from Kerman Plain, Iran. Comput Environ Urban Syst 50:66–73. doi:10.1016/j.compenvurbsys.2014.11.004

Napolitano P, Fabbri AG (1996) Single-parameter sensitivity analysis for aquifer vulnerability assessment using DRASTIC and SINTACS. IAHS Publications-Series of Proceedings and Reports-Intern Assoc Hydrological Sciences, 235:559–566

Puckett LJ, Tesoriero AJ, Dubrovsky NM (2011) Nitrogen contamination of surficial aquifers—a growing legacy. Environ Sci Technol 45(3):839–844. doi:10.1021/es1038358

Refsgaard JC, Thorsen M, Jensen JB, Kleeschulte S, Hansen S (1999) Large scale modeling of groundwater contamination from nitrate leaching. J Hydrol 221:117–140. doi:10.1016/S0022-1694(99)00081-5

Salemi E, Colombani N, Aschonitis VG, Mastrocicco M (2011) Assessment of specific vulnerability to nitrates using LOS indices in the Ferrara Province, Italy. In: Advances in the research of aquatic environment. Springer, Berlin, pp. 283–290. doi:10.1007/978-3-642-24076-8_33

Shaffer MJ, Halvorson AD, Pierce FJ (1991) Nitrate leaching and economic analysis package (NLEAP): model description and application. In: Managing nitrogen for groundwater quality and farm profitability. Soil Science Society of America, Madison, pp. 285–322

Šimůnek J, van Genuchten MT, Šejna M (2008) The HYDRUS-1D software package for simulating the one-dimensional movement of water, heat, and multiple solutes in variably-saturated media. Version 4.0. HYDRUS Software Ser. 3. Dep. of Environmental Sciences, Univ. of California, Riverside

Tesoriero AJ, Duff JH, Saad DA, Spahr NE, Wolock DM (2013) Vulnerability of streams to legacy nitrate sources. Environ Sci Technol 47(8):3623–3629. doi:10.1021/es305026x

Van Stempvoort D, Ewert L, Wassenaar L (1992) AVI: a method for groundwater protection mapping in the prairie provinces of Canada. Prairie Provinces Water Board Report 1–14, Regina, SK

Voudouris KS (2006) Report on the hydro-meterological and hydrogeological data of Sarigkiol basin Kozani prefecture, Western Macedonia, Greece. Development and utilization of vulnerability maps for the monitoring and management of groundwater resources in the Archimed area (Water-Map) (eds) Polemio M, Dragone V, Watermap, Intereg III B Archimed, 8–21

Wang Y, Merkel BJ, Li Y, Ye H, Fu S, Ihm D (2007) Vulnerability of groundwater in Quaternary aquifers to organic contaminants: a case study in Wuhan City, China. Environ Geol 53(3):479–484. doi:10.1007/s00254-007-0669-y

Winter TC, Harvey JW, Franke OL, Alley WM (2013) Ground Water and Surface Water A Single Resource. USGS circular 1139

Zwahlen F (2003) Vulnerability and risk mapping for the protection of carbonate (karst) aquifers. Eur Comm Cost Action 620:42