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Toward operational methods for the assessment of intrinsic groundwater vulnerability: A review

Przemysław Wachniew^a, Anna J. Zurek^b, Christine Stumpp^c, Alexandra Gemitzi^d, Alessandro Gargini^e, Maria Filippini^e, Kazimierz Rozanski^a, Jessica Meeks^f, Jens Kværner^g, and Stanislaw Witczak^b

^aFaculty of Physics and Applied Computer Science, AGH University of Science and Technology, Krakow, Poland; ^bFaculty of Geology, Geophysics and Environmental Protection, AGH University of Science and Technology, Krakow, Poland; ^cHelmholtz Zentrum München, Institute of Groundwater Ecology, Neuherberg, Germany; ^dDepartment of Environmental Engineering, School of Engineering, Democritus University of Thrace, Xanthi, Greece; ^eBiological, Geological and Environmental Sciences Department, Alma Mater Studiorum University of Bologna, Bologna, Italy; ^fCentre for Hydrogeology and Geothermics, University of Neuchâtel, Neuchâtel, Switzerland; ^gDivision for Environment and Natural Resources, NIBIO—Norwegian Institute of Bioeconomy Research, Ås, Norway

ABSTRACT

Assessing the vulnerability of groundwater to adverse effects of human impacts is one of the most important problems in applied hydrogeology. At the same time, many of the widespread vulnerability assessment methods do not provide physically meaningful and operational indicators of vulnerability. Therefore, this review summarizes (i) different methods used for intrinsic vulnerability assessment and (ii) methods for different groundwater systems. It particularly focuses on (iii) timescale methods of water flow as an appropriate tool and (iv) provides a discussion on the challenges in applying these methods. The use of such physically meaningful indices based on timescales is indispensable for groundwater resources management.

KEYWORDS Groundwater; intrinsic vulnerability; residence time

1. Introduction

Assessing the vulnerability of groundwater to adverse effects of human activities is one of the most important problems in applied hydrogeology (Gorelick and Zheng, 2015). For example, according to the Water Framework Directive of the European Union (EC, 2000), the likelihood of groundwater bodies failing to meet the objectives for groundwater protection, set out by the same Directive, has to be assessed. The groundwater bodies found to be at risk are subject to more precise risk assessments, which encompass evaluation of groundwater vulnerability. The Groundwater Directive of the European Union (EC, 2006) indicates water supply for human

CONTACT Christine Stumpp ✉ christine.stumpp@helmholtz-muenchen.de 📧 Helmholtz Zentrum München, Institute of Groundwater Ecology, Ingolstädter Landstrasse 1, 85764 Neuherberg, Germany.

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consumption and groundwater-dependent ecosystems as two receptors with respect to which groundwater should be protected from deterioration and chemical pollution. From this perspective it is even more appropriate to assess groundwater vulnerability not for the whole groundwater body but for particular receptors like abstraction wells or groundwater-dependent ecosystems.

A fundamental difficulty in assessing groundwater vulnerability is the complexity of groundwater systems. The intertwined processes of groundwater flow and pollutant transport occur in three spatial dimensions, in the inherently heterogeneous and anisotropic geological media, over a great range of distances and times, and are typically nonstationary. Also, the pressures on groundwater quality have complex or unknown spatial and temporal distribution characteristics. The vulnerability of a particular groundwater receptor is therefore a complex function of the following:

- spatial and temporal distribution of pressures, for example, location of source areas of pollution, pollutant loads, fertilization levels, location of pumping wells and their pumping regimes, patterns of land-use change;
- distribution of water flow paths in the groundwater body;
- dilution, retardation, attenuation, and transformations of contaminants in the subsurface that affect their levels at the receptor;
- rates at which impacts of pressures propagate along the flow paths, that is, time lags associated with the responses of the receptor to the commencement or cessation of pressures.

The task of assessing groundwater vulnerability can thus be seen as essentially equivalent to predicting contaminant concentrations within the groundwater body or at the groundwater receptors. A direct and comprehensive assessment of groundwater vulnerability is in most cases not feasible due to insufficient availability of monitoring data and the inherent complexity of groundwater systems. Instead, groundwater vulnerability indicators are defined, quantified, and mapped in order to reflect the actual or to predict the potential severity of human-induced deterioration in groundwater quality. Furthermore, because of time lags inherent to the groundwater flow and contaminant transport, responses in groundwater quality to changes in contaminant inputs may not be visible over short periods of time of the order of years that are typically considered by policy makers, groundwater managers, and the general public. Setting up of deadlines for the improvement of surface water quality—as, for example, in programs of measures required by the Water Framework Directive—involves consideration of such time lags (Witczak et al., 2007; Fenton et al., 2011; Aquilina et al., 2012; Hamilton, 2012; Herrman et al., 2012; Stumpp et al., not published yet).

This work presents different understandings of the groundwater vulnerability concept and gives an overview of methods for assessing the intrinsic vulnerability. Among those, only the physically based methods can provide physically meaningful and operational indicators of the intrinsic groundwater vulnerability based on the knowledge of timescales of groundwater flow. This work reviews applications

in which various approaches were used to estimate mean residence times (MRTs) of water or residence time distributions (RTDs) and to derive indicators of vulnerability. Chapter 2 summarizes different understandings of the vulnerability concept. In chapter 3, an overview on different vulnerability assessment methods is given. Chapter 4 reviews applications in which vulnerability assessments are based on the quantification of residence times of water. Chapter 5 presents challenges in assessing vulnerability related to the often misunderstood and overlooked features of groundwater flow and contaminant transport, such as heterogeneity, transient conditions, or role of aquitards.

2. Concept of groundwater vulnerability

The concept of vulnerability (Fig. 1) is often considered in the context of the source-pathway-receptor (SPR) paradigm of groundwater risk assessment (EC, 2003; Liggett and Talwar, 2009; EC, 2010). The receptor itself can be, for example, the groundwater table, any point in the groundwater, a groundwater dependent ecosystem (GDE), or any shallow and deep groundwater well used for water supply. Groundwater vulnerability is, in this approach, related to the pathway components of conceptual models built to identify processes and interactions governing contaminant spreading. Vulnerability assessments may be limited to those properties of groundwater systems that control patterns of subsurface water flow—the intrinsic vulnerability—but may as well encompass the compound-specific

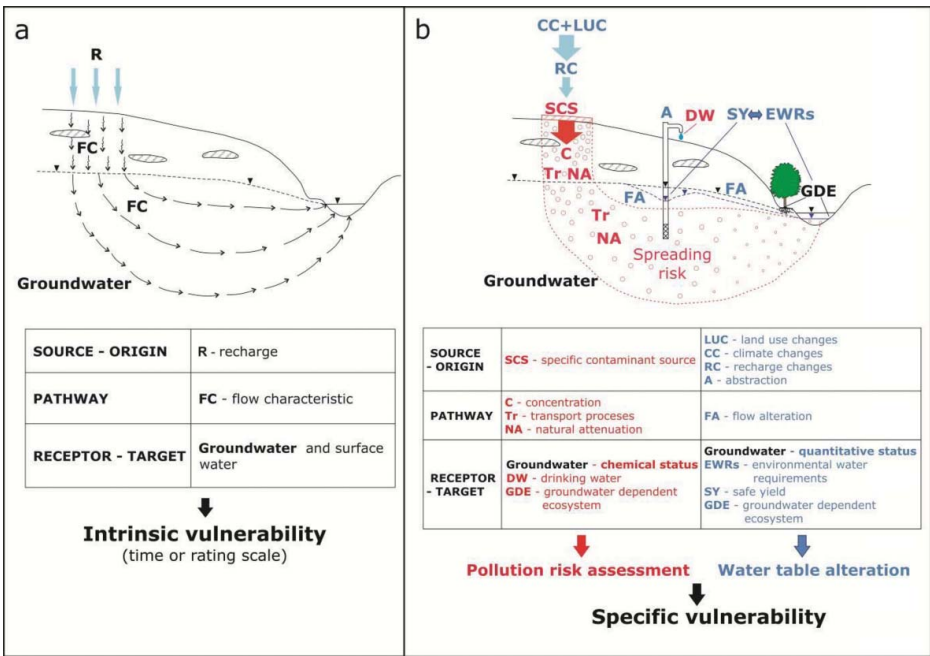


Figure 1. Basic concepts defining the (a) intrinsic and (b) specific vulnerability.

physical and biogeochemical attenuation processes that control the fate of particular contaminants—the specific vulnerability ((Zwahlen, 2004), cf. Fig. 1); the latter is not part of this study, but readers are referred to the extensive literature (e.g., Vrba and Zaporozec, 1994; Gogu and Dassargues, 2000a; Margane, 2003; Zwahlen, 2004) for more detailed information about specific vulnerability assessment. A similar concept for intrinsic vulnerability assessment based on the origin-pathway-target model was applied within the COST Action 620 (Goldscheider et al., 2000; Daly et al., 2002; Zwahlen, 2004). Based on the same idea the hazard-pathway-receptor model was used for groundwater vulnerability assessment by Dochartaigh et al. (2005). Groundwater vulnerability might be also considered in the framework of the system of environmental indicators, known as the DPSIR model (Driving forces, Pressures, State, Impacts, and Responses) (EEA, 2003; Kristensen, 2004) applied for the integrated analysis of the social-economic and environmental aspects in the field of sustainability assessment (Bottero, 2011). An example of such an approach was presented by Beaujean et al. (2014), based on vulnerability assessment of the calculation of a series of sensitivity coefficients for a user-defined groundwater state (S), for which several physically based indicators, which relate impacts (I) to pressures (P), were proposed.

The development of the concept of vulnerability in the field of groundwater resources protection has been reviewed in several works (National Research Council, 1993; Vrba and Zaporozec, 1994; Foster et al., 2002; Frind et al., 2006; Popescu et al., 2008). For the first time the term vulnerability was used in the hydrogeological context in France and those vulnerability assessments were presented in the form of maps (Margat, 1968; Albinet and Margat, 1970), which later became a standard way of communicating assessment results. In the 1980s the term groundwater vulnerability was used widely (Vierhuff, 1981; Aller et al., 1987; Civita, 1987; van Duijvenbooden and van Waegeningh, 1987; Foster and Hirata, 1988; Johnston, 1988) but with a rather intuitive understanding of its meaning. At the same time, Andersen and Gosk (1987) suggested that vulnerability mapping could be better carried out for individual contaminants in specific pollution scenarios and Foster (1987) proposed the concept of groundwater pollution risk, which involved natural aquifer pollution vulnerability and man-made subsurface pollution loading. Vrba and Zaporozec (1994) used the term specific (or integrated) vulnerability as related to intrinsic (natural) vulnerability complemented with “potential impacts of specific land uses and contaminants, which may prove detrimental—in space and time—to the present or future uses of the groundwater resource (p. 7).”

A commonly referred to definition of groundwater vulnerability is the one formulated by the US Committee on Techniques for Assessing Ground Water Vulnerability (National Research Council, 1993), according to which groundwater vulnerability is “the tendency or likelihood for contaminants to reach a specified position in the groundwater system after introduction at some location above the uppermost aquifer (p. 1).” Many of the proposed definitions are either based on this formulation or carry the same concept using terms synonymous or similar to

“tendency or likelihood” such as risk, degree, or possibility (Aldwell, 1994). Another influential definition was presented by Vrba and Zaprozec (1994), who defined groundwater vulnerability as “an intrinsic property of a groundwater system, depending on the sensitivity of that system to human and/or natural impacts (p. 7).” Vrba and Zaporozec (1994) provided a general framework for vulnerability assessments, according to which soil and strata overlying groundwater table provide limited and extremely variable “natural protection” of groundwater from contaminants. This observation, present in the literature since the 1980s (Vierhuff, 1981; Foster, 1987; Johnston, 1988), constitutes a conceptual basis for designing indices of vulnerability. These two above-mentioned definitions are complementary rather than exclusive as the first implicitly expresses the SPR paradigm and the second advises on how to assess “the tendency or likelihood” of the former definition. In fact, many authors refer to both definitions simultaneously as exemplified by the following excerpt from the work of Majandang and Sarapirome, (2012) (p. 2026):

Groundwater vulnerability is a concept based on the assumption that the physical environment provides some natural protection to groundwater against human impacts, especially with regard to contaminants entering the subsurface environment. Groundwater vulnerability is defined as the tendency or likelihood of contaminants reaching the groundwater system after introduction at the surface and is based on the fundamental concept that some land areas are more vulnerable to groundwater contamination than others.

Vulnerability assessments are performed not only in groundwater resources management but also in the wider context of socio-environmental systems affected by the global environmental change (Eakin and Luers, 2006). The vagueness of the proposed definitions hinders the development of operational methods of vulnerability assessment (Hinkel, 2011). Similarly, due to the abundance of available definitions, the concept of groundwater vulnerability is perceived as ambiguous and lacking clear definition (Daly et al., 2002; Stigter et al., 2005; Frind et al., 2006). This ambiguity stems partly from the fact that in large part the definitions are not logically rigorous (Belnap, 1993; Jureta, 2011) as they do not explain in a strict way the meaning of the term “groundwater vulnerability” and only ascribe to it some attributes (“intrinsic property,” “depending on the sensitivity”). Some definitions introduce circularity because they explain vulnerability by the related terms such as “susceptibility” or “sensitivity.” It is also often repeated after Vrba and Zaporozec (1994) that vulnerability of groundwater is a relative, nonmeasurable, and dimensionless property. Indeed, as appears from the preceding discussion, groundwater vulnerability has not been defined as a physical property that could be unambiguously quantified by application of a standardized procedure. Recently, there is an increasing understanding of the need for the stricter, physically based, and operational understanding of vulnerability based on the quantitative

representation of the physical processes that take place in the hydrogeological systems (Focazio et al., 2002; Popescu et al., 2008; Yu et al., 2010; Beaujean et al., 2014). It needs to be emphasized that in the concept of vulnerability, only qualitative (chemical) aspects of the water body are assessed. In many areas of the world, the quantity of groundwater resources (Plummer et al., 2012) and groundwater availability to the dependent ecosystems is even more seriously affected, requiring new solutions for the management of groundwater and GDEs (Kløve et al., 2014).

3. Overview of groundwater vulnerability assessment methods

Methods for assessing the intrinsic vulnerability belong to two major categories: objective (physically based and statistical) and subjective methods defined and reviewed by some authors (e.g., Vrba and Zaporozec, 1994; Gogu and Dassargue, 2000a; Focazio et al., 2002; Margane, 2003; Zwahlen, 2004; Liggett and Talwar, 2009; Pavlis et al., 2010; Shirazi et al., 2012; Faybishenko et al., 2015; Marín and Andreo, 2015). These reviews thoroughly discuss different understandings of the groundwater vulnerability concept (Vrba and Zaporozec, 1994) and differences between the intrinsic and specific vulnerability (Foster, 1987; Vrba and Zaporozec, 1994; Focazio et al., 2002; Zwahlen, 2004), list factors influencing vulnerability (Foster, 1987; Vrba and Zaporozec, 1994), and compare and provide guidance for use of the subjective methods (Gogu and Dassargues, 2000a; Margane, 2003). Gogu and Dassargues (2000a) discuss challenges in the development of vulnerability assessment analysis and call for the integration of process-based models with vulnerability methods. A recurring theme of these works is also the need for standardization of the terminology and methods of vulnerability assessment. Groundwater is a critical resource in those parts of the world where rapid population growth leads to deterioration of groundwater in terms of quantity and quality (Foster and Chilton, 2003), with improper sanitation being a significant cause of groundwater pollution (Graham and Polizzotto, 2013). Shirazi et al. (2012) provide a review of vulnerability assessments performed in Asia where DRASTIC appears to be the method of choice (Rahman, 2008). In Africa, Ouedraogo et al. (2016) demonstrated the use of DRASTIC for the assessment of groundwater vulnerability at the continent scale.

The present work provides some additional overview of the subjective methods, but focuses on those physically based methods that rely on the evaluation of time-scales of groundwater flow. In few of the above-mentioned reviews (Foster, 1987; Vrba and Zaporozec, 1994; Focazio et al., 2002; Zwahlen, 2004; Liggett and Talwar, 2009; Faybishenko et al., 2015), timescales of groundwater flow and/or contaminant transport are considered as vulnerability indices (VIs). However, our work provides a systematic exposition of the time-based approaches to groundwater vulnerability analysis relating them to the current needs of groundwater management

and presenting them as a bridge between the simple subjective methods and complex and data-demanding physically based methods.

Methods used for assessing the specific vulnerability are not discussed here because they are usually dedicated to specific cases and contaminants and their generalization and classification are difficult (Morris et al., 2003). However, evaluation of the specific vulnerability can be to some extent based on assessments of the intrinsic vulnerability. It is considered as corresponding to a typical scenario of pollution with a universal contaminant (Foster et al., 1988), which, when transported with groundwater, is subjected to processes of advection and dispersion only (e.g., chloride ion or nitrate ion in oxidizing conditions) and its behavior in the groundwater system is indistinguishable from that of water. Pavlis et al. (2010) review vulnerability assessment methods in the context of contamination by plant protection products considering the evaluation of the intrinsic vulnerability as a first step in the assessments performed for particular substances. Not considered or difficult to predict in intrinsic vulnerability assessment are contamination incidences where sources are not known or difficult to identify such as direct mismanagement due to dumping of chemical into the groundwater.

Intrinsic vulnerability assessments are often performed in regional scales and presented in the form of vulnerability maps. Such assessments constitute a basis for evaluating threats from potential diffuse pollution originating mainly from agriculture (e.g., nitrates and pesticides) and atmospheric deposition of pollutants (e.g., sulfates). If the time necessary for the contaminant to reach an aquifer or receptor was used as the measure of vulnerability, then the intrinsic vulnerability would provide a worst case scenario for the vulnerability to specific contaminants. There are, however, exceptions when contaminants are normally transported conservatively but move faster than the bulk of water due to density effects like NAPLs (cf. Chapter 5.4) or due to size exclusion like microbial contamination in karst aquifers (Göppert and Goldscheider, 2008; Sinreich et al., 2009). For nonconservative (i.e., reactive) transport, additionally degradation/decay and sorption need to be considered. Here, transport depends not only on the properties of the contaminant but also on rock/sediment properties, microbiological aspects, and water chemistry. Generally, retardation of contaminants with respect to water due to sorption, but also due to matrix diffusion and other processes, slows down their transport.

3.1. Subjective methods

The most commonly used are the subjective, often referred to as parametric, methods. In the subjective methods various physical factors of vulnerability are rated, usually as layers of information within a GIS system. The relative indices of groundwater vulnerability provided by these methods are combined from subjective ratings of the importance of these physical parameters, which is not an

objective process and requires judgment of groundwater practitioners or scientists involved in vulnerability assessment.

The most commonly used subjective methods are summarized in Table 1 for all aquifer types and in Table 2 for methods specifically developed for Karst aquifers. More details about these methods are given in chapters 3.1.1 and 3.1.2. Table 1 and 2 present basic parameters and spatial scales relevant to each of methods.

In a similar way, Vrba and Zaporozec (1994) summarized basic attributes of groundwater vulnerability methods and their parameters and divided the parametric methods into: (i) matrix systems (MS); (ii) rating systems (RS), and (iii) point count system models (PCSM). The subjective methods have their obvious advantages and disadvantages, the former being their flexibility and conceptual simplicity (Neukum et al., 2008), and the latter being related to the subjective nature of vulnerability evaluation and to the oversimplifications in the hydrogeological characterization. Furthermore, previously established methods appeared to be not appropriate for karstic aquifers (Ray and O'dell, 1993; Rosen, 1994; Van Stempvoort et al., 1993; Panago-poulos et al., 2006; Denny et al., 2007) for which dedicated methods were developed (cf. chapter 3.1.2). Nevertheless, their use could be focused on screening applications in order to unveil areas of high vulnerability where detailed research should concentrate on.

The subjective methods provide only relative measures of vulnerability (Gogu and Dassargues, 2000a). Despite the need to address the reliability of these methods, the attempts to evaluate their uncertainty and to validate them against the objective measures of vulnerability, such as water transit times estimates (Neukum et al., 2008; Marin et al., 2015) or contaminant transport simulations (Yu et al., 2010), are rare—see also review by Neukum (2013). More common are comparisons of results obtained by different methods for the same object and set of data—several of them are mentioned below. It is noteworthy that such comparisons show in some cases large discrepancies between the methods. For example, Gogu et al. (2003) compared five methods for assessing the intrinsic aquifer vulnerability, noting large differences between their results and concluding that the vulnerability assessments must incorporate physically based methods.

3.1.1. Commonly used subjective methods

Among the most established methods are GOD (Foster, 1987; Foster et al., 1988; 2002) and DRASTIC (Aller et al., 1987). The GOD system is named after the examined factors: identification of the type of Groundwater confinement, with consequent indexing of this parameter on a scale of 0 (none or overflowing) to 1.0 (unconfined); description of the strata Overlying the aquifer saturated zone (vadose zone or confining beds) in terms of lithological character and degree of consolidation; this leads to a second value on a scale of 0.4 (e.g., estuarine clays) to 1.0 (karst limestones); assessment of the Depth to groundwater table (unconfined aquifers) or depth of first major groundwater strike (confined aquifers) with consequent ranking on a scale of 0.6 (> 50 m) to 1.0 (all depths for karstic aquifers)

Table 1. Subjective methods applicable to all aquifer formations.

Method	Basic parameters										Spatial scale		
	Characteristic of soil			Characteristic of vadose zone			Characteristic of aquifer media						
	Type ¹⁾	Confining conditions	Net recharge, to water infiltration	Depth table	Lithology	Attenuation potential	Lithology	Conductivity	Thickness	Topography slope		Karst comprising (aquifer or basin scale)	
GOD	RS	x		x		x							Foster, 1987
DRASTIC	PCSM		x	x	x	x		x		x		x	Aller et al., 1987
DRASTIC-Fm	PCSM		x	x	x	x		x		x		x	Denny et al., 2007
SINTACS	PCSM	x	x	x	x	x		x		x		x	Civita, 1990a,b
ISIS	PCSM		x	x				x		x		x	Sappa and Lega, 1998
SEEPAGE	hybrid			x	x	x			x			x	Moore and John, 1990
KARSTIC	PCSM		x	x	x					x		x ²⁾	Davis et al., 2002
DRISTPI	PCSM		x	x	x			x		x		x ²⁾	Jiménez-Madrid et al., 2013
PI	RS		x	x ³⁾				x ³⁾				x ²⁾	Goldscheider et al. 2000
EUROPEAN APPROACH	RS		x	x ³⁾				x ³⁾				x ²⁾	Daly et al. 2002

¹⁾RS: rating system; PCSM: point count system model (Vrba and Zaporozec, 1994)

²⁾methods with a specific tool adapted for karst—preferential infiltration

³⁾the complex parameter—protective function of the layers above aquifer—is used

Table 2. Subjective methods dedicated to Karst.

Method	Type ¹⁾	Basic parameters										Spatial scale	References	
		Confining conditions	Infiltration conditions	Karstification			Protective cover/ overlying layers		Characteristic of aquifer media					Local (aquifer or basin scale)
				Epikarst network	Karst features	Karstic features	Vadose zone	Thickness	Lithology	Hydraulic properties	Precipitation			
DIVERSITY	hybrid			X	X	X					X ²⁾	X	Ray and O'dell,, 1993	
EPIK	PCSM		X	X		X						X	Doerfliger and Zwahlen, 1997	
REKS	RS		X		X	X				X		X	Malik and Svasta, 1999	
RISKE	PCSM		X	X	X	X			X			X	Petelet-Giraud et al., 2000	
PRESK	PCSM		X	X	X	X			X		X	X	Koutsi and Stoumaras, 2011	
PaPRIKA	PCSM		X	X ³⁾	X	X ³⁾	X ³⁾		X			X	Doerfliger et al., 2010	
COP	RS	X			X	X	X	X		X		X	Vías et al., 2005, 2006	
COP+K Slovene approach	RS	X		X	X	X	X	X		X		X	Andreo et al., 2009	
Ravbar, 2007			X ⁴⁾											
VURASS	PCSM						X ⁴⁾					X	Laimer, 2005	

¹⁾RS: rating system; PCSMS: point count system model (Virba and Zaporozec 1994)

²⁾“Potential dispersal pattern”: flow directions

³⁾the complex parameter (Protection) includes soil, vadose zone, and epikarst

⁴⁾infiltration criterion results from soil type and aquifer lithology

(Foster et al., 2002; Debernardi et al., 2008). The integrated aquifer vulnerability index (AVI) is calculated by multiplying the values of these three parameters.

The most popular and widely used is the DRASTIC method (Aller et al., 1987), which has been applied in numerous studies, from the municipality to the national scale (e.g., Ehteshami et al., 1991; Kalinski et al., 1994; Napolitano and Fabbri, 1996; Lobo-Ferreira and Oliveira, 1997; Lynch et al., 1997; Melloul and Collin, 1998; Johansson et al., 1999; Kim and Hamm, 1999; Rupert, 2001; Al-Zabet, 2002; Stigter et al., 2005; Qamhie, 2006; Tilahun and Merkel, 2010; Fijani et al., 2013; Krogulec, 2013) despite the criticism it has been subjected to (Garrett et al., 1989; Ray and O'dell, 1993; US EPA, 1993; Van Stempvoort et al., 1993; Rosen, 1994; Foster and Skinner, 1995; Frind et al., 2006; Panagopoulos et al., 2006; Dassargues et al., 2009). The name of this method is an acronym for the parameters used to assess vulnerability: Depth to water table, net Recharge, Aquifer media, Soil media, Topography, Impact of the vadose zone, and hydraulic Conductivity. These parameters are transformed from the physical range scale to a 10-grade relative scale (rating). Parameters are multiplied by weighting coefficients varying from 1 (Topography) to 5 (Depth to water table and Impact of vadose zone) (Aller et al., 1987). The DRASTIC index of the intrinsic vulnerability is obtained as a sum of individually weighted parameters. A major breakthrough in the DRASTIC method, when compared to the preexisting methods, was the application of parameter weighting, a tool used to express the relative importance of the above parameters in controlling groundwater vulnerability. This methodology, however, does not provide a unique vulnerability classification scheme and its users may interpret the produced indices according to their experience and knowledge of the hydrogeological system.

Use of GIS techniques facilitates handling of large data sets and preparation of vulnerability maps resulting in a better viability of DRASTIC models (Evans and Myers, 1990; Barrocu and Biallo, 1993; Engel et al., 1996; Lobo-Ferreira, 1998; Bedessem et al., 2005; Panagopoulos et al., 2006; Rahman, 2008; Kazakis and Voudouris, 2011; Shirazi et al., 2012; Fijani et al., 2013; Edet, 2014). There exist many modifications of the DRASTIC method with modified weights or additional parameters (Bedessem et al., 2005; Evans and Myers, 1990; Witkowski et al., 2003). The multitude of such modifications makes comparisons between vulnerability assessments obtained by different versions of the method impossible. Attempts were undertaken to modify the method for fissured and karstic aquifers, because the poor performance of DRASTIC in such system was criticized as the main drawback of this method (Rosen, 1994). One of such attempts is DRASTIC-Fm proposed by Denny et al. (2007), where an additional parameter (Fm—fractured media) was introduced taking into account orientation, length, and density of fractures. Some of the improvements made in DRASTIC stemmed from the need to assess threats resulting from agriculture (Rupert, 2001; Stigter et al., 2005; Panagopoulos et al., 2006; Berkhoff, 2008; Martinez-Bastida et al., 2010; Fijani et al., 2013). There were also attempts to combine DRASTIC with simple statistical

techniques (Rupert, 2001; Panagopoulos et al., 2006) and with the approaches using fuzzy logic or artificial intelligence (Fijani et al., 2013).

SINTACS and ISIS, both proposed in Italy, are examples of PCSM. The SINTACS method, based on DRASTIC, was designed to be suitable also for the highly diverse and largely karstic Italian hydrogeology (Civita, 1990a, b; 1994; 2010; Civita and De Maio, 1997, 2000; 2004; Ramos Leal et al., 2010). SINTACS includes seven parameters: depth to groundwater (*Soggiacenza*), effective infiltration (*Infiltrazione*), unsaturated (*Non saturo*) zone attenuation capacity, soil/overburden attenuation capacity (*Tipologia della copertura*), hydrogeological characteristics of the aquifer (*Acquifero*), hydraulic conductivity range of the aquifer (*Conducibilità*), and slope of the topography (*Superficie topografica*). The ISIS considers seven parameters: annual mean net recharge, topography, soil type, lithology of the unsaturated zone, depth to the water table, aquifer lithology, and aquifer thickness (Sappa and Lega, 1998). The VIs in SINTACS and ISIS are calculated similarly as in DRASTIC (i.e., as weighted sums of individual parameters), but the latter adapts ratings from DRASTIC and SINTACS and weights from GOD (Civita and De Regibus, 1995; Sappa and Lega, 1998).

The SEEPAGE method (Moore and John, 1990; Navulur and Engel, 1996; Richert et al., 1992) focuses on soil properties and considers the following parameters: soil slope, depth to water table, vadose zone material, aquifer material, soil depth, and attenuation potential. The attenuation potential is further subdivided into texture of surface soil, texture of subsoil, surface layer pH, organic matter content of the surface, soil drainage class, and soil permeability (least permeable layer). Each factor is assigned a weight ranging from 1 to 50 based on its relative significance, with the most significant parameter affecting the water quality assigned a weight of 50 and the least significant assigned a weight of 1. The weights are different for point and diffuse sources. The SEEPAGE Index Number is obtained by summing the scores of the six individual parameters, resulting in four categories of vulnerability.

3.1.2. Methods dedicated to karst

Karstic aquifers comprise highly soluble rocks such as limestone, and are marked by well-developed secondary porosity, which results from dissolution enlargement along preexisting fissures and fractures (Ford and Williams, 2007). The consequence of this process is a landscape characterized by sinking streams, dolines, springs, and bedrock containing highly heterogeneous and spatially and volumetrically unpredictable cave networks. Precipitation may diffusely percolate through the soil zone and epikarst prior to entering underlying cave networks and emerging at down gradient discharge areas and/or springs. Alternatively, precipitation may directly infiltrate through highly permeable swallow holes or karrenfields and residence through vertical shafts to merge with groundwater in the phreatic zones. Thus swallow holes, fractures, and other open conduits provide routes for the direct entry of water and surface-derived contaminants into the subsurface

(Ravbar, 2007). Therefore, rapid infiltration, high flow velocities, swift spatial distribution of waters, and short residence times result in karstic aquifers lacking a substantial self-cleaning capacity and enable rapid dispersal of contaminants (Zwahlen, 2004). Even in the context of karst's inherent anisotropy, prediction of transport processes is further complicated by two factors. First, direction of flow within karst can be largely dependent on the recharge volume flushing through the system at a given time. Increased subsurface flow may max out the capacity of a given karst conduit, activating flow in overlying conduits, which had been historically abandoned (Kübeck et al., 2013). Second, karstic rocks by nature are continuously undergoing dissolution. Therefore, with time, new conduits are forming and being abandoned and flow is rerouted with these changes.

Two categories of vulnerability assessment tools can be applied to karstic settings: those specifically configured for karstic settings (e.g., DIVERSITY, EPIK, REKS, PaPRIKA) and those applicable to all aquifer formations with a specific tool adapted for karst (e.g., KARSTIC, PI, DRISTPI). DIVERSITY (Dispersion/Velocity-Rated/Sensitivity) applied to regional scale assessments (Ray and O'dell, 1993; Ray et al., 1994) is an example of hybrid methods (Vrba and Zaporozec, 1994) as the physical parameters (pore size, groundwater flow velocity, and potential dispersion) are taken into account. KARSTIC (Davis et al., 2002) is a PCSM method derived from DRASTIC and bases the evaluation on the following factors: Karst sinkholes with surface recharge; Aquifer medium; Recharge rate; Soil medium; Topography; Impact of the unsaturated zone (includes lithology and depth to water; their weights and ratings are multiplied together); and hydraulic Conductivity of the aquifer. The EPIK method was the first in Europe multi-parameter intrinsic vulnerability mapping tool developed specifically to take into consideration the hydrological characteristics in karst aquifers (Doerfliger, 1996; Doerfliger et al., 1999; Doerfliger and Zwahlen, 1995; 1997; Tulipano et al., 2002). This PCSM method evaluates the protection factor F_p by weighing the following factors: Epikarst development, Protective cover effectiveness, Infiltration conditions, and Karst network development. Based on EPIK, the RISKE method (Petelet-Giraud et al., 2000) and its improvement RISKE 2 (Plagnes et al., 2005) (PCSM both) introduced modifications to mitigate overlapping of criteria (ex. in Infiltration and in Epikarst definition) in addition to introducing consistency in the weighting and RS. The PRESK method (Koutsi and Stournaras, 2011), an adaptation of RISKE, considers the protective role of topography in combination with vegetation. Another method based on EPIK but belonging to the RS category is REKS—Rocks, Epikarst, Karstification, and Soil cover (Malik and Svasta, 1999). Marsico et al. (2004) integrated into the SINTACS method typical karst features (dolines, caves, and superficial lineament arrangement).

Vulnerability assessments of karstic areas were a subject of COST Action 620 (Zwahlen 2004), which resulted in defining the RS-type PI method (Goldscheider et al., 2000; Goldscheider, 2005) based on assessing the Protective function of the layers above the saturated zone and of the Infiltration conditions. The P factor is

calculated according to a slightly modified version of the German (GLA) method (Hölting et al. 1995; von Hoyer and Sofner, 1998) and divided into five classes (from $P = 1$ for a very low degree of protection to $P = 5$ for very thick and protective overlaying layers). The I factor describes the infiltration conditions and varies from 0.0 when the protective cover is completely bypassed by a swallow hole to 1.0 for diffuse infiltration in flat area. The final protection factor π is the product of P and I and is subdivided into five classes. The PI method served as a basis for the further development of the European approach (Daly et al., 2002; Zwahlen, 2004) based on the hazard-pathway-target model. It takes into account the specific properties of the karstic environments not excluding applicability of the method to other geological conditions. This general approach specifies neither component factors necessary for measurement nor guidelines for vulnerability mapping, but presents a board method with an array of elements for possible application, the selection of which is contingent upon site configuration and intended use. Four factors are considered: overlaying layers (O), concentration of flow (C), precipitation regime (P), and karst network development (K) (Daly et al., 2002; Zwahlen, 2004). A number of vulnerability assessment methods originated from the European approach. The COP method was designed for resource vulnerability mapping to include the overlaying layers factor (O), the concentration of flow factor (C), and the precipitation regime factor (P) (Andreo et al., 2006; Vías et al., 2005; 2006). The O factor refers to the protection of the unsaturated zone against a contaminant event and plays a critical role in vulnerability assessment. The C and P factors are used as modifiers that correct the degree of protection provided by the overlaying layers (O factor) (Zwahlen, 2004). To obtain the COP VI the final numerical representations of the C , O , and P factors are multiplied (Vías et al., 2005; 2006). The values of the COP index range between 0 and 15 and are grouped into five vulnerability classes. The COP method was extended into the COP+ K method (Andreo et al., 2009), named also the Slovene approach (Ravbar, 2007), which is dedicated to water source (spring or well) vulnerability assessment. In this method the “Karst saturated zone (K) factor” is proposed, which considers the horizontal flow in the saturated zone, depicted as the karst network development. The value of the K factor is based on the groundwater travel time, the information on karst network development, and the degree of connection to the spring or well (Andreo et al., 2009). To obtain the final source VI, the K index is added to the COP index. The source vulnerability maps can be used as a basis for the delineation of the protection zone (Andreo et al., 2009; Ravbar and Goldscheider, 2007). The COP and the COP+ K methods are RS, while a simplified methodology proposed by Nguyet and Goldscheider (2006) is an MS acc. Vrba and Zaporozec (1994) classification. In this simplified methodology groundwater vulnerability in karst area is assessed on the basis of two factors only: the overlaying layers (O) and the concentration of flow (C). The resulting maps can be a basis for groundwater management and land-use planning (Nguyet and Goldscheider, 2006; Ravbar and Goldscheider, 2009). VURASS (vulnerability and risk assessment for alpine aquifer systems)

(Laimer, 2005) dedicated to alpine karst aquifer is the PCSM method emphasizing the infiltration criterion.

Yildirim and Topkaya (2007) compared four vulnerability mapping methods: DRASTIC, SINTACS, PI, and COP applied in a karst aquifer in Turkey. This study shows that the COP method gives the best results in evaluating the karst groundwater vulnerability to pollution. Another comparison of methods (GOD, DRASTIC, SINTACS, EPIK, PI, and COP) was performed at a karstic test site in SE Italy by Polemio et al. (2009). EPIK, PI, and COP supplied satisfactory results, highly coherent with karstic and hydrogeological features, especially in the case of PI and COP.

As a resource and source vulnerability mapping tool based on EPIK, RISK, PI, and COP, the PaPRIKa (PCSM) method takes into consideration both aquifer structure (resource vulnerability) and function (source—spring, well—vulnerability) (Doerfliger et al., 2010; Huneau et al., 2013; Kavouri et al., 2011; Marín et al., 2012). The acronym PaPRIKa stands for **P**rotection of **a**quifer assessed on the base of the four factors: **P**rotection (including soil cover, unsaturated zone, and epikarst behavior parameters); **R**ock type, **I**nfiltration, and **K**arstification degree. The PaPRIKa method generates two vulnerability maps: (i) the resource-vulnerability map useful to control diffuse pollution and to prevent further deterioration of the aquifer; and (ii) the source catchment vulnerability used to delineate the protection zones and prevent contamination from accidental pollution. The *I* factor map for source vulnerability assessment (I_{source}) applies transit time isochrones, which take into account the active conduit network. Other vulnerability methods developed under COST 620: VULK (Jeannin et al., 2001), which became the base for the “Vi & Cv” method (Butscher and Huggenberger, 2009), and Time-Input (Kralik and Keimel, 2003), which evolved to the Residence Time Method (Brosig et al., 2008), are presented in chapter 4.2.

A PCSM method DRISTPI was proposed by Jiménez-Madrid et al. (2013) for evaluation of the intrinsic vulnerability in different types of aquifers with emphasis on karst area. The rationale of this method is to protect the groundwater (the resource) rather than the water supply (the source). DRISTPI takes as the starting point the DRASTIC approach but eliminates the A (aquifer material) and C (hydraulic conductivity) factors that are mainly related to the movement of water through the saturated zone. The DRISTPI method incorporates a new factor called PI to characterize areas of preferential infiltration.

While vulnerability assessment methods need to be reliable and universal for cross-site comparison, the inherent anisotropy and heterogeneity of karstic settings, flow switching with recharge volume, and flow rerouting due to aquifer dissolution, along with region-specific climate dictates a need for regional adaptation of the assessment methods. Given that one exact, inadaptable method cannot be ubiquitously applied to all carbonate aquifers, the need for validation of vulnerability methods is necessary (Gogu and Dassargues, 2000b). Validation

procedures should be applied rigorously considering on the one hand integrated tracers (nitrates, pesticides such as developed in the framework of the EU FOOTPRINT project (FOOTPRINT, 2006–2009)) and on the other hand artificial tracers applied under variable hydrological conditions such as suggested by Ravbar (2007), Nguyet and Goldscheider (2006), Perrin et al. (2004), Rupert (2001), or Sinreich and Pochon (2015) as well as the environmental tracers used for vulnerability validation (Dimitriou and Zacharias, 2006; Goldscheider and Drew, 2007).

3.2. Objective methods

Application of the objective methods does not involve subjective categorization. These methods allow for predicting groundwater responses to pollution by use of statistical or physically based approaches. The statistical methods attempt at predicting contaminant concentrations or probabilities of contamination on the basis of correlations between selected parameters describing aquifer properties, sources of contamination, and contaminant occurrences derived from sufficiently extensive sets of monitoring data (e.g., FOOTPRINT, 2006–2009). As such, the statistical methods are concerned with the specific vulnerability. They may well incorporate a wide range of input factors related to both the anthropogenic and natural conditions of the groundwater system (Masetti et al., 2008, 2009; Boy-Roura et al., 2013). The statistical methods try to minimize uncertainty of assessments by determining suitable factor coefficients instead of importance weights (Shirazi et al., 2012). However, for the establishment of reliable statistical parameters, it is required that sufficient and proper monitoring data exist. Masetti et al. (2009) categorized the statistical methods of vulnerability assessment into Logistic regression (Eckardt and Stackelberg, 1995; Tesoriero and Voss, 1997; Nolan et al., 2002) and Bayesian methods (Worrall and Besien, 2005; Arthur et al., 2007; Masetti et al., 2007 and Masetti et al., 2008). Other sophisticated statistical techniques make use of the Artificial Neural Networks in order to establish relationships between the driving factors (input layers) and the water deterioration status (output layers). Examples of such applications can be found in the recent literature (Aguilera et al., 2001; Kralisch et al., 2003; Sharma et al., 2003; Dixon, 2005; Daliakopoulos et al., 2005; Mohammad and Jagath, 2005; Chaves and Kojiri, 2007; Gemitzi et al., 2009). Masetti et al. (2009) noticed that among the advantages of the statistical methods is their ability to be easily updated as new information becomes available and tested against new groundwater observations. Other statistical methodologies developed for vulnerability assessment incorporate the use of sophisticated tools such as neuro-fuzzy techniques (Dixon, 2005) or the fuzzy quantification approach combined with the Ordered Weighted Average procedure (Gemitzi et al., 2006). Both methodologies validated their approaches by comparing the results with water-quality data and trying to form a sensitivity analysis. Moreover, attempts are

made to combine methods belonging to different categories (Focazio et al., 2002; Yu et al., 2010).

The physically based (process based) methods of vulnerability assessment were initially seen as requiring “analytical or numerical solutions to mathematical equations that represent coupled processes governing contaminant transport (p. 6)” (National Research Council, 1993) with large data requirements, upscaling and downscaling problems, and difficulties with representation of preferential flow seen as their disadvantages. Indeed, the task of assessing groundwater vulnerability can be seen as essentially equivalent to predicting contaminant concentrations within a groundwater body or at groundwater receptors. However, as the data density for large-scale models is usually scarce and cannot represent local heterogeneity of hydraulic parameters, such models are highly uncertain (Voss 2005, 2011a, 2011b; Konikow, 2011; Refsgaard et al., 2012). According to Focazio et al. (2002) the physically based methods take into account the physical processes of flow and transport, but do not have to rely on deterministic simulations. A promising, but still not widely used, physically based approach grounds assessments of vulnerability on estimates of the temporal characteristics of contaminant transport such as residence time or residence time distributions (RTDs) of water (Van Stempvoort et al., 1992; Voigt et al., 2004; Zwahlen, 2004; Witczak et al., 2007; Eberts et al., 2012).

4. Importance of timescales in vulnerability assessment

4.1. Indicators of the intrinsic vulnerability based on timescales of groundwater flow

The relevance of vulnerability assessments to the present requirements of water resources managements depends on their ability to address time lags associated with contaminant transport. The longer the time necessary for the contaminants to reach the groundwater table or the groundwater receptor, the greater is the effect of contaminant dilution, retardation, and attenuation. Mean residence time (MRT) of water appears in this context as a pragmatic indicator of the intrinsic groundwater vulnerability. There is some terminological confusion concerning terms used to describe temporal characteristics of mass transport. For the purpose of this work we treat different terms used in the literature (travel time, residence time, transit time, turnover time) as synonymous in the steady-state conditions. The MRT equals the turnover time of water and thus the ratio of water volume in reservoir to water flux. In contrast, mean travel time or transit time (MTT) of water can be evaluated using Darcy's law and represents the advective flow timescale. For a detailed discussion of the physical meaning of those terms see Bolin and Rodhe (1973).

A more comprehensive, than the MRT, quantitative characteristic of delays in solute transport through groundwater systems is provided by RTD (Etcheverry and Perrochet, 2000; Kazemi et al., 2006; Leibundgut et al., 2009, Eberts, 2012).

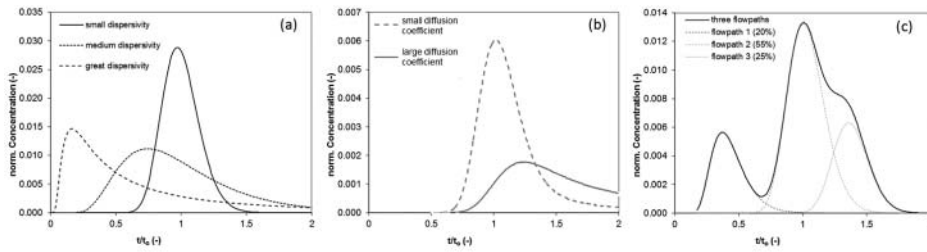


Figure 2. Schematic illustration of normalized residence time distributions in saturated sediments (a) with different dispersivities, (b) for two solutes with different diffusion coefficients in heterogeneous sediments containing immobile water, and (c) in heterogeneous sediments containing three flowpaths with different fractions of flow components; t_0 : mean residence time.

The RTD represents response of the system to the instantaneous pulse of contamination and as such provides information on the time lags in propagation of changing contaminant inputs. RTDs can be mathematically coupled with transient contaminant inputs to predict their output concentrations (Maloszewski and Zuber, 1996; Bohlke, 2002; Marcais et al., 2015). Some examples of RTDs for steady-state flow conditions in saturated sediments are schematically illustrated in Fig. 2; all RTD are normalized to the concentration and MRT. Further examples of RTD and a detailed description of different mathematical model approaches and parameters are given in Leibundgut et al. (2009). For systems containing mobile water only, transport is described by the advection dispersion equation. Here, the shape of the RTD depends on the dispersivity; the larger the dispersivity, the more skewed is the RTD, and the maximum peak concentration appears at times smaller than the MRT (Fig. 2a). For systems containing immobile water, the RTD of the solutes additionally depends on the diffusion properties of the solutes. The larger the diffusion coefficient, the more solute diffuses into immobile water regions and the longer is the tailing of the RTD. Experimental evidence for immobile water regions can be gained from artificial tracer experiments using multiple tracers with different diffusion properties resulting in different concentration curves as illustrated in Fig. 2c and in Knorr et al. (in press). Pronounced tailing of RTD can also be the result of multiple flow paths. Here experiments with multiple tracers having different diffusion properties result in identical RTD. The RTD in such heterogeneous multiple flowpaths systems strongly depends on the transport properties of the individual flowpaths and their relative contribution to the total flow, as for example shown for three individual flowpaths in Fig. 3c. From these examples it is obvious that MRT is related to only one of the statistics (mean) of the RTD, which might not be appropriate to characterize cases of multiple flow components or multiple porosity (Zwahlen, 2004). Multiple flow components result from preferential flow through the unsaturated zone (Stumpp et al., 2007; Nimmo, 2012) or from the horizontal stratification of aquifers (Etcheverry and Perrochet, 2000). In such cases, knowledge of the full RTD allows for quantification of the relative

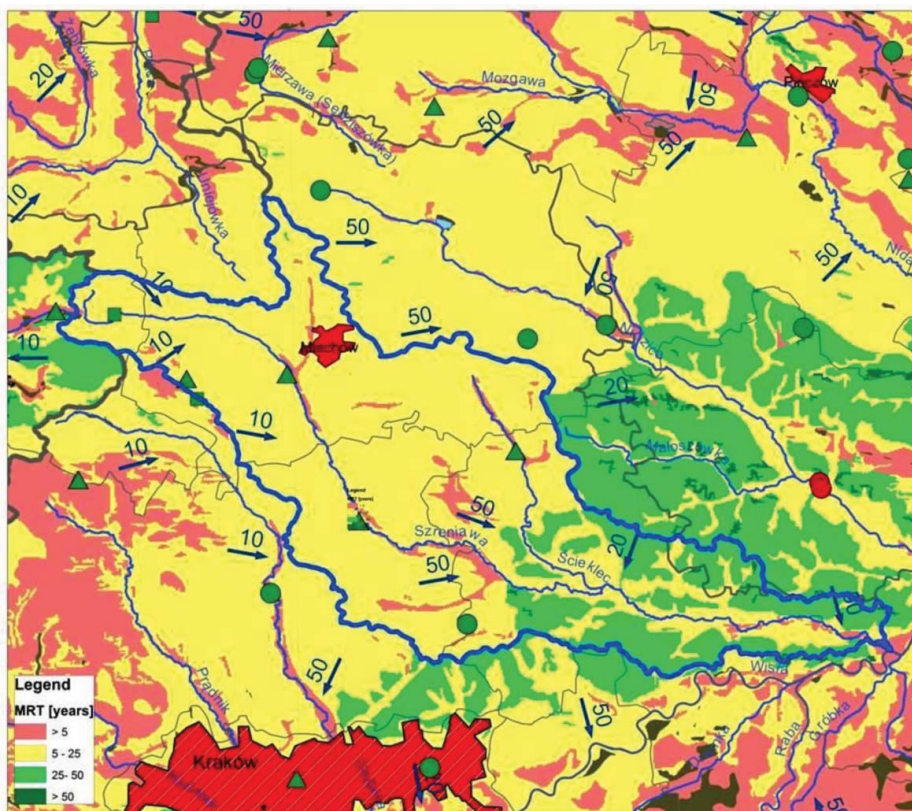


Figure 3. Selected part of the groundwater vulnerability map of Poland (Witczak, 2011; modified) with the Szreniawa river catchment marked with bright blue line. Colors represent MRT in the unsaturated zone. Arrows with individual labels reflect lateral travel time of water in years through saturated zone over the distance of the corresponding length of the arrows (3 km). The map provides estimates of time lags between contaminant entrance and its appearance in surface water of a given catchment.

importance of particular flow components (Fig. 2c). The highly skewed RTDs, which arise due to multiple porosity or pronounced heterogeneity of geological medium, can be characterized by other than MRT statistics of RTD (e.g., mode, quantiles). The RTD statistics may be used to design more sophisticated vulnerability indicators as illustrated by some of the examples given below. Nevertheless, use of MRT as a vulnerability indicator is a reasonable compromise because of the effort, skills, and information on the groundwater system required for determination of the full RTD. As an indicator of vulnerability, the time necessary for water to reach a drinking water well is also more easily understandable by the general public than indicators built on more abstract properties like hydraulic conductivity.

The RTDs are obtainable through modeling (Ginn, 1999; Etcheverry and Perrochet et al. 2000; Cornaton and Perrochet, 2006), which relies on the knowledge of hydrogeological characteristics and is subject to uncertainties stemming from

heterogeneities inherent to groundwater systems. The temporal characteristics of groundwater flow can be, however, more directly derived through analysis of environmental tracer data. In the simplest mode of tracer application, lack or low levels in groundwater of substances introduced into the atmosphere by men (e.g., bomb tritium, freons) indicates vulnerability of groundwater to contamination released after the 1950s. Full RTDs are obtained by fitting of tracer data to RTDs of different lumped parameter transport models (Maloszewski and Zuber, 1982; Maloszewski et al., 2006; Stumpp et al., 2009b) or by application of the nonparametric approaches where no particular shape of the RTD is presumed (Visser et al., 2013; Massoudieh et al., 2014). An advantage of environmental tracers is their ability to integrate information on groundwater flow patterns between recharge areas and groundwater sampling points over a wide range of possible spatial and temporal scales (Newman et al., 2010). The RTDs obtained in such a way reflect the influence of the heterogeneities in all relevant scales without a need to characterize them quantitatively.

4.2. Review of vulnerability assessments based on timescales

Methods using timescales for vulnerability assessment are summarized in Table 3 and discussed in more detail below. The table facilitates a comparison of the methods concerning their type of timescale used for vulnerability assessment, their applicability to different groundwater systems and scales as well as the basic methods for timescale analysis.

Probably the first practical use of time as vulnerability indicator was proposed by Zampetti (1983) in the TOT (time of travel) method, in which the time required for a contaminant to move through the vadose zone from a specific point to the aquifer is assessed (Debernardi et al., 2008). The TOT values were divided into six classes of vulnerability varying between very low (TOT > 20 years) and extreme (TOT < 24 hr) (De Luca and Verga, 1991). Marcolongo and Pretto (1987) use time indirectly as a VI on the map of the aquifer near Vicenza, Italy. The VI (I_v) was assessed taking into account the specific retention and infiltration capacities of soil:

$$I_v = \frac{R}{z \cdot \theta} \quad (1)$$

where θ is the actual soil volumetric water content [L^3/L^3], z is the thickness of the unsaturated zone [L], and R is the infiltration rate per unit surface (recharge)[L/T].

For the purpose of Groundwater Resources Maps of Europe (CEC, 1982) residence time in piston-flow conditions was implemented as the VI in the vulnerability mapping in France (BRGM, 1979), the Netherlands (Meinardi et al., 1982), Denmark (Villumsen et al., 1982), and the United Kingdom (Vrba and Zaporozec, 1994). The vulnerability maps of the United Kingdom

Table 3. Approaches based on timescales.

Method/ reference	Groundwater system			Spatial application		Modeling approach				
	Vulnerability indicator ¹⁾	Vadose zone	Saturated zone	Karst ²⁾	Local (aquifer or basin scale)	regional	Turnover time (water content vs. infiltration)	Darcy's flow (advection)	Numerical modeling	Isotopes and lumped parameter model
TOT Zampetti, 1983	TT	x			x			x		
Marcolongo and Pretto, 1987	1/MRT	x			x		x			
Groundwater Resources Maps of Europe CEC, 1982	MRT	x				x	x			
Bachmat and Collin, 1987	TT ³⁾				- ⁴⁾ x	- ⁴⁾	x	x		
MGWB Kleczkowski, 1991;	RT	x	x			x	x	x		
Kleczkowski and Witzczak, 1990					x					
AVI Van Stempvoort et al., 1993	c: "hydraulic resistance" (Tab. 4)	x	x					x		
Maxe and Johansson, 1998	TT	x	x		x		x	x		corresponding to RT
The German method (GLA) (hybrid method) Hölting et al, 1995; von Hoyer and Söfner, 1998; Voigt et al., 2004	point rating									
x										
VULK Jeannin et al., 2001; Cornaton, 2004; Sinreich et al., 2007	TT	x	x	x	x				x	
Vi & Cv Butscher and Huggenberger, 2008; 2009	VI ⁵⁾			x	x				x	
Time-Input (hybrid method) Kralik and Keimel, 2003	TT ⁶⁾	x	x	x	x			x		
Frind et al., 2006	TT		x		x ⁷⁾				x	
Schwartz, 2006	MRT	x				x			x	
Neukum, 2008	MTT	x		x	x				x	x
Neukum and Azzam, 2009	TTD (TT ^{75%} , TT ^{50%} , TT ^{25%})	x			x				x	
Heuvelmans and D'hont, 2012	TTD ⁸⁾	x			x				x	

(Continued)

Table 3. (Continued)

Method/ reference	Groundwater system			Spatial application		Modeling approach				
	Vulnerability indicator ¹⁾	Vadose zone	Saturated zone	Karst ²⁾	Local (aquifer or basin scale)	regional	Turnover time (water content vs. infiltration)	Darcy's flow (advection)	Numerical modeling	Isotopes and lumped parameter model
Popescu et al., 2008; Dassargues et al., 2009	TT ⁹⁾	x	x	x	x				x	
Transit Time Brosig et al., 2008	TT			x	x			x		
Eberts et al., 2012	TTD		x	x	x				x	x
Fenton et al., 2011	time lag	x	x		x ¹⁰⁾		x	x		
Herrmann et al., 2012	RT	x				x	x			
Hrachowitz et al., 2011 Heidb üchel et al., 2012	MTT				x ¹⁰⁾					x
van der Velde et al., 2012 Basu et al., 2012	TTD				x ¹⁰⁾					x
	time lag (TTD)		x		x			x	x	
Sophodeous, 2012	time lag (TT)		x		x				x	
GWMP Witczak et al. 2007; 2011	MRT	x				x	x			

1) TT: transit (travel) time; TTD: transit time distribution; (M)RT: (mean) residence time

2) dedicated to karst or karst comprising

3) the authors used the term "travel time" but it is calculated as turnover time

4) no application is evidenced

5) VI (vulnerability index): relative proportions of spring water discharging from the conduit and diffuse systems as a function of time

6) travel time classes are modified by groundwater recharge correction factor

7) well

8) the vulnerability index is defined as the number of the age class containing the 10th percentile of the age distribution

9) final vulnerability indicator depends on three factors: (i) the contaminant transfer time from the source to the target, (ii) the contaminant duration at the target, and (iii) the level of contaminant concentration reached at the target.

10) catchment.

were elaborated using the vulnerability categorization into four classes based on a single parameter—the residence time in the unsaturated zone of a conservative, nonabsorbable pollutant with the physical properties not different from those of water (Lobo-Ferreira, 1998). Based on the methodologies of the above-mentioned groundwater vulnerability maps, Andersen and Gosk (1987) considered their applicability and discussed whether vulnerability could be quantified as dependent on the travel time of pollutants to the aquifer. They stated that the travel time of a pollutant from the source to the aquifer plays an important role in vulnerability mapping and can be used as a vulnerability indicator where removal of the pollutant is dependent on time only. The idea of assessing vulnerability through consideration of timescales was recommended by Fried (1987) for the second phase of elaboration of hydrogeological maps of Groundwater Resources of the European Community. Bachmat and Collin (1987) have proposed a complex technique of quantifying vulnerability as the sensitivity of groundwater quality to anthropogenic activities in which the anticipated change in concentration of a given substance in the groundwater per its unit flux to the ground surface is a function of residence time of this substance depending on the thickness of the unsaturated zone and the average downward velocity of the pollutant. However, Vrba and Zaporozec (1994) suggested that the technique proposed by Bachmat and Collin (1987) is based on too large an amount of data, most of which are difficult to gather.

In the late 1980s the countrywide project of identification of the Major Groundwater Basins (MGWB) was performed in Poland (Kleczkowski, 1991; Kleczkowski et al., 1990; Kleczkowski and Witczak, 1990; Witczak et al., 2007; 2011). The intrinsic vulnerability of the MGWBs and their recharge areas was expressed as the total of the vertical residence time of conservative contaminants from the surface to the aquifer and the horizontal transport time of these contaminants to the border of the MGWB (Witczak, 2011). The piston-flow model was adopted to estimate the residence times. The intrinsic vulnerability of the MGWBs and their recharge areas was classified and mapped (Kleczkowski et al., 1990) as follows: (i) extreme and high vulnerability— $RT < 5$ years—requiring extreme protection (Maximum Protection Areas); (ii) moderate vulnerability— RT in the range 5–25 years—requiring high protection and (High Protection Areas); (iii) low and very low vulnerability— $RT > 25$ years—requiring usual protection (Standard Protection Areas). The MPAs and HPAs were presented on the map at a 1:500000 scale (Kleczkowski et al., 1990).

In the AVI method proposed by Van Stempvoort et al. (1993), as the alternative to the DRASTIC method (Aller et al., 1987), the measure of groundwater vulnerability is based on two physical parameters: (i) thickness of each sedimentary layer above the uppermost, saturated aquifer surface d , and (ii) estimated hydraulic conductivity K of each of these sedimentary layers. Based

on these two physical parameters, the hydraulic resistance c can be calculated for n layers as follows:

$$c = \sum_{i=1}^n \frac{d_i}{K_i} \quad (2)$$

The parameter c [T] is a theoretical factor used to describe the resistance of an aquitard to vertical flow. Thus, the weighing of the two factors, thickness d [L] and hydraulic conductivity K [L/T] of each sediment layer above the uppermost saturated aquifer surface, is not arbitrary, but it based on physical theory (Van Stempvoort et al., 1992; 1993; Van Stempvoort and Martin, 2003). The physical dimension of the hydraulic resistance c is time and this parameter indicates the approximate time necessary for water to seep downward through the various porous media above the uppermost saturated aquifer surface. However, it should be noted that in a strict sense, c is not a residence time either for water—unless all water is mobile—or contaminants because this formula assumes Darcy flow at the unit hydraulic gradient and because diffusion and sorption are not considered. The calculated c or $\log c$ values can be used directly to generate vulnerability map, because the vulnerability classes are derived directly from the relationships of AVI to hydraulic resistance c . It must be noted that the K values used for calculation of c correspond to the saturated conditions, which are not typical in the unsaturated zone. Furthermore, vulnerability classes are based on the logarithms of c (Table 4), which hinders the relation to time lags. Because of that the AVI method should be classified as a hybrid method.

In Sweden (Maxe and Johansson, 1998), travel time was used as the indicator of groundwater vulnerability for the hypothetical scenario of accidental spills of liquids generating a hydraulic surcharge. For the situation when the contaminants are transported by the natural groundwater recharge, the groundwater vulnerability was related to retention capacity determined from the total surface area of the overburden material in the unsaturated zone. The travel time of water for deeper parts of the profile was roughly estimated by Darcy's law, assuming temporary saturation and a unit hydraulic gradient.

Table 4. Relationship of aquifer vulnerability index (AVI) to hydraulic resistance (according to Van Stempvoort et al, 1992; 1993).

Hydraulic resistance (c) [years]	$\log c$	Aquifer vulnerability index (AVI)
0–10	<1	extremely high
10–100	1–2	high
100–1000	2–3	moderate
1000–10,000	3–4	low
>10,000	>4	extremely low

By assuming complete saturation, a worse case was obtained for matrix-flow situation. As the maximum values of possible recharge (natural and additional from accidental spill), the infiltration capacities of typical soils were considered.

The “German” method (also known as the GLA method) (Hölting et al., 1995; von Hoyer and Sofner, 1998) puts considerable emphasis on travel time as a measure of the protective function of the unsaturated zone. The basic assumption is that infiltration occurs diffusely and therefore this method is not recommended to karstic area (Zwahlen, 2004). This protective function is dependent on the main factors controlling the travel time: the thickness of each stratum of the unsaturated zone (topsoil, subsoil, and unsaturated bedrock) and the properties of the material. The protective function of the topsoil is assessed according to effective field capacity, that of the subsoil by considering grain-size distribution, and that of the unsaturated bedrock according to lithology (Zwahlen, 2004). The German method is a hybrid method because the vulnerability assessment bases on the indirect point rating, which corresponds to residence time of percolating water in the unsaturated zone (Hölting et al., 1995; Voigt et al., 2004). The protection function of the unsaturated zone is acknowledged, respectively, as follows: (i) very high when residence time (RT) is >25 years, (ii) high—RT in the range of 10–25 years, (iii) moderate—RT in the range of 3–10 years, (iv) low—for RT varying from several months to about 3 years, and (v) very low—when RT is generally shorter than 1 year (range: few days to about 1 year, in karstic rock even less) (Hölting et al., 1995; Voigt et al., 2004). The basic assumptions of the German approach were used in the PI method coming from COST 620 group (Goldscheider et al., 2000; Zwahlen, 2004).

The physically based vulnerability method that has been created especially for quantitative intrinsic vulnerability assessment in karst settings according to the European COST Action 620 is VULK (the acronym for **VUL**nerability and **Karst**) (Jeannin et al., 2001; Cornaton, 2004; Sinreich et al., 2007). The VULK code is an analytical one-dimensional transport solver (steady-state flow, transient transport) (Jeannin et al., 2001). Here, the dual-porosity approach was applied to account for preferential flow in enlarged fissures and karst conduits. Five layers (topsoil, subsoil, epikarst, unsaturated karst, and karst phreatic zone) are considered in the VULK model. The key output parameters are: the dominant transit time (arrival time of the maximum contaminant concentration, C_{\max}) and attenuation (C_0/C_{\max} : ratio of the input to the maximum concentration). The VULK model was improved to simulate an array of physical and geochemical reactions and implemented to assess specific vulnerability (Sinreich et al., 2007). The improved model was validated by field experiments with tracers (Perrin et al., 2004).

The VULK method became the base for the “Vi & Cv” method (Butscher and Huggenberger, 2008; 2009) dedicated to karst aquifers. In this approach the vulnerability assessment is based on an intrinsic property of a karst system, which is the relative proportions of spring water discharging from the conduit and diffuse systems as a function of time. VI is assessed on the base of numerical modeling and defined as the ratio of the contributions of karst conduit systems to spring

discharge. High values of VI (i.e., a high proportion of water from the conduit system) indicate that the spring is highly sensitive to short-lived contaminants (e.g., microorganisms). Vulnerability Concentration CV is calculated in spring water as the result of a continuous input of a standard contaminant with different degradation rates and can be used to assess the specific vulnerability.

The other method coming from COST Action 620 is the Time-Input method (Kralik and Keimel, 2003), to assess groundwater vulnerability especially in mountainous areas (Zwahlen, 2004). Two main factors taken into account in this approach are the travel **Time** from the surface to groundwater (weight 60%) enhanced by the amount of precipitation **Input** as groundwater recharge (weight 40%) (Kralik and Keimel, 2003). The travel time is calculated as the sum of the hydraulic conductivity multiplied by the thickness of each stratum. Vulnerability is mainly expressed as travel Time classes (in seconds) modified by the Input-correction factor based on groundwater recharge (mm/year). Since the time values are not the exact MTT to groundwater, the Time-Input method should be classed as a vulnerability assessment hybrid method. The Time-Input method evolved into the Residence Time Method (Brosig et al., 2008), which is mentioned in the following.

Referring to the concept of groundwater vulnerability within the European COST Action 620, Frind et al. (2006) presented a quantitative approach for water intake protection (well vulnerability). This approach, developed by Molson and Frind (2012), focuses on the relative expected impact of potential contaminant sources at unknown locations within a well capture zone, providing relative measures of intrinsic well vulnerability. It includes the expected times of arrival of a contaminant, the dispersion-related reduction in concentration, the time taken to breach a certain quality objective, and the corresponding exposure times. This approach supplements the advective travel time used in conventional wellhead protection analysis with a set of selected quantitative measures expressing the expected impact. The technique combines forward- and backward-in-time flow-path modeling using a standard numerical flow code.

The vulnerability of groundwater in Namibia was assessed by Schwartz (2006) through numerical modeling. The net infiltration rate together with the water storage in the unsaturated zone and groundwater depth were used to calculate the residence time of pore water in the unsaturated zone. To simulate the water balance (precisely the net infiltration) in the vadose zone, taking into account preferential flow in macroporous soils of vegetation sites, the physically based numerical modeling approach MACRO4.3 (Jarvis, 2002) was applied. The calculated residence times range from <1 year in areas with carbonate rocks to >500 years in desert areas in accordance with the respective timescales of groundwater response to rainfall. Five vulnerability classes were based on residence time following Hölting et al. (1995): very high (<1 year), high (1–3 years), medium (3–10 years), low (10–25 years), and very low (>25 years).

Neukum and Hötzl (2007) performed a comparative assessment of four vulnerability methods: DRASTIC, PI, EPIK, and GLA in a karst area in SW Germany.

The consistency of the maps produced by different methods was improved after the introduction of new class limits defined through the MTT of water in the unsaturated zone calculated by the GLA method (Neukum and Hötzl, 2007). Neukum et al. (2008) presented the more advanced methodology for validation of the above-mentioned mapping method. Maps were validated by estimates of the MTT through the unsaturated zone derived from field investigation and numerical modeling. The results of stable isotopes and tritium measurements were interpreted by lumped parameter models (“black-box” models) (Maloszewski and Zuber, 1982, 1996). Transit times (arrival times for C_{\max} and C_{mean}) for each hydrogeological layer in the unsaturated zone were modeled separately. Vertical one-dimensional water flow and transport in all the hydrological layers were modeled with HYDRUS-1D (Šimůnek et al., 2005). Drawing from these results, Neukum and Azzam (2009) defined new vulnerability indicators using numerical simulation of water flow and solute transport with transient boundary conditions. Based on the first, second, and third quartiles of solute mass breakthrough at the lower boundary of the unsaturated zone and on the solute dilution, four vulnerability indicators were extracted. The t_{50} transit time is the time where 50% of solute mass breakthrough passes the groundwater table. The dilution is the maximum solute concentration C_{\max} in the percolation water upon entering the groundwater table in relation to the injected mass or solute concentration C_0 at the ground surface. The duration of solute breakthrough is defined as the difference of arrival times for the first and third quartiles of solute mass ($t_{75\%}-t_{25\%}$). A similar approach was proposed in the framework of the IMVUL project (IMVUL, 2008–2012) by Heuvelmans and D’hont (2012), who defined the VI as the number of the age class containing the 10th percentile of the age distribution.

The approach of Neukum and Hötzl (2007) was followed by several researchers. Yu et al. (2010) performed comparative vulnerability assessments using the index system and transport simulation in a catchment in Shandong province of China. The transit time of 75% of a hypothetically injected contaminant was considered as the vulnerability indicator. Primary approximation of transit time values in selected subareas was simulated by the HYDRUS 1D transport model (Šimůnek et al., 2005). Next, the Monte-Carlo simulation was used to improve vulnerability assessment using the statistics of the transit time. It was concluded that transport simulations can provide validation or improvement of the index methods.

Pragmatic solutions for groundwater vulnerability assessment using physically based modeling were proposed by Popescu et al. (2008), who followed the idea of Brouyère et al. (2001). The definition of the vulnerability was based on three factors describing a pollution event, which are: (i) the contaminant transfer time from the source to the target, (ii) the contaminant duration at the target, and (iii) the level of contaminant concentration reached at the target. Practically, this method needs to describe and simulate the contaminant migration in the unsaturated zone and possibly in the saturated zone in order to assess the breakthrough

curve at the target. A final vulnerability indicator depends on the decision makers who can decide about the relative importance for each of these three physically based criteria according to their locally agreed priorities. This approach was tested in a limestone basin in Belgium (Popescu et al., 2008; Dassargues et al., 2009). The weighting coefficients for a final vulnerability indicator were assumed as follows: 0.45 to the transient time, 0.45 to duration of the contamination, and 0.10 to the maximum concentration.

Brosig et al., (2008) in their study of a karst groundwater in Northern Jordan, based vulnerability assessment on the idea that areas close to the final infiltration point (e.g., sinkholes) within the dry valleys allow rapid infiltration and are thus more vulnerable. The vulnerability is related to the transit time of lateral water flow along the slope within the epikarst toward the final infiltration points or dry valleys. The transit time is calculated as the ratio of flow path length to the average pore water velocity.

Eberts et al. (2012) compared two assessments of the vulnerability of production wells to contamination based on a particle-tracking and on a lumped-parameter model. Selected characteristics of the age distributions obtained by both models for each investigated well were compared to identify the model differences that affect contaminant predictions. In addition, results from piston-flow models calibrated to tracer data were used to illustrate the importance of full age distributions, rather than apparent tracer ages or model mean ages, for trend analysis and forecasting.

Assessments of groundwater vulnerability are an indispensable part of catchment-scale water resources management because groundwater constitutes a considerable component of catchment run-off in all climatic and hydrogeological settings. Moreover, in baseflow conditions, the ecological status of streams depends largely on the quality of discharging groundwater. At the same time, transport of contaminants with groundwater may be considerably delayed with consequences for risk assessment and planning of protective measures. Fenton et al. (2011) state that evaluation of catchment time lag issues offers a more realistic scientifically based timescale for expected water-quality improvements in response to mitigation measures implemented under the WFD. They presented a simplified methodology for the estimation of vertical and horizontal travel and flushing timescales to nitrate threshold concentrations in Irish aquifers. Horizontal travel time was estimated for the first occurrence of nutrients in a surface of water body assuming piston flow under steady-state conditions. The travel time was calculated using effective porosity instead of the mean water content as introduced later in chapter 5.1.

The relevance of vulnerability assessments to the WFD requirements was also recognized by Herrmann et al. (2012), who, in the regional study in Germany, developed a conceptual hydrogeological model for the evaluation of residence times of water percolation in soil and the unsaturated zone and of groundwater in upper aquifers. The residence time of water in soil was derived from the water storage capacity of soils (field capacity) and the infiltration rate. Determination of

residence times in the groundwater covering layers was evaluated indirectly applying the procedure developed by Hölting et al. (1995). The residence times of groundwater in the upper aquifer were evaluated based on the WEKU model (Kunkel and Wendland, 1997) using the Darcy equation. Residence times determined for unconsolidated rock areas typically ranged between 10 and 25 years, whereas residence times <5 years were assessed for consolidated rock areas.

Sensitivity of MTT estimates to model conditioning and data availability was analyzed by Hrachowitz et al. (2011) for a small catchment in the Scottish Highlands. The analysis was based on seasonal fluctuations of marine-derived Cl^- using the gamma distribution as a TTD function in the convolution integral. The authors concluded that MTT estimations depend strongly not only on data availability and a priori assumptions of the modeler, which include choice of TTD function and representation of the warm-up period, but also on the tracer used. MTT estimates should be seen as indicative rather than absolute and care must be taken when comparing MTT estimates from different studies.

Heidbüchel et al. (2012) analyzed thoroughly the TTD of variable-flow catchment systems. The authors suggested that though the distribution of water transit times is best characterized by a time-variable probability density function, it is often assumed that the variability of TTD is negligible and catchments are characterized by a unique TTD. Application of the method using several years of rainfall-runoff and stable water isotope data yields an ensemble of TTD with different moments. The combined probability density function was proposed and examined in two research catchments. It represents the master TTD and characterizes the variability of catchment storage and flow paths.

At the catchment scale, van der Velde et al. (2012) considered TTD variations with time as the effect of dependency on rainfall and evapotranspiration. To quantify the relation between subsurface mixing and TTD dynamics the authors, referring to Botter et al. (2011), proposed a new TT transformation that yields transformed TTD, called Storage Outflow Probability (STOP) functions. The STOP function can be used as the tool to explore the effects of catchment mixing behavior, seasonality, and climate change on travel time distributions and the related catchment vulnerability to pollution spreading.

Basu et al. (2012), Fenton et al. (2011), and Herrmann et al. (2012) emphasize the critical importance of the policy makers' and water resources managers' awareness of the lag times between application of measures and improvements of groundwater status. For solutes like nitrate that are transported primarily by the groundwater pathway, the lag time is a function of the groundwater TTD. In an approach to solving the time lag problem (Basu et al., 2012), three models of varying levels of complexity were used to estimate the steady-state TTD of a shallow unconfined aquifer in a small (52 km²) watershed (Iowa, USA): (i) an analytic model, (ii) a GIS approach, and (iii) the MODFLOW model. The analytic method, proposed by Haitjema (1995), was derived for steady-state, two-dimensional groundwater flow and neglected flow variation in the vertical direction by

assuming the Dupuit–Forchheimer conditions to be valid. The TTD was derived using a simple water balance for an area enclosed by a representative isochrone. The GIS-based approach was proposed by Schilling et al. (2006) who used the resulting groundwater TTD to estimate the time lags that would be associated with selected land-use changes in the watershed. MODFLOW was used to simulate steady-state, two-dimensional, groundwater flow. Travel times in the watershed were subsequently computed using the particle tracking postprocessing model, MODPATH. The resulting TTDs displayed an exponential distribution with good agreement among all three methods. Results indicated that for shallow aquifers with similarities between the land surface and the water table, simpler approaches (analytic and GIS) can be used to estimate RTDs with accuracy corresponding to disseminate lag times issues to the public.

Sophocleous (2012) provides an exposition on dimensional scaling analysis, followed by an overview of aquifer response time for simplified aquifer systems. It is pointed out that understanding the time lag between land-use changes and groundwater response is fundamental to identifying where in watershed to undertake mitigation programs aimed at changing conditions within a specified time frame. Incorporating time-lag principles into water-quality regulations will provide regulators with more realistic expectations when implementing such policies (Sophocleous, 2012). Especially this issue concerns the implementation date for Programs of Measures, which was set by the Water Framework Directive at 2015 (EC, 2000).

A useful indicator of time lag after cessation of contaminant loads was proposed by Kania et al. (2006). Typically, the catchment response has exponential character like many processes of natural attenuation and the half-time ($t_{1/2}$) of conservative contaminant reduction can be used as an indicator of attenuation after changes in contaminant load. In the case of Quaternary phreatic aquifers in Poland $t_{1/2}$ is about 20 years

An operational approach based on evaluation of timescales was adopted for preparation of the 1:500,000 Groundwater Vulnerability Map of Poland (GVMP) (Witczak et al., 2007; 2011). The GVMP illustrates the intrinsic vulnerability of shallow groundwater systems in Poland to conservative pollutants. The adopted approach relies on MRT of water in the strata separating the saturated aquifer from the land surface as an integrated VI. The classification of groundwater vulnerability adopted for preparation of the map is based on the classification proposed by Foster et al. (2002), which links vulnerability classes to MRT ranges. The MRT is defined in the framework of the piston-flow model of water movement and is equal to the ratio of the total water column present in the vadose zone profile, divided by the mean annual recharge. The total MRT is a sum of partial turn-over times of water in the soil layer and in the rocks (permeable and low permeable) comprising the unsaturated zone. Five information layers were used to calculate the MRT: (i) volumetric water content of the soil profile down to 1.5 m depth, (ii) groundwater recharge, (iii) depth to the water table, (iv) volumetric

water content of dominating lithotypes of rocks present in the vadose zone, and (v) contribution of low-permeable rocks in the vadose zone profile. The MRT classes are the principal information on the GVMP. To quantify the time lag of river systems with respect to changes in the pollutant load (e.g., nitrate) on the given catchment, the directions and the characteristic times of groundwater flow between the recharge areas and the drainage areas (surface waters) are visualized on the GVMP by a system of arrows (Fig. 3). The individual numbers next to the arrows reflect lateral travel time of water in years through saturated zone over the distance of the corresponding length of the arrows (3 km).

It can be seen from the above review that the distinction between the subjective and objective methods is not always clear. Many applications have features of both approaches because the overlay and index framework allows for the operational integration and presentation of the physically based flow characteristics of the system. Furthermore, due to the limited data availability use of educated guesses is unavoidable in most cases. The complementarities of both approaches can be seen in practical realizations of vulnerability assessments like for example the European approach (Zwahlen, 2004) or the Polish approach (Witczak et al., 2007; Witczak, 2011). Table 5 relates the parameters of the DRASTIC approach to the vulnerability assessment method based on estimation of timescales of water flow (Witczak et al., 2007; Witczak, 2011). Incorporation of timescales in groundwater vulnerability mapping facilitates transfer of knowledge and information to decision makers. Yet, there are only few examples of such vulnerability assessment applications, all of them developed for shallow aquifers (Witczak et al., 2007, 2011; Neukum et al., 2008). According to Witczak et al. (2007) time lag for vertical transport of conservative contaminants from the surface to shallow aquifer can be a basis for vulnerability classification. These time lags can be calculated either from known soil hydraulic properties (water retention and hydraulic conductivity relationships) of soil layers or as the ratios of exchangeable water content in the unsaturated zone to recharge flux (typically natural infiltration). The first method requires more detailed knowledge of hydraulic parameters and application of the nonlinear

Table 5. Correspondence between parameters of the DRASTIC method and the MRT method used in groundwater vulnerability map of Poland (GVMP) (Polish approach) (according to Witczak et al., 2007; 2011).

DRASTIC	MRT
Depth to water	Vadose zone thickness (d) in Eq. (1).
Net recharge	Net recharge (R) used Eq. (1)
Aquifer media	This parameter of the DRASTIC index is strongly correlated with hydraulic conductivity. In the MRT methods hydraulic conductivity and active porosity of aquifer media used to calculate MRTs of shallow aquifers visualized on the GVMP by a system of arrows.
Soil media	Volumetric water content in the soil profile (θ) in Eq. (1). Topography (slope) and land use are used as a basis for estimation of
Topography	the effective infiltration rate.
Impact of vadose zone	Volumetric water content (θ) in rocks of the vadose zone in Eq. (1).
Hydraulic conductivity	See "Aquifer media"

equations governing flow and transport in unsaturated media. In the second method the time lag is practically equal to the MRT for piston flow. However, in the unsaturated zone the uncertainty of hydraulic conductivities estimates is many times higher than the uncertainty of estimates of exchangeable water content and recharge flux. Hence, MRT evaluation should be based on the second method. The total MRT of the vadose zone is a sum of these partial MRTs separately for soils and for permeable and low-permeable rocks. Time lags of the phreatic zone are calculated from hydraulic conductivity and effective porosity of rocks and visualized on the Groundwater Vulnerability Maps by a system of arrows. The length and the labeling of the arrows (in years) characterize the timescale of transport of conservative contaminant over the distance marked by the arrow.

5. Challenges

5.1. Unsaturated zone

According to the original concept of Vrba and Zaporozec (1994) soil and strata overlying the groundwater table provide protection of groundwater from contaminants. This broad (including soil and rock), variable saturated over time and space, zone between the surface and the groundwater table is thus a primary factor in groundwater vulnerability. Consequently, information about residence times is indispensable for determining filter functions and fate of contaminants in the unsaturated zone. Residence times of water cannot be ignored even for shallow aquifers (Broers and van der Grift, 2004) and the unsaturated zone alone can considerably retard the movement of contaminants. However, flow paths in the unsaturated zone are sometimes ignored in vulnerability studies arguing about shallow water tables and short RTs (Basu et al., 2012; Eberts et al., 2012). In catchment studies, the unsaturated zone often is not considered explicitly but integrated information is gained at the catchment outlet to determine RTs (McGuire and McDonnell, 2006). The importance of residence time in the unsaturated zone (RT_{unsat}) depends on its relative contribution to the entire residence time on the pathway between the source and the receptor. Therefore, a first recommendation is to estimate the order of magnitudes of RT_{unsat} and of residence times on the total flow paths (RT_{tot}) and to decide whether RT_{unsat} can be neglected or whether it has to be considered (Sousa et al., 2013). Generally, RT_{unsat} can be ignored if the uncertainty of RT estimation for the entire pathway is higher compared to the RT_{unsat} . It is important to note that not only the length of the pathway is important, but also the hydraulic properties of the aquifer (hydraulic conductivity, mean effective water content/effective porosity) influence water flow velocities and thus residence times. Water flow velocities in the saturated zone can be significantly larger compared to the unsaturated zone. Therefore, RT_{unsat} are often larger compared to RT_{sat} , emphasizing the importance of the unsaturated zone as a natural buffer zone to reduce the input of pollutants into groundwater. Still, a thick unsaturated zone does not necessarily mean great RT_{unsat} . To get a first idea about RT_{unsat} ,

several methods are available (Sousa et al., 2013; Voigt et al., 2004). The simplest approximation based on the piston-flow assumption is the sum of partial RT_{unsat} s ($T_{\text{unsat}}[T]$) calculated for i individual permeable layers in the unsaturated zone:

$$T_{\text{unsat}} = \sum_{i=1}^n \frac{z_i \cdot \theta_i}{R} \quad (3)$$

where R [L/T] is the direct groundwater recharge rate, z [L] is the thickness of the unsaturated zone, and θ [L^3/L^3] is the mean volumetric water content. If R is not available, it can be approximated by several methods (Healy and Cook, 2002; Healy and Scanlon, 2010; Scanlon et al., 2002; Thomas and Tellam, 2006). As an example, the RT_{unsat} equals five years in a 10 m unsaturated zone with a mean volumetric water content of 0.25 and a recharge of 500 mm/a. In contrast, RT_{sat} can be calculated from lateral Darcy velocities and, for instance, equals one year along 10 m distance in saturated porous media with a hydraulic gradient of 0.001, a hydraulic conductivity of about 10^{-4} m/s, and a mean porosity of 0.3.

5.2. Heterogeneity

Heterogeneity, a ubiquitous feature of the groundwater environment, complicates flow patterns from the microscale to the regional scale and gives rise to a wide spectrum of timescales; affecting thus the predictability of flow and transport. Microscale heterogeneities give rise to dispersion, diffusion, and retardation of contaminants. At the aquifer scale, rates and directions of groundwater flow are controlled by the spatial distribution of hydraulic conductivity and, to a lesser extent, of effective porosity. Hydraulic conductivity may range over several orders of magnitude within one geological formation, which influences the dispersion of contaminants because it is primarily governed by spatial variations of groundwater velocity. Furthermore, stratified deposits, fractures, discontinuities, and other distinct structural heterogeneities of geological medium are obvious controls on groundwater flowpaths (Sudicky, 1986).

Merely in very homogeneous sediments and soils with low dispersion and thus with advective dominant transport, the MTT is similar to the arrival time of the peak concentration. In all other systems with larger dispersion, which is the rule rather than the exception, particularly in the unsaturated zone, the MTT is greater compared to the time of the peak concentration. Further, the dispersion parameter itself also defines the decrease in maximum concentration at the receptor compared to its initial maximum concentration at the source; however, the dilution effect for the peak concentration and the dispersion parameter are not linearly related (see also Fig. 2). The dilution is low for small and large dispersion parameters (Leibundgut et al., 2009). Particularly for estimations of the specific vulnerability, TTDs are of importance to encompass the entire exposure time of the pollutant

at the receptor (Fig. 2a). Here, retardation and (bio-) degradation need to be considered in addition to the intrinsic vulnerability of the system.

Flow heterogeneities in the unsaturated zone are one of the major challenges in vulnerability assessment. Preferential flow, which is a very fast flow component bypassing the matrix, can be caused by fractures, earthworm activities, root channels, or other structural heterogeneities (Gerke, 2006). Flow and transport through these larger pore regions are rapid, particularly during heavy rainstorm events or when soils are close to saturation (Nimmo, 2012). Preferential flow is of main importance when the receptor is vulnerable to the first appearance and, therefore, the fastest travel time. Particularly, in the unsaturated zone, where TTs are often great (weeks to years), filter and buffer functions can be impaired by preferential flow. Thus, contaminants can leach extremely fast (<days) through fractures or preferential flow paths; too fast for degradation. This concern is another important reason for not neglecting the unsaturated zone in vulnerability assessments.

Besides preferential flow, regions with immobile water and multiple porosity might also influence the TT. These zones (e.g., dead-end pores, clay lenses, pores in the rock matrix) do not actively contribute to water flow and, thus, the effective mean water content is smaller than the total mean water content. Solutes (like pollutants) can be transported into and out of immobile water regions by diffusion, which increases the TT of pollutants compared to water. Consequently, the specific TT is greater compared to the intrinsic TT and depends on the diffusion properties of the solute/pollutant (see also Fig. 2b). Again, use of MTT instead of the full TTD may obscure important features of contaminant transport, particularly the persistence of contamination in systems with immobile water.

In recent years, heterogeneities associated with patterns of infiltration and groundwater recharge and their influence on vulnerability assessments, particularly in cold and mountainous regions, have received increased attention (e.g., Stähli et al., 1999; Flerchinger et al., 2006). In climates with soil frost, snow, and snowmelt, water will sometimes not infiltrate during winter and large volumes of melt water from winter precipitation may gather and temporarily store in local terrain depressions until early spring (Hayashi et al., 2003). When the frozen soil subsequently thaws, the temporary stored water can rapidly infiltrate the subsurface in these depressions (Hayashi et al. 2003, Stumpp and Hendry, 2012). Such areas with focused recharge are considerate to represent “hot spots” with increased risk of rapid downward transport of contaminants (Fetter, 1999, Hayashi et al. 2003, Gerke et al., 2010). For groundwater systems with local vulnerable hot spots, with focused groundwater recharge, timescale-based methods will be particularly suited.

For some aquifers in narrow valley bottoms surrounded by large catchments, the recharge from bottom and valley sides can be large compared to the infiltration from precipitation throughout the catchment and determine the patterns of flow and transport of water and contaminants. The patterns of groundwater recharge flow and transport will be an important part of the hydrological framework for vulnerability also for this kind of aquifers, but it might be a particular challenge to

describe variability and quantify recharge through different fracture zones in crystalline rocks beneath and along such aquifers (Sililo and Tellam, 2000; de Vries and Simmers, 2002).

Statistical and stochastic approaches are used to describe heterogeneity and predict contaminant transport in heterogeneous aquifers (e.g. Elfeki et al., 2012), but they are still evolving and their application is not widespread in hydrogeological practice. More commonly, standard numerical models of flow and transport are used. Here again, tracers (environmental isotopes, artificial dyes, soluble salts, and other) are an added value and help tackle the above-mentioned difficulties. For simple flow systems, theoretical relationships between depth in the aquifer and the groundwater age can be developed with the help of environmental tracers allowing predictions on conservative contaminant migration to specific points of interest in the flow system (Cook et al., 1995; Broers and Van der Grift, 2004; Stauffer et al., 2011). In complex systems, environmental tracers are often indispensable for calibration and validation of numerical transport models (Zuber et al., 2005, 2011; Newman et al., 2010). Tracer observations are used to infer not only timescales but also flow paths and values of effective hydraulic conductivities and diffusivities (Kazemi et al., 2006; Leibundgut et al., 2009), all of which are crucial components of vulnerability assessments. Thanks to their versatility, tracers integrate information over a wide range of distances and times, thus providing the effective values of hydraulic characteristics for the relevant scales.

5.3. Transient nature of transport processes

Because of the inherently transient nature of contaminant transport processes, the steady-state representations might not provide reliable results in predictions of contaminant behavior. Additionally, a basic feature of solute transport in groundwater is that its timescales are different than for propagation of hydraulic heads. This dichotomy arises because flow and transport are governed by different physical processes (Konikow, 2011). According to the general groundwater flow equation, rates at which hydraulic disturbances propagate through the aquifer are directly determined by its properties, namely, by hydraulic diffusivity, which is the ratio of hydraulic conductivity (transmissivity) to specific storage (storativity). Rates of pressure propagation are much faster than rates of solute transport because the latter is controlled by advection and dispersion of solute particles, which in turn depend on the velocity field and on the presence of immobile water. Spatial distributions of hydraulic heads and of concentrations of solutes transported with groundwater flow are created by different processes and cannot be used to define parameters of the same model (Voss, 2011a,b; Konikow, 2011). Transport depends on flow, but characterization of flow does not suffice to describe all transport phenomena (Konikow, 2011). Therefore, different approaches of groundwater age evaluation based on hydraulic and tracer observations might give inconsistent results.

Transient conditions are strongly regulated by the boundary and initial conditions. This includes changes in precipitation, (evapo)transpiration, soil water content, depth to the water table over time and space as well as changes in hydraulic gradients. Thus, MTT and TTD are only representative for a specific observation time being analyzed and may change through time (Kania et al., 2006; Zuber et al., 2011). Even for the period of observation, the intrinsic vulnerability is suggested to be an integrative and average value indicator masking short-term changes in TT_{unsat} . For example, heavy rainstorms can increase the water flow velocity in the unsaturated zone by several orders of magnitudes compared to average water flow velocities. Consequently, TT_{unsat} is dramatically decreased and the vulnerability of the receptor increased in case of negligible other buffer or storage compartments (river, aquifer, deeper vadose zone layers, etc.). Still, methods using MTT or TTD completely ignore the response of short-term changes like heavy rainstorms. Therefore, further studies are warranted considering uncertainties and sensitivities of such short-term high-risk scenarios in vulnerability assessment for example by generally considering dynamic processes. Whether such short-term TT variability can actually cause a potential threat depends on the response of the receptor. The exposure–response relationship of short-term and high concentration input loads is assumed to be quite different compared to long-term and low concentration input loads (e.g., when considering toxicity).

Methods to determine dynamic TTD or time-variable TTD are limited to date. Recently, time-variable RTDs have been applied to the catchment scale (Kania et al., 2006; Zuber et al., 2011; Birkel et al., 2012; Botter et al., 2011; Heidbüchel et al., 2012; van der Velde et al., 2012). Similarly, one can think of transferring these methods to the unsaturated zone or heterogeneous aquifers by superimposing local TTD specific for a soil or sediment unit to larger scales. Such a method would be valuable when the specific vulnerability of diffuse sources is of interest. Another possibility—and more appropriate for point sources—is the estimation of changes in TTD or MTT over time like it was shown for different vegetation periods (Stumpp et al., 2009a) and treatment methods (Stumpp et al., 2012) emphasizing the impact of land use on RT_{unsat} . Thus, land-use-specific TTD and MTT can be derived for a certain soil type (Stumpp and Maloszewski, 2010; Stumpp et al., 2009a,b,c; Stumpp et al., 2007). They can be used for vulnerability assessment as well as management strategies for land-use changes.

For the estimation of MTT or TTD based on environmental tracer approaches, a major challenge is the determination of the correct concentration input function of environmental tracers, which can be different from time series of the tracers in precipitation (e.g., McGuire and McDonnell, 2006). Thus, the actual infiltration signal contributing to the recharge can be different due to surface runoff, fractionation processes (when water isotopes are used as tracers), or evapotranspiration. Adjustment of this input function and estimation of isotope ratios in the effective precipitation are prerequisite for calculation of TTDs (Stumpp et al., 2009a).

However, for fully describing the transient nature of water flow and transport changes in water fluxes over time and space need to be considered. For homogeneous, variably saturated flow conditions in the unsaturated zone, this is given by the Richards equation, taking into account gravity and matrix forces. Here, knowledge about hydraulic properties such as water retention and hydraulic conductivity functions are required, which are described by empirical functions (e.g., Brooks and Corey, 1966; Durner, 1994; Kosugi, 1996; Mualem, 1976; Priesack and Durner, 2006; van Genuchten, 1980). Water retention and saturated hydraulic conductivity functions are specific for different sediments and vary according to the grain/pore size distribution. They can be determined from lab or in situ measurements or approximated from pedotransfer functions, which particularly are of importance for large-scale vulnerability assessments or only having limited information about intrinsic soil and sediment properties (Stumpp et al., 2009a; Vereecken et al., 2007; Vereecken et al., 2010). Then, transient flow and transport processes for vulnerability assessment can be approximated by models with analytical and semi-analytical or numerical solutions of the Richards equation combined with the advection–dispersion equation (Connell and van den Daele, 2003; Neukum and Azzam, 2009; Neukum et al., 2008; Šimůnek and Bradford, 2008; Šimůnek and van Genuchten, 2008). In contrast to lumped parameter modeling, numerical models require extensive additional data about the unsaturated zone for calibration though. The great challenge next to calibration and validation is the extraction of flow information from numerical models for vulnerability assessment as the TT will be a function of time.

Even though variable flow and transport modeling covers dynamic processes the best and should be applied where enough data are available, care still needs to be taken when choosing the model approach, particularly in heterogeneous systems. Independent of the model and method to determine MTT or TTD, uncertainty and sensitivity analysis is required to provide a range of possible impacts and how reliable model results are, particularly for assessments with limited data availability (Hrachowitz et al., 2011). This is of particular interest for the unsaturated zone where heterogeneities and dynamics of fluxes can cause distinct differences in TTs. An idea would be to provide different TT or TTD depending on the effective water content of the system or according to extreme conditions (like drought or heavy precipitation events).

5.4. Aquitards

It is necessary to underline that, historically, hydrogeologists believed that fractures, in relatively unweathered clayey aquitards, were unimportant because of the expectation that natural plasticity would cause fractures to “heal” (e.g., close naturally). Open fractures were recognized as abundant in unweathered zones in the majority of clayey aquitards (Norris, 1959; Lissey, 1962; Ziezel et al., 1962; Meyboom, 1966; Rozkowski, 1967; Cherry et al., 1971; Cherry et al., 1973; Grisak et al., 1976). This kind of fractures, in apparently unweathered materials, could have

been originated long ago due to contraction of the clay caused by cycles of wetting and drying and freezing and thawing or due to a variety of other depositional and postdepositional processes.

Aquitards have usually been thought to provide underlying aquifers with protection from contamination. However, nowadays, a hydrogeologic perspective is more appropriate in which the groundwater domain encompasses both aquitards and aquifers as the components of a single system in which the two components are interdependent and interactive in the context of flow and contaminant migration (Cherry et al., 2004).

In recent years particularly dense nonaqueous phase liquids (DNAPLs) in aquitards have received attention (e.g., Parker et al., 1994; Hinsby et al., 1996; Jørgensen et al., 1998; Parker et al., 2004) since aquitards, with a strong capability to protect underlying aquifers from dissolved contamination, should not necessarily be expected to provide strong protection in situations where contaminants moved in the DNAPL state. This kind of contaminants can move through aquitard's discontinuities, as a free liquid phase, in ways solute phase cannot. The literature identifies various types of preferential pathways for contaminant migration also through unlithified porous aquitards (Hanor, 1993; McKay and Fredericia, 1995; Aslan and Autin, 1996; Bierkens, 1996; EddyDilek et al., 1997; Weissmann and Fogg, 1999; Brockman and Szabo, 2000); however, only minimal guidance is provided on how to go about conducting field studies to locate and characterize these pathways (Cherry et al., 2004). In the main, where lithological heterogeneity such as sand lenses or erosional windows are not a cause of preferential pathways in clay-rich, unlithified aquitards, fractures are the most probable pathway for preferential flow.

Indeed DNAPLs have the propensity to migrate through fractured aquitards and cause impacts on underlying aquifers, because they can move downward under the combined influence of different driving forces: higher density and lower interfacial tension and kinematic viscosity with respect to water, nonpolarity of the molecules (Kueper and McWhorter, 1991; McWhorter and Kueper, 1996; Pankow and Cherry, 1996). DNAPLs, particularly chlorinated solvents, once accumulated on the top of an aquitard, are thus capable of entering very small fractures, even those with apertures smaller than 10 μm , moving downward very rapidly, with respect to water, even where groundwater flow is upward directed (Kueper and McWhorter, 1991; McWhorter and Kueper, 1996; Chown et al., 1997).

Fractured flow in aquitards is not limited to DNAPLs only. Also water and other solutes can be transported preferentially through fractures and increase the vulnerability. Although deep penetration of contaminants in fractured clayey aquitards has been documented at several sites (e.g., from north-American literature: McIlwain et al., 1989; Wills et al., 1992; Hanor, 1993; PPG Industries, 1995), intensive field studies also show some aquitards capable of preventing contaminant penetration and others allowing partial but not full penetration (e.g., Roberts et al., 1982; Schwartz et al., 1982; Brewster et al., 1995; Parker, 1996; Morrison et al., 1998).

Thus, some aquitards have excellent integrity even when DNAPLs are the contaminant source.

However, when looking at large timescales, another issue concerning DNAPL diffusion in the aquitards arises. Indeed DNAPLs, during their diffusion-controlled migration through aquitards, can strictly interact with low-permeability deposits, especially with the ones having a significant organic matter content, where they can be trapped and later released back into the aquifers (Chapman et al., 2012). In this way these fine deposits become a “secondary source” of pollution, having persistence with time estimated up to hundreds of years (Chapman and Parker, 2005). Low-permeability deposits can release then significant mass of pollutants in groundwater, leading to the accumulation of risky concentrations, by means of the “back diffusion” process described above (Parker et al., 2004).

As a consequence, in assessing the vulnerability of a site with a clayey aquitard the notion of Aquitard integrity must be underlined, which means the degree to which an aquitard is protective of groundwater quality in underlying aquifers. It depends on the capability of the aquitard to prevent, delay, or strongly attenuate the flux of contaminants into an underlying aquifer and is controlled by three factors: (i) state of the hydrologic system (hydraulic head distribution), (ii) contaminant characteristics (dissolved, NAPL, particulate, microbial, reactive, or degrading), and (iii) hydrogeologic characteristics (hydraulic conductivity, porosity, thickness, etc.). In many urban areas important aquifers have been found as strongly contaminated by DNAPLs also if apparently well protected by overlying aquitard layers (Nijenhuis et al., 2013), considering a classical hydrogeological evaluation of relationships between the different bodies. Thus, a site-specific evaluation of aquitard integrity becomes a mandatory issue in settings where the occurrence of immiscible contaminants is supposed or verified.

While simple geologic criteria such as sediment or rock type are sometimes used in the consideration of wellhead protection (US EPA, 1991), information on hydrogeological setting (Belitz and Bredehoeft, 1990; Neuman and Neretnieks, 1990; Simpkins et al., 1996), hydraulic head (Roppe et al., 1992; Eaton, 2002; Eaton and Bradbury, 2003), hydraulic conductivity (Williams and Farvolden, 1967; Shaw and Hendry, 1998; van der Kamp, 2001), and hydrochemistry and isotopes (Remenda et al., 1996; Hendry 1988; Nativ and Nissim, 1992; Nativ et al., 1995; Pucci, 1998; Pucci, 1999; Hendry et al., 2000; Stimson et al., 2001) are typically necessary for a proper assessment of the aquitard integrity. Determining the degree of protection that aquitards provide to underlying aquifers is a challenging task because field data needed to develop reliable predictions are commonly unattainable due to funding limitations and/or unquantifiable complexities in the hydrogeologic system.

A complex evaluation cannot be examined by standard approaches for intrinsic vulnerability assessment (such as subjective parametric methods), which generally does consider the occurrence of aquitards as a protective element and not as a possible carrier of contaminants downward into underlying aquifers.

6. Summary and conclusions

The evaluation of groundwater vulnerability to man-derived impacts represents one of the main issues for the protection of groundwater resources and is an inherent element of the risk assessment schemes. At the same time, there are significant ambiguities in the very understanding of the groundwater vulnerability concept and in the commonly used assessment methods. A more definite approach toward assessing the intrinsic vulnerability can be based on the essential characteristic of contaminant migration, which is the residence time of water between the source areas of contamination and either the groundwater table or the groundwater receptors. Such an approach reflects the basic notion that the longer the residence times of water, the less vulnerable are groundwater resources to any kind of man-made nonpersistent contamination. Grounding of vulnerability assessment on the temporal characteristics of groundwater flow meets the requirements of the present-day groundwater resources management where timeframes set for the improvement of groundwater status have to take into account time lags associated with the responses of the receptors to the commencement or cessation of pressures on groundwater quality.

MRT of water appears as a first-choice index of the intrinsic groundwater vulnerability as it can be estimated by use of relatively simple methods and is intuitive and easy to comprehend even for nonexperts, which is an important requirement for a pragmatic vulnerability management. The MRT can be directly estimated from the hydrogeological data or by use of those dating methods that provide absolute groundwater ages. For cases that can be approximated by piston flow, the MRT is evaluated from the water budget data as the turnover time of water.

The MRT is not a reliable indicator of vulnerability for the spatial and temporal scales at which heterogeneities control flow patterns. In such cases, the RTD conveys information about the number of flow components and their arrival times. The RTD quantifies also the degree of contaminant dilution due to mixing and dispersion. Various statistics of the RTD are used to build indices of vulnerability.

The major challenge in the evaluation of timescales and their distribution is related to the inherent heterogeneities of water flow in the subsurface, which manifest themselves in various spatial and temporal scales. Specific examples are karstic systems with the irregular network of conduits and triple porosity or aquitards protective characteristics can be compromised due to the presence of the preferential flow pathways. The integrative properties of the environmental help overcome these difficulties at the relevant scales.

The review and discussion presented in this work are limited to intrinsic groundwater vulnerability. Consequently, the indices of vulnerability presented herein are based on the residence time of water and not of contaminants. Such indices will in most cases overestimate the vulnerability as the contaminants are

subject to retardation and attenuation processes that slow down their spreading and can reduce their concentrations down to the background levels. On the other hand, the timescale approach can be applied to the specific vulnerability for the cases where historical data on the responses of groundwater quality to the known contaminant loads are available. In such cases, the timescale and its distribution can be evaluated for the specific contaminant.

This review sets out the conceptual background and recommendations for application of residence time of water as a physically based and operational index of the intrinsic groundwater vulnerability. Use of such indices is indispensable for incorporation of the time lags in contaminant spreading into groundwater resources management. It will support groundwater managers and decision makers in the implementation of programs of measures aimed at the protection of groundwater resources.

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