

## 1. METHODS OF GROUNDWATER VULNERABILITY AND PROTECTABILITY ASSESSMENT

Step 1 in an assessment of groundwater vulnerability and protectability from pollution within a certain area includes the evaluation of hydrogeological and physicochemical processes and factors followed by subdivision of the studied area into zones with similar geological and hydrogeological conditions. *Methods of hydrogeological zoning* were used for groundwater vulnerability assessment by Margat [1968], Vrana [1968, 1984], Albinet and Margat [1970], Rogovskaya [1976], Josopait and Schwerdtfeger [1979], Ostry et al. [1987]. Then, there were developed parametric methods and corresponding scoring and *index* system methods that were used to quantify the most significant characteristics of the geological medium (lithology, hydraulic conductivity, infiltration, etc.). Among these methods are DRASTIC [Aller et al., 1987; Rosen, 1994], SINTACS [Civita and De Maio, 2004], GOD [Foster, 1987; Foster and Hirata, 1988], and other index-rating assessment methods [Villumsen et al., 1983; Engelen, 1985; Zaporozec, 1985; Andersen and Gosk, 1987; Carter et al., 1987; Marcolongo and Pretto, 1987; Schmidt, 1987; Sotornikova and Vrba, 1987; Palmer, 1988; Doerfliger et al., 1999; Magiera, 2000; Rogachevskaya, 2002]. With development of modern geographic information systems (GISs) and mapping techniques (maps overlay, three-dimensional (3D) data processing and visualization, etc.), these methods became more complex and detailed, taking into account an increasing number of hydrogeological, geological, climatic, and other parameters and criteria [Engel et al., 1996; Burkart et al., 1999; Zhou et al., 1999; Gogu and Dassargues, 2000; Zaporozec, 2002; Daly et al., 2002; Zwahlen, 2004; Sinreich, et al., 2007; Liggett and Talwar, 2009].

On the other hand, in parallel to the development of zoning and index-rating methods, even before the appearance of groundwater vulnerability and protectability concepts in the 1960s, many researches used characteristic unified physicochemical parameters of the geological medium, such as *travel time* necessary for the contamination front to reach groundwater from the contamination source, the *retardation factor* (ratio of velocities of seepage water and contaminant particles), or *hydraulic resistance* of covering and water-bearing deposits. These characteristic

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parameters became the basis for the groundwater vulnerability and protectability assessment, and the corresponding methods can be called methods of *parametric assessment*. This approach was developed in publications of the former USSR researchers [Goldberg, 1983, 1987; Mironenko and Rumynin, 1990; Belousova and Galaktionova, 1994; Belousova, 2001, 2005; Pityeva, 1999; Pashkovskiy, 2002; Rogachevskaya, 2002; Zektser, 2007] as well as by Western authors [e.g., Van Stempvoort *et al.*, 1995]. Parametric methods of the assessment of groundwater vulnerability were then combined with numerical modeling techniques to incorporate the effect of complex hydrogeological and geological conditions along with physicochemical parameters characterizing the geological medium and interactions in the “contaminant-water-rock” system [Rumynin, 2003; Loague *et al.*, 1998; Shestopalov *et al.*, 2006; Zhang *et al.*, 1996].

In this chapter, the authors will discuss in more detail existing methods of groundwater vulnerability assessment based on hydrogeological zoning, index rating, parametric, and modeling methods.

### 1.1. Method of Hydrogeological Zoning

Starting from the early works of the 1960s, the methods of groundwater vulnerability assessment and mapping were developed based on subdividing the studied area into a number of zones with different degree of vulnerability based on zoning by hydrogeological conditions, relief, thickness and composition of soil and vadose zone, etc. The groundwater vulnerability is represented by qualitative categorization of groundwater into several “homogeneous” zones, for example, of very low, low, medium, high, and very high vulnerability. The resulted zones with different vulnerability degree in most cases are obtained using the procedure of “overlying maps” of basic initial data on which the homogeneous zones are first contoured corresponding to different types or degree of the initial (basic) characteristic. This procedure became easier to perform in detail using modern GIS technologies. Strictly speaking, the initial data zoning and categorization procedure is a necessary and useful preliminary stage for any groundwater vulnerability assessment.

The method of area zoning by hydrogeological features was used in the first groundwater vulnerability assessments [Vrana, 1968; Albinet and Margat, 1970; Olmer and Rezac, 1974]. A case study is presented by Sililo *et al.* [2001]. They developed a system of regional qualitative groundwater protectability assessment for South Africa in the scale 1:250,000 using GIS overlay of initial maps in the scale 1:50,000 of relief, climatic characteristics, and type and composition of soil. After performing the zoning procedure on the initial data, they built maps of clay fraction and iron content and obtained resulting maps of attenuation potential of soil separately for cation- and anion-forming groups of contaminants. The maps include three classes of attenuation potential: low, medium, and relatively high.

Another example of the zoning method combined with modern GIS technology is the development of a regional groundwater vulnerability map of Scotland (in scale 1:100,000) by *Ball et al.* [2004] in the framework of the SNIFFER project. They performed the initial data analysis by overlaying maps of soil and vadose zone thickness, lithology and permeability, character of aquifer occurrence, hydraulic conductivity, porosity, and fracturing degree of rocks. As a result they classified the study area into seven characteristic types of hydrogeological conditions determined by most frequently occurring lithological sections of vadoze zone and character of groundwater occurrence: (1) highly permeable alluvium-delluvium deposits (drift), (2) exposed hard fractured rocks, (3) hard fractured rocks covered by soil layer, (4) hard fractured rocks covered by drift layer, (5) fractured open rocks with double porosity, (6) fractured rocks covered by soil layer, and (7) fractured rocks covered by drift layer. According to these types, seven scenarios of groundwater vulnerability categorization have been developed which include 199 different vulnerability codes (possible combinations of gradations for thickness and hydraulic conductivity of layers for the above seven section types). In the study area of Scotland, only 46 of these 199 gradations occur. The resulting map of groundwater vulnerability is obtained after the GIS zoning procedure according to the above seven types of groundwater occurrence. The authors conclude that the majority of the studied area of Scotland has maximum or very high groundwater vulnerability because of wide occurrence of highly fractured weathered hard rocks, often uncovered or covered by thin layers of soil and highly permeable drift.

The hydrogeological zoning method is able to provide broad-scale regional groundwater vulnerability maps, including modern GIS-based maps with high resolution which use large volumes of data of hydrogeological, geological, climatic, relief, and other characteristics. An assessment system and gradations developed using this method in most cases are targeted only to the assessment area for which it was developed, and they cannot be used without special adaptation for groundwater vulnerability assessments of other areas.

## 1.2. Index Methods

The necessity of fast and effective assessments of the groundwater pollution risks related with increasing requirements of municipal services of water supply, farms, environment protection agencies, etc., in the United States, France, Italy, Germany, and other countries, starting from the 1980s, stimulated the development of different index-type and rating-type assessment systems of groundwater contamination risks, groundwater vulnerability and protectability based on simple algorithms of unification (summation, generalization) of parameters, and factors characterizing the hydrogeological conditions and protection ability of the

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geological medium containing the assessed groundwater. The appearance of modern GIS technologies allowed for the development of several, effective methods which have already been used in different countries.

The *DRASTIC* method was proposed by *Aller et al.* [1987] for the U.S. Environmental Protection Agency (EPA) and was applied in the United States, Canada, South Africa, and many other countries. The method is based on the calculation (at each point of the assessed area) of a unified groundwater vulnerability index, *DRASTIC*, as a sum of seven rating indicators (*D*, *R*, *A*, *S*, *T*, *I*, *C*) multiplied by the corresponding weight factors  $r_1$  through  $r_7$ :

$$\text{DRASTIC} = r_1 \cdot D + r_2 \cdot R + r_3 \cdot A + r_4 \cdot S + r_5 \cdot T + r_6 \cdot I + r_7 \cdot C,$$

where *D* is the groundwater table depth, *R* the net recharge, *A* the aquifer media (determined by lithology), *S* the soil type (by texture), *T* the topography (by slope), *I* the impact of the vadose zone, and *C* the aquifer hydraulic conductivity.

Each indicator is assessed by the corresponding local hydrogeological characteristic in a 10-point scoring system [*Aller et al.*, 1987]. For weight coefficients  $r_1$ – $r_7$ , determining the relative “importance” of the corresponding indicator, two sets of values are proposed: (1)  $r_1$ – $r_7 = 5, 4, 3, 2, 1, 5, 3$  and (2)  $r_1$ – $r_7 = 5, 4, 3, 5, 3, 4, 2$ . The first set determines the standard *DRASTIC* index used in most cases for assessing the *intrinsic* groundwater vulnerability, and the second set (“agricultural” *DRASTIC*) is designed for *special* vulnerability to contamination with pesticides. Thus determined, the assessed *DRASTIC* index can vary within the range of 23–230 (intrinsic vulnerability) or 26–260 (vulnerability to pesticides). The proposed values of weight coefficients to some degree have the judgmental character and/or are based on experimental results. It is clear from the above formula for the *DRASTIC* index that, in case of pesticides, the soil type and slope angle appear to be more important, but the influence of the vadose zone and the aquifer conductivity are less important.

Higher values of the *DRASTIC* index correspond to higher groundwater vulnerability. In real practical applications, the *DRASTIC* index usually varies in the range of 5–200.

For example, *Zektser et al.* [2004] used *DRASTIC* (with the second set of weight coefficients) for building a vulnerability map of the main aquifer in Castelporciano province (Italy). They obtained the *DRASTIC* index in the range 26–256 and determined five groundwater vulnerability categories: 26–72, very low; 72–118, low; 118–164, medium; 164–210, high; and 210–256, very high. *Denny et al.* [2007] proposed to modify the *DRASTIC* method in order to incorporate the structural characteristics of bedrock aquifers with large-scale fracture zones and faults acting as primary conduits for flow at the regional scale. The methodology is applied to the southern Gulf Islands region of southwestern British Columbia, Canada. Bedrock geology maps, soil maps, structural measurements, mapped lineaments, water well information, and topographic data assembled within a

comprehensive GIS database are used to assess the traditional DRASTIC indices, and additional structural indices are considered for accounting the regional structural elements during the recharge and well capture zone determinations.

SINTACS was developed in works by *Civita and De Maio* [2004] and *Civita* [2008] for use in Italy. It represents a more detailed and refined variant of DRASTIC. Similarly to DRASTIC, the SINTACS index is determined as a sum of seven weighted indicators (ratings): *S* (*sorgicenza*), depth to groundwater (range 0–100m); *I* (*infiltrazione*), recharge (0–550 mm/year); *N* (*non saturo*), vadose zone lithology with account of fracturing; *T* (*tipologia della copertura*), soil type (composition); *A* (*acquifero*), saturated zone (aquifer) characteristic (composition, disturbance, including karst occurrence); *C* (*conducibilità*), hydraulic conductivity; and *S* (*superficie topografica*), topography (slope).

In contrast to DRASTIC, the table of scores for each SINTACS indicator contains more detailed lithological differences and disturbances (fractures, karst). Authors have developed the five series of weight coefficients,  $r_1-r_7$ , according to types of hydrogeological conditions of the study area and an additional set for assessment of the special groundwater vulnerability to nitrate contamination:

1. Normal recharge:  $r_1-r_7 = 5,4,5,3,3,3,3$
2. High (technogenic recharge):  $r_1-r_7 = 5,5,4,5,3,2,2$
3. Temporarily flooded areas, with account of watercourse density:  $r_1-r_7 = 4,4,4,2,5,5,2$
4. Karst rocks:  $r_1-r_7 = 2,5,1,3,5,5,5$
5. Fractured rocks:  $r_1-r_7 = 3,3,3,4,4,5,4$
6. Nitrate contamination:  $r_1-r_7 = 5,5,4,5,2,2,3$

An important feature of the method is its attempt to account implicitly for hydraulic conditions of the vadose and saturated zones, including types of rocks, technogenic recharge, flooding, etc.

*GOD* is an index-rating method of assessing regional groundwater vulnerability proposed by *Foster* [1987, 1988] for geological conditions of Great Britain where the groundwater occurs mainly in fractured rocks (limestones, sandstones) overlaid with unconsolidated deposits of the vadose zone and soil. The method is based on the evaluation of three groundwater vulnerability indicators:

1. Types of an aquifer — unconfined, confined, or confined-unconfined groundwater
2. Overall lithology — composition of covering deposits, aquifer rocks, degree of consolidation
3. Depth to groundwater

The authors of this method stress attention to accounting for fracturing and other rock heterogeneities. Each of three indicators ranges in value from 0 (minimum vulnerability) to 1 (maximum vulnerability). The resulting *GOD* index is determined as the product of all three indicators, and the groundwater vulnerability map is obtained as a distribution of the *GOD* index over the studied area.

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*SUPRA* is a regional mapping method for groundwater vulnerability. It is an index method using the matrix ranging procedure for the indicators and GIS overlay to obtain the resulting areal groundwater vulnerability. The method is proposed by Zaporozec [2002] and was applied in mapping the groundwater vulnerability of northern Wisconsin. The assessment is based on five indicators:

1. Soil characteristics
2. Unsaturated zone thickness
3. Permeability of vertical sequences in the unsaturated zone
4. Groundwater recharge
5. Aquifer characteristics (lithology, flow regime, recharge)

The resulting vulnerability index is assessed in three stages that correspond to the assessment objectives and stages of downward migration of contaminants from the soil surface into groundwater aquifers:

- I. Evaluation of the soil capacity to attenuate contaminants
- II. Evaluation of the contamination potential of shallow groundwater
- III. Evaluation of the contamination potential of deeper aquifers

In the conclusion of each stage, a map is built which can be used alone or in compiling the combined composite map. Use of the independently evaluated components (soil, upper aquifer, deeper aquifers) makes the method flexible to requirements of different users.

The assessment and mapping of vulnerability of deeper aquifers (stage III) is based on geological and hydrogeological characteristics such as aquifer deposit lithology, integrity of the overlying confining bed, location, area and character of the recharge zones, as well as the regional groundwater flow direction.

The evaluation of attenuation capacity of soil can be carried out using the soil contamination attenuation model (SCAM) developed by Zaporozec [1985]. With its aid the soil attenuation capacity is assessed in relation to contaminant sources, located within or out of the soil, based on a two-layer model (soil and subsoil), using characteristic indicators such as the soil texture, pH, depth, drainage degree, and content of organic material. Each indicator is assessed by its score, and the sum of the scores is found using GIS. Depending on the total score range in the area, it is classified based on the four categories of soil attenuation capacity: best, good, average, and least.

The second assessment stage for the upper groundwater aquifer is performed using GIS based on the three parameters: unsaturated zone thickness, vertical hydraulic conductivity, and average groundwater recharge assessed by means of the evaluation of net infiltration. Each of these parameters is assessed using three gradations (low, medium, and high). After that, for each assessed subarea, the GIS matrix overlaying procedure is performed successively for these three indicators, in the result of which the groundwater vulnerability is assessed as low, medium, or high, and a three-color map (green, yellow, red) of the corresponding vulnerability zones is drawn for the studied area.

As is noted by Zaporozec, the method is designed as a base for general land use and construction planning.

The *DRAW method* is described by Zhou *et al.* [2010]. The method was developed in China for groundwater vulnerability assessments in arid areas. For calculating the overall vulnerability index, the method combines four main assessment characteristics: *D*, the depth; *R*, the net recharge of the aquifer; *A*, the aquifer characteristics; and *V*, the lithology of the vadose zone. As a case study, the Zhou *et al.* [2010] paper assesses the vulnerability of a phreatic aquifer in Tarim Basin of Xinjiang. As reported by the authors, the groundwater vulnerability zones with vulnerability index ranging within 2–4, 4–6, 6–8, and >8 account for 10.1, 80.4, 9.2, and 0.2%, respectively, of the total plain area of the Tarim Basin. The areas with the latter two higher vulnerability ranges (6–8 and >8) are mainly located in the irrigation districts with thin soil layer (20–30 cm thick near-surface soil of vadose zone, mainly with underlying sandy gravel) and with silty and fine sand layer. Such a vadose zone generally lacks low permeability sandy loam and clayey soil, resulting in greater recharge due to infiltration of irrigation water.

The *EPIK method* was designed specially for use at karst areas in Switzerland by Doerfliger *et al.* [1999] for assessment of groundwater vulnerability of karstic alpine areas. The method is based on the classification of lithology and permeability of the unsaturated zone, recharge conditions, and karst development. The following four indicators are used:

1. Epikarst (weathered fractured bedrock layer beneath the soil or at the surface)
2. Protective cover
3. Infiltration conditions (with account of relief)
4. Karst development

The scores of these indicators are summed and weighted using the expert evaluation. The final assessment gives three categories of groundwater vulnerability: average, high, and very high. The method was used to assess the influence of karst on the groundwater vulnerability at test sites in Switzerland, Spain, and Germany during the implementation of the COST-620 Project [Zwahlen, 2004].

The *German State Geological Survey (GLA) method* was developed by Hoelting *et al.* [1995] for regional protectability assessment of the upper groundwater aquifer. The method accounts for the protective effectiveness of soil (down to a depth of 1 m, the average rooting depth) and the unsaturated zone. The assessment is based on the scores of the following indicators:

1. Effective moisture capacity of soil, *S* (mm), takes scores 10 (0–49 mm), 50 (50–89 mm), 125 (90–139 mm), 250 (140–199 mm), 500 (200–249 mm), and 750 ( $\geq 250$  mm).
2. Percolation rate, *W* (mm/year) takes scores from 2.25 to 0.5 for increasing groundwater recharge from 0 to over 400 mm/year.
3. Type of rock is given as  $R = O \cdot F$ , where *O* and *F* are defined as follows:
  - O* is the rock type with scores 5 (conglomerate, breccia, limestone, dolomite, etc.); 10 (porous sandstone, porous tuff); 15 (sandstone,

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quartzite, massive igneous and metamorphic rock); 20 (claystone, siltstone, shale, marlstone);

$F$  is the jointing and karstification indicator with values: 0.3 (strongly jointed, fractured, or karstic), 0.5 (moderately karstic), 1 (moderately jointed, slightly karstic; or no data), 4 (slightly jointed), and 25 (nonjointed).

4. Unsaturated zone thickness  $T$  (sum of layer thicknesses  $T_n$ ).

The resulting groundwater protectability index  $P_T$  is calculated as

$$P_T = P_1 + P_2 + Q + HP,$$

where

$$P_1 = S \cdot W$$

is the protective effectiveness of the soil;

$$P_2 = W (R_1 T_1 + R_2 T_2 + \dots + R_n T_n)$$

is the total protective effectiveness of the unsaturated zone layers, accounting for lithology and rock disturbance (fracturing, karst); and  $Q = 500$  and  $HP = 1500$  are scores added a perched aquifer and a confined aquifer, respectively, if present. Using the  $P_T$  index, the groundwater protectability categories are determined as follows: very low ( $P_T < 500$ ), low (500–1000), average (1000–2000), high (2000–3000), and very high (3000–4000).

The most problematic procedure of the method is the selection and substantiation of the separate indicator scores for a given area.

The method was used in Germany [Von Hoyer and Söfner, 1998] and other countries [Margane et al., 1999]. It became the base for the PI method described below.

The *PI method* of regional assessment of intrinsic groundwater vulnerability was developed by Goldscheider [2005] especially for karst areas, but it can be used for any other hydrogeological conditions. Although based on the German method described above, in contrast, it specifically takes into account the zones of fast infiltration related with the accumulation of surface runoff in depressions and direct influx of water into the upper aquifer through the open karst forms (caves, holes, etc.).

The resulting index of groundwater vulnerability is assessed as a product of two indicators:

1. Protective capacity of soil and unsaturated zone,  $P$ , with scores 1 (very low), 2 (low), 3 (average), 4 (high), and 5 (very high). Increasing scores by one point corresponds to a tenfold increase of protective capacity.
2. Infiltration conditions,  $I$ , is an indicator of the influence of fast infiltration zones, with scores 0–0.2 (maximum), 0.2–0.4 (high), 0.4–0.6 (average), 0.6–0.8 (low), and 0.8–1 (very low).

The protective capacity is assessed by score tables accounting for lithology, effective capacity, granulometry, fracturing, and karst. The detailed score tables are given in the COST-620 Project report [Zwahlen, 2004].

The final gradations of groundwater vulnerability PI index are as follows: PI = 4–5 (very low vulnerability), 3–4 (low), 2–3 (average), 1–2 (high), and 0–1 (maximum). In fact, this index gives the groundwater *protectability* rather than vulnerability, as it increases with the decrease in vulnerability (increase in protectability) of the assessed groundwater.

The PI method is used in the “European approach” to groundwater vulnerability assessment of karstic areas [Daly *et al.*, 2002] developed during the European Community (EC) COST-620 Project. In the result of this project, the *COP method* was designed based on three main indicators: (1) concentration of flow, (2) overlying layers, and (3) precipitation regime. The first of these indicators (*C* and *O*) correspond to the *I* and *P* indicators, respectively, of the PI method described above, and the third one (*P*) is a climatic indicator accounting for the annual atmospheric precipitation, frequency, duration, and intensity of precipitation events [Zwahlen, 2004].

The modified European approach was developed by Shestopalov *et al.* [2009] in Ukraine (called by authors “the Mountain Crimea approach”) for assessment of karst groundwater vulnerability. In this approach the COP method was adapted and modified for specific conditions of the area of Ai-Petri karst massif in mountainous Crimea representing the main recharge area of the regional groundwater system. The modification of the European approach includes accounting for the special properties of the epikarst and concentration of the underground runoff by karst caves. The GIS-based resulting map of assessed groundwater vulnerability in the PI method scale is obtained for the research area.

From the above consideration, it can be concluded that the common feature of the index-rating methods is in a significant degree “judgmental” approach to the definition of rating scores and scales for main factors and indicators of groundwater vulnerability.

### 1.3. Parametric Methods

The most known system of *groundwater protectability assessment* standardized in the former USSR was developed by Goldberg [1983, 1987], who determined the *groundwater protectability* to be the state of overlaying of an aquifer by deposits, first of all low-permeable ones, which prevent the penetration of contaminants from the land surface into groundwater. According to his representation, the groundwater’s protectability depends on a number of factors which can be classified into three main groups, natural, technogenic, and physicochemical, as follows:

1. *Natural Factors* Presence of low-permeable deposits in the vertical section; depth to groundwater table; thickness, lithology, and permeability properties of rocks (first low-permeable) overlying the aquifer; capacity (sorption)

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properties of rocks; and interrelation of groundwater heads (levels) in the studied and overlying aquifers.

2. *Technogenic Factors* Presence of contaminants on the land surface (waste collectors, slurry tanks, pits, outflow of wastewater over the watershed areas, irrigation with wastewater, etc.) and character of contaminant influx to groundwater determined by these conditions.
3. *Physicochemical* Specific properties of contaminants, their migration, sorption, and degradation properties chemical stability, and interaction with groundwater and rocks.

According to *Goldberg* [1983], the complete groundwater protectability assessment requires all the above factors to be taken into account. As a complex characteristic determining the risk of groundwater contamination, *Goldberg* introduces the groundwater *susceptibility*  $\Pi$  to contamination as determined by the ratio

$$\Pi = M_T / \varepsilon, \quad (1.1)$$

where  $M_T$  is the module of the technogenic load assessed in thousands of tons of contaminant fallout per square kilometer of land surface in a year, and  $\varepsilon$  is the dimensionless *groundwater protectability index* assessed in relative units.

From the above three main groundwater protectability factors, the natural ones are of primary importance because they determine the degree of the natural protection of an aquifer from any contaminants and conditions of their penetration from the land surface. Among the natural factors, the most important is the presence of overlying low-permeable deposits: clays, heavy loams, loams, sandy loams, and loamy sands with hydraulic conductivity  $k$  below 0.1 m/day.

Quantitatively the groundwater protectability can be characterized by the dimensionless index  $\varepsilon$  as described below.

As the main parameter of groundwater protectability, *Goldberg* used the *percolation time*  $t_w$  that is the time needed for percolating contaminated water from the land surface to reach the groundwater table. For the upper (unconfined) aquifer the time  $t_w$  is assessed for the following two scenarios:

1. Flow of contaminated (waste) waters from the surface basins with constant level  $H_c$ . The percolation time is determined by the formula

$$t_w = (n - n_e) H_c / k \left[ (m / H_c) - \ln(1 + m / H_c) \right], \quad (1.2)$$

where  $H_c$  is the height of the wastewater column in the basin (the average value  $H_c = 5$  m is usually taken in groundwater protectability assessments),  $k$  the unsaturated zone hydraulic conductivity (m/day),  $m$  the unsaturated zone thickness (m),  $n$  the porosity, and  $n_e$  the initial soil moisture content in the unsaturated zone.

2. Flow of contaminated water with constant flow rate  $Q_c$  ( $m^3/day$ ) with corresponding percolation rate  $w_c = Q_c/F$ , where  $F$  ( $m^2$ ) is the recharge surface area. In the case of  $w_c \leq k$ , where  $k$  ( $m/day$ ) is the hydraulic conductivity of the unsaturated zone, the percolation time is determined by the formula

$$t_w = \frac{mn}{\sqrt[3]{w_c^2 k}} \quad (1.3)$$

For  $w_c > k$  (a temporary layer of contaminated water is formed on the surface), the time  $t_w$  is determined by the formula

$$t_w = \frac{m}{\frac{(1-n)k}{2n} + \sqrt{\frac{(1-n^2)k^2}{4n^2} + \frac{qk}{n}}}. \quad (1.4)$$

In a heterogeneous stratified unsaturated zone, the equivalent hydraulic conductivity of the averaged section can be determined by the formula

$$k_e = \frac{m}{m_1/k_1 + m_2/k_2 + \dots + m_i/k_i}, \quad (1.5)$$

where  $m_1, m_2, \dots, m_i$  and  $k_1, k_2, \dots, k_i$  are the thicknesses and hydraulic conductivities, respectively, of the layers.

The groundwater protectability index  $\varepsilon$  for the *upper (unconfined) groundwater* is assessed using Goldberg's qualitative groundwater protectability assessment by an integer sum of two scores: (1) for the depth to groundwater table,  $H$ , and (2) for the low-permeable layers in the unsaturated zone (if present). The first one takes values 1–5 for corresponding intervals of groundwater table depth, as determined in Table 1.1.

If low-permeable deposits ( $k \leq 0.1$ ) are present in the unsaturated zone then the second (additional) score is determined by the total thickness  $m_0$  and hydraulic conductivity  $k$  as given in Table 1.2 for different lithology groups. The resulting groundwater protectability index  $\varepsilon$  is assessed by finding the sum of the scores (Tables 1.1 and 1.2) ranging from 1 to 30; according to this range, Goldberg determined six groundwater protectability categories:

- Category I:  $\varepsilon \leq 5$
- Category II:  $5 < \varepsilon \leq 10$
- Category III:  $10 < \varepsilon \leq 15$
- Category IV:  $15 < \varepsilon \leq 20$
- Category V:  $20 < \varepsilon \leq 25$
- Category VI:  $\varepsilon > 25$

**Table 1.1** Scores for groundwater table depth  $H$ .

Depth range	$H \leq 10\text{ m}$	$10\text{ m} < H \leq 20\text{ m}$	$20\text{ m} < H \leq 30\text{ m}$	$30\text{ m} < H \leq 40\text{ m}$	$H > 40\text{ m}$
Score	1	2	3	4	5

**Table 1.2** Scores for low-permeable deposit thickness and lithology.

Thickness of Low-Permeable Deposits, $m_0$ , m	Lithology Group of Deposits/(Hydraulic Conductivity, $k$ , m/day)		
	A ( $0.01 \leq k < 0.1$ ), Loamy Sands, Light Sandy Loams	B ( $0.001 \leq k < 0.01$ ), Mixed A and C	C ( $k < 0.001$ ), Heavy Sandy Loams, Clays
$m_0 \leq 2$	1	1	2
$2 < m_0 \leq 4$	2	3	4
$4 < m_0 \leq 6$	3	4	6
$6 < m_0 \leq 8$	4	6	8
$8 < m_0 \leq 10$	5	7	10
$10 < m_0 \leq 12$	6	9	12
$12 < m_0 \leq 14$	7	10	14
$14 < m_0 \leq 16$	8	12	16
$16 < m_0 \leq 18$	9	13	18
$18 < m_0 \leq 20$	10	15	20
$m_0 > 20$	12	18	25

Less favorable groundwater protectability conditions correspond to category I, and most favorable ones correspond to category VI. Suppose, for example, that the groundwater table is at depth 7 m from the land surface (score 1 according to Table 1) and there is a 3 m thick layer of loamy sand and light sandy loam in the unsaturated zone (score 2 by lithology group A, Table 1.2). Then, by the sum of the scores  $\varepsilon = 3$ , the groundwater protectability category is I. If the groundwater table is at depth 14 m (score 2, Table 1.1) and there is a 5 m thick layer of clays (score 6 by group C, Table 1.2), then  $\varepsilon = 8$ , which corresponds to the groundwater protectability category II.

*Confined groundwater protectability* can be assessed using Goldberg's qualitative groundwater protectability assessment by the thickness of the overlying (low-permeable) confining bed,  $m_0$ , also taking into account the data on the ratio of groundwater hydraulic head in the confined and upper unconfined aquifers. If the hydraulic conductivity  $k_0$  of the confining bed is known, then a more refined groundwater protectability assessment can be performed using the parameter  $\alpha = m_0/k_0$ , physically determining the water percolation time through the confining bed at a unit groundwater hydraulic head gradient (flow directed downward). Taking  $k_0$  as ranging from

$10^{-5}$  to  $10^{-3}$  m/day and characteristic  $m_0$  values of 5, 10, 20, 30, 40, and 50 m, Goldberg obtained the range of  $\alpha = m_0/k_0$  to be approximately  $10^3 - 10^7$  days, and determined six categories for the confined groundwater protectability assessment as follows:

- Category I:  $m_0 \leq 5$  m, or  $\alpha \leq 10^3$
- Category II:  $5 \text{ m} < m_0 \leq 10$  m, or  $10^3 < \alpha \leq 10^4$
- Category III:  $10 \text{ m} < m_0 \leq 20$  m, or  $10^4 < \alpha \leq 10^5$
- Category IV:  $20 \text{ m} < m_0 \leq 30$  m, or  $10^5 < \alpha \leq 10^6$
- Category V:  $30 \text{ m} < m_0 \leq 50$  m, or  $10^6 < \alpha \leq 10^7$
- Category VI:  $m_0 > 50$  m, or  $\alpha > 10^7$

The higher the category, the higher the groundwater protectability.

In addition, Goldberg determined three basic groups of confined groundwater protectability based on the confining bed thickness  $m_0$  and ratio of groundwater heads (levels) in the upper (unconfined) aquifer,  $H_1$ , and in the assessed confined aquifer,  $H_2$ :

- I. *Protected.* The groundwater is confined by a continuous (in area) permeability formation with thickness  $m_0 > 10$  m and  $H_2 > H_1$ .
- II. *Conditionally Protected.* The groundwater is confined by a continuous (in area) low-permeability formation with thickness  $5 \text{ m} \leq m_0 < 10$  m and  $H_2 > H_1$  (case a) or thickness  $m_0 > 10$  m and  $H_2 \leq H_1$  (case b).
- III. *Unprotected.* The groundwater is confined by a thin confining formation with  $m_0 < 5$  m and  $H_2 \leq H_1$  (case a) or when the confining formation is discontinuities (presence of lithological “windows,” zones of intensive fracturing, faults) at any ratio between  $H_2$  and  $H_1$  (case b).

Confined groundwater should also be considered as *unprotected* in the following cases: in the river valleys when the confining layer is cut through by the river in the karst areas when the confining layer is subjected to karst processes, and under the unfavorable tectonic conditions (presence of intensive neotectonic movements in the active water exchange zone, high conductivities in faults).

In group I the groundwater protectability is guaranteed by the high thickness of the confining layer and by hydrodynamic conditions at which the downward groundwater flow from the unconfined aquifer is impossible.

A quantitative *upper groundwater protectability assessment* by Goldberg is performed directly by the calculation of percolation time  $t_w$  using formula (1.1), (1.2), or (1.3). Setting the base at the *maximum contaminant lifetime*, which is assessed to be 400 days for most of bacteria, and some kinds of pesticide contamination, Goldberg determined six groundwater protectability categories, as given in Table 1.3.

For the *confined groundwater*, the time of groundwater percolation through the confining bed (at downward flow direction,  $H_1 > H_2$ ) is calculated as

$$t_w = \frac{m_0^2 n}{k_0 \Delta H}, \tag{1.6}$$

**Table 1.3** Categories of Goldberg’s quantitative upper groundwater protectability assessment.

Groundwater protectability category	I	II	III	IV	V	VI
Percolation time $t_w$ , days	$t_w \leq 10$	$10 < t_w \leq 50$	$50 < t_w \leq 100$	$100 < t_w \leq 200$	$200 < t_w \leq 400$	$t_w > 400$

**Table 1.4** Groups and gradations of confined groundwater protectability by percolation time  $t_w$  through low-permeable confining bed.

Groundwater protectability group	Unprotected	Conventionally protected			
Gradations $t_w$ , years	1 $t_w < 1$	2 $1 < t_w \leq 5$	3 $5 < t_w \leq 10$	4 $10 < t_w \leq 20$	5 $t_w > 20$

where  $n$  is the porosity of the confining bed (usually taken to be 0.01). Corresponding confined groundwater protectability gradations and groups are given in Table 1.4.

Comparing the assessed  $t_w$  value with known lifetimes for definite contaminants, a special groundwater protectability assessment can be done for these contaminants.

The groundwater protectability assessment system described above and developed by Goldberg was the first theoretically grounded solution of the given problem. The system has been used with different modifications and generalizations in Russia until recent times [Goman, 2005; Michnevich, 2011].

It should be noted, however, that a groundwater protectability assessment based on the time of water percolation through the overlying deposits determined for different cases by formulas (1.2)–(1.4) and (1.6) is in most cases not complete enough because it assesses only *cover* groundwater protectability and does not account for the protective capacity of the aquifer itself.

In the case of infiltration of contaminated water from the surface, calculations of the water percolation time  $t_w$  through the unsaturated zone by formula (1.3) show that the assessed percolation time appears to be small enough. For example, at infiltration rate  $w_c = 100$  mm/year and a 10 m thick unsaturated zone with effective porosity 0.01 composed of heavy loams and clays with hydraulic conductivity 0.001 m/day, formula (1.3) gives a  $t_w$  equal to only 239 days. This result is in agreement with the conclusion by *Haustov* [2007] that the cover protectability of upper groundwater, even in a thick unsaturated zone (over 10 m) composed of low-permeability deposits (loams, clays) is always insufficient for groundwater protection from contaminants. For this reason, the

upper groundwater can never be “well protected” or “protected enough” but only “relatively” or “conditionally.”

Thus, although the groundwater protectability assessment by water percolation time from the land surface to the groundwater table accounts for the hydraulic conductivity of covering deposits, this method does not account for the presence of geochemical barriers as well as the hydraulic and geochemical capacity properties of the assessed aquifer itself.

After Goldberg, the development of groundwater protectability assessment methods in the former USSR is associated with the works of *Mironenko and Rumynin* [1990, 1999], *Pashkovskiy* [2002], *Pityeva* [1999], and *Zektser* [2001]. Their efforts were directed at accounting not only for hydraulic properties but also for physicochemical properties of soil, in both unsaturated and saturated zones.

In particular, *Mironenko and Rumynin* [1990] determined the percolation time  $t_w$  of a conservative contaminant from the soil surface to the groundwater by the balance equation

$$wt_w = \int_0^{m_A} \theta(z) dz, \quad (1.7)$$

where  $\theta(z)$  is the volumetric water content that can in turn be related to infiltration  $w$ , full moisture saturation  $\theta_m$  (equal to effective porosity), field capacity  $\theta_0$  of soil (water content held in soil after excess water has drained) and hydraulic conductivity  $k$  by the formula

$$\theta = \theta_0 + (\theta_m - \theta_0) \sqrt[4]{\frac{w}{k}}. \quad (1.8)$$

*Rumynin* [2003] studied the sorption properties of groundwater geological medium and their effect on radionuclide migration.

*Pashkovskiy* [2002] proposed to assess the *contaminant travel time*  $t_c$  taking into account sorption in soil and the unsaturated zone:

$$t_c = \frac{mR}{w}, \quad R = 1 + K_d \frac{\delta}{g}, \quad (1.9)$$

where  $m$  (m) is the thickness of the unsaturated zone,  $K_d$  (dm<sup>3</sup>/kg) the distribution coefficient,  $\delta$  (kg/dm<sup>3</sup>) the volume (specific) weight of rock,  $\theta$  the volumetric water content (usually substituted by effective porosity  $n$ ),  $w$  (m/day) the infiltration velocity, and  $R$  the retardation factor determined as the ratio of water and contaminant velocities.

*Zektser* [2001] used the same approach to determine the contaminant travel time in the unsaturated zone. The author also introduced the concepts of the *full residence time* of a contaminant and the *time of water exchange* in the groundwater system considered based on the balance of the groundwater recharge and discharge. Considering a more general approach to the groundwater protectability assessment, *Zektser* also gave a more generalized determination of groundwater protectability as the property of a natural system which allows the groundwater composition and quality to be preserved as satisfying the requirements of the groundwater practical use during a forecast period. This means that requirements for groundwater protectability are different depending on its use, e.g., for potable, technical, or industrial purposes.

For a groundwater protectability assessment in any groundwater system (saturated or unsaturated), *Zektser* [2001] and *Rogachevskaya* [2002] determined the full residence times  $T_w$  and  $T_c$  for nonsorbed and sorbed contaminants, respectively, by the formulas

$$T_w = V/Q, \quad (1.10)$$

$$T_c = VR/Q, \quad (1.11)$$

where  $V$  is the volume of the system,  $Q$  is the rate of groundwater flow passing through the system, and  $R$  is the retardation factor determined by equation (1.9).

The geochemical aspects of groundwater were studied *Kraynov and Shvets* [1987], *Kraynov et al.* [2004], *Pityeva* [1999], and *Pityeva et al.* [2006] based on the concept of geochemical barriers of geological medium. This concept was first proposed by *Perelman* [1961], who determined the geochemical barrier as a zone in which a sharp change of hydrogeochemical conditions of chemical element migration takes place at short distances, causing their precipitation to a solid phase.

*Pityeva* [1999] proposed the concept of “geochemical groundwater protectability” determined by a series of physicochemical processes causing the removal of contaminants from the groundwater, such as sorption in porous or fractured media. According to *Pityeva*, geochemical groundwater protectability includes:

- identification and quantitative assessment of physicochemical processes along the travel paths of contaminants to groundwater;
- their;
- assessment of the potential manifestation of these processes in different conditions and objects determining the groundwater protectability.

Assessment of groundwater protectability is conducted the depending on types and properties of water-bearing rocks, as well as the thickness of the unsaturated zone.

Further development of the hydrogeochemical aspects of groundwater vulnerability assessment is found in the work by *Goman* [2007] as related to the migration of organic contaminants through low-permeable hydrogeological beds in areas of common solid waste repositories.

“The *Russian methodology*” [Belousova and Galaktionova, 1994; Belousova, 2005]. The Chernobyl catastrophe provided significant amount of information on a large scale on groundwater contamination with radionuclides, in particular with  $^{137}\text{Cs}$  and  $^{90}\text{Sr}$  [Shestopalov, 2001, 2002]. The accident groundwater protectability assessments have been implemented for Chernobyl-born  $^{137}\text{Cs}$  by Belousova and Galaktionova [1994] based on the contaminant travel time through the unsaturated zone taking into account its thickness, lithology, and sorption properties. The same approach was used for a regional assessment of upper groundwater vulnerability to Chernobyl-born  $^{137}\text{Cs}$  for the Dnieper Basin areas of Ukraine and Russia performed during the Russian-Belorussian-Ukrainian Cooperated Research Project in 2003 [Shestopalov, 2003]. As part of this research we used the base Russian methodology of intrinsic groundwater vulnerability assessment [Belousova and Galaktionova, 1994]. As a result, a regional groundwater vulnerability assessment by contamination was performed for the area of the Kyiv region, including the Chernobyl Exclusion Zone (CEZ), and a groundwater vulnerability map in scale 1:20,0000 was drawn. The methodology is based on the assessment of the contaminant travel time from the contaminated surface to the groundwater table,  $t_c$ , according to formula (1.9) [Pashkovsky, 2002] applicable for both conservative and sorbed pollutants. Depending on the  $t_c$  value, the score scale for the upper groundwater vulnerability to  $^{137}\text{Cs}$  is determined as shown in the Table 1.5.

As shown in the Table 1.5, groundwater vulnerability is classified into seven categories: catastrophic, very high, high, medium, low, very low, and absent. The two lowest categories, very low and absent, are often unified as “conditionally invulnerable.”

Rogachevskaya [2002] used materials obtained in the above study as well as data from field observation of  $^{137}\text{Cs}$  migration in the unsaturated zone obtained at special test sites. She considered groundwater vulnerability as a concept inverse to groundwater protectability based on the hydraulic and geochemical barriers of the unsaturated zone, influence of forestation degree as a regional factor, and hydrogeological properties of the assessed upper aquifer. As important factors of groundwater vulnerability to radioactive contamination, the sorption capacity

**Table 1.5** Gradations of groundwater vulnerability by  $^{137}\text{Cs}$  as determined by surface contamination density ( $\text{Ci}/\text{km}^2$ ) and radionuclide travel time  $t_c$  from surface to groundwater table.

$t_c$ Range, years	Groundwater Vulnerability Grade				
	>40 Ci/km <sup>2</sup>	15–40 Ci/km <sup>2</sup>	5–15 Ci/km <sup>2</sup>	1–5 Ci/km <sup>2</sup>	<1 Ci/km <sup>2</sup>
$t_c < 30$	Catastrophic	Very high	High	Medium	Very low
$30 < t_c < 60$	Very high	Very high	High	Medium	Very low
$60 < t_c < 100$	Very high	High	Medium	Low	Very low
$t_c > 100$	Medium	Low	Low	Low	Absent

(retardation), dispersion, and radioactive decay are considered. As the basic parameter of groundwater vulnerability assessment, *Rogachevskaya* [2002] used the radionuclide full residence time  $T_c$  in the hydrogeological system as determined above by equations (1.10) and (1.11):

$$T_c = T_w R, \quad (1.12)$$

where, as before,  $T_w$  is the residence time in the hydrogeological system of a nonsorbed chemicals moving with groundwater flow velocity, and  $R$  is the retardation factor determined by equation (1.9). During construction of the resulting groundwater vulnerability map, the zoning map of protective properties for the unsaturated zone is overlaid with the map of radionuclide residence time in groundwater determining the self-cleaning aquifer ability.

Based on results of experimental studies of  $^{137}\text{Cs}$  migration in areas contaminated after the Chernobyl Nuclear Power Plant (NPP) accident in Russia (Bryansk region) and experiments with artificial radionuclide injection at special observation plots, *Rogachevskaya* came to the conclusion that the soil is not a perfect protective barrier against radionuclide migration from the soil surface to groundwater. The share of “fast migration component” of the nonsorbed contaminant appeared to be near 10%. This part is determined by fast migration pathways such as “breakthrough” pores of the unsaturated zone and local “migration windows.” Of key importance are the relief microforms which influence the infiltration and depot properties of the soil and unsaturated zone.

The above conclusions are in agreement with our representation of the existence and importance of preferential flow and migration zones (PFMZs) of different scales in the geological medium. The assessed share of PFMZs in the total groundwater contamination (10% from total initial contamination) determined just on the local site scale (without accounting for larger PFMZs such as depressions and lineaments) is rather significant. Moreover, the effects of the landscape type (forested, meadow, plowed, etc.) also provide important input into the assessment of groundwater protectability.

*Polyakov and Golubkova* [2007] also used the water exchange time and retardation factor. However, they estimated the residence time of a nonsorbed tracer (or water exchange time),  $T_w$ , using a nonsorbed radioactive tracer (tritium). The tritium concentration was measured, and the time  $T_w$  was determined by “input” and observed tritium concentrations according to the methodology proposed by *Maloszevski and Zuber* [1996]. As an “input function,” they used historical data on tritium concentration in atmospheric precipitation starting from 1953 (when nuclear weapon tests were conducted in the atmosphere). The authors accounted for the retardation factor and lifetime of the radionuclide. They developed a score assessment system for groundwater vulnerability as applied to the area of Azov-Kuban artesian basin (score range 0–7) corresponding to the average water exchange time from over 1000 years to 5 years and determined tritium concentrations from

1 to 14 TU (tritium units, 1 TU=0.119 Bq/L). The wide use of this method requires implementation of special field works for groundwater sampling and sample analysis for determination of isotopes Tr,  $\delta D$ ,  $\delta^{18}O$ ,  $\delta^{13}C$ , and  $\delta^{14}C$ .

*AVI method.* Among the parametric groundwater vulnerability assessment methods, one should mention the aquifer vulnerability index (AVI), which was developed at the National Hydrogeology Research Institute of Saskatoon (Canada) by *Van Stempvoort et al.* [1995]. The authors used the total flow resistance of the covering deposits taking into account the lithology:

$$r = \sum_i \frac{m_i}{k_i}, \quad (1.13)$$

where  $m_i$  are layer thicknesses and  $k_i$  are the corresponding hydraulic conductivities. The method is equivalent to the assessment using groundwater percolation time because the total resistance  $r$  can be treated as the time of water percolation through the whole formation at a unit vertical hydraulic head gradient.

The method was by *Tovar and Rodriguez* [2004] for a groundwater vulnerability assessment in the area of Leon, Mexico. The hydraulic conductivities were determined by pumping tests and direct measurements with a constant head permeameter. The assessment required a significant volume of initial information that was provided by detailed GIS maps of relief, geological conditions, and conditions of land use. The obtained results were compared with an alternative assessment using the DRASTIC method. Authors noted that the AVI method gave a higher vulnerability, particularly in zones of tectonic dislocations.

Overall, parametric groundwater vulnerability assessments by water percolation time or flow often lead to underestimation or overestimation of the potential groundwater contamination depending on whether or not the physico-chemical interaction in the “contaminant-water-rock” system is taken into account. The approach uses the representation of a contamination front with a definite concentration at a definite depth below which the groundwater medium is still considered clean at each time moment. The approach often takes no account of areal distribution PFMZs of different dimensions (from macropores to areal zones related with depressions, geodynamically active zones, etc.). With an increase in the assessed area, the heterogeneities of larger dimensions should be brought into consideration, and the assessed groundwater vulnerability should be determined by their total “degree of openness.”

#### 1.4. Modeling Methods

Among the modeling methods used by different authors for groundwater vulnerability assessments, two methods should be distinguished: deterministic and statistical.

Most deterministic methods are based on general flow and transport balance (conservation) equations for the modeling domain with corresponding boundary conditions determining a boundary or initial-boundary (in the transient case) problem, using a system of partial differential (or integral) equations. These boundary problems mathematically describe the principal physical processes determining contaminant transport in a water-bearing system, the most important of which are *advection* (transport with groundwater flow velocity), *dispersion* of the contaminant front (caused by different deviations of contaminant particles from their “advection” paths and positions), and *sorption* of the contaminant by water-bearing rock.

The partial differential equation describing the contaminant transport in groundwater in saturated conditions can be written in the form [Ciang and Kinzelbach, 2001]

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x_i} \left( D_{ij} \frac{\partial C}{\partial x_j} \right) - \frac{\partial}{\partial x_i} (v_i C) + \frac{q_s}{n} C_s + \sum_{k=1}^N R_k, \quad (1.14)$$

where  $C$  is the concentration of a dissolved contaminant in groundwater (in units of mass or activity per unit volume,  $M/L^3$ ),  $t$  is time ( $T$ ),  $x_i$  are linear distances along the corresponding axes of the Cartesian coordinate system ( $L$ ),  $D_{ij}$  is the hydrodynamic dispersion tensor ( $L^2 T^{-1}$ ),  $v_i$  is the real flow velocity ( $LT^{-1}$ ),  $q_s$  is the volume water flow rate per unit volume of water-bearing medium representing sources of water recharge and discharge ( $T^{-1}$ ),  $C_s$  is the contaminant concentration in the recharge and discharge sources ( $ML^{-3}$ ),  $n$  is the porosity (dimensionless), and  $\sum_{k=1}^N R_k$  is a chemical reaction term, or the contaminant mass recharge or discharge sources ( $ML^{-3} T^{-1}$ ).

When only the equilibrium sorption and irreversible reactions of first-order chemical reactions are considered, the chemical reaction term in equation (1.14) can be represented in the form [Grove and Stollenwerk, 1984]

$$\sum_{k=1}^N R_k = -\frac{\rho_b}{n} \frac{\partial \bar{C}}{\partial t} - \lambda \left( C + \frac{\rho_b}{n} \bar{C} \right), \quad (1.15)$$

where  $\rho_b$  is the specific weight of rock ( $mL^{-3}$ ),  $\bar{C}$  the concentration of contaminant sorbed by rock per unit rock mass ( $Mm^{-1}$ ), and  $\lambda$  the first-order chemical reaction rate constant ( $T^{-1}$ ). The contaminant transport equation (1.14) is coupled with the groundwater flow equation by the relation

$$v_i = -\frac{K_{ii}}{n} \frac{\partial h}{\partial x_i}, \quad (1.16)$$

where  $K_{ii}$  is the main component of the hydraulic conductivity tensor ( $L/T$ ) and  $h$  is the hydraulic head ( $L$ ). The hydraulic head distribution is determined by the groundwater flow equation

$$\frac{\partial}{\partial x_i} \left( K_{ii} \frac{\partial h}{\partial x_j} \right) + q_s = S_s \frac{\partial h}{\partial t}, \quad (1.17)$$

where  $S_s$  ( $L^{-1}$ ) is the specific storage coefficient (storativity, or specific yield) of a water-bearing porous medium.

For numeric solution of the 3D boundary problems of groundwater flow and transport described by equations (1.14)–(1.17), various computer codes have been developed. The most well-known are the MODFLOW code for groundwater flow [McDonald and Harbaugh, 1988] and the MT3D code for contaminant transport [Zheng, 1990].

Depending on the case assessment and its objectives, different simplified versions of the 3D equation system (1.14)–(1.17) can be used: 1D (vertical), 2D (cross-section), etc.

For example, Zhang *et al.* [1996] assessed the intrinsic groundwater vulnerability of the Goshen County, Wyoming, using a 1D advection-dispersion model for the unsaturated zone. To determine the vertical distribution of the contaminant concentration, they solved a 1D equation of the type 1.14 without accounting for sorption in which, instead of porosity, they considered the water content as a function of the hydraulic conductivity of *van Genuchten* [1980]. The governing equations of water flow and chemical transport with the specified initial and boundary conditions were solved using a computer code HYDRUS (developed at the US Salinity Laboratory) using the finite-element method [Vogel *et al.*, 1995]. The authors calculated 130 vertical concentration distributions of the relative contaminant concentration  $c/c_0$ , where  $c_0$  is contaminant concentration in water infiltrating from the surface. The resulting groundwater vulnerability assessment has been compared to the corresponding assessment using the modified DRASTIC method (with procedures of GIS map overlays). The authors [Vogel *et al.*, 1995] note that the index-rating methods with GIS are appropriate for large study areas and the modeling method is better for use at smaller sites.

In the work of Loague *et al.* [1998] a 3D model is developed based on the MODFLOW-MT3D code for the regional groundwater vulnerability assessment of Fresno County, California, to contamination with DBCP (1,2-dibromo-3-chloropropane), which was used since 1940 until its prohibition in 1977. The authors reconstructed the historic data on atmospheric precipitation, land use (state of soil), irrigation, and groundwater contamination with DBCP and developed a 3D groundwater flow and contaminant transport model. In the result of the epignostic (past-time) simulation for the period 1960–1994 the authors built the

map of groundwater contamination with the pesticide. The results obtained in this work were further analyzed by *Loague and Corwin* [1998], they came to the conclusion that 3D modeling using GIS technologies is, in many cases, most effective for groundwater vulnerability assessment. The GIS provides the direct data support for modeling (preprocessing, postprocessing, reformatting, mapping, etc.), especially in the analysis of non-point source vulnerability. It helps to characterize the full information content of the spatially variable data required by solute transport models.

The same conclusion is made by *Zaporozec* [1985] as the result of a groundwater vulnerability assessment in Wisconsin using the SUPRA indexing method. He notes that the step after the preliminary assessment should be development of a regional hydrogeological flow transport model for the study area.

*Statistical* models of groundwater flow and transport used for groundwater vulnerability assessments are in most cases equivalent to deterministic ones because their general solutions also satisfy the groundwater flow and contaminant mass balance equations. However, the problem solution methods are based on stochastic algorithms such as the Monte Carlo method. Another aspect of statistical models is represented by the use of special probability density functions for the solution of groundwater migration problems. For groundwater modeling applications, this approach was developed by *Jury and Roth* [1990].

Statistical algorithms and data processing methods (regression analysis, interpolation and extrapolation methods, gridding methods, etc.) are directly employed in groundwater vulnerability assessment *by analogy*, that is, by associating a given research area with known areas in which groundwater contamination already occurred. If the analogue area is the same as the studied area, then we have the case of groundwater vulnerability assessment *by real contamination*. For example, *Evans and Maidment* [1995] used such a method for a statistical assessment of the groundwater vulnerability in Texas to nitrate contamination using linear regression analysis. They built a spatial distribution map for groundwater contamination probability based on water sampling data from 29,485 wells in the study area. It is clear that this method requires high volumes of initial information available only using the monitoring network facilities. An extended review of statistical methods for groundwater vulnerability assessment is presented in the National Research Council reports [*NRC*, 1993a,b].

Among all groundwater vulnerability assessment methods described above, in a higher or lesser degree, only a few consider the pathways and zones of preferential flow and transport. An attempt at the experimental assessment of a “fast migration component” for Chernobyl-born  $^{137}\text{Cs}$  was implemented by *Rogachevskaya* [2002]. In other methodologies the preferential flow phenomena were taken into account indirectly, particularly in the German, EPIC, PI, and COP methods for karst areas [*Hoelting et al.*, 1995; *Doerfliger et al.*, 1999; *Zwahlen*, 2004].

In the present work an attempt is made to assess the groundwater vulnerability of the upper (Quaternary) and first confined (Eocene) aquifers of the Dnieper River basin area (Kyiv region) in Ukraine to contamination with Chernobyl-born  $^{137}\text{Cs}$ , taking into account the PFMZ associated with depressions. A methodology is proposed for this purpose based on the 1D contaminant transport model and 3D groundwater flow model of the study area as well as available data of observed groundwater contamination obtained during the postaccident period.

As *Shestakov* [2003] notes, it is necessary to formulate the question of possible manifestations of heterogeneity in the geological medium during the solution of any hydrogeodynamic problem. Any study of hydrogeodynamic processes cannot be considered complete if the influences of rock heterogeneity on these processes have not been analyzed. This conclusion is especially acute in questions of groundwater vulnerability and protectability assessments.

