Chapter 2

Groundwater Vulnerability and Pesticide Leaching Modelling: A Literature Review

This chapter presents the main concepts associated with groundwater vulnerability and pesticide leaching modelling. The objective is to introduce a number of notions useful to the reader of this thesis and to identify the important methodological issues associated with the assessment of pesticide leaching at the regional scale. First, a section is devoted to groundwater vulnerability. The processes governing the environmental fate of pesticides are then described, before a number of methodological issues related to the implementation of a spatially distributed assessment of pesticide leaching.

2.1 Groundwater vulnerability

2.1.1 Definition

Vulnerability in a broad sense is defined as the quality or state of being vulnerable, i.e. capable of being wounded, liable to injury, assailable. This work deals with groundwater contamination by pesticides, and hence vulnerability is tackled through the vulnerability of ecosystems.

In climate change studies for instance, vulnerability is commonly defined in terms of sensitivity (i.e. the degree to which a system will respond to a given change), adaptive capacity (i.e. the degree to which spontaneous or planned adjustments are possible in practices, processes, or structures of

systems), and the degree of exposure of the system to climate change (IPCC, 2001).

Both qualitative and quantitative issues are concerned by groundwater vulnerability (De Smedt et al., 2001). The quantitative aspect deals with the balance between groundwater discharge and extraction, and groundwater recharge. The next paragraph examines how groundwater vulnerability is defined for quality issues.

Groundwater vulnerability

In hydrogeology, Foster et al. (2002) dated the origin of the use of the term 'vulnerability' to the early 1970s in France (Albinet and Margat, 1970). Many different definitions of groundwater vulnerability are now available in the literature, but all agree in the sense that vulnerability is a relative property (NRC, 1993). The National Research Council (1993) defined groundwater vulnerability to contamination, in the case of non-point sources or distributed point sources of pollution, as:

> 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.16).

The ideas of sensitivity and exposure are present, but the concept of adaptive capacity is not relevant for groundwater. It should also be noted that groundwater vulnerability appears as a probabilistic notion.

The reference location mentioned in the above definition is most often the water table (NRC, 1993; Connell and van den Daele, 2003). However, some authors argue that assessments of vulnerability of groundwater resources require analysis of not only the vadose zone, but also of the groundwater system itself (Fogg et al., 1999). Indeed, the choice of the reference location (e.g. the water table, well intakes, recharge or discharge zones) can depend on the purpose of the study.

It should be noted here that definitions of vulnerability differ across research disciplines. Kelly and Adger (2000) noted that some analysts regard assessment of vulnerability as the end point of any impact appraisal, others as the focal point, and yet others as the starting point. Depending on

the field of study (e.g. natural hazards, food security, etc.), definitions of vulnerability may intrisically include a social dimension. In this case, vulnerability is 'human' in nature and is defined as the 'capacity to anticipate, cope with, resist, and recover from the impact of a natural hazard' (Blaikie et al., 1994, cited by Kelly and Adger, 2000).

In this thesis, vulnerability is limited to the NRC's definition presented above, and does not consider the human aspects (e.g. water consumption and exposure) that could be associated with groundwater contamination.

Intrinsic vs. specific vulnerability

A question intensely debated about the definition of groundwater vulnerability is whether or not vulnerability depends on the nature and properties of the contaminant, and on land use management. Some studies considered that vulnerability is an intrinsic characteristic of the hydrogeological system (Foster, 1987; Palmer and Lewis, 1998). Others find that vulnerability depends on the properties of individual contaminants or contaminant groups, but is independent of land management practices (e.g. the amount of pesticide applied) (NRC, 1993). A distinction is then sometimes made between intrinsic and specific vulnerability (NRC, 1993; Burkart et al., 1999a). The latter is used when vulnerability is related to a specific contaminant, contaminant class, and/or human activity.

It is now widely recognized that the degree of contaminant attenuation can vary significantly with the type of pollutant in any given situation (Foster et al., 2002). Moreover, Worrall et al. (2002) showed in an analysis of variance that, in order to explain groundwater contamination, the interactions between the pollutant and in-situ properties are statistically even more important than chemical vs. land-use, soil and aquifer properties. The scientific justification of intrinsic vulnerability assessments and maps is therefore highly questionable (Foster et al., 2002; Lobo-Ferreira, 2003).

The use of intrinsic vulnerability is thus often motivated by the easier implementation of intrinsic vulnerability assessment methods or by the scarcity of data and information about the interactions between contaminants and the environment (Burkart et al., 1999a; Lobo-Ferreira, 2003). Intrinsic vulnerability also allows the production of a unique vulnerability map for a given area and is therefore often perceived as appropriate to land

use planning proposals (Robins et al., 1994).

Vulnerability assessments with a sound scientific basis tend to turn to methods considering the specificity of vulnerability to a single compound or to a class of contaminants (e.g.; Burkart et al., 1999a; Worrall and Kolpin, 2004; Posen et al., 2006). By considering a number of different pesticides, Worrall and Kolpin (2004) were able to evaluate the influence of pesticide properties upon groundwater vulnerability. A recent assessment of groundwater vulnerability in the Scheldt catchment also implemented a method specific to pesticides (Pinte et al., 2005).

2.1.2 Factors affecting groundwater vulnerability to contamination by pesticides

Various physical, chemical, and biological processes determine the environmental fate of pesticides (see section 2.2). The rates and importance of each of these processes are, in turn, affected by different factors (Soutter and Pannatier, 1996). Table 2.1 presents the influence of these factors on groundwater specific vulnerability to pesticides. The following paragraphs discuss the different points in more details.

Table 2.1: Factors affecting groundwater vulnerability to contamination by pesticides.

Factor	Examples
Land use/management	Pesticide application rate and timing, tillage
Soil and crop properties	Organic matter content, texture, structure, plant uptake
Climate	Timing of first rainfall, temperature, potential evapotranspiration
Subsoil, vadose zone	Thickness, degradation sites
Groundwater	Groundwater flow, dilution
Pesticide properties	Sorption, degradation

Land use and land management

Land use (including the crop rotation scheme) is an important factor affecting groundwater vulnerability, as it is directly linked with the type and amount of pesticide applied (Addiscott and Mirza, 1998). Obviously, leaching cannot be expected if no pesticide input is attributed to a given land use. The concept of risk is perhaps more appropriate to take the influence of land use into account. Risk is often defined as the combination of hazard and vulnerability: risk = hazard × vulnerability (Passarella et al., 2002). Thus defined, risk includes the quantification of the probability that a pesticide will be applied at a given space/time location (i.e. hazard); this probability is further combined with the vulnerability of that location to the pesticide applied.

However, management practices also affect groundwater vulnerability. Indeed, by influencing crop and soil properties, land management can play a non-negligible role. For example, conventional tillage has the potential to limit preferential flow[1] and to subsequently affect the rate and amount of pesticide transport (Isensee et al., 1990; Elliott et al., 2000). However, the overall effect of tillage (no-till, conservation tillage or conventional tillage) on macroporosity and pesticide leaching remains unclear because of contrasted results obtained by different experimental studies (Flury, 1996; Malone et al., 2003).

The pesticide application rate, formulation and timing are also key parameters to estimate pesticide leaching (NRC, 1993; Flury, 1996). For example, it is known that the apparent adsorption of pesticides in the field increases with time. It can therefore be expected that the mass of pesticides leached to groundwater is inversely proportional to the time elapsed between pesticide application and the first infiltration event (Flury, 1996).

Soil and crop properties

Most of the processes causing degradation and/or attenuation of pollutants concentration in the unsaturated zone occur at much higher rates in

[1] Preferential flow phenomena are defined in the sense that water and solutes move only through a portion of the available pore space (Flury, 1996). An important characteristic of preferential flow is its non-equilibrium nature. Even for uniform flow conditions, most of the water and solutes generally move through the largest continuous pores that are filled with water at a particular tension (Šimunek et al., 2003).

the biologically active soil zone (Robins et al., 1994). For example, pesticide sorption on organic matter and clay minerals is of paramount importance for the attenuation of pesticide leaching (Hutson, 1993; Robins et al., 1994).

Using a multivariate analysis, Burkart et al. (1999b) determined for a regional data set that soil characteristics explained 33% of the variability in concentrations of atrazine in groundwater. Organic matter content plays a dominant role in the sorption of pesticides and transformation products (e.g. Ahmad et al., 2001). Soil organic matter has a great number of binding sites, because it has a very large surface area and is chemically reactive. Thus, the sorption capacity of a pesticide influences considerably its mobility in soils.

Textural and structural characteristics determine the hydrological behaviour of soils and hence the percolation rate of contaminants. Soil structure and the occurrence of preferential flow may significantly affect groundwater vulnerability. Soil macroporosity is an important factor affecting pesticide movement to drains or surface water, but also to shallow groundwater in some cases (Shipitalo et al., 2000; Haria et al., 2003).

There is evidence that the effects of the initial water content on pesticide leaching depend on soil texture: under dry conditions, sandy soils tend to show less leaching, whereas loamy and clayey soils show more leaching when exposed to a strong rainfall shortly after pesticide application (Flury, 1996).

Finally, crop properties such as root distribution, root depth, and pesticide uptake rates, may also significantly influence groundwater vulnerability (NRC, 1993).

Climate

The impact of both the precipitation regime and the timing of the first rainfall after pesticide application on pesticide leaching has been abundantly investigated (e.g. Jury and Gruber, 1989; Hutson, 1993; Van Alphen and Stoorvogel, 2002). Timing of the first rainfall is particularly important because it determines the initial soil moisture conditions and thus water percolation rate (Flury, 1996; Shipitalo and Edwards, 1996).

However, pesticide leaching is generally found to be much less sensitive to climatic variability than to soil variability (Jury and Gruber, 1989; Bleecker

et al., 1995). Besides, it has been suggested that these two factors act independently on pesticide leaching (Van Alphen and Stoorvogel, 2002), but this implies that the study is not conducted at a scale reflecting pedogenic influence of climate.

Temperature, radiation, wind and humidity are also climatic factors affecting groundwater vulnerability, e.g. by determining potential evapotranspiration and hence affecting the water balance. Finally, soil temperature acts upon pesticide degradation (i.e. pesticide degradation is temperature-dependent) and hydrological processes, and thus affects groundwater vulnerability under different climatic conditions (Paraíba et al., 2003).

Subsoil, vadose zone

For aquifers with the water table deeper than the soil layer, the thickness and nature of the vadose zone may be important to evaluate groundwater vulnerability. In general, pesticide attenuation and degradation are slower below the soil layer (Robins et al., 1994), although in some cases small sites or horizons with a high degradation potential may occur in the vadose zone (Vanderheyden, 1997).

However, it is recognized that vadose zone transport processes are very complex, and data on vadose zone parameters (e.g. retention curve and unsaturated hydraulic conductivity) are seldom available (Fogg et al., 1999). Therefore, vadose zone influence on groundwater vulnerability has often been estimated using weighting factors or vulnerability classes in index methods (see section 2.1.3; Gogu and Dassargues, 2000).

Groundwater

If the vulnerability analysis is not restricted to contaminants reaching the water table, then the saturated zone properties can influence groundwater vulnerability estimates e.g. at pumping wells. Fogg et al. (1999) argued that it is highly relevant to consider groundwater flow in the vulnerability assessment, particularly for groundwater resources at important depths, because of the significant time lag existing between the solute arrival at the water table and its presence in water supply wells.

Pesticide properties

Consideration of pesticide pollution purely in chemical terms has largely been developed as part of methods to identify priority pollutants for monitoring or to pre-screen new compounds for their environmental behaviour. Most of these approaches have been based on the use of sorption and degradation parameters (e.g. K_{OC} and half-life), which are dependent on soil properties (Worrall and Kolpin, 2004). This illustrates the key role played by pesticide properties in pesticide leaching assessments.

However, it is worth to note here that the best approach to discriminate between leachers and non-leachers on the basis of molecular parameters is rarely in terms of sorption and degradation (Gustafson, 1989). Alternatively, molecular descriptors derived from the compounds structure (e.g. connectivity parameters) have been successfully used to discriminate between pesticides found to leach to groundwater and those not found in groundwater (Worrall, 2001). Aqueous solubility, Henry's constant, and saturated vapour density among others complete the pesticide parameters that determine the environmental fate of compounds in interaction with site properties (NRC, 1993).

2.1.3 Vulnerability assessment methods

Overlay and index methods

These methods are based on combining maps of various physiographic attributes by assigning an index or score to each attribute (NRC, 1993). Qualitative or quantitative indices are derived, that bring together the key factors believed to determine pesticide transport processes (Connell and van den Daele, 2003). Early examples of this type of assessment are the DRASTIC index (Aller et al., 1985) and the GOD index (Foster, 1987). A number of similar index-based systems have been developed, sometimes extending the range of parameters included in the vulnerability assessment (e.g. Secunda et al., 1998). Vulnerability maps based on these methods have proved popular tools and are a common feature of groundwater quality management throughout the world, as documented for example by Worrall and Kolpin (2004).

However, this category of methods in general does not differentiate between contaminants and hence they are applicable to the assessment of in-

trinsic vulnerability only (Connell and van den Daele, 2003). Moreover, overlay and index methods have a number of conceptual flaws. Firstly, weightings are chosen arbitrarily and solely based on expert opinion (NRC, 1993; Worrall, 2002; Connell and van den Daele, 2003). Secondly, systems based on indices do not capture the probabilistic nature or the uncertainty of groundwater vulnerability (Worrall, 2002). Thirdly, uncertainties in the data themselves and in the actual relevance of each weighted factor question the reliability of the vulnerability maps (Merchant, 1994; Fogg et al., 1999). Fourthly, the use of indices makes validation difficult. Merchant (1994) noticed that, apart from the use of 'visual validation', very few attempts have been made to validate the numerous DRASTIC applications. Worrall (2002) stressed that validation may be inherently impossible for this category of methods that assess vulnerability outside of a probabilistic framework. Finally, these methods have a greater focus on the distribution of environmental attributes rather than on processes directly controlling groundwater contamination by pesticides (Fogg et al., 1999; Connell and van den Daele, 2003).

These numerous limitations suggest that overlay and index methods will receive decreasing support in the future, although Gogu and Dassargues (2000) argued that they could still be useful in combination with methods using process-based models.

Methods employing process-based simulation models

Groundwater vulnerability can be assessed through the use of process-based simulation models. Assessment methods in this category are usually more elaborated than simple overlay or index methods, and include different degrees of complexity from process-based indices to complex 3-D simulation models.

Simple models such as the Behavior Assessment Model (BAM; Jury and Ghodrati, 1989) or the Attenuation Factor (AF; Rao et al., 1985) can be used to map groundwater vulnerability, but they can also serve for screening purposes (i.e. to compare the environmental fate of a new compound with other pesticides). The AF is an analytical solution of the convection-dispersion equations. Indices can also be based on numerical solutions of the transport equations. For example, Meeks and Dean (1990) used a one-dimensional advection-dispersion transport model to develop a leaching potential index,

which simulates vertical movement through a soil to the water table. Soutter and Pannatier (1996) expressed groundwater vulnerability as the ratio between the cumulative pesticide flux reaching mean water table depth and the total quantity of pesticide applied.

The derivation of such indices is not necessarily a common feature of vulnerability assessments using process-based models. The selection of a single relevant variable can serve the purpose of estimating groundwater vulnerability. For example, using the results of Monte Carlo simulations, Morgan (2002) selected the pesticide mass loading at the 90% probability of non-exceedence as a means to map aquifer vulnerability. Connell and van den Daele (2003) chose the maximum contaminant concentration at the water table as a proxy for groundwater vulnerability.

Vulnerability assessments can also be based on metamodels. A metamodel is basically a 'model of a model'. It is a statistical significant response function that approximates outcomes of a complex simulation model (Wu and Babcock, 1999; Piñeros Garcet et al., 2006). In environmental sciences, metamodels are usually based on multiple regression analyses, artificial neural networks, transfer functions, multidimensional kriging, etc. For example, Holman et al. (2004) used a meta-version of the leaching model MACRO (Jarvis, 1991) coupled with AF to assess the risk of groundwater contamination by pesticides. Tiktak et al. (2006) mapped groundwater vulnerability at the pan-European scale using a combination of AF and a metamodel of GeoPEARL.

Monitoring based statistical inference methods

Statistical methods use response variables such as the frequency of contaminant occurrence, contaminant concentration, or contamination probability. These methods are based on the concept of uncertainty, which is described in terms of probability distributions for the variable of interest (NRC, 1993). One possible goal in applying statistical methods to vulnerability assessment is to identify variables that can be used to define the probability of groundwater contamination (Burkart et al., 1999a). Typically, one seeks to describe in mathematical terms (function or model) a relationship between water quality and natural and/or human-induced variables in a discrete area.

For example, Teso et al. (1996) developed a logistic regression model containing independent variables related to the soil texture. The dependant variable was defined as the contamination status of soil sections (uncontaminated vs. contaminated) and groundwater vulnerability was thus assessed through the estimation of a section's likelihood of its containing a contaminated well. Other statistical approaches, such as principal components analysis, discriminant analysis and cluster analysis, have been used to describe relationships between soil attributes and groundwater vulnerability (e.g. Teso et al., 1988; Troiano et al., 1999).

These methods may also be used to discriminate between different sources of pesticide leaching. Lapworth and Gooddy (2006) examined the relationships between land use and pesticide concentrations in monitoring wells and concluded that observed diuron contamination resulted from non-agricultural applications.

Worrall (2002) and Worrall and Kolpin (2003) used Bayesian statistics to measure the vulnerability of the catchment of a borehole to groundwater pollution, based on observation of contaminant occurrence in the borehole and the region. This vulnerability assessment is thus based solely on monitoring data and does not need explanatory variables. However, the application of this method requires extensive data sets (and hence is limited to large, intensively monitored areas) and appears to be less sensitive for boreholes with a low relative vulnerability (Worrall, 2002). Moreover, for regulation purposes, this approach implies that borehole catchments can actually be delineated.

Worrall and Kolpin (2004) developed a logistic regression model of groundwater pollution that brings together variation in chemical properties with land-use, soil and aquifer properties. They found that vulnerability, as explained by the independent factors that produced the best regression fit, could be viewed as having two parts: an intrinsic vulnerability factor (consisting of variables related to the depth to groundwater, the organic matter and the sand content) and a molecular factor (consisting of variables related to molecular connectivity). However, the regression output is limited to the presence/absence of a compound, and hence limits the discrimination to vulnerable vs. invulnerable wells. Although the mapping of such a vulnerability assessment might prove to be problematic, this study is—to our knowledge—the first application of a statistical vulnerability assessment

which explicitly accounts for the variability of both chemical and site properties.

2.2 Process-based models of pesticide leaching

2.2.1 Modelling approaches

Addiscott and Wagenet (1985) and Vanclooster et al. (2000a) reviewed the different modelling approaches of solute leaching in soils. A key distinction is made between deterministic models, which presume that a system or process operates such that the occurrence of a given set of events leads to a unique outcome, and stochastic models, which presuppose the output to be uncertain and are structured to account for this uncertainty.

Other modelling classification keys include numerical vs. analytical, and mechanistic vs. functional models (Addiscott and Wagenet, 1985). Alternative classification keys are sometimes based on considerations of spatial or temporal scale (pore vs. global scale; instantaneous vs. decades), level of complexity (scientific vs. decision making models) or level of integrity (holistic vs. reductionistic approach) (Vanclooster et al., 2000a).

Index models integrate the effect of the different fate and transport processes into lumped-parameters, and are inherently subject to simplifications, which limit their predictions (Hantush et al., 2000). Examples of such models include LEACH (Laskowski et al., 1982) and LPI (Meeks and Dean, 1990). They are widely used for relative ranking of chemicals, but are also potential tools for the assessment of groundwater vulnerability (Hantush et al., 2000).

A number of process-based, deterministic models have been developed, for example LEACHP (Wagenet and Hutson, 1989), MACRO (Jarvis, 1991; Larsbo and Jarvis, 2003), PEARL (Tiktak et al., 2000), PRZM (Carsel et al., 1998), WAVE (Vanclooster et al., 1994), among others. The AF model (Rao et al., 1985) is also process based, but is used as a screening model unless combined with metamodelling. These models are all one-dimensional. HYDRUS-2D (Šimunek et al., 1999) is an example of a two-dimensional model of water and solute transport.

2.2.2 Processes governing the environmental fate of pesticides

As pesticide leaching models aim at predicting the fraction of pesticide percolating the soil and subsoil, it is important to know what are the other environmental pathways through which pesticides are transported. Some of the processes presented here are closely related to those developed in section 2.1.2 dedicated to groundwater vulnerability.

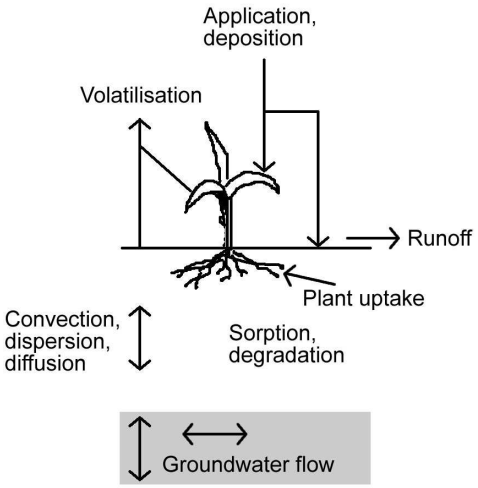

Figure 2.1: Overview of the main processes governing the environmental fate of pesticides.

In the following paragraphs, the equations used for modelling pesticide fate (e.g. Richards convection-dispersion equation) will not be presented. The objective is rather to review the key processes governing the environmental fate of pesticides. For an introduction to the equations governing water and solute movement, the reader is referred to e.g. Addiscott and Wagenet (1985) or van Genuchten et al. (1999). Figure 2.1 represents the main processes governing pesticides fate in the atmosphere-plant-soil-groundwater system, which will be described below.

Volatilisation

The presence of pesticides in the atmosphere can occur as a result of drift

during application or, subsequently, volatilisation from soil, plants or surface water (Bedos et al., 2002). Volatilisation is a major source of pesticide residues in air, and thus may lead to a long-range transport of residues remote from their application. This can for instance lead to subsequent deposition of pesticides in rainwater (Dubus et al., 2000). Volatilisation is therefore likely to have a major impact on the environmental balance of pesticides (Vanclooster et al., 2003).

Volatilisation can occur from both the bare soil and the crop canopy (if pesticide is applied in post-emergence), and has been shown to occur within the first days or weeks after application (Bedos et al., 2002). It results from a series of dynamic processes occurring in the soil-crop canopy-atmosphere continuum, which can be seen as a diffusive vapour flux across a thin air-boundary layer (Vanclooster et al., 2003; Hantush et al., 2000).

The most important factors affecting volatilisation are the physico-chemical properties of a pesticide (vapour pressure being a key parameter), atmospheric conditions (air temperature, humidity, wind), soil conditions (moisture, temperature, soil density, clay and organic matter content), and agricultural practices (application dose and date, tillage) (Bedos et al., 2002; Kubiak, 2006).

Runoff

Runoff and leaching are mutually dependent processes (Flury, 1996). During runoff, a portion of the water is removed laterally from the surface, and does not contribute to pesticide leaching anymore. Increased runoff is therefore related to decreased leaching. This might not be generally true for preferential flow processes through drainage wells (Troiano et al., 1999) or macropores, but certainly for the leaching of contaminants through bulk soil (Flury, 1996).

Plant uptake

Although this process has limited relevance for autumn-applied compounds, plant uptake of pesticides may be important in some cases. Uptake is often simulated using a factor to describe the relative uptake of the compound into the plant roots compared to the removal of water (Vanclooster

et al., 2000b). The capacity of plants to uptake chemicals is frequently used for the remediation of contaminated soils (e.g. Sun et al., 2004).

Water and solute flow

Water flow in the soil and subsoil is usually described by two processes: flow through the matrix pore-space and preferential flow. Flow in porous media is usually described by a capacity type or by an advection-dispersion model (Flury, 1996; Vanclooster et al., 2000b). In their classification of modelling approaches for soil matrix flow, Addiscott and Wagenet (1985) explained the difference between rate and capacity models:

> A rate model for solute movement combines the description of several transport processes. It first defines the instantaneous rate of change of water content in terms of the product of a hydraulic gradient and a rate parameter, the hydraulic conductivity, and then defines the rate of change of solute concentration in terms of convection and diffusion processes. A capacity model defines changes (rather than rates of change) in amounts of solute and water content, using capacity factors such as the volumetric water content at field capacity. Rate models are by definition driven by time, while capacity models are usually driven by the amounts of rainfall, evaporation, or irrigation (p.412).

The importance of preferential flow has already been underlined. This process can act as a by-pass of the upper soil layers, thus strongly preventing the attenuation and retardation of pesticide leaching (Robins et al., 1994). Preferential flow may take place in macropores, or in the form of unstable flow ('fingering') induced by soil textural layering, water repellency and air entrapment. It may also be caused by funnelling of water through high-conductivity layers, or as being redirected by sloping less-permeable layers (van Genuchten et al., 1999; Jarvis, 1999).

Šimunek et al. (2003) reviewed modelling approaches for the description of preferential and non-equilibrium flow and transport. Existing approaches range from relatively simplistic models to more complex physically based dual-porosity, dual-permeability, and multi-region type models. It is generally assumed that the porous medium consists of two interacting regions,

one associated with the macropore system, and one comprising micropores inside soil aggregates (Šimunek et al., 2003). A different approach was introduced by Deurer et al. (2003) who determined drainage networks in the field using hydraulic properties of the soil, and described preferential flow as a piston flow through the network.

Sorption and degradation

Once in the soil, pesticide molecules partition between the aqueous and solid phases of the soil. The degree to which a pesticide molecule prefers one phase to the other will affect every other aspect of its fate: sorption will determine whether the pesticide will persist or not, be transported to groundwater or not (Wauchope et al., 2002). Soil sorption is usually characterized by a partition constant, K_d, which is a ratio of solid phase to solute concentrations. High values of K_d indicate that a pesticide is strongly sorbed and will be immobile in soil, and also resistant to microbial degradation (Wauchope et al., 2002).

The thousands of K_d measurements made in a variety of soils have showed that there is generally a high correlation between the organic matter content of the soils and K_d (Ahmad et al., 2001). This observation leads to the assumption that it is soil organic matter, acting as a non-polar phase, that is the main sorbent in soils, attracting pesticides because they are typically non-polar organic molecules (Wauchope et al., 2002). Binding of pesticides to organic matter can occur by sorption (Van der Waal's forces, hydrogen bonding, hydrophobic bonding), but also by electrostatic interactions (charge transfer, ion exchange or ligand exchange), covalent bonding or combinations of these reactions (Bollag et al., 1992).

The experimental observation of a gradual decrease in the sorption coefficient K_d with increasing pesticide equilibrium concentration has lead to the definition of the Freundlich sorption isotherm. In this case, equilibrium sorption is described by:

$$X_{eq} = K_{f,eq} \times {C_L}^{N} \tag{2.1}$$

where X_{eq} is pesticide content in the equilibrium sorption phase, $K_{f,eq}$ is the Freundlich coefficient for the equilibrium-sorption phase, C_L is the concentration in the liquid phase, and N is the Freundlich exponent (Jacques

et al., 1999). N indicates the extent to which adsorption depends on the concentration. If $N = 1$, the sorption isotherm is linear and K_d is used.

Degradation is a fundamental attenuation process for pesticides and is generally described using the substance half-life (i.e. the time needed to transform half of the pesticide mass). This process is affected by many biotic and abiotic factors involved in the interactions among microorganisms, chemical and soil constituents (Guo et al., 2000; Vanclooster et al., 2000a). It is generally accepted that sorption limits the degradation of pesticides by reducing their partitioning into the soil liquid phase. It is assumed that sorbed pesticides are less accessible to microorganisms that utilize exclusively or preferentially chemicals in solution. Guo et al. (2000) listed the studies providing evidence of the negative dependence of degradation on sorption for a variety of compounds.

When adsorption is assumed to be instantaneous, and equilibrium conditions exist at all times between liquid and solid phases, overall degradation is determined directly by the kinetics of degradation of the individual phases (Guo et al., 2000). However, equilibrium is typically only apparent, and sorption and desorption involve a complex system of processes with fast and slow kinetics (Wauchope et al., 2002). Under non-equilibrium assumptions, where adsorption is time-dependent, the dependence of degradation on sorption is more complex even if degradation of each phase is first order (Guo et al., 2000).

Degradation parameters obtained for soils are not directly transferable to saturated-zone materials, because of different microbial populations, pesticide concentrations, and anaeroby conditions (Hoyle and Arthur, 2000). In the case of atrazine, degradation in saturated conditions has most often been found to be null or very low (see the review of Hoyle and Arthur, 2000).

Groundwater flow

Pesticide leaching through the soil and vadose zone can eventually cause residues to reach the saturated zone. From there, pesticide fate is mainly driven by groundwater flow and degradation. Retardation and dispersion of pesticides in groundwater may be estimated *in situ* using an appropriate network design of monitoring wells (e.g. at the field scale; Springer and Bair, 1998).

Groundwater flow may be simulated using analytical models, such as the mass balance equation (steady flow, no dispersion) presented in Beltman et al. (1995). Another example is given by Hantush et al. (2000), who developed an analytical solution for a two-dimensional advective-dispersive transport (flushing) of the solute in the aquifer.

In analytical element models, analytical solutions for different processes (such as groundwater pumping, recharge, seepage boundaries) are combined spatially and superimposed (e.g. Moorman, 1999).

Solute transport in groundwater may also be simulated with numerical techniques, such as the widely used MODFLOW (Harbaugh et al., 2000) 3-D finite-difference groundwater flow model. In this case, the saturated zone is represented as a collection of cells (blocks and layers) filling a three-dimensional space. These types of models generally have heavy input data requirements (hydraulic parameters, boundary conditions, and stresses).

2.2.3 Validation of pesticide leaching models

The FOCUS (FOrum for the Coordination of pesticide fate models and their USe) group defined the validation process as a

> comparison of model output with data independently derived from experiments or observations of the environment; this implies that none of the input parameters is obtained via calibration

to those data (FOCUS, 1995). Vanclooster et al. (2000b) gave a selection of indicators useful for testing of pesticide leaching models (e.g. root mean square error, modelling efficiency, Nash-Sutcliffe coefficient, etc.). These indicators basically measure the goodness of fit between simulations and observations. More generally, performance criteria are not restricted to residual error analysis, but also include statistical criteria, hypothesis testing, linear regression and graphical comparisons (Mulla and Addiscott, 1999).

Ideally, a pesticide leaching model should be validated (or evaluated; Beck, 2002) against a range of different environmental conditions (weather conditions, irrigation practices, soil types, positions of groundwater table, tillage system, types of pesticides) so that a model user could be confident

enough before a new application. However, in environmental systems, complete validation of a model is a priori an impossible task (Konikow and Bredehoeft, 1992; Oreskes et al., 1994), but acceptable modelling results in different conditions and with different substances enhance the reliability of a pesticide leaching model and its probability of success at a new site (Vanclooster et al., 2003). In this sense, model validation is never totally achieved, but the validation status can be qualified via the model performance in different case studies (*increasing confirmation*; Beven, 1995).

2.2.4 Uncertainty in pesticide leaching modelling

The importance of assessing and communicating uncertainties in scientific research is now well established (Brown, 2004). Recently the European Water Framework Directive required scientific uncertainty to be addressed within the development of integrated water management plans (EU, 2000).

2.2.4.1 Sources of uncertainty

Dubus et al. (2002b) reported the different sources of uncertainty in pesticide fate modelling. They provided a comprehensive review of uncertainty sources, which will be summarized here. In the following section, only references other than Dubus et al. (2002b) are specified.

Uncertainty in the primary data

The primary data are defined as the basic physical, chemical and environmental properties, which are either directly fed into a model or used to derive input parameters for the model. Primary data include both parameters and variables : site characteristics, soil properties, weather conditions, pesticide properties or results of field experiments. Uncertainty in the primary data will arise from the spatial and temporal variability of environmental variables, from sampling procedures in the field, and from analyses in the laboratory.

The spatial and temporal variability of environmental properties influences predictions of pesticide leaching models. In particular, the spatial variability of pesticide sorption has received a lot of attention (see section

2.3.2). Variability in the sorption distribution coefficient K_d can generally be reduced by normalising it to the organic carbon content, but the variability of the resulting K_{OC} often remains considerable. Geostatistics can be used for example when soil or pesticide properties show some spatial dependency. However, describing uncertainty using geostatistics is not a method exempt from uncertainty itself as variogram uncertainty may be large and spatial interpolation may be undertaken using different techniques.

There is definitively some uncertainty originating from the sampling in the field and the determination of physical or chemical properties of samples. Measurement errors, but also differences in sampling and laboratory procedures are likely to introduce considerable bias in laboratory measurements of e.g. sorption and degradation properties of pesticides.

Uncertainty in the derivation of model input parameters

Some uncertainty may originate from the derivation of parameters from primary data. For example, different decay equations and curve fitting programs may introduce significant differences in the derivation of degradation parameters. However, a considerable reduction of this latter source of uncertainty can be obtained by implementing identical or similar boundary conditions and settings (FOCUS, 2006).

Uncertainty is also introduced by the non-linearity of pesticide fate models. For example, if different sorption coefficient values are available, the modelling results are known to be strongly affected by the choice of either (i) deriving a single sorption input parameter and then running the model, or (ii) performing several simulations for the different input parameters and then averaging the results.

Procedures to derive input parameters using limited information also introduce some uncertainty. A typical example is the use of pedotransfer functions (PTFs) to derive input parameters. For soil hydrological properties, PTFs express relationships between basic soil properties and parameters that are difficult to measure or not available. However, these functions introduce some uncertainty and have a defined domain of validity that cannot be neglected (e.g. Espino et al., 1995). Pachepsky et al. (1999) and Cornelis et al. (2001) reviewed the accuracy and reliability of the main types of PTFs currently available.

For spatially distributed applications of pesticide fate models, the derivation of distributed input parameters is an important source of uncertainty, e.g. via the interpolation of spatially referenced variables (Brown and Heuvelink, 2005). This issue is further discussed in section 2.3.2.

Other sources of uncertainty in the derivation of input parameters include the treatment of outliers and replicates in a data set, the selection of a representative variable (e.g. arithmetic mean, geometric mean or median), the use of inadequate units or the rounding of values.

Uncertainty in the modelling procedure

Selecting an appropriate model is not an easy task and may have considerable consequences on pesticide fate modelling. Mathematical models necessarily need to simplify the complex processes found in nature for their simulations. As the various models sometimes contain different process descriptions, the way in which processes are conceived in the models will also influence model output (FOCUS, 1995). This variability between predictions obtained by different leaching models indicates that the choice of the model to be used is a significant source of uncertainty.

The fact that a model is unable to simulate experimental observations even when the most appropriate model and parameters are used has been referred to as structural or conceptual error(s) in the model. Excellent fit for simulations of field leaching data have rarely been reported in the literature. These uncertainties most often originate from the non-inclusion or inappropriate representation of processes in the model. This type of error may be exposed in a sensitivity analysis or through a validation exercise, but no specific test can be defined for the model error (Addiscott and Tuck, 2001).

Modeller subjectivity may introduce a significant uncertainty in the modelling process. Brown et al. (1996) noted that user-dependency of the results could be attributed to the existence of key input parameters which could not be derived from the information provided to the user. Boesten (2000) reported an exercise in which different modellers received raw data from laboratory degradation studies and were asked to derive model input parameters of degradation and sorption distribution coefficients. The results suggested that the subjective influence of the model user was even greater

than the variability introduced by the use of different models. Beulke et al. (2006) found that user subjectivity biased also the treatment of uncertainty in Monte Carlo analysis (truncation, type and parameterisation of the distributions, correlation between parameters, methods for sampling and size of random samples).

Model calibration can help reduce the modelling uncertainty through the derivation of values for input parameters that help to improve the simulation of experimental data, but this might not always be the case. The calibration may be ill-posed and uncertainty will arise from the issue of equifinality (Beven and Freer, 2001). The equifinality concept states that in complex environmental systems, there are many different model structures and many different parameter sets within a chosen model structure that may be behavioural or acceptable in reproducing the observed behaviour of that system. Equifinality is in fact, as far as modelling is concerned, the equivalent of the functional similarity observed in the real environment (Beven et al., 1999), i.e. different parts of the landscape exhibit similar functional responses although they are characterised by different physical, biological and chemical attributes.

Due to the presence of equifinality in modelling, the concept of an optimal model and parameter set should be rejected in favour of multiple possibilities for producing simulations that are acceptable simulators in some sense (Beven and Freer, 2001). If different combinations of input parameters provide similar fit to the experimental data, the uncertainty on the input parameters is not reduced, even though it is quantified. However, the uncertainty estimates provided are dependent on subjective choices, such as the selection of an objective function or the limit from which it is considered that the model is not calibrated anymore (Beven, 2001b).

Another reason that may prevent a decrease in uncertainty resulting from calibration is 'parameter lumping' (Dubus et al., 2002a). Parameter lumping results from the flexibility of the modelling system, which allows for changes in specific parameters to compensate for uncertainties and errors associated with other input data and modelling procedures. The curve-fitting nature of calibration may thus result in an increase in the parameter uncertainty, although maybe not perceptible by the modeller.

Contribution of the individual sources of uncertainty to the overall uncertainty

The above list of sources of uncertainty definitively shows that significant uncertainties are inherently associated with pesticide fate modelling. However, most of the uncertainties are difficult or impossible to quantify. Also, parameter uncertainty may be transferred differently through the modelling, from suppression to large exaggeration, depending on the sensitivity of the model. Dubus et al. (2002b) noted that very few attempts to differentiate between the contributions of the various sources of uncertainty to the overall uncertainty in pesticide fate modelling have been reported.

A sensitivity analysis can help to identify those parameters the uncertainty of which is likely to have the strongest influence on the overall modelling uncertainty. The primary concern of a sensitivity analysis is to assess the propagation of error between model components (Corwin et al., 1997). It is usually accepted that predictions of pesticide fate models for leaching will mainly be influenced by sorption and degradation parameters, and by hydrological parameters.

However, the contribution of sources of uncertainty other than those in model input parameters is in general largely unknown. Most often, Dubus et al. (2002b) found that uncertainty analyses reported in the literature have investigated the effects of input uncertainty on model predictions, implicitly assuming that (i) the major sources of uncertainty are those associated with input parameters; (ii) error in the model structure and modeller subjectivity are negligible; and, (iii) an adequate parameterisation of the model is possible. Beven (2006) argued that it is generally not possible to separate the different sources of uncertainty, because certain parameter sets may compensate for the different types of error.

2.2.4.2 Methods for propagating uncertainty

To tackle the equifinality issue, Beven and Binley (1992) proposed the GLUE (generalised likelihood uncertainty estimation) methodology, in which prior distributions of parameter sets are assessed in terms of some likelihood measure relative to the observations. A posterior distribution is then calculated in a Bayesian framework and can be used in prediction. GLUE is thus able to account for the predictive uncertainty arising from the lack of a unique

solution to the calibration problem (Dubus et al., 2002b). This may also be achieved using multi-objective optimization techniques such as the Pareto Optimal Set procedure (Yapo et al., 1998).

Dubus et al. (2002b) reviewed the studies investigating the propagation of uncertainty in pesticide fate modelling. It is important to distinguish between sensitivity and uncertainty analysis. The two approaches can determine the impact of parameter imprecision on the model results, but only the uncertainty analysis actually estimates the imprecision of input parameters (Freissinet et al., 1998). Sensitivity analysis can be particularly useful to study the system non-linearity and the propagation of parameter error through the model (Addiscott and Tuck, 2001). Uncertainty analyses have been performed using three main techniques, which will be briefly presented here: differential analysis, Monte Carlo analysis and fuzzy logic. However, it must first be specified that these uncertainty analyses have only considered the effects of input uncertainty on model predictions. Dubus et al. (2002b) noted that many of the sources of uncertainty described above are not accounted for by current approaches.

Differential analysis

Differential analysis (of which first-order uncertainty analysis is part) is based on developing a Taylor-series approximation to the model under consideration (Helton and Davis, 2003) and allows the uncertainty to be expressed analytically (Dubus et al., 2002b). The first-order approximation of functionally related variables is obtained by truncating the Taylor-series expansion (about the mean) for the function after the first two terms and thus corresponds to a linearisation of the function (Loague et al., 1996).

In regional assessments of groundwater vulnerability, Loague et al. (1996) and Diaz-Diaz and Loague (2000) used first-order uncertainty analysis to characterize data uncertainty with the AF and RF (Retardation Factor) indices. Loague et al. (1996) found that the distinction between mobile and immobile classes was substantially blurred when the uncertainties on the AF and RF parameters were included (coefficient of variation greater than unity for AF). In the same way, Diaz-Diaz and Loague (2000) found that levels of uncertainty (standard deviations) in the AF and RF estimates were of similar magnitude to the estimates themselves. Diaz-Diaz et al. (1999) found comparable results with the Leaching Index. Due to the non-linearity

of the equations, Diaz-Diaz and Loague (2000) also showed that reducing uncertainties in estimates of the input variables had an uneven effect on the overall uncertainty.

The main drawback of differential analysis is its inherently local nature. Other drawbacks, but also the main desirable properties of differential analysis can be found in Helton and Davis (2003).

Monte Carlo analysis

Monte Carlo analysis is a stochastic technique of characterizing the uncertainty in complex response model simulations (Loague and Corwin, 1996). Monte Carlo simulations are based upon a large number of realizations, from every input parameter distribution, created through sampling of the different probability density functions. The resulting output distribution provides a representation of the uncertainty associated with the model response. Three main sampling procedures are possible: random, stratified and Latin hypercube sampling (Helton and Davis, 2003).

Numerous applications of the Monte Carlo technique have been made in contaminant transport modelling. For example, Soutter and Pannatier (1996) used Monte Carlo simulations at different soil profiles to produce local distributions of a groundwater vulnerability index. Soutter and Musy (1998) performed Monte Carlo simulations using three different deterministic pesticide leaching models, along with geostatistical interpolation techniques, to analyse the differences between the models and to map both groundwater vulnerability and levels of uncertainties. Thorsen et al. (2001) analysed how uncertainty in input data propagates to model output for nitrate leaching. Dubus and Brown (2002) used the Monte Carlo approach to perform a sensitivity analysis, and then used the results as a first step assessment of the uncertainty associated with the modelling.

Dubus and Brown (2003) tested the robustness of the Monte Carlo technique on a pesticide leaching model. Monte Carlo results were found to be inherently unstable even with a relatively large number of model runs. Results were also found to be affected by slight changes in the parameterisation of probability density functions and in the assignment of correlation between parameters. More discussion on Monte Carlo sampling strategies is provided by Helton and Davis (2003).

Fuzzy logic

Freissinet et al. (1998) presented a framework in which uncertainty around the mean response of the model is evaluated through fuzzy logic application. The mathematical formulation of the process under study is split into independent elementary processes from which closed mathematical solutions can be obtained. For each process, using fuzzy numbers, a fuzzy result is obtained. The combination of all fuzzy results yields the relative imprecision of the mean result. Freissinet et al. (1998, 1999) applied a fuzzy approach to the uncertainty analysis of respectively an advective flow calculation, and AF and RF indices.

Dou et al. (1997) applied fuzzy sets theory and fuzzy arithmetic to the transport modelling of solute material in groundwater flow, in both one- and two-dimensional uniform flow fields. One of the main advantages of fuzzy arithmetic is to allow the inclusion of imprecise data and expert knowledge through the use of membership functions that can be defined in a variety of shapes. However, the accuracy of fuzzy numerical models for solving the transport equations is debatable when compared to the analytical solutions.

2.3 Pesticide leaching models at the catchment/ regional scale

2.3.1 Problems of scale

Beven et al. (1999) identified two problems of scale in hydrological modelling: the scale problem and the scaling problem. These are defined as follows (Beven et al., 1999):

> The scale problem denotes the expectation that different processes may dominate hydrological processes at different scales so that different theories and models may be appropriate at different scales. The scaling problem denotes the development of a consistent theory that would allow a process description at one scale to be formally transformed to represent the hydrological response at a different scale (p.725).

These two issues evoke the same concepts and are closely related, as discussed in the next two paragraphs.

The scale problem

An issue of significant importance is to know how pesticide fate models developed for small areas of land can be used at the catchment or regional scales, and indeed, whether it is appropriate to use them in this way (Corwin et al., 1999b). The problem of scale is inherently linked to that of non-linearity, because there are no measurement techniques that give information directly at the element grid scales (Beven, 2001a). Heuvelink (1998) reported two other reasons why models are scale-specific. First, the relative importance of different processes is variable at different scales. As spatial scale increases, the complex local patterns of solute transport are attenuated and dominated by macroscale characteristics (Corwin et al., 1999b). Secondly, the aggregation level of model inputs and outputs is also a function of the modelling scale and this may affect the relationship between them.

Broadly, three different approaches have been used in hydrology to model transport processes at coarse (e.g. catchment) scales (Baveye and Boast, 1999). At one extreme are the so-called 'lumped conceptual' models. At the other end are the 'physically-based, spatially distributed' models that explicitly account for spatial variability in inputs, processes, and parameters. Between these two extremes, one finds 'semi-distributed, semi-physically-based' models, which combine some degree of lumping with a partial consideration of the spatial variability of processes. A complementary point of view is expressed by Corwin et al. (1999b), who perceived the scale debate as a conflict between deterministic and stochastic approaches. Fully deterministic models, solving the 3-D flow equations are nearly impossible to apply at coarse scales (Corwin et al., 1997). Moving towards larger scales would therefore require more stochastic approaches (Vanclooster et al., 2000a; Corwin et al., 2006). However, stochastic modelling at the catchment scale will in general provide information only on catchment-aggregated values of fluxes and thus prevent the location of sensitive areas in terms of pollution risk (Vachaud and Chen, 2002).

To date, the vast majority of models of non-point source pesticides in the vadose zone have used one-dimensional deterministic models of contaminant transport (regression models, overlay and index models, and process-based

models) coupled to a geographic information system (GIS) (Corwin et al., 1999a). In comparison to deterministic models, the coupling of a stochastic solute transport model to a GIS is relatively unexplored (Corwin et al., 1997). Wilson (1999) examined the role and advantages of GIS for assessing the environmental impacts of non-point source pollutants. The use of deterministic transport models with GIS at coarse scales has been justified on practical grounds based upon availability, usability, widespread acceptance, and the assumption that a heterogeneous medium macroscopically behaves like a homogeneous medium with properly determined parameters (Corwin et al., 1999a), although this assumption is hardly questioned (e.g. Beven et al., 1999). In general, assessments of groundwater vulnerability at the regional scale rest upon soil, climate, and chemical data that are extremely sparse and contain considerable uncertainty (Loague et al., 1999). Some authors have used one-dimensional deterministic models and uncertainty propagation methods (usually Monte Carlo simulations) coupled with a GIS to account for the variability at the regional scale (e.g. Petach et al., 1991; Soutter and Pannatier, 1996; Soutter and Musy, 1998).

A number of studies have looked at the impact of the spatial resolution of input data. Wilson et al. (1996) simulated pesticide movement in the vadose zone by coupling a leaching model with a GIS. They investigated the effects of soil and weather input data at two different scales and found that the mean leaching depths were significantly affected by the spatial resolution of input data. Wagenet and Hutson (1996) found that modelling results at the regional scale are significantly dependent on available database. Bleecker et al. (1995) integrated a capacity-type model and environmental databases (soil, crop and weather data) to map leaching potential at the regional scale. They concluded that translation from the local to regional scale was possible, although scientifically tenuous because results were subject to a lot of uncertainties due to database quality, and spatial and temporal variability of environmental variables. Therefore, it is recognized that regional scale estimates of pesticide transport are limited to the resolution and the quality of input data.

At coarse scales, comparisons between model predictions and observations may become more difficult for a number of reasons (Wagenet, 1998; Mulla and Addiscott, 1999). First, the model outputs at coarse scales are less likely to involve measurable properties such as pesticide concentration

depth profiles. Experimental observations may not be available at coarse scales to test model predictions. Second, the effects of spatial and temporal variability on model predictions may be much greater at coarser scales than at finer scales (Mulla and Addiscott, 1999). For example, if observations of pesticide concentrations are available at a pumping well, they somehow represent the average response from a relatively large surface capture zone and a relatively long-time scale. Indeed, Corwin et al. (1999a) noted that very few attempts towards validation of leaching models have been made at field or larger scales.

The scaling problem

Refsgaard and Butts (1999) summarized the different scaling approaches available to determine grid scale parameters from local scale parameters. Three main cases were retained: (i) the finer scale equations are assumed valid without change; (ii) the finer scale equations are extended in a theoretical/stochastic framework to account for the spatial variability of finer scale parameters; and, (iii) new equations are developed specifically for the coarser scale. Aggregation is considered apart from upscaling, as the process equations are applied at the finer scale and the coarse-scale results are obtained by aggregating the fine-scale results at the coarser scale. Addiscott and Mirza (1998) proposed to use variogram analysis to investigate whether the non-linearity effect will intensify as the modelling area increases. By knowing how parameter variance changes with increasing scale, one could assess the effect of models non-linearity at a coarser scale. A critical assumption of some regional scale studies is the existence of effective soil properties. Scaling problems are sometimes overcome through scale-specific calibration (Refsgaard and Butts, 1999).

Baveye and Boast (1999) argued that there is at this stage no theoretical framework in vadose zone transport to guide upscaling efforts toward field or catchment scales. Processes showing fractal properties are found in many areas of hydrology (e.g. Pachepsky and Timlin, 1998; Kirchner et al., 2001; Caniego et al., 2005), but they do not really provide an upscaling theory. In general, scaling is performed via empirical approaches based on a combination of aggregation and model simplification (e.g. Vereecken et al., 2003; Van Bodegom et al., 2002a). Blöschl (2001) recognised that *ad hoc* upscaling relationships with little theoretical justification will probably re-

main the rule in the near future. Beven et al. (1999) even asserted that the scaling problem will prove to be impossible to apply at the catchment or regional scale in hydrology, mainly because of the 'uniqueness of place'. They evoked the apparent impossibility to measure all of the parameters that are necessary for landscape scale modelling. Thus spatial heterogeneity and temporal variability would prevent the application of scaling theory. On the contrary, Blöschl (2001) believes that scaling has the potential to become a unifying theory of hydrology, by providing a connection between all hydrologic subdisciplines.

Applying physically-based transport models at the catchment scale does not ensure that these models will effectively simulate the processes occurring at that scale. Baveye and Boast (1999) suggested that lumped, conceptual models may be relevant for studying catchment scale processes, but only if the description of transport processes is adapted to the dynamics occurring at that scale (case (iii) above).

2.3.2 Spatial variability of pesticide and soil properties

Independently of scale, the variability of soil and pesticide properties has strong effects on pesticide leaching, and hence on groundwater vulnerability to pesticides (Di and Aylmore, 1997).

Some of the input variables and parameters needed for transport models are dominated by the bulk characteristics of the soil matrix; consequently, the spatial variability of these properties (porosity, bulk density, water content at field capacity) is relatively small, which reflects the uniformity of soil genesis processes (Corwin et al., 1997). In contrast, water transport parameters including saturated hydraulic conductivity, infiltration rate, and hydraulic conductivity - water content relationships are characterized by a high variability (Corwin et al., 1997). Soil physical and chemical properties vary considerably across the field, but substantial local scale variability (within a few meters or less) may also be found (Corwin et al., 2006). Local scale variability occurs because of the variation in structural properties, textural composition, and the human activity influence (i.e. soil management practices).

Field analyses have shown the importance of spatial variability of soil and

pesticide properties, although the variability of soil properties often varies with measurement scale (Corwin et al., 1999b). In a study at the pedon scale, Jacques et al. (1999) analysed the 3-D spatial variability of atrazine sorption isotherm parameters (K_f and N; see section 2.2.2) and their correlation with soil textural variables, cation exchange capacity (CEC) and organic carbon content. After removing the vertical and horizontal trends, the authors found that organic carbon content, CEC and N revealed spatial structure, while the variograms of textural variables and K_f exhibited pure nugget effect. Besides, the correlation between the variables differed for different spatial increments (Jacques et al., 1999). In a study at the field scale, Novak et al. (1997) found that for atrazine, K_d and K_{OC} showed strong spatial dependence (with a correlation range of 87 and 71 m). Using geostatistics, the authors were then able to produce K_d and K_{OC} maps at the field scale. Finally, Coquet (2002) explored the variability of pesticide sorption parameters at the catchment scale. He found that more than 97% of the K_f catchment-scale variations could be explained by the variations of soil organic carbon content.

Simulation studies have also emphasized the impact of soil and pesticide properties variability on pesticide leaching. Van Alphen and Stoorvogel (2002), performing simulations for 19 different pesticides, found that leaching was strongly affected by soil heterogeneity at the within-field, field, and farm levels. Jury and Gruber (1989) used a stochastic approach to study the influence of soil variability on the leaching of 10 pesticides. The effect of soil variability was found to be significant on the distribution of the residual mass under all conditions. They also showed that soil (and climatic) variability can introduce a small probability that some mass of even relatively immobile compound will migrate below the soil surface even when the projected mass is negligible as determined from models neglecting variability by using average values. Van der Zee and Boesten (1991) presented similar findings, using both a stochastic approach and Monte Carlo simulations to incorporate variability.

An important issue in pesticide fate modelling at coarse scales is therefore to capture and represent the spatial variability of soil properties in an appropriate way. For transport models based on non-linear equations such as the Richards equation, there is a risk of inaccurate results when the model is used with a single-valued parameter based on a soil property known to be

spatially variable (Addiscott and Mirza, 1998). Di and Aylmore (1997) developed a simple leaching model incorporating the variations in soil and pesticide parameters. For each input parameter, random data were generated from normal input distributions. The predicted pesticide residue fractions at different depths were described by beta-distributions, and the corresponding travel times by normal distributions. Foussereau et al. (1993) assessed the uncertainty of soils input by generating pseudo-profiles of soils from pedon characterization data within a given map unit. These pseudo-profiles were then used in Monte Carlo simulations that captured the variance of selected soil parameters. Yost et al. (1999) proposed several methods to incorporate spatial variability and uncertainty into existing soil databases. Three sources of input soil data are usually considered: measurement methods, estimation methods (e.g. PTFs), and existing soil databases (Corwin et al., 1997). The first source should be preferred, but is limited by the current inability of remote measurement techniques and instrumentation to meet input data requirements. Estimation methods are the next best alternative, while coarse-scale soil databases (such as STATSGO in the USA or SPADE in Europe) do not meet minimum data requirements for many parameters (Corwin et al., 1997).

McBratney et al. (2003) carried out an extensive review of the different methods used for fitting quantitative relationships between soil properties or classes and their environment. These include linear models, classification and regression trees, neural networks, fuzzy systems and geostatistics. A few examples are given below, but the reader is referred to McBratney et al. (2003) for a detailed overview of soil mapping.

Geostatistics have been abundantly used to study the spatial variability of soil properties. Goovaerts (2001) discussed the opportunities offered by kriging-based and simulation-based techniques. The two approaches are found to yield similar models of local uncertainty, although the simulation-based approach has several advantages over kriging (see details in Goovaerts, 2001). However, the correlation range of certain soil or pesticide properties (e.g. about 80 m for atrazine K_d and K_{OC}; Novak et al., 1997) hampers the application of geostatistics to interpolate these properties at coarse scales with limited data sets.

To represent detailed soil spatial information, Zhu (1999) used a fuzzy inference scheme consisting of a fuzzy logic-based model and a set of infer-

ence techniques. This allowed the realistic characterization of the spatial covariation of landscape parameters at the catchment scale. Another example of the use of fuzzy logic for mapping soil variability and uncertainty is given by Lark and Bolam (1997).

Haskett et al. (1995) aggregated the values of individual soils within a soil association to account for the variability of soil properties. This variability was parameterised using a beta-function distribution. In multiple simulation runs, this method allows the inclusion of the soil variability found within the soil association.

Remote sensing techniques also have the potential to incorporate soil variability in spatially distributed studies. For example, Ben-Dor et al. (2002) processed data acquired from a hyperspectral airborne sensor to yield quantitative maps of soil properties, including organic matter content. Barnes et al. (2003) discussed how remote and ground-based sensor techniques may be used to map a variety of soil properties, while Odeh et al. (2001) showed how these techniques can be combined with geostatistical methods.

Even if appropriate techniques have allowed to take into account the spatial variability of soil properties, a question remains as to whether pedotransfer functions applied afterwards are able to quantify spatial variability. Romano and Santini (1997) suggested that PTFs are able to describe the structure of spatial variability of soil water retention properties.

Finally, an interesting comment was made by Baveye (2002), who noted that little attention is devoted to the questions of when, where and why, from a practical standpoint, one should be concerned with soil variability, and what the appropriate scale is at which to observe soil variation in given circumstances. In the field of groundwater contamination by pesticides, Baveye (2002) cited the study of Worrall (2001), who showed that the molecular topology of the pesticide molecules is a good basis to discriminate between polluting and non-polluting pesticide compounds. Although Worrall (2001) and Worrall and Thomsen (2004) used this approach for screening purposes, their results indicate that groundwater vulnerability may be assessed to some extent without a complete description of soil spatial variability.

2.3.3 Second-order Monte Carlo analysis

Second-order Monte Carlo analysis has been developed to put a clear distinction between variability and uncertainty in risk assessment (EUFRAM, 2005). The objective is to characterize both the variability of the output variable and the uncertainty we have about what that true distribution of variability really is (Vose, 2000).

The variability of a quantity (also named stochastic uncertainty, or aleatory uncertainty) is defined as the inherent heterogeneity of this quantity over time, space, or some population of individuals (McKone, 1996; Cullen and Frey, 1999; Counil et al., 2005). Additional effort may yield a better estimate of the magnitude of variability, but it will not tend to reduce it (Ferson and Ginzburg, 1996). On the other hand, uncertainty (also called epistemic uncertainty) is caused by our incomplete knowledge of the system (Apel et al., 2004).

In this context, variability and uncertainty may both be quantified using probability distributions but their interpretation somehow differs: variability may be viewed in terms of frequency, while the uncertainty distribution may be considered as a degree of belief (Cullen and Frey, 1999).

A second-order Monte Carlo analysis works as follows. Each variable is classified as a source of either uncertainty or variability. First, a single value from each variable that is classified as a source of uncertainty is sampled at random. Using the values from this single sample, a complete first-order Monte Carlo analysis is then performed for all variables that are classified as a source of variability. The process is repeated many times and has the effect of separating uncertainty from variability (EUFRAM, 2005).

Although the suitability of probability theory for dealing with epistemic uncertainty has been challenged (Hall and Anderson, 2002) and alternative methods have been proposed (e.g. a combination of probability and interval analysis; Ferson and Ginzburg, 1996), second-order Monte Carlo analysis is now widely used in risk assessments. An important number of applications were made in ecotoxicology (exposure) assessments (e.g. Wu and Tsang, 2004; Counil et al., 2005; Delignette-Muller et al., 2006). In this case, uncertainty usually concerns the distribution of input parameters in the exposure model and variability is applied to the individuals of a population (Counil

et al., 2005).

McKone (1996) applied a second-order Monte Carlo analysis to the modelling of contaminant fate in soils and compared the results of two different models. Soil and pesticide properties were classified as 'variable' and 'uncertain', respectively. In surface hydrology, Apel et al. (2004) developed a second-order Monte Carlo framework for a flood risk assessment.

2.4 Conclusions from the literature cited

In this thesis, groundwater vulnerability will be considered to be dependent on both land use and pesticide properties (i.e. vulnerability is specific to a pollutant or a class of substances). Overlay and index methods have been popular tools to assess groundwater vulnerability (mainly due to facility and lower data requirements), but monitoring based statistical inference methods or approaches using process-based models seem now to be preferred. In this thesis, we use the GeoPEARL model to assess the vulnerability of the Brusselian aquifer. However, this type of models are generally based on equations developed on point support. Although the literature indicates that no scaling theory–if ever possible–is available at the moment, a scale issue exists in the application of GeoPEARL at the catchment or regional scale.

For example, the version of GeoPEARL used in this thesis does not account for preferential flow, which has repeatedly been shown to be an important process in pesticide leaching studies. Although the available data would have hardly allowed the parameterisation of preferential flow at the catchment scale, particular attention is needed in the interpretation of GeoPEARL results.

We therefore conclude that GeoPEARL predictions at the catchment scale should not be expected to compare exactly with monitoring data. However, if distributed predictions are required, one can accept that accuracy in local predictions is necessarily limited, but predictions of 'where' rather than 'how much' may become acceptable. Indeed, as Beven (2001a) suggested, a relative assessment of the spatial distribution of risk, including an assessment of uncertainty, might be sufficient for risk-based decision making in some cases.

Simpler, analytical models could be used, but there is a risk of underestimating the leaching fraction if vertical heterogeneity is not taken into account (van der Zee and Boesten, 1991). This difference could be overcome by introducing effective model parameters, but these parameters are site-specific, and can only be obtained by calibration (Tiktak et al., 2003). In this study, no calibration (leaching) data were available at the regional scale, but a detailed database of soil profiles was available that allowed a relatively comprehensive parameterisation of soil properties in GeoPEARL. Moreover, several chapters of this thesis deal with the implications of modelling issues for pesticides management. In this context, the advantage of GeoPEARL is also its capacity to predict leaching fractions in a detailed way, in order to derive absolute values of leaching for registration procedures in which clear-cut thresholds are defined (e.g. 0.1 μg/L).

To summarize, the choice of GeoPEARL was motivated by the following points: spatially distributed model, access to the model code, value given to available soil profile data, and good validation status notably in registration procedures (one of the four models selected in FOCUS).

Monte Carlo simulations are frequently used for the analysis of uncertainty propagation. The literature review provided numerous applications of Monte Carlo analysis to pesticide leaching modelling. However, it should be noted that in this framework it is generally impossible to separate the different sources of uncertainty (Dubus et al., 2002b).

In the case of spatially distributed models, probabilistic risk assessment may inspire the distinction between variability and uncertainty. Only one application of this concept to pesticide fate modelling has been found, but we propose to adapt the methodology and test it for the case study presented in this work.

Finally, an important point for our research is that we can make the reasonable assumption—derived from the literature review—that virtually no atrazine degradation occurs in saturated conditions.