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Review

The mobility and degradation of pesticides in soils and the pollution of groundwater resources

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Abstract

Pesticides, the most cost-effective means of pest and weed control, allow the maintenance of current yields and so contribute to economic viability. Concern about the environmental impact of repeated pesticide use has prompted research into the environmental fate of these agents, which can emigrate from treated fields to air, other land and waterbodies. How long the pesticide remains in the soil depends on how strongly it is bound by soil components and how readily it is degraded. It also depends on the environmental conditions at the time of application, *e.g.*, soil water content. Pesticide use must ensure public safety and environmental protection with regards to both the chemical itself and their potentially harmful metabolites. This paper reviews what is known of the influence of the physical and chemical characteristics of the soil system, such as moisture content, organic matter and clay contents, and pH, on the sorption/desorption and degradation of pesticides and their access to groundwater and surface waters. An understanding of the fate of pesticides is essential for rational decision-taking regarding their authorization. To reach an adequate understanding will require the concourse of soil science, clay mineralogy, physical chemistry, surface chemistry, environmental microbiology, plant physiology and, no doubt, other disciplines. Only through a multidisciplinary approach to environmental research will it be possible to plan, manage, pursue and integrate the results of the studies that will be necessary for the development of tools and techniques allowing effective environmental decision-making. There seems to be a great potential to develop microbially derived pesticides, which are effective, reliable and have a low environmental risk. In addition, new application techniques, for example precision band spraying, can reduce the dose, which can be a very effective way to minimize transport and emission but also to avoid a build-up of resistance in target organisms. Improved formulations will also be needed to reduce off-target deposition, improve retention on target, and enhance uptake and translocation.
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Contents

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1. Introduction

1.1. Pesticides

Any substance or mixture of substances intended for preventing, destroying, repelling, or mitigating any pest or weed is a pesticide. Pesticides can be classified according to their target, their mode or period of action, or their chemistry (Table 1). More than 500 different pesticide formulations are being used in our environment, mostly in agriculture (Azevedo, 1998), although the control of biological public health hazards also continues to be an important field of application. In the last 50 years, the use of pesticides has greatly increased the quantity and improved the quality of food for the growing world population. However, with increasing amounts used, concern about their adverse effects on nontarget organisms, including human beings, has also grown. Nontarget pesticide poisoning has been identified as the cause of fish kills, reproductive failure in birds, and illness in humans (Rao et al., 1993). In fact, it has been estimated that less than 0.1% of the pesticide applied to crops actually reaches the target pest; the rest enters the environment gratuitously, contaminating soil, water and air, where it can poison or otherwise adversely affect nontarget organisms (Pimentel and Levitan, 1986). Furthermore, many pesticides can persist for long periods in an ecosystem—organochlorine insecticides, for instance, were still detectable in surface waters 20 years after their use had been banned (Larson et al., 1997); and once a persistent pesticide has entered the food chain, it can undergo "biomagnification", *i.e.*, accumulation in the body tissues of

Table 1
Classifications of pesticides

By target		By mode or time of action		By chemical structure
Type	Target	Type	Action	
Bactericide (sanitizers or disinfectants)	Bacteria	Contact	Kills by contact with pest	Pesticides can be either organic or inorganic chemicals. Most of today's pesticides are organic
Defoliant[a]	Crop foliage	Eradicant	Effective after infection by pathogen	
Desiccant[a]	Crop foliage	Fumigants	Enters pest as a gas	
Fungicide	Fungi	Nonselective	Toxic to both crop and weed	
Herbicide	Weeds	Post-emergence	Effective when applied after crop or weed emergence	Commonly used inorganic pesticides include copper-based fungicides, lime-sulfur used to control fungi and mites, boric acid used for cockroach control, and ammonium sulfamate herbicides
Insecticide	Insects	Pre-emergence	Effective when applied after planting and before crop or weed emergence	
Miticide (acaricide)	Mites and ticks	Preplant	Effective when applied prior to planting	
Molluscicide	Slugs and snails	Protectants	Effective when applied before pathogen infects plant	
Nematicide	Nematodes	Selective	Toxic only to weed	Organic insecticides can either be natural (usually extracted from plants or bacteria) or synthetic. Most pesticides used today are synthetic organic chemicals. They can be grouped into chemical families based on their structure
Plant growth regulator[a]	Crop growth processes	Soil sterilant	Toxic to all vegetation	
Rodenticide	Rodents	Stomach poison	Kills animal pests after ingestion	
Wood preservative	Wood-destroying organisms	Systemic	Transported through crop or pest following absorption	

  [a] In U.S. law the term "pesticide" is defined to cover not only pesticides proper, but also these other classes of agrochemical.

organisms, where it may reach concentrations many times higher than in the surrounding environment (Brewer, 1979). It is presumably because of the similarity of the threats they pose to health and the environment that in U.S. law the term ''pesticide'' is defined to cover not exclusively pesticides, but also defoliants, desiccants and plant growth regulators used for different purposes than pest control.

1.2. Environmental residues

Information on the actual input of pesticides into the environment is crucial for proper risk assessment and the rational design of risk reduction measures. The greatest concern regarding human exposure to pesticides is their presence in water (Younes and Galal-Gorchev, 2000). In 1999, the U.S. Geological Survey found widespread contamination of U.S. water resources; in particular, more than 95% of samples collected from streams, and almost 50% of samples collected from wells, contained at least one pesticide (Robert et al., 1999). The U.S. Environmental Protection Agency (EPA) had previously reported that normal agricultural use had led to the presence of at least 46 pesticides in groundwater and 76 in surface waterbodies (Larson et al., 1997; USEPA, 1998); the most frequently found was atrazine (Hallberg, 1989; Stoltenberg et al., 1990; Jayachandran et al., 1994), more than 4000 tonnes of which were used in North American agriculture in 1989 (Environment Canada, 1993). Atrazine was also the herbicide found most often in the period 1993–1995 in surface waters of central and north-western New South Wales, although the pesticide found most often was endosulfan, due to its widespread use in irrigated cotton production and oilseed crops; other pesticides detected included pronofos, dimethoate, chlordane, diuron, prometryn and fluometuron (Cooper, 1996). All pesticides in groundwater, and most residues present in surface water enter via the soil. There are two main routes by which pesticides enter the soil: spray drift to soil during foliage treatment plus wash-off from treated foliage (Rial-Otero et al., 2003) and release from granulates applied directly to the soil (López-Pérez et al., 2006) (Fig. 1). It is of paramount importance to study the dynamics of pesticides in soil: sorption–desorption (Arias-Estévez et al., 2005a,b), transport (López-Blanco et al., 2005), and the dependence of transport on entry dynamics and transformation processes. When studying these issues, especially in field experiments, it is essential to use robust analytical techniques allowing complete pesticide extraction and interference-free quantification (Rial-Otero et al., 2004).

1.3. Transport models

The continually growing amount of information on the behaviour of pesticides in soil, and in the environment in general, has deepened our understanding of these phenomena. This has also allowed the parameterization and testing of increasingly sophisticated mathematical models and the corresponding computer simulation programs (Larson
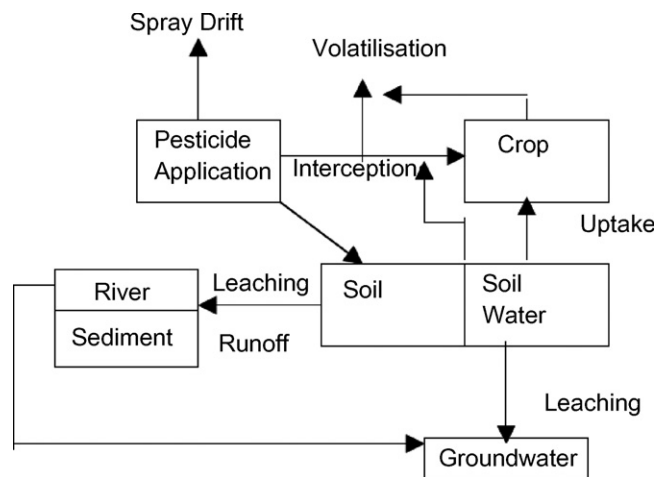

Fig. 1. Pathways of a pesticide applied to a crop. Ideally, at least one includes its contact with the targeted pest.

et al., 1997; Azevedo, 1998; Reichman et al., 2000; Chen et al., 2001; Li et al., 2001). Run-off models such as CREAMS (Knisel, 1980), AGNPS (Young et al., 1986) or RZWQM (USDA-ARS, 1995), and models of pesticide transport in soil such as SWACRO (Belmans et al., 1983), MACRO (Jarvis, 1991), LEACHP (Hutson and Wagenet, 1992) or PRZM-2 (Mullins et al., 1993), have been applied to many pesticides, though generally within limited spatial and temporal windows. Well-tested integral models of this kind are necessary if simulations are to lay a basis for the formulation of rational pollution control policies and regulations. The development of geographic information system (GIS) technology, and of remote sensing, offers hopes for the imminent evolution of comprehensive pesticide transport models.

1.4. Review objectives

The mobility of pesticides in soil, and hence their bioavailability and transfer to other environmental compartments (the atmosphere, waterbodies), depends on the mechanisms and kinetics of their sorption on and desorption from soil particles (Moorman et al., 2001). An understanding of these processes is essential for transport modelling and the rational design of remedial and measures against pollution (Struthers et al., 1998). The main subject of this review is to study the processes that determine pesticide sorption-mobility and persistence-degradation in soils; all this with the purpose of providing advice for the development of risk assessment tools in groundwater pollution and policies on pesticide use.

2. Factors influencing the persistence of pesticides in soil

2.1. Degradation and sorption

The behaviour of pesticides in soils is governed by a variety of complex dynamic physical, chemical and

Table 2
Factors influencing the persistence of pesticides in soil

Pesticide	Soil/site	Climate	Experimental variables
• Chemical nature	• Site	• Wind, air movements	• Plot size, arrangement
• Volatility	- Elevation, slope, aspect, geographical location	• Temperature, solar radiation	• Number of replicates
• Solubility	- Plant cover (species, density, distribution, history at site)	• Rainfall, relative humidity, evaporation	• Frequency of sampling
• Formulation	- Fauna (species, density, distribution, history at site)		• Sample size, shape
• Concentration	- Microbial populations (species, density, distribution, history at site)		• Techniques for measuring variables
• Application	- Use of "fertilizers", lime, mulches and green manures		
- Method	- Use of other pesticides and chemicals		
- Time (of year and day)	- Tillage, cultivation, drainage, irrigation (type, depth, amount, timing, frequency)		
- Frequency	- Fire, *e.g.*, burning of crop residues		
- Amount	- Adjacent environments (hedges, field borders, woodlots, waterbodies)		
	- Presence of pollutants		
	• Soil type		
	- Texture, especially clay content		
	- Structure, compaction		
	- Organic matter and humus contents		
	- Soil moisture, leaching		
	- pH		
	- Mineral ion content		

biological processes, including sorption–desorption, volatilization, chemical and biological degradation, uptake by plants, run-off, and leaching (Table 2). These processes directly control the transport of pesticides within the soil and their transfer from the soil to water, air or food. The relative importance of these processes varies with the chemical nature of the pesticides and the properties of the soil, but two processes stand out: degradation and sorption (Linn et al., 1993).

Degradation is fundamental for attenuating pesticide residue levels in soil (Guo et al., 2000). It is governed by both abiotic and biotic factors (the latter including enzymatic catalysis by microorganisms), and can follow complex pathways involving a variety of interactions among microorganisms, soil constituents, and the pesticide (Topp et al., 1997). Thus, degradation rates depend on many microbiological, physical and chemical properties of the soil, as well as the properties of the pesticide (Rao et al., 1983).

Sorption plays a fundamental role in the advective–dispersive transport dynamics, persistence, transformation and bioaccumulation of pesticides (De Jonge et al., 1996). The sorption of neutral compounds has been extensively investigated (Gao et al., 1998), and appears to depend on soil organic matter content (Spark and Swift, 2002; Coquet, 2003). The molecular nature of soil organic matter has been proved to be key in determining sorption of nonionic pesticides (Ahmad et al., 2006). The pesticides which are most likely to bind covalently to soil humic matter have functionalities similar to the components of humus. Oxidative coupling reactions contribute to link humus together during humification and are mediated not only by

abiotic catalysts (inorganic chemicals, clay, etc.) but also by biotic catalysts, including plant and microbial enzymes. Therefore, microorganisms have been reported to mediate in both soil-bound pesticide formation and pesticide degradation (Gevao et al., 2000). The sorption of weak organic acids in soils has also attracted considerable research (Dubus et al., 2001); kinetic studies have shown that bentazone and 2,4-D are weakly sorbed by a variety of soils just after their application (Boivin et al., 2004), but the sorption of these and other weak organic acids depends on soil pH (Clausen and Fabricius, 2002). This is partly because of their acid–base equilibria (Fig. 2; Wauchope et al., 2001), but also partly because of the effects of pH on other soil properties such as electric charge and ionic strength (Clausen and Fabricius, 2002). Other soil constituents than organic matter, including clays and Fe-oxides, are important sorbents for the sorption of ionic pesticides. Lots of studies have determined sorption isotherms in order to investigate the influence of soil parameters (organic matter content, clay content, pH, etc.) on the sorption of weakly acidic, weakly basic and neutral pesticides by a wide array of soils.

Kinetic studies have revealed several interactions between sorption and degradation (Gevao et al., 2000; Guo et al., 2000). It is commonly accepted that sorbed chemicals are less accessible to microorganisms, and that sorption accordingly limits their degradation as well as their transport (Selim et al., 1999; Koskinen et al., 2001). For example, Guo et al. (1999, 2000) reported that the degradation rates of both 2,4-D and aldicarb in soil treated with activated carbon were 65 times faster in the solution phase than in the sorbed phase. However, though slower than in solution, the degradation of sorbed chemicals is not
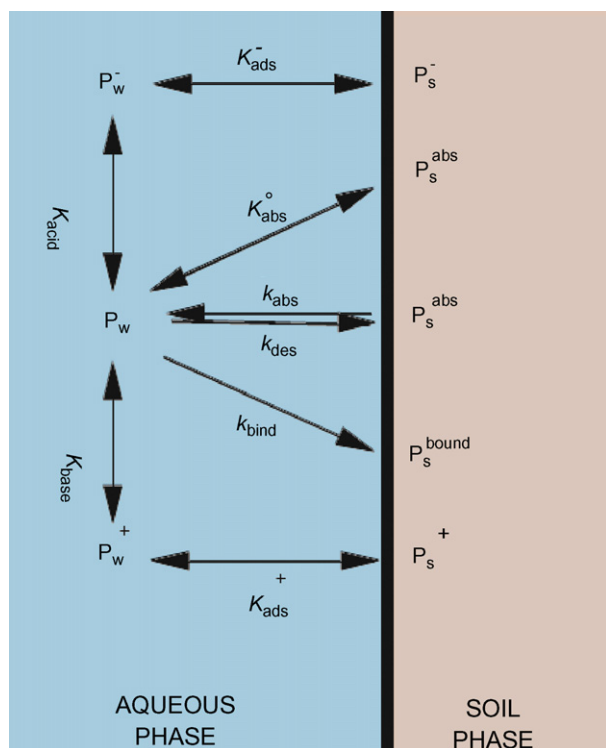
Fig. 2. Schematic diagram of the sorption reactions (small k) and instantaneous sorption equilibria (capital K) which may occur with a pesticide in soil water, as neutral basic or acidic molecule. Slow sorption reactions may also occur with cationic or anionic species. P_s and P_w are the potentially available adsorbed-phase and dissolved phase pesticide levels.

necessarily negligible, and an increase in sorption does not necessarily give rise to a proportional reduction in degradation (Moyer et al., 1972). In a study, in which measurements of the rate of microbial degradation of atrazine were performed, Park and coworkers concluded that in some soils, under certain conditions, bacteria can access and degrade at least part of the sorbed pesticide (Park et al., 2003). Studies of the relationship between sorption and degradation rate in various soils have been carried out for a number of individual pesticides (Bolan and Baskaran, 1996; Dyson et al., 2002). Dyson et al. (2002) found a negative correlation between the two, but in a study of 2,4-D in 10 natural soils Bolan and Baskaran (1996) observed a negative correlation only up to a certain soil sorption capacity, above which the degradation rate increased again; this behaviour was attributed to higher microbial activities in the soils with strongest sorption. When the influence of sorption on degradation rates is studied, the effects of other variables on degradation can be discounted by using a single soil to which various quantities of sorbent material are added, preferably a sorbent with properties similar to those of some soil components. This approach was adopted by Moyer et al. (1972) and Helweg (1975) some 30 years ago, and was used by Guo et al. (2000) in the studies noted above. In a study of how the sorption and mineralization of 2,4-D might be altered by adding compost to the treated soil, Barriuso et al. (1997) found that mineralization kinetics were unaffected by

the addition of this sorbent, but that a smaller proportion of the pesticide was mineralized when compost was added. Correlation between sorption and degradation has not been observed in studies in which the soil was treated with sorbent (Baskaran et al., 1996; Socías-Viciana et al., 1999). As noted above, for dissociating pesticides, sorption properties of the molecule can be modified by a pH adjustment (Spadotto and Hornsby, 2003). This may affect several other conditions in the soil system, *e.g.*, the ion strength thereby also influencing the sorption properties. Furthermore, it may affect the microorganisms, thereby influencing the degradation rate of the pesticide.

2.2. Pesticide aging in soil and bioavailability

In characterizing the relationship between sorption and degradation it is useful to distinguish among different pesticide pools defined conceptually by their different degrees of bioavailability. These pools are defined operationally and quantified by performing successive extractions with increasingly powerful extractants (Oi, 1999; Cupples et al., 2000). Typically, the extractant series consists of water, followed by an organic solvent, and finally a strong extractant (the last step may be replaced by combustion of the residue left by the previous steps). Attempts have also been made to characterize or predict bioavailability using mild extractants (Chung and Alexander, 1998; Alexander, 2000), but results have been inconsistent. For example, Chung and Alexander (1998) were unable to establish a strong correlation between extractability with mild solvents and characterization of bioavailability. By contrast, Barriuso et al. (2004) found that in soils with aged atrazine the quantity of atrazine extractable with 0.01 M CaCl$_2$/methanol could be used to estimate the quantity of bioavailable pesticide ($r^2 > 0.93$). The establishment of such correlations would be useful to predict the quantities available for uptake, thus allowing the assessment of actual risks resulting from the application of pesticides to soil.

Kinetically, the sorption of most organic chemicals is a two-step process: an initial fast step that accounts for the greater part of total sorption is followed by a much slower step tending towards final equilibrium (Pignatello, 1998). Increased sorption as a pesticide ''ages'' in soil has been observed for a variety of pesticide classes using a variety of methods (Barriuso et al., 1997; Koskinen et al., 2003; Park et al., 2003, 2004). This means that batch equilibrium partitioning coefficients based on freshly treated samples under slurry conditions can seriously overestimate the availability of aged pesticide: the biological availability and biodegradation rate of pesticides in soil will often decrease markedly with increasing time since application (Barriuso et al., 1997; Kristensen et al., 2001; Park et al., 2003, 2004). Furthermore, with longer contact times between soil and chemical, the fraction of strongly bound residues increases at the expense of extractable residues (Boivin et al., 2004). In some instances, the sorbed fraction of the pesticide becomes

totally resistant to microbial metabolism, although in others, as noted above, sorption does not totally preclude biodegradation. The mechanisms of aging are poorly understood: slow diffusion within small pores of soil aggregates, hydrophobic partitioning into solid humic materials (Kristensen et al., 2001; Mordaunt et al., 2005), entrapment in nanopores in hydrophobic surfaces (Brusseau et al., 1991a) and sorption at irreversible sorption sites of soil organic matter (Park et al., 2004) have all been proposed as possible mechanisms involved in the aging process. With longer residence times in the soil, bound pesticide residues tend to lose their biological activity and become even more resistant to degradation and extraction (Brusseau et al., 1991b; Nam and Alexander, 1998). However, relatively few laboratory studies have been carried out to assess the influence of pesticide residence time on the dynamic interplay between sorption and degradation. As is highlighted both by the effect of aging on binding strength and by the experiments of Park and coworkers commented on above (Park et al., 2003, 2004), pesticide sorption sites exhibit several degrees of binding strength. The bioavailability of pesticides will depend not only on the amount sorbed, but also on its distribution among sorption sites of different strengths (Sharer et al., 2003). That this distribution varies during successive wetting–drying cycles is suggested by the fact that sorption–desorption processes in soil characteristically exhibit hysteresis (Gramatica and Di Guardo, 2002; Walker et al., 2005). As in the case of aging, the exact mechanisms responsible for this remain largely unknown (Zhu and Selim, 2002; Selim, 2003). According to Park et al. (2004), sorption into non-desorbable sites of soil organic matter is a primary source of increased atrazine sorption in soils during aging.

2.3. Sorption enhancement

At present, organic amendment added to soil is becoming a common practice. This is why its influence on pesticide sorption and movement through the soil profile is studied with the intention of reducing the risk of water pollution associated with rapid run-off or leaching of pesticides in soil (Albarrán et al., 2002; Morillo et al., 2002). Other studies with physicochemically modified soils are of interest mainly when the sorption capacity of soils with low organic matter contents has to be increased to decrease pesticide mobility in soils from pollution point sources (high concentration in a small area), and to prevent the pollution of waters (Sánchez-Camazano, 2006).

3. Factors influencing the pollution of water by pesticides via soil

3.1. Pesticide fluxes in soil

There is evidence that chemicals applied to the soil surface may be transported rapidly to groundwater,

bypassing the unsaturated soil zone (Johnson et al., 1995). The hypotheses proposed to explain this rapid transport include preferential flow (Elliott et al., 2000; Roulier and Jarvis, 2003), co-transport with colloidal matter (Worall et al., 1999; Hesketh et al., 2001), and a combination of both these processes (Williams et al., 2000). The rate and magnitude of rapid transport seem to be influenced by multiple factors, including not only pesticide properties, but also soil properties (structure, organic matter, clay content, iron oxides, etc.), soil hydrological processes and management (*e.g.*, time of application). Especially for the hydrophobic pesticides, their mobility, and therefore the risk of their leaching into groundwater (Fig. 3) (Wauchope et al., 2001), has been correlated with weak sorption on the soil matrix, as quantified by K_{oc}, the ratio of adsorbed to solution-phase pesticide normalized with respect to organic matter content. However, pesticides with $K_{oc} \geq 1000$ have also been observed in groundwater and drainage water (Elliott et al., 2000), presumably as the result of leaching: transport to groundwater may be caused by heavy rainfall shortly after application of the pesticide to wet soils with preferential flow paths.

The flow patterns of soil water and its dissolved agrochemicals can be very heterogeneous. In the tropics, most preferential flow under typical intense rainstorms passes through animal burrows such as termite galleries (McGarry et al., 2000), although other exceptionally conductive regions of the soil also play a role (fingering infiltration; Hillel and Baker, 1988; Reichenberger et al., 2002). Preferential flow is beneficial in so far as it can lead to the replenishment of groundwater even when evaporation exceeds precipitation; but it also constitutes a process of potential water pollution, especially since pesticide concentrations peak in preferential flow. There is an urgent need for a better understanding of the temporal and spatial variation of water and pesticide fluxes in soils under intense rains.
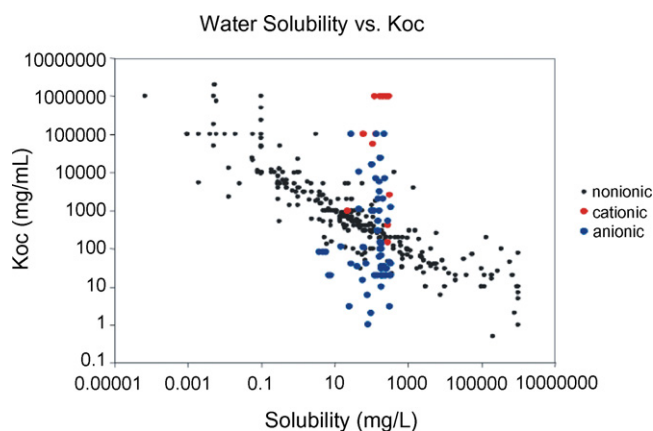
Fig. 3. Influence of K_{oc} on the water solubility of pesticides in soil. About one-third of pesticides are acidic or basic and, depending on the pH of the soil and the strength of the pesticides dissociation constant, these compounds may be present mainly as anions and cations in the soil. These pesticides do not fit the excellent regression observed for non-ionic pesticides between water solubilities and soil sorption coefficients.

All common approaches to the evaluation of water and contaminant fluxes in the field have limitations when applied to the measurement of preferential flow. In macroporous soils, where water bypasses the soil matrix, pesticide concentrations in the soil solution cannot be estimated from pesticide concentrations in the bulk soil (Malone et al., 2000). Sampling leachate in lysimeters may yield a quantitative estimate of the cumulative leaching efflux (Laabs et al., 2002), but the large surface area of typical lysimeters can lead to relevant peak concentrations in preferential flow pathways being diluted by unloaded adjacent matrix flow. Suction cups reflect the small-scale variation of water and solute concentrations in the field, but they do not sample soil water quantitatively (Magid and Christensen, 1993). Suction-plate lysimeters combine these approaches. Van Grinsven et al. (1998) introduced tensiometer-controlled suction lysimeters with adjustable vacuums. This type of extraction system was used with lysimeters that consisted of porous glass plates sintered into glass frames; in this way these suction plates are free of seals and glues that might adsorb fractions of the sample or contaminate it (Siemens and Kaupenjohann, 2003). The suction-plate technique has been used successfully to analyze seepage water fluxes and chemistry in sandy German soils (Siemens and Kaupenjohann, 2004).

3.2. Water pollution risk

The variables that jointly determine the susceptibility of groundwater to pollution via the soil include climate and land use as well as soil and hydrogeological conditions and the nature of the pollutants to which the soil is exposed. A concept that is by definition independent of the nature of possible pollutants, and which thus depends only on site variables and is amenable to mapping (Palmer et al., 1995), is that of "groundwater vulnerability" (Palmer and Lewis, 1998). Note, however, that the USEPA (1993) and other organizations (National Research Council, 1993) use a concept of groundwater vulnerability that does include pesticide characteristics among its defining variables, together with a concept of "aquifer sensitivity" that excludes both pesticide characteristics and land use or management practices (Table 3). To standardize the evaluation of groundwater pollution potential, in the late 1980s the USEPA developed the DRASTIC system (Aller et al., 1987), which ranks sites with respect to a linear combination of hydrogeological variables. DRASTIC has been applied, for example, in South Korea and South Africa (Lynch et al., 1997; Kim and Hamm, 1999), and other countries have developed similar indices (Zetsker et al., 1995; Madl-Szonyi and Fule, 1998). Extensions of DRASTIC include the incorporation of land use variables (Secunda et al., 1998) or 1D transport equations (Meeks and Dean, 1990). These ideas have been taken forward to develop regional vulnerability maps (Palmer et al., 1995). DRASTIC and related schemes have a number of significant drawbacks. Firstly, the variables they employ have often been chosen intuitively and weighted on the basis of expert opinion rather than by systematic evaluation (Palmer and Lewis, 1998). Secondly, these indices are typically not based on observations or measurements of groundwater contamination, and even when they incorporate physical models they are prone to errors in the assumptions of the models or the choice of input parameters. Thirdly, these indices have rarely been validated or tested against observed data (Merchant, 1994). When validation is performed evidence can be contradictory, *e.g.*, for the DRASTIC system, see refs. from Maas et al. (1995) and Close (1993). More fundamentally there is an underlying assumption that such site factors can be differentiated from the chemical properties of the contaminants of concern in terms of processes affecting transport. In other words, it is possible that the variation observed in the occurrences of, for example, pesticides is due only to variations in soil or climatic conditions without reference to the properties of the contaminant concerned.

As well as methods for evaluating the risk inherent to site characteristics, there are methods for evaluation of the pollution risk inherent in the characteristics of a given potential pollutant. Most are based on measures of sorption, degradation and/or solubility (Gustafson, 1989) and, as in the case of groundwater vulnerability assessment schemes, the methods based solely on chemical properties have tended to develop scores and indices based on expert opinion of the weighting of chemical parameters. Gustafson, however, developed an index of risk of leaching that was based on observations of groundwater contamination rather than expert opinion or arbitrary classification schemes (Gustafson, 1989). These observations have since been reprocessed to allow prediction of the actual probability of a compound being found in groundwater, rather than just to give an index or score (Worrall et al., 1998). However, all such approaches are open to essentially the same fundamental criticism as has been raised at the site-oriented indices of pollution risk that ignore pollutant properties: that they assume that chemical properties totally control the transport of contaminants to groundwater, or at least that interactions between site and chemical are of no account. Even methods that, like Gustafson's, are based on observations of groundwater contamination rather than on *a priori* combinations of parameters, have been found, unsurprisingly, to be generally inapplicable outside the region for which they were developed (Wooff et al., 1999). Thus, classifications of compounds in mobility classes, or as polluting or non-polluting, which are based on such schemes are prone to error due to natural variation in the parameters they use, such as K_{oc} (Fig. 3) and half-life in soil (half-life in soil may be confusing because it does not differentiate between degradation and sequestration; Wooff et al., 1999). Despite such variation it is possible to make a distinction between polluting and non-polluting compounds (*i.e.*, between compounds that are never found in groundwater and those that have been detected) that at least holds in a statistical sense (Worrall et al., 2000). Thus, it is feasible to

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Table 3
Comparison of risk assessment methods categories for water pollution

Methods category	Application	Expertise required	Data requirements	Output	Limitations
Aquifer sensitivity					
- Hydrogeologic setting classification - Scoring	Screening tool for broad decisions on the scale of political units (*i.e.*, counties, townships), or for areas larger than 100 acres	Review of method and application by individuals experienced in local hydrogeology, soils, and contaminant fate and transport is recommended	Variable. Sensitivity methods require as few as two and as many as seven or more factors. Scale for assessment decisions dictates the quantity of data required	Hydrogeological setting classification methods output consists of sensitivity classes (*i.e.*, low, medium, high). The output from scoring methods is a numerical score. Outputs of both may be mapped or listed	Intended for assessing sensitivity or relatively large areas (smaller than 1:100,000, *e.g.*, county or larger). Not intended for use in making field-level decisions (*i.e.*, areas <100 acres). Pesticide leaching characteristics and loading are not taken into account
Ground water vulnerability					
- Pesticide loading methods	For use in similar applications as sensitivity methods, but where pesticide-specific information is desired in the decision-making process	Review of method and application by individuals experienced in local hydrogeology, soils, and fate and transport is recommended	Pesticide loading methods require similar data requirements as sensitivity methods, but also require use/loading information	Output is similar to that of sensitivity methods	Pesticide use/loading information is often based on pesticide sales, which may be a misleading indicator of pesticide loading
- Simulation models	For detailed assessments of ground water vulnerability at many levels or scales	Generally require a high level of expertise, although some models are not as complicated as others. Experts in hydrogeology, soils, computer science, chemistry, and agronomy may be useful	Depending on use objective, simulation models may have large data requirements, including site- and pesticide-specific information	The flexibility of output varies between methods, but these methods generally present different views of pesticide movement and concentration in different media over time	If extensive data collection is necessary, it may be expensive and time-consuming to collect. Expensive verification may be necessary. Substantial ground water modelling skills may be required
- Pesticide leaching subcategory	For the prediction of pesticide leaching potentials in soil. Pesticide leaching methods are often used to assess a particular pesticide's tendency to leach from benchmark soils	Several off-the-shelf methods may be used with minimal experience or expertise. Review of method and application by individuals experienced in soils, chemistry, and statistics is recommended	Not extensive, depending on scale. Data for several of the methods may be obtained from the literature or from public databases	May be in the form of the proportion of pesticide predicted to leach through the soil zone over time, or the likelihood that the leachate from the soil zone will contain detectable levels of pesticides. May be expressed as leaching indices	Generally not suitable over large land areas. Pesticide travel times and resulting concentrations in different media are not addressed. Not usually used for field-by-field assessments

screen compounds for their pollution potential solely on the basis of chemical properties. However, the relative importance of chemical properties and site properties in controlling the transport of contaminants is not known.

That both chemical and site characteristics do need to be taken into account in evaluating the risk of groundwater pollution is illustrated by the fact that while both nitrate and organic pesticides are found in groundwater, one is often found without the other at sites exposed to both (Worrall et al., 2002). More generally, the expectation that certain soil properties should have different effects on the transport behaviour of different kinds of chemical (hydrophilic and hydrophobic compounds, for example) has been justified empirically both qualitatively (Blanchard and Lerch, 2000) and by application of a general linear statistical model to the results of extensive groundwater surveys in the southern U.K. and in the Midwest U.S. (Worrall et al., 2002). Accordingly, rather than an index of risk for sites that is universal for all pollutants, or an index of the risk posed by chemicals that is universal for all sites, what is required is to characterize sites by means of a series of indices corresponding to different types of chemical, and to characterize chemicals by means of a series of indices corresponding to different types of site. Thus, although Palmer et al. (1995) originally defined groundwater vulnerability as independent of the nature of potential pollutants, the soil classification of Palmer and Lewis (1998) does take pollutant type into account.

4. Future prospects

4.1. Improved formulations and application techniques

Use of pesticides in agriculture will lead to their occurrence in non-agricultural environments. Therefore, the present environmental concerns over agrochemical residues in the atmosphere, water, soil and foodstuffs will not vanish. To guarantee minimal negative side-effects in ecosystems other than the soil–plant system, pesticides, whether natural or synthetic, should have no or low toxicity, except for the target organisms. There seems to be a great potential to develop microbially derived pesticides, which are effective, reliable and have a low environmental risk. In addition, new application techniques, for example precision band spraying, can reduce the dose, which can be a very effective way to minimize transport and emission but also to avoid a build-up of resistance of target organisms.

Improved formulations will be needed to reduce off-target deposition, improve retention on target, and enhance uptake and translocation. It is also necessary to use the lowest rates of pesticides for each treatment on an annual basis. The difficulties in forecasting formulation behaviour and the cost of empirical field screening can only be reduced by developing a better understanding of the mode and action of adjuvants in spray formulations. This approach, in turn, leads itself to the development of either empirical or

physically based process-driven models, which may be incorporated into computer-based decision support systems. Future formulations will be made in the laboratory, performance tested by computer, evaluated under controlled conditions for efficacy and then applied under expert system control, which may be part of the spray application equipment. Such control in estimating crop protection performance and potential pesticide residues, together with the development of nanomechanical biosensors for their detection, may be the only defence against even more stringent regulations.

4.2. Geographical information systems

GIS provide a mean of extracting relevant information on pesticide fate from databases containing geo-referenced basic soil properties. The most relevant role of GIS in the analysis of pesticide fate in soil is that it can be used as a powerful tool to process together both input data and results of distribution model-based simulations of pesticide transport (Fig. 4; Ares et al., 2006). In this way analyzing the alternative strategies for the sustainable use of pesticides in agriculture and assessing the risk of human exposition to pesticides by the consumption of agricultural products is possible (Jones and Mangels, 2002).

Some recent examples of the potential of using distribution models with GIS in the assessment of the environmental fate of pesticides follow. In Argentina, Ares et al. (2006) coupled results of landscape analyses supported with the field-scale GIS, field data and information about management scenarios of citrus crops in Argentina to inspect the behaviour of a field-scale pesticide model Groundwater Loading Effects of Agricultural Management Systems (GLEAMS v.3.0; Leonard et al., 1987). Probability distribution functions of model parameters relevant to hydrology, geo-forms and crop distribution were derived from satellite imagery, while crop characteristics, information on soils and pesticides were obtained from field data. For the Mediterranean countries of Europe, Mediterranean Land Evaluation Information System Decision Support System (MicroLEIS DSS; De la Rosa et al., 2004) is a set of useful tools for decision-making in a wide range of agro-ecological schemes. The design philosophy follows a toolkit approach, integrating many software tools: databases, statistics, expert systems, neural networks, Web and GIS applications, and other information technologies. The aim of this software is to provide opportunities for greater cooperation in interdisciplinary research and in the application of knowledge to solve problems of soil protection. Other recent scientific contributions with GIS are based on the use of indicators for the estimation of the pesticide catabolic activity. Posen et al. (2006) produced a GIS layer representing levels of catabolic activity for the dissimilar soils across 30 km × 37 km area of river catchment to the north–west of London. After combining with other GIS data the authors produced a map showing risk of groundwater contamination by isoproturon. The authors stated that there appears to be
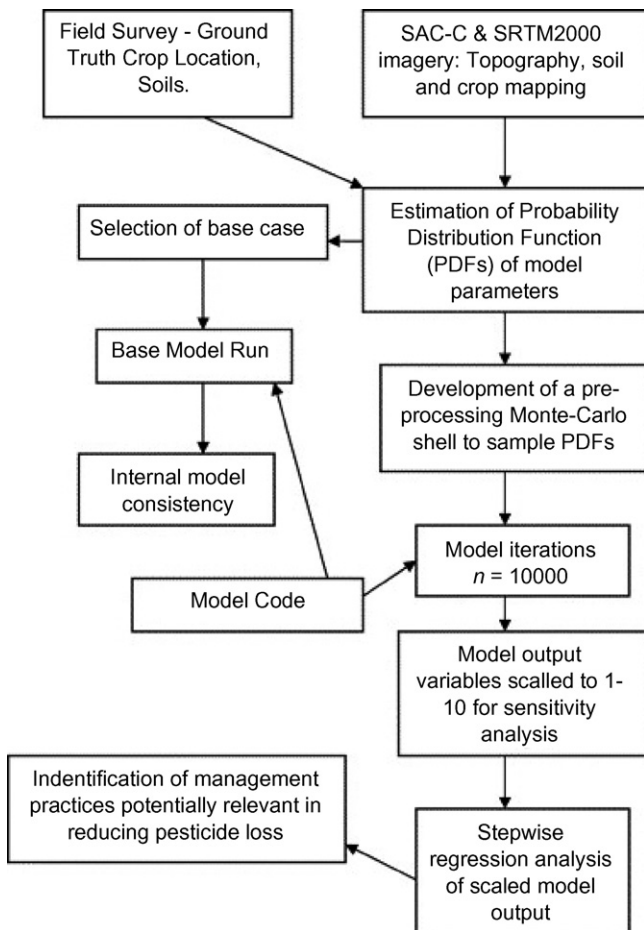
Fig. 4. Flow scheme of the use of distribution models with GIS in the assessment of the environmental fate of pesticides. SAC-C (Satélite de aplicaciones científicas-C) and SRTM2000 (Shuttle Radar Topography Mission launched on February 11, 2000 to collect 3D measurements of the Earth's surface).

limited benefit in including pesticide catabolic activity in this regional-scale groundwater risk model.

GIS have already been used for pesticide risk assessment for at least 10 years. However, in a recent article, Stenemo et al. (2007) recognized that the control of the uncertainties is necessary to restrict the interpretation of the results. Therefore, they used a conservative approach with respect to interpretation of the results and selection of pesticide parameters used. Not only scientists but legislators, together with social and economical agents, come together in the search for robust risk assessment methods. The techniques used for the risk assessment of consumers' exposure to pesticides have been normalized in the USA with the Food Quality Protection Act (FQPA, 1996), but not yet in Europe. The progress in the development of methods for ecological impact assessment (EUPRA, 2001) has not yet granted the chance for a consensus in the methodology to follow for the analysis of human exposure to pesticides. However, it is necessary to mention the 'Footprint' initiative (*e.g.*, http://www.eu-footprint.org/), a multidisciplinary, multinational European programme that aims at developing functional

tools for pesticide risk assessment and management. The main obstacles are based on the lack of data for a quantitative analysis together with the lack of experience in the use and interpretation of the models to use. For this reason, their application is not general although its usefulness is being admitted. Therefore, it is of key importance to normalize the different soil information systems used and to deliver new and improved databases for the application of fate models. These are the European future challenges for the understanding of the mobility and degradation of pesticides in soils and the pollution of waterbodies.

5. Recommendations

5.1. Multidisciplinary approach to environmental research

An understanding of the fate of pesticides is essential for rational decision-taking regarding their authorization. The retention of a pesticide by soil can prevent its short-term access to ground or surface waters and its effects on nontarget organisms, but the persistence of the undegraded pesticide or of harmful metabolites constitutes an ever-present – and cumulative – risk to the environment and, eventually, to human health. Thus, it is necessary to understand both the processes involved in the retention and release of pesticides by soil – and the factors influencing these processes – and the processes by which degradation occurs. To reach an adequate understanding will require the concourse of soil science, clay mineralogy, physical chemistry, surface chemistry, plant physiology and, no doubt, other disciplines. Only through a multidisciplinary approach to environmental research will it be possible to plan, manage, pursue and integrate the results of the studies that will be necessary for the development of tools and techniques allowing effective environmental decision-making.

5.2. Pesticide use policies

The authors' recommendations to implement policies on pesticide use follow:

1. It should be encouraged to continue surveys of national pesticide sales and to make annual summaries for policy purposes.
2. Sector and producer groups should be encouraged to gather end-user data on pesticides. The spray diary recording systems used by many sectors are a good basis but more emphasis should be put on entry of full data, including all dormant season sprays and herbicide applications.
3. Other regular market surveys (retail or end-user) should be encouraged for determining pesticide use patterns in

sectors such as pastoral agriculture which are less amenable to spray diary recording systems.

4. It is still necessary strategies for sustainable agriculture (alternative plant protection strategies, safer pesticide handling and more targeted application), increasing end-user confidence to adopt alternative practices.

5. Sectors should be given guidance and encouragement to implement these policies on pesticide use as part of a global strategy.

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