



Available online at www.sciencedirect.com



Agriculture, Ecosystems and Environment xxx (2007) xxx–xxx

**Agriculture
Ecosystems &
Environment**

www.elsevier.com/locate/agee

Review

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

Manuel Arias-Estévez^a, Eugenio López-Periago^a, Elena Martínez-Carballo^b,
 Jesús Simal-Gándara^{b,*}, Juan-Carlos Mejuto^c, Luis García-Río^d

^a *Soil Science and Agricultural Chemistry Group, Department of Plant Biology and Soil Science, Science Faculty, University of Vigo, E-32004 Ourense, Spain*

^b *Nutrition and Bromatology Group, Department of Analytical and Food Chemistry, Science Faculty, University of Vigo, E-32004 Ourense, Spain*

^c *Physical Chemistry Department, Science Faculty, University of Vigo, E-32004 Ourense, Spain*

^d *Physical Chemistry Department, Chemistry Faculty, University of Santiago de Compostela, E-15782 Santiago de Compostela, Spain*

Received 20 February 2007; received in revised form 20 July 2007; accepted 23 July 2007

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 concurrence 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.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Pesticides in soil; Sorption; Persistence; Degradation; Transport; Fate; Water pollution

Contents

| | |
|---------------------------------------|-----|
| 1. Introduction | 000 |
| 1.1. Pesticides | 000 |
| 1.2. Environmental residues | 000 |

* Corresponding author.

E-mail address: jsimal@uvigo.es (J. Simal-Gándara).

1.3. Transport models 000
 1.4. Review objectives 000
 2. Factors influencing the persistence of pesticides in soil 000
 2.1. Degradation and sorption 000
 2.2. Pesticide aging in soil and bioavailability 000
 2.3. Sorption enhancement 000
 3. Factors influencing the pollution of water by pesticides via soil 000
 3.1. Pesticide fluxes in soil 000
 3.2. Water pollution risk 000
 4. Future prospects 000
 4.1. Improved formulations and application techniques 000
 4.2. Geographical information systems 000
 5. Recommendations 000
 5.1. Multidisciplinary approach to environmental research 000
 5.2. Pesticide use policies 000
 Acknowledgements 000
 References 000

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 | 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 |
| Herbicide | Weeds | Post-emergence | Effective when applied after crop or weed emergence | |
| 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 | 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 |
| Nematicide | Nematodes | Selective | Toxic only to weed | |
| 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.

Please cite this article in press as: Arias-Estévez, M., et al., The mobility and degradation of pesticides in soils and the pollution of groundwater resources, Agric. Ecosyst. Environ. (2007), doi:10.1016/j.agee.2007.07.011

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

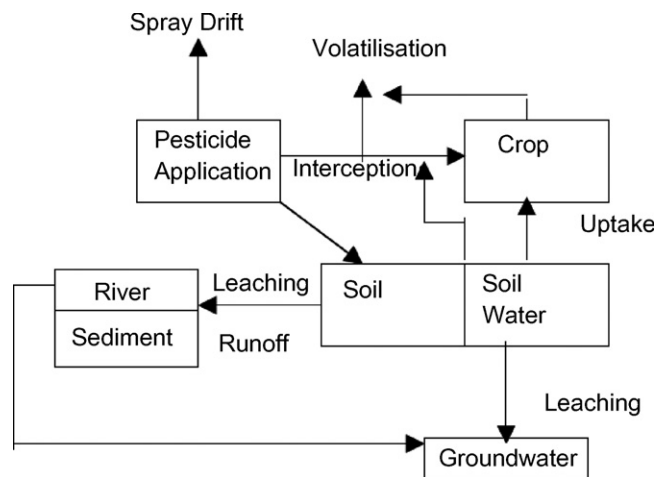


Fig. 1. Pathways of a pesticide applied to a crop. Ideally, at least one includes its contact with the targeted pest.

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 |
|--|--|---|---|
| <ul style="list-style-type: none"> • Chemical nature • Volatility • Solubility | <ul style="list-style-type: none"> • Site <ul style="list-style-type: none"> - Elevation, slope, aspect, geographical location - Plant cover (species, density, distribution, history at site) - Fauna (species, density, distribution, history at site) - Microbial populations (species, density, distribution, history at site) | <ul style="list-style-type: none"> • Wind, air movements • Temperature, solar radiation • Rainfall, relative humidity, evaporation | <ul style="list-style-type: none"> • Plot size, arrangement • Number of replicates • Frequency of sampling |
| <ul style="list-style-type: none"> • Formulation • Concentration | <ul style="list-style-type: none"> - Use of “fertilizers”, lime, mulches and green manures - Use of other pesticides and chemicals | | <ul style="list-style-type: none"> • Sample size, shape • Techniques for measuring variables |
| <ul style="list-style-type: none"> • Application <ul style="list-style-type: none"> - Method - Time (of year and day) - Frequency - Amount | <ul style="list-style-type: none"> - Tillage, cultivation, drainage, irrigation (type, depth, amount, timing, frequency) - Fire, e.g., burning of crop residues - Adjacent environments (hedges, field borders, woodlots, waterbodies) - Presence of pollutants • Soil type <ul style="list-style-type: none"> - 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

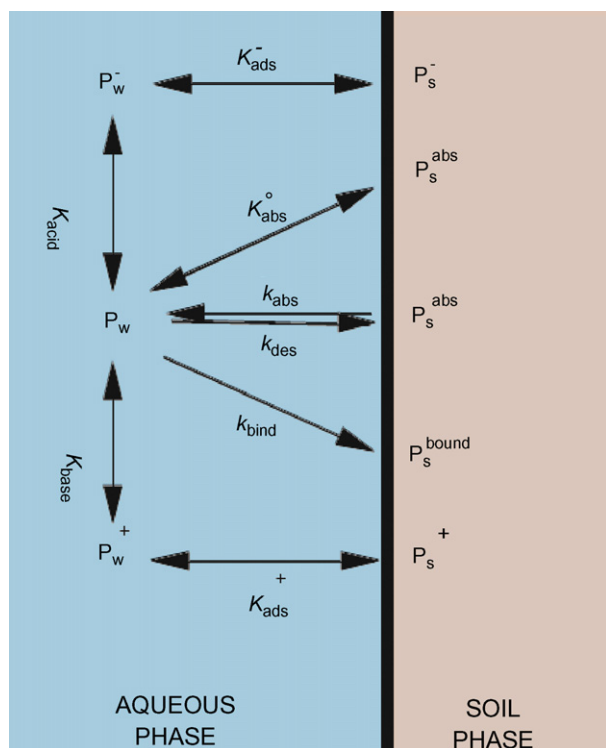


Fig. 2. Schematic diagram of the sorption reactions (small k) and instantaneous sorption equilibria (capital K) which may occur with a pesticide in soil water, as neutral basic or acidic molecule. Slow sorption reactions may also occur with cationic or anionic species. P_s and P_w are the potentially 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-Viciano 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.

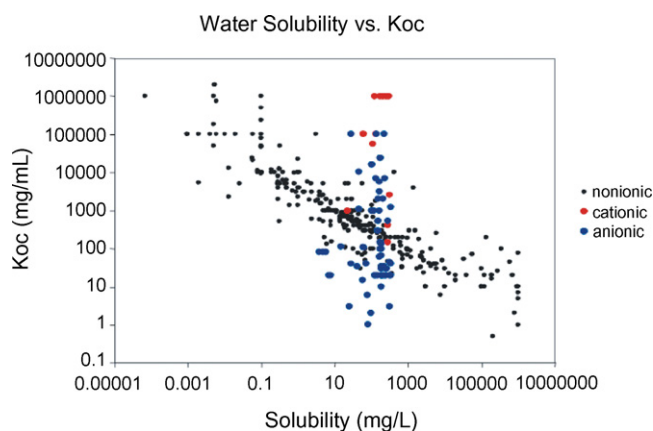


Fig. 3. Influence of K_{oc} on the water solubility of pesticides in soil. About one-third of pesticides are acidic or basic and, depending on the pH of the soil and the strength of the pesticides dissociation constant, these compounds may be present mainly as anions and cations in the soil. These pesticides 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

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 | Screening tool for broad decisions on the scale of political units (<i>i.e.</i> , 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>i.e.</i> , 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, <i>e.g.</i> , county or larger). Not intended for use in making field-level decisions (<i>i.e.</i> , areas <100 acres). Pesticide leaching characteristics and loading are not taken into account |
| - Scoring | | | | | |
| 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 |

Please cite this article in press as: Arias-Estévez, M., et al., The mobility and degradation of pesticides in soils and the pollution of groundwater resources, Agric. Ecosyst. Environ. (2007), doi:10.1016/j.agee.2007.07.011

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

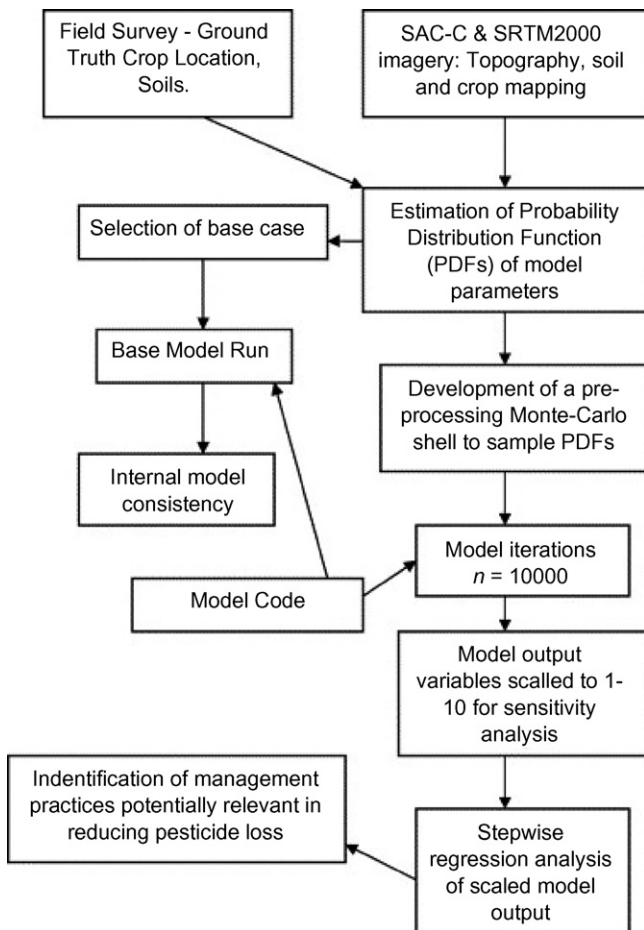


Fig. 4. Flow scheme of the use of distribution models with GIS in the assessment of the environmental fate of pesticides. SAC-C (Satélite de aplicaciones científicas-C) and SRTM2000 (Shuttle Radar Topography Mission launched on February 11, 2000 to collect 3D measurements of the Earth's surface).

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 concurrence 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.

Acknowledgements

This work was supported by the Xunta de Galicia under contracts PGIDIT03PXIB38302PR, PGIDIT03RAG38301-PR, PGIDIT03PXIC20905PN and PGIDIT04TMT209003PR, and by the Spanish Ministry of Science and Technology under contracts AGL2003-02244, CTQ2005-04779, AGL2006-04231 and AGL2007-62075. We are also grateful by the Ramón y Cajal contracts awarded to Manuel Arias-Estévez and Eugenio López-Periago, and also by the Parga Pondal contract to Elena Martínez-Carballo.

References

- Ahmad, R., Nelson, P.N., Kookana, R.S., 2006. The molecular composition of soil organic matter as determined by ¹³C NMR and elemental analyses and correlation with pesticide sorption. *Eur. J. Soil Sci.* 57, 883–893.
- Albarrán, A., Celis, R., Hermosín, M.C., López-Piñeiro, A., Cornejo, J., 2002. Effect of solid olive-mill waste amendment on pesticide sorption and leaching in soil. *Waste Management and the Environment*. In: International Conference on Waste Management and the Environment, Cadiz, Spain, September 4–6, pp. 351–359.
- Alexander, M., 2000. Aging, bioavailability, and overestimation of risk from environmental pollutants. *Environ. Sci. Technol.* 34, 4259–4265.
- Aller, L., Bennett, T., Lehr, J.H., Petty, R.J., Hackett, G., 1987. DRASTIC: A standardised system for evaluating groundwater pollution potential using hydrogeologic settings. US Environment Protection Agency, Ada, Oklahoma, EPA/60012-87/035.
- Ares, J.O., Del Valle, H.F., Olinuck, J.A., 2006. Exploring improved pesticide management in sub-tropical environments with GIS-supported fate modeling. *Agric. Syst.* 91 (3), 189–210.
- Arias-Estévez, M., Soto-González, B., López-Periago, E., Cancho-Grande, B., Simal-Gándara, J., 2005a. Atrazine sorption dynamics in organic matter rich-soils. *Bull. Environ. Contam. Toxicol.* 75, 264–271.
- Arias-Estévez, M., Torrente, A.C., López-Periago, E., Soto-González, B., Simal-Gándara, J., 2005b. Adsorption–desorption dynamics of cyprodinil and fludioxonil in vineyard soils. *J. Agric. Food Chem.* 53 (14), 5675–5681.
- Azevedo, A.S.O.N., 1998. Assessment and simulation of atrazine as influenced by drainage and irrigation. An interface between RZWQM and ArcView GIS. Doctor Thesis. Iowa State University, Ames, Iowa.
- Barriuso, E., Houot, S., SerraWittling, C., 1997. Influence of compost addition to soil on the behaviour of herbicides. *Pesticide Sci.* 49, 65–75.
- Barriuso, E., Koskinen, W.C., Sadowsky, M.J., 2004. Solvent extraction characterization of bioavailability of atrazine residues in soils. *J. Agric. Food Chem.* 52, 6552–6556.
- Baskaran, S., Bolan, N.S., Rahman, A., Tillman, R.W., 1996. Effect of exogenous carbon on the sorption and movement of atrazine and 2,4-D by soils. *Aust. J. Soil Res.* 34, 609–622.
- Belmans, C., Wesseling, J.G., Feddes, R.A., 1983. Simulation model of the water balance of a cropped soil: SWATRE. *J. Hydrol.* 63, 271–286.
- Blanchard, P.E., Lerch, R.N., 2000. Watershed vulnerability to losses of agricultural chemicals: interactions of chemistry, hydrology and land-use. *Environ. Sci. Technol.* 34, 3315–3322.
- Boivin, A., Cherrier, R., Perrin-Ganier, C., Schiavon, M., 2004. Time effect on bentazone sorption and degradation in soil. *Pesticide Manage. Sci.* 60 (8), 809–814.
- Bolan, N.S., Baskaran, S., 1996. Biodegradation of 2,4-D herbicide as affected by its adsorption–desorption behaviour and microbial activity of soils. *Aust. J. Soil Res.* 34, 1041–1053.
- Brewer, R., 1979. *Principles of Ecology*. Saunders College Publishing, Philadelphia, pp. 249–258.
- Brusseau, M.L., Jessup, R.E., Rao, P.S.C., 1991a. Nonequilibrium sorption of organic chemicals: elucidation of rate-limiting processes. *Environ. Sci. Technol.* 25, 134–142.
- Brusseau, M.L., Larsen, T., Christensen, T.H., 1991b. Rate-limited sorption and non-equilibrium transport of organic chemicals in low organic carbon aquifer materials. *Water Resour. Res.* 27, 1137–1145.
- Chen, B., Huang, G., Li, J., Li, Y.R., Li, Y.F., 2001. Integration of GIS with pesticides losses runoff model. In: Proceedings of DMGIS & Geoinformatics Conference, ISPRS, vol. XXXIV, Part 2W2, Bangkok, Thailand, May 25–28, pp. 37–44.
- Chung, N., Alexander, M., 1998. Differences in sequestration and bioavailability of organic chemicals aged in dissimilar soils. *Environ. Sci. Technol.* 32, 855–860.
- Clausen, L., Fabricius, I., 2002. Atrazine, isoproturon, mecoprop, 2,4-D, and bentazone adsorption onto iron oxides. *J. Environ. Qual.* 30 (3), 858–869.
- Close, M.E., 1993. Assessment of pesticide contamination of groundwater in New Zealand 2. Results of groundwater sampling. *N. Z. J. Marine Freshwater Res.* 27, 267–273.
- Cooper, B., 1996. Central and North West Regions Water Quality Program. 1995/1996 Report on Pesticide Monitoring. TS96.048; NSW Department of Land & Water Conservation, Sidney, Australia.
- Coquet, Y., 2003. Sorption of pesticide atrazine, isoproturon, and metamitron in the Vadose Zone. *Vadose Zone J.* 2, 40–51.
- Cupples, A.M., Sims, G.K., Hultgren, R.P., Hart, S.E., 2000. Effect of soil conditions on the degradation of cloransulam-methyl. *J. Environ. Qual.* 29, 786–794.
- De la Rosa, D., Mayol, F., Diaz-Pereira, E., Fernandez, M., De la Rosa, D., 2004. A land evaluation decision support system (MicroLEIS DSS) for agricultural soil protection: with special reference to the mediterranean region. *Environ. Model. Software* 19 (10), 929–942.
- De Jonge, R.J., Breure, A.M., van Anandel, J.G., 1996. Reversibility of adsorption of aromatic compounds onto powdered activated carbon (PAC). *Water Res.* 30 (4), 883–892.
- Dubus, I.G., Barriuso, E., Calvet, R., 2001. Sorption of weak organic acids in soils: clofencet, 2,4-D and salicylic acid. *Chemosphere* 45 (6–7), 767–774.
- Dyson, J.S., Beulke, S., Brown, C.D., Lane, M.C.G., 2002. Adsorption and degradation of the weak acid mesotrione in soil and environmental fate implications. *J. Environ. Qual.* 31, 613–618.
- Elliott, J.A., Cesna, A.J., Best, K.B., Nicholaichuk, W., Tollefson, L.C., 2000. Leaching rates and preferential flow of selected herbicides through tilled and untilled soil. *J. Environ. Qual.* 29, 1650–1656.
- Environment Canada, 1993. Environment Canada-Agriculture Canada. Pesticide Registrant Survey, 1990 Report. Commercial Chemicals Branch, Conservation and Protection, Environment Canada, Ottawa.
- EUPRA, 2001. Probabilistic risk assessment for pesticides in Europe: Implementation & research needs. In: Hart, A. (Ed.). Report of the European Workshop on Probabilistic Risk Assessment for the Environmental Impacts of Plant Protection Products (EUPRA). Central Science Laboratory, York, UK, pp. 1–105.
- FQPA, 1996. Food quality protection act of 1996. Public Law 104–107:101–501.

- Gao, J.P., Maguhn, J., Spitzauer, P., Kettrup, A., 1998. Sorption of pesticides in the sediment of the Teufelsweiher pond (Southern Germany). I: equilibrium assessments, effect of organic carbon content and pH. *Water Res.* 32 (5), 1662–1672.
- Gevao, B., Semple, K.T., Jones, K.C., 2000. Bound pesticide residues in soils: a review. *Environ. Pollut.* 108, 3–14.
- Gramatica, P., Di Guardo, A., 2002. Screening of pesticides for environmental partitioning tendency. *Chemosphere* 47 (9), 947–956.
- Guo, L., Wagenet, R.J., Jury, W.A., 1999. Adsorption effects on kinetics of aldicarb degradation: equilibrium model and application to incubation and transport experiments. *Soil Sci. Soc. Am. J.* 63, 1637–1644.
- Guo, L., Jury, W.A., Wagenet, R.J., Flury, M., 2000. Dependence of pesticide degradation on sorption: nonequilibrium model and application to soil reactors. *J. Contam. Hydrol.* 43 (1), 45–62.
- Gustafson, D.I., 1989. Groundwater ubiquity score: a simple method for assessing pesticide leachability. *Environ. Toxicol. Chem.* 8, 339–357.
- Hallberg, G.R., 1989. Pesticide pollution of groundwater in the humid United States. *Agric. Ecosyst. Environ.* 26, 299–367.
- Helweg, A., 1975. Degradation of ¹⁴C-maleic hydrazide in soil as influenced by adsorption on activated carbon. *Weed Res.* 15, 129–133.
- Hesketh, N., Brookes, P.C., Addiscott, T.M., 2001. Effect of suspended soil material and pig slurry on the facilitated transport of pesticides, phosphate and bromide in sandy soil. *Eur. J. Soil Sci.* 52, 287–296.
- Hillel, D., Baker, R.S., 1988. A descriptive theory of fingering during infiltration into layered soils. *Soil Sci.* 146, 51–56.
- Hutson, J.L., Wagenet, R.J., 1992. Leaching Estimation and Chemistry Model, Version 3. Department of Soil, Crop and Atmospheric Sciences, Research Series No. 92-3. Cornell University, New York.
- Jarvis, N.J., 1991. MACRO—a model of water movement and solute transport in macroporous soils. Reports and Dissertations No. 9. Department of Soil Sciences, Swedish University of Agricultural Sciences, Uppsala.
- Jayachandran, K., Steinheimer, T.R., Somasundaram, L., Moorman, T.B., Kanwar, R.S., Coats, J.R., 1994. Occurrence of atrazine and degradates as contaminants of subsurface drainage and shallow groundwater. *J. Environ. Qual.* 23 (2), 311–319.
- Johnson, D.C., Selim, H.M., Ma, L., Southwick, L.M., Willis, G.H., 1995. Movement of Atrazine and Nitrate in Sharkey Clay Soil. Evidence of Preferential Flow. Report No. 846. Louisiana State University Agricultural Center, Louisiana Agricultural Experimental Station, Baton Rouge, LA.
- Jones, R.L., Mangels, G., 2002. Review of the validation of models used in Federal Insecticide, Fungicide, and Rodenticide Act environmental exposure assessments. *Environ. Toxicol. Chem.* 21 (8), 1535–1544.
- Kim, Y.J., Hamm, S.Y., 1999. Assessment of the potential for groundwater contamination using the DRASTIC/EGIS technique, Cheongju area, South Korea. *Hydrogeol. J.* 7, 227–235.
- Knisel, W.G. (Ed.), 1980. CREAMS: A Field Scale Model for Chemical, Runoff, and Erosion from Agricultural Management Systems. Conservation Research Report, No. 26. U.S. Dept. Agric. Washington, DC.
- Koskinen, W.C., Cox, L., Yen, P.Y., 2001. Changes in sorption/bioavailability of imidacloprid metabolites in soil with incubation time. *Biol. Fert. Soils* 33, 546–550.
- Koskinen, W.C., Anhalt, J.A., Sakaliene, O., Rice, P.J., Moorman, T.B., Arthur, E.L., 2003. Sorption–desorption of two “aged” sulfonylaminocarbonyltriazolinone herbicide metabolites in soil. *J. Agric. Food Chem.* 51, 3604–3608.
- Kristensen, G.B., Johannesen, H., Aamand, J., 2001. Mineralization of aged atrazine and mecoprop in soil and aquifer chalk. *Chemosphere* 45, 927–934.
- Laabs, V., Amelung, W., Pinto, A., Zech, W., 2002. Fate of pesticides in tropical soils of Brazil under field conditions. *J. Environ. Qual.* 31, 256–268.
- Larson, S.J., Capel, P.D., Majewski, M.S., 1997. Pesticides in surface waters—distribution, trends, and governing factors. In: Gilliom, R.J. (Ed.), *Series of Pesticides in Hydrologic System*, vol. 3. Ann Arbor Press, Chelsea, Michigan.
- Leonard, R.A., Knisel, W.G., Still, D.A., 1987. GLEAMS: groundwater loading effects of agricultural management systems. *Trans. Am. Soc. Agric. Eng.* 30 (5), 1403–1418.
- Li, Y.R., Struger, J., Fischer, J.D., Li, Y.F., Huang, G.H., 2001. Predicting runoff losses of atrazine from agricultural lands in the Kintore Creek watershed using two statistical models. In: *The 36th Central Canadian Symposium on Water Pollution, Research*, Canada Centre for Inland Waters, Burlington, ON.
- Linn, D.M., Carski, T.H., Brusseau, M.L., Chang, F.H. (Eds.), 1993. *Sorption and Degradation of Pesticides and Organic Chemicals in Soil*. Soil Science Society of America, Madison, WI, p. 260.
- López-Blanco, C., Cancho-Grande, B., Simal-Gándara, J., López-Periago, E., Arias-Estévez, M., 2005. Transport of commercial endosulfan through a column of aggregated vineyard soil by a water flux simulating field conditions. *J. Agric. Food Chem.* 53 (17), 6738–6743.
- López-Pérez, G.C., Arias-Estévez, M., López-Periago, E., Soto-González, B., Cancho-Grande, B., Simal-Gándara, J., 2006. Dynamics of pesticides in potato crops. *J. Agric. Food Chem.* 54 (5), 1797–1803.
- Lynch, S.D., Reynders, A.G., Schulze, R.E., 1997. A DRASTIC approach to groundwater vulnerability in South Africa. *S. Afr. J. Sci.* 93, 59–60.
- Maas, R.P., Kucken, D.J., Patch, S.C., Peek, B.T., Van Engelen, D.L., 1995. Pesticides in eastern North Carolina rural supply wells: land-use factors and persistence. *J. Environ. Qual.* 24, 426–431.
- Madl-Szonyi, J., Fule, L., 1998. Groundwater vulnerability assessment of the SW trans-Danubian central range. *Central Range, Hungary. Environ. Geol.* 35, 9–18.
- Magid, J., Christensen, N., 1993. Soil solution sampled with and without tension in arable and heath land soils. *Soil Sci. Soc. Am. J.* 57, 1463–1469.
- Malone, R.W., Shipitalo, M.J., Douglass, L.W., Owens, L.B., Nelsen, T.C., Warner, R.C., Byers, M.E., 2000. Assessing herbicide movement using soil samples versus percolate samples. *Trans. Am. Soc. Agric. Eng.* 43, 343–348.
- McGarry, D., Bridge, B.J., Radford, B.J., 2000. Contrasting soil physical properties after zero and traditional tillage of an alluvial soil in the semi-arid subtropics. *Soil Tillage Res.* 53, 105–115.
- Meeks, Y.J., Dean, J.D., 1990. Evaluating ground-water vulnerability to pesticides. *J. Water Resour. Plan Manage.* 116, 693–707.
- Merchant, J.W., 1994. GIS-based groundwater pollution hazard assessment—a critical review of the DRASTIC model. *Photogram. Eng. Remote Sensing* 60, 1117–1128.
- Moorman, T.B., Jayachandran, K., Reungsang, A., 2001. Adsorption and desorption of atrazine in soils and subsurface sediments. *Soil Sci.* 166 (12), 921–929.
- Mordaunt, C.J., Gevao, B., Jones, K.C., Semple, K.T., 2005. Formation of non-extractable pesticide residues: observations on compound differences, measurement and regulatory issues. *Environ. Pollut.* 133 (1), 25–34.
- Morillo, E., Maqueda, C., Reinoso, R., Undabeytia, T., 2002. Effect of two organic amendments on norflurazon retention and release by soils of different characteristics. *Environ. Sci. Technol.* 36, 4319–4325.
- Moyer, J.R., Hance, R.J., McKone, C.E., 1972. The effects of adsorbents on the rate of degradation of herbicides incubated with soil. *Soil Biol. Biochem.* 4, 307–311.
- Mullins, J.A., Carsel, R.F., Scarbrough, J.E., Ivery, A.M., 1993. PRZM-2, A Model for Predicting Pesticide Fate in the Crop Root and Unsaturated Soil Zones: Users Manual for Release 2.0. US EPA, Athens, GA, 30605-2720.
- Nam, K., Alexander, M., 1998. Role of nanoporosity and hydrophobicity in sequestration and bioavailability: tests with model solids. *Environ. Sci. Technol.* 32, 71–74.
- National Research Council, 1993. *Ground Water Vulnerability Assessment: Contamination Potential Under Conditions of Uncertainty*. National Academy Press, Washington, DC.

- Oi, M., 1999. Time-dependent sorption of imidacloprid in two different soils. *J. Agric. Food Chem.* 47, 327–332.
- Palmer, R.C., Holman, I.P., Robins, N.S., Lewis, M.A., 1995. Guide to Groundwater Vulnerability Mapping in England and Wales. National Rivers Authority, Bristol.
- Palmer, R.C., Lewis, M.A., 1998. In: Groundwater pollution, Aquifer Recharge, Vulnerability, Robins, N.S. (Eds.), Assessment of Groundwater Vulnerability in England and Wales. Special Publications, vol. 130. Geological Society, London, pp. 191–198.
- Park, J.H., Feng, Y.C., Ji, P.S., Voice, T.C., Boyd, S.A., 2003. Assessment of bioavailability of soil-sorbed atrazine. *Appl. Environ. Microbiol.* 69, 3288–3298.
- Park, J.H., Feng, Y.C., Cho, S.Y., Voice, T.C., Boyd, S.A., 2004. Sorbed atrazine shifts into non-desorbable sites of soil organic matter during aging. *Water Res.* 38, 3881–3892.
- Pignatello, J.J., 1998. Soil organic matter as a nanoporous sorbent of organic pollutants. *Adv. Colloid Interface Sci.* 76–77, 445–467.
- Pimentel, D., Levitan, L., 1986. Pesticides: amounts applied and amounts reaching pests. *Bioscience* 36, 86–91.
- Posen, P., Lovett, A., Hiscock, K., Evers, S., Ward, R., Reid, B., 2006. Incorporating variations in pesticide catabolic activity into a GIS-based groundwater risk assessment. *Sci. Total Environ.* 367 (2–3), 641–652.
- Rao, P.S.C., Mansell, R.S., Baldwin, L.B., Laurent, M.F., 1983. Pesticides and their Behavior in Soil and Water. Soil Science Fact Sheet. Florida Cooperative Extension Service, Institute of Food and Agricultural Sciences, University of Florida.
- Rao, P.S.C., Bellin, C.A., Brusseau, M.L., 1993. In Sorption and Degradation of Pesticides and Organic Chemicals in Soil. SSSA Special Publication Number 32, Wisconsin, pp. 1–26.
- Reichenberger, S., Amelung, W., Laabs, V., Pinto, A., Totsche, K.U., Zech, W., 2002. Pesticide displacement along preferential flow pathways in a Brazilian Oxisol. *Geoderma* 110, 63–86.
- Reichman, R., Wallach, R., Mahrer, Y., 2000. A combined soil-atmosphere model for evaluating the fate of surface-applied pesticides. 1. Model development and verification. *Environ. Sci. Technol.* 34, 1313–1320.
- Rial-Otero, R., Cancho-Grande, B., Arias-Estévez, M., López-Periago, E., Simal-Gándara, J., 2003. Procedure for the measurement of soil inputs of plant-protection agents washed off through vineyard canopy by rainfalls. *J. Agric. Food Chem.* 51 (17), 5041–5046.
- Rial-Otero, R., González-Rodríguez, R., Cancho-Grande, B., Simal-Gándara, J., 2004. Parameters affecting extraction of selected fungicides from vineyard soils. *J. Agric. Food Chem.* 52 (24), 7227–7234.
- Robert, J.G., Barbash, J.E., Kolpin, D.W., Larson, S.J., 1999. Testing Water Quality for Pesticide Pollution. *Environ. Sci. Technol.* 33 (7), 164 A–169 A.
- Roulier, S., Jarvis, N., 2003. Modeling macropore flow effects on pesticide leaching: Inverse parameter estimation using microlysimeters. *J. Environ. Qual.* 32, 2341–2353.
- Sánchez-Camazano, M., 2006. Comparison of pesticide sorption by physicochemically modified soils with natural soils as a function of soil properties and pesticide hydrophobicity. *Soil Sediment Contam.* 15 (4), 401–415.
- Secunda, S., Collin, N.I.L., Melloui, A.L., 1998. Groundwater vulnerability assessment using a composite model combining DRASTIC with extensive agricultural land use in Israel's Sharon region. *J. Environ. Manage.* 54, 39–57.
- Selim, H.M., Ma, L., Zhu, H., 1999. Predicting solute transport in soils: second-order two site models. *Soil Sci. Soc. Am. J.* 63, 768–777.
- Selim, H.M., 2003. Retention and runoff losses of atrazine and metribuzin in soil. *J. Environ. Qual.* 32, 1058–1071.
- Sharer, M., Park, J.H., Voice, T.C., Boyd, S.A., 2003. Aging effects on the sorption-desorption characteristics of anthropogenic organic compounds in soil. *J. Environ. Qual.* 32, 1385–1392.
- Siemens, J., Kaupenjohann, M., 2003. Dissolved organic carbon is released from sealings and glues of pore water samples. *Soil Sci. Soc. Am. J.* 67, 795–797.
- Siemens, J., Kaupenjohann, M., 2004. Comparison of three methods for field measurement of solute leaching in a sandy soil. *Soil Sci. Soc. Am. J.* 68, 1191–1196.
- Sociás-Viciano, M.M., Fernández-Pérez, M., Villafranca-Sánchez, M., González-Pradas, E., Flores-Céspedes, F., 1999. Sorption and leaching of atrazine and MCPA in natural and peat-amended calcareous soils from Spain. *J. Agric. Food Chem.* 47, 1236–1241.
- Spadotto, C.A., Hornsby, A.G., 2003. Soil sorption of acidic pesticides: modeling pH effects. *J. Environ. Qual.* 32, 949–956.
- Spark, K.M., Swift, R.S., 2002. Effect of soil composition and dissolved organic matter on pesticide sorption. *Sci. Total Environ.* 298 (1–3), 147–161.
- Stenemo, F., Chittaranjan, R., Russell, Y., Steven, M., 2007. A screening tool for vulnerability assessment of pesticide leaching to groundwater for the islands of Hawaii, USA. *Pest Manage. Sci.* 63 (4), 404–411.
- Stoltenberg, D., Pope, R., Most, J., 1990. Atrazine management rules for Iowa. Iowa State University. Coop. Ext. Bull. Pm-1390, pp. 1–6.
- Struthers, J.K., Jayachandran, K., Moorman, T.B., 1998. Biodegradation of atrazine by *Agrobacterium radiobacter* J14a and use of this strain in bioremediation of contaminated soil. *Appl. Environ. Microbiol.* 64 (9), 3368–3375.
- Topp, E., Vallaey, T., Soulas, G., 1997. In: van Elsas, J.D., Trevors, J.T., Wellington, E.M.H. (Eds.), *Modern Soil Microbiology*. Marcel Dekker, New York, pp. 547–575.
- USDA-ARS, 1995. Root Zone Water Quality Model (RZWQM) V.3.0. User's Manual. GPSR Technical Report No. 5. USDA-ARS Great Plains Systems Research Unit, Ft. Collins, CO.
- USEPA, 1993. A Review of Methods for Assessing Aquifer Sensitivity and Ground Water Vulnerability to Pesticide Contamination. USEPA, Office of Water, Washington, DC.
- USEPA, 1998. Research program description-Groundwater research. U.S. Environmental Protection Agency, EPA/600/9-88/005: Washington, DC.
- Van Grinsven, J.J.M., Booltink, H.G.W., Dirksen, C., van Breemen, N., Bongers, N., Waringa, N., 1998. Automated in situ measurement of unsaturated soil water flux. *Soil Sci. Soc. Am. J.* 52, 1215–1218.
- Walker, A., Rodríguez-Cruz, M.S., Mitchell, M.J., 2005. Influence of ageing of residues on the availability of herbicides for leaching. *Environ. Pollut.* 133 (1), 43–51.
- Wauchope, R.D., Yeh, S., Linders, J.B.H., Kloskowski, R., Tanaka, K., Katayama, A., Kördel, W., Gerstl, Z., Lane, M., Unsworth, J., 2001. Pesticide soil sorption parameters: theory, measurement, uses, limitations and reliability. In: Poster presented at the IUPAC Congress/General Assembly.
- Williams, C.F., Agassi, M., Letey, J., Farmer, W.J., Nelson, S.D., Ben-Hur, M., 2000. Facilitated transport of napropamide by dissolved organic matter through soil columns. *Soil Sci. Soc. Am. J.* 64, 590–594.
- Wooff, D.A., Seheult, A.H., Coolen, F.P.A., Worrall, F., 1999. Bayesian discrimination with uncertain covariates for pesticide contamination. In: Barnett, V., Stein, A., Turkman, K. (Eds.), *Statistics for the Environment 4: Pollution Assessment and Control*. John Wiley and Sons, Chichester, pp. 337–353.
- Worrall, F., Wooff, D.A., Seheult, A.H., Coolen, F.P.A., 1998. A Bayesian approach to the analysis of environmental fate and behaviour data for pesticide registration. *Pesticide Sci.* 54, 99–112.
- Worrall, F., Parker, A., Rae, J.E., Johnson, A.C., 1999. A study of suspended and colloidal matter in the leachate from lysimeters and its role in pesticide transport. *J. Environ. Qual.* 28, 595–604.
- Worrall, F., Wooff, D.A., Seheult, A.H., Coolen, F.P.A., 2000. New approaches to assessing the risk of groundwater contamination by pesticides. *J. Geol. Soc.* 157, 877–884.

- Worrall, F., Besien, T., Kolpin, D.W., 2002. Groundwater vulnerability: interactions of chemical and site properties. *Sci. Total Environ.* 299, 131–143.
- Younes, M., Galal-Gorchev, H., 2000. Pesticides in drinking water e a case study. *Food Chem. Toxicol.* 38 (1), 87–90.
- Young, R.A., Onstad, C.A., Bosh, D.D., Anderson, W.P., 1986. Agricultural Nonpoint Source Pollution Models: A Watershed Analysis Tool, Model Documentation, Agricultural Research Service. U.S. Department of Agriculture, Morris, MN.
- Zetsker, I.S., Belousova, A.P., Dudov, V.Y., 1995. Regional assessment and mapping of groundwater vulnerability to contamination. *Environ. Geol.* 25, 225–231.
- Zhu, H., Selim, H.M., 2002. Retention and mobility of deltamethrin in soils: 1. Adsorption–desorption. *Soil Sci.* 167, 513–523.