Session 5

Risk Assessment and Regulatory Implications

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ASSESSMENT, ACCEPTABILITY AND REGULATION OF RISK FROM RESIDUES IN WATER

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ABSTRACT

Safe levels in drinking water are calculated by allocating a small proportion of the Acceptable Daily Intake, usually 10%, and assuming a 70 kg person drinks two litres per day. There is normally no risk to aquatic ecosystems if the initial concentration in water is <1/10 EC_{50} or <NOEC for fish, invertebrates and algae. Regulations follow these approaches, with some notable exceptions. In the EU, a pseudo zero value, 0.1 µg/litre has been set for drinking water. This is forcing water supply companies to waste billions of pounds removing safe, trace levels of pesticides. The EU regulations presume no risk to aquatic organisms if the exposure concentration is <1/100 EC_{50} or <1/10 NOEC for fish and *Daphnia*. The labelling of pesticides is based on a risk assessment, *ie* takes into account potential exposure as well as toxicity.

INTRODUCTION

Data are used to:

1.   Assess possible risks to humans and environment.

2.   Help define what risks are acceptable/unacceptable

3.   Regulate the use of pesticides.

4.   Inform pesticide users how to minimise risks and maximise benefits.

There are numerous definitions of risk. In this paper it is equated to the probability of injury occurring under a specific set of circumstances. Risk assessment requires a knowledge of both the toxicity of a chemical and the level of exposure of the organism(s) to the chemical, as well as the ecology of ecosystems. In the case of humans, we are concerned about risk to individuals while, with the environment, we are concerned about risk to populations of a given species or to an ecosystem (OECD, 1989).

The assessment of risk must not be confused with the separate process of managing risks and deciding what risks are acceptable in relation to the benefits from using a pesticide and the risks from alternative pest management procedures. Although this is a political as well as scientific process, decisions should still be based on good science, *ie* on real risks and benefits and not short term, unfounded scare stories. Of course, policies change with time. In Europe, in the decades following the Second World War, priority was given to minimising the risk of insufficient food. The public now consider food supplies not to be at risk, and increasing priority is given to human and environmental safety, including the

"quality" of water.

Regulations give guidance on data required, methods for assessing risk and how to decide if a risk is acceptable. They include defining how a pesticide can be used, not just an "approval" of the active ingredient. Regulations also give guidance on how information should be communicated to the user via the product label. They also provide a legal framework for enforcing the proper use of pesticides.

RISK ASSESSMENT

Humans

The increasing sensitivity of analytical methods has lead to the detection of trace amounts of pesticides in groundwater and surface water. Thus it is necessary to establish what levels should be permissible in drinking water.

Pesticide safety evaluations include tests designed to mimic potential routes and conditions of exposure for man. Short and long term toxicological tests are conducted to identify immediate and long term effects to assess potential human health implications. The following indices are included: lethality; irritation; sensitisation or allergic responses; toxicity to major organs such as the liver, kidney, reproductive system; effects on the developing foetus; the potential to cause mutations or genetic damage; and the potential to produce tumours.

Procedures have been developed which utilise the toxicological database to assess human health risks posed by dietary pesticide exposures. They are used for pesticide registrations worldwide. The Acceptable Daily Intake (ADI) is used as the basis for estimating the amount of pesticide residues in crops which can be consumed safely during an entire lifetime by the public.

The ADI is usually derived from the no observed effect level (NOEL) in long term feeding studies for the most sensitive laboratory animal species tested. An uncertainty factor (UF) is incorporated in the calculation to account for potential differences in sensitivity between species and variability within species. The UF is usually assigned a value of 100 for chronic effects. Pesticides having data showing "limited" evidence of carcinogenicity in animals (*eg* those compounds that produced tumours in only one species, strain or experiment, or an increase in the incidence of tumours that occur spontaneously in unexposed animals) might be assigned an uncertainty factor of 1000. ADIs are expressed as mg/kg bodyweight/day.

It is reasonable to consider drinking water as a constituent of the daily diet and allocate a fraction of the ADI to establish safe levels in water. There is a strong desire by society to give an extremely high level of protection to water (precautionary principle). Therefore, normally only a small percentage of the ADI is allocated to water; the WHO frequently recommend 10% of the ADI (WHO, 1993). To calculate the permissible concentration in water (mg/litre), it is assumed a 70 kg person consumes 2 litres water/day. Thus:

$$\text{Permissible level} = \frac{10}{100} \times \text{ADI (mg/kg/day)} \times \frac{70 \text{ kg}}{2 \text{ litres/day}}$$

<u>Environment</u>

The quotient ratio method is widely used to assess risks to the aquatic environment. The quotient is the ratio of a no observed effect level (NOEL) or LC_{50} to the predicted environmental concentration (PEC). A key area of debate is what ratio should be equated with a conclusion that a pesticide does not present a risk to the aquatic environment. Thus, laboratory measured EC_{50} and NOEL values for fish, invertebrates and algae have been compared with effects of pesticides on pond ecosystems (Figure 1). This has shown that there will be no concern if the predicted environmental concentration is <1/10 of LC_{50}, or <chronic NOEL to fish, invertebrates and algae, *ie* there is unlikely to be any significant effect on the aquatic ecosystem (Rijtema *et al*., 1993). Although the aquatic ecosystem might contain organisms more sensitive to the pesticide than those tested in the laboratory, this is counterbalanced by a more rapid decline in residue concentrations due to degradation, adsorption and dilution. Laboratory toxicity studies are normally carried out in 'clean' water; in some studies, the concentration of the pesticides is also maintained constant by using a flow-through system. Effects under field conditions are also balance by natural population processes.

FIGURE 1 Effects on aquatic organisms, comparison of lowest laboratory results and ecosystem NOEC
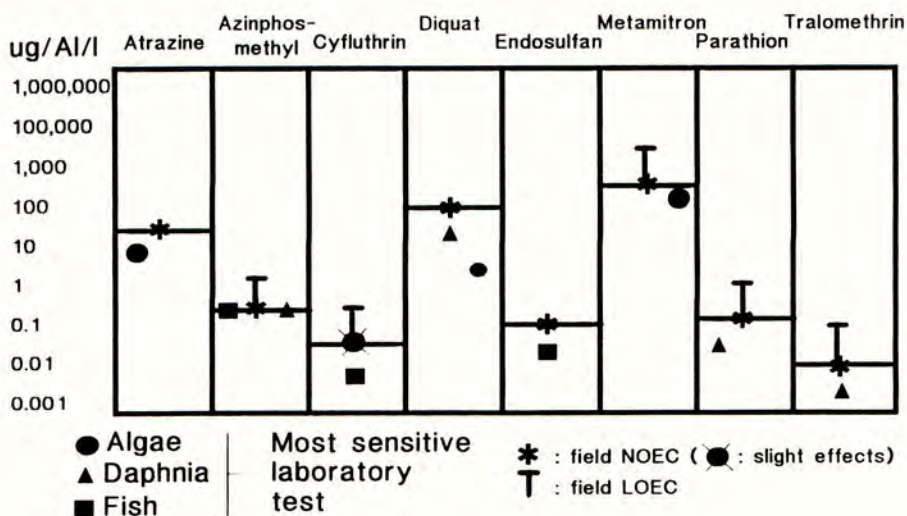
NOEC = No observed effect concentration
LOEC = Lowest observed effect concentration

The PEC values are normally estimated from generic databases generated under a range of conditions, rather than measured for each new pesticide. In order to minimise the risks to aquatic environment, typical worst case values are used rather than average values. Examples for spray drift are given in Table 1. These values are then used to calculate the PEC value. For example, 0.6% drift of an application of 100 g ai/ha is equivalent to 0.00006 mg ai/litre in water 1 m deep.

TABLE 1   Drift rates (% of application rate) for various crops/cultures at different distances from the treated area used in aquatic risk assessments (Ganzelmeier, 1993a and b)

Distance (m)	Arable/ field crops	Vineyards		Orchards		Hops
		With leaves	Without leaves	With leaves	Without leaves	
1	4.0	-	-	-	-	-
2	1.6	-	-	-	-	-
3	1.0	7.5	4.9	15.5	29.6	-
5	0.6	4.0	1.6	10.0	19.5	11.0
10	0.3	1.5	0.4	4.0	10.6	7.0
15	0.2	1.0	0.2	2.0	6.2	4.5
20	0.1	0.5	0.1	1.5	4.2	3.0
30	0.1	0.2	0.05	0.7	2.0	1.5
40			0.05		0.4	
50			0.05		0.2	0.25

There is a growing interest in probablistic approaches to risk assessment (Brown and Shaw, 1994), for example, in estimating the amount of run-off or spray drift into the aquatic environment, which is obviously very variably. Similarly, rather than using the toxicity to individual species, procedures have been developed using distribution models for sets of chronic data. The distribution is then used to calculate the Maximum Acceptable Risk level in water which safeguards 95% of the species. Although such approaches appear more scientific, they often include many invalid assumptions, *eg* that the NOEC values follow a log-logistic distribution and the organisms tested are a random selection of all the species present. It also presumes all species are of equal importance and ignores interactions between species in an ecosystem. It has been concluded that empirical use of $NOEC_{field} = NOEC_{lab}$ or $NOEC_{field} = 0.1 \ LC_{50lab}$ works just as well, or better than the log-logistic model (Rijtema *et al.*, 1993).

ACCEPTABILITY OF RISKS

Human

Society has a desire to achieve zero risk for pesticides in water. Coupled with an exaggerated perception of the risks from pesticides, this has lead to extremely demanding standards and a willingness to bear much higher costs than those expended on reducing other risks. For example, in the USA it has been estimated that the 'cost per premature death averted' for the atrazine and acetochlor standards is $92,000 M compared to $3.2 M for car rear seat belt standards (UK, 1993).

The setting of such low risk levels is a major challenge to toxicologists, *eg* for estimating pesticide levels which would cause extremely small increases in cancers, such as one in a million (US EPA, 1990).

Environment

Processes for defining acceptable environmental effects of pesticides on ecosystems are poorly developed and it is usually done on an *ad hoc* case by case basis.

One of the few examples of the scientific assessment of acceptable risk is in the area of soil microbial ecology (Domsch *et al.*, 1983). Side effects of pesticides on populations and functions of soil microorganisms are evaluated by comparison with the effects inflicted by natural stress factors such as fluctuations of temperature, rainfall, pH, physical disturbance of soil, nutrient supply and biotic interactions. Based on an extensive database, it was proposed that reversible side effects causing delays of restitution of microbial parameters up to 30 days are normal, those resulting in delays of 60 days tolerable, but those with delays of more than 60 days may be critical.

A similar approach could be adopted for a range of types of aquatic bodies. For example, localised effects of pesticides on aquatic organisms in a farm ditch would be acceptable if the size and duration of the effect was less than that caused by other stresses, such as the ditch drying out in summer or the mechanical dredging out of the ditches. In contrast, much smaller effects might not be acceptable in a natural stream in a nature reserve.

REGULATION

Pesticides are highly regulated. For example, EU Community legislation in summarised in Figure 2. Many Directives relate to water, for example:

Placement of plant protection products on the market (91/414/EEC)

Groundwater (80/68/EEC)

Surface water (75/440/EEC)

Drinking water (80/778/EEC)

Discharges of dangerous substances into water (76/464/EEC)

Ecological quality of water (COM(93)680 final)

Many of these are still under development or being revised.

Human

Many countries have adopted standards for pesticides in drinking water, based on their toxicity, using procedures similar to those recommended by WHO. For example, the US EPA have issued drinking water standards for a range of pesticides (US EPA, 1993). The UK Department of Environment have also published advisory values for some 40 pesticides (UK, 1993).

In contrast, the EC Drinking Water Directive (80/778/EEC) sets a level of 0.1 µg/litre for individual pesticides and a total of 0.5 µg/litre for

all pesticides combined. The 0.1 µg/litre limit is believed to have been based upon a one time detection limit for organochlorine insecticides (in particular DDT) and as such is widely regarded as a surrogate for zero. This limit was thus set with regard to the limitations in detection methods, rather than on the basis of toxicological data. Toxicological based limits are 10 to 1000 times higher for most pesticides (UK, 1993). The EU drinking water limit is not only unscientific, but completely illogical considering the EU uses toxicity based limits for setting residue limits in food and for residues of other types of chemicals in water. Compliance with the 0.5 µg/litre limit for all pesticides combined can not be monitored. This would require analytical methods with limits of detection of less than 0.001 µg/litre for each pesticide, which generally is not feasible.

The 0.1 µg/litre is an extremely difficult target. For example, it is equivalent to only 0.01% of a pesticide applied at 1 kg/ha/year, assuming a typical groundwater recharge rate of 20 cm/year. There have been many detects of pesticides in drinking water at levels between 0.1 µg/litre and the toxicological based limits. This is forcing water suppliers to spend large sums of money in order to comply with the Drinking Water Directive. In the UK alone, the cost has been estimated to be around £1 billion (UK, 1993). This money would give a much greater benefit to society if spent on other projects, such as removing lead pipes or improving sewage treatment facilities. The alternative of banning a wide range of pesticides would put European farmers at a severe disadvantage compared to their competitors in countries which take a more scientific approach to risk assessment. It would also greatly increase the risks associated with increased mechanical weed control, such as:

Increased deaths and injury to farmers and wildlife through physical injury by tractors and machinery.

Increased erosion due to excessive soil tillage, damage to soil structure, loss of soil organic matter by stimulation of microbial activity, reduction in some beneficial organisms, such as earthworms.

Reduced areas devoted to forests and wildlife habitats due to need to drain wetlands and remove more tropical forests to compensate for reduced crop yields.

The EU Drinking Water Directive is being reviewed and revised, and it would be hoped that it would include a more scientific approach to setting pesticide limits. Unfortunately, the signs are not encouraging, *ie* politics is still overruling good science and this will continue to divert funds from areas where it could be spent with much greater benefit to society. In the latest proposal, the 0.1 µg/litre limit has been retained, although the 0.5 µg/litre limit for total of all pesticides has been dropped.

Annex VI to the EU Pesticide Directive (91/414/EEC) lays down the criteria for setting limits in ground and surface waters. An area of great controversy was whether or not the Drinking Water Directive limits should be extended to groundwater. Some countries, such as UK preferred toxicologically based limits while others, such as Denmark and the Netherlands, preferred to extend the 0.1 µg/litre limit to groundwater. The compromise was that countries can either extend the Drinking Water limits to groundwater or give a conditional authorisation for five years;

the conditions being related to further monitoring or changing use patterns to reduce concentrations in groundwater to the drinking water limit.

<u>Environment</u>

Most countries have adopted the quotient method to protecting aquatic ecosystems. However, the values of quotients equated to presumption of no risk differ (Table 2), although these differences can be counterbalanced by different procedures for estimating the PEC values. The EU limits are particularly severe. However, Annex VI to 91/414/EEC allows registration of the product if "it is clearly established through an appropriate risk assessment that under field conditions no unacceptable impact on the viability of exposed species (predators) occurs - directly or indirectly - after use of the plant protection product according to the proposed conditions of use".

TABLE 2 Evaluation criteria (fish/aquatic invertebrates). There is no concern if predicted environmental concentration (PEC) is less than specified values.

Scientific evidence	US EPA	EU (Annex VI)
$<1/10$ LC_{50} $<NOEL$	$<1/10$ LC_{50} $<NOEL$	$<1/100$ LC_{50} $<1/10$ NOEL

The probablistic approach to risk assessment has not been formally incorporated into regulatory schemes. However, it is increasingly used in Tier 2 risk assessments.

Regulations are placing an increasing emphasis on mitigating risks, usually by developing use patterns which minimise exposure of humans and wildlife.

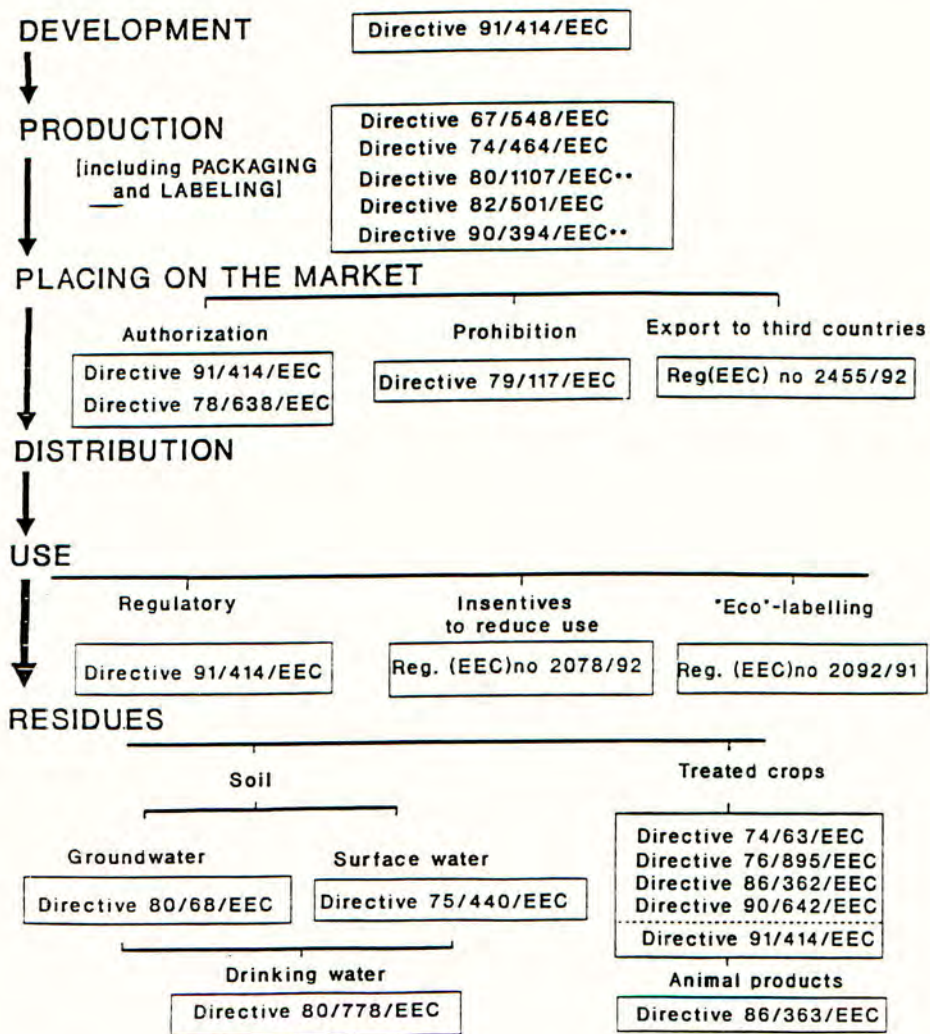CLASSIFICATION AND LABELLING

For general chemicals, classification and safety labelling is mainly aimed at accidental releases into the environment. The classification is based on the intrinsic properties of the chemical, *eg* fish toxicity and the percentage of the chemical in the final product. The R (Risk) and S (Safety) phrases are related to the classification.

Labelling of pesticides is very detailed, often consisting of attached pull-out sheets or small booklets, rather than just a simple stick on label. Labelling is based on risk assessment, rather than just the intrinsic properties of the chemical, *ie* it takes into account the likely exposure as well as toxicity. The EU Pesticide Directive includes Annexes aimed at harmonising R & S phrases, although these have not yet been written. An area of current debate is whether or not the classification of pesticides should be included in the General Chemical Directives or in a separate Pesticide Directive.

Scientists should play an active role in developing the classification and labelling schemes, rather than leave it solely in the hands of the regulators and politicians.

FIGURE 2 Overview of existing Community legislation related to plant protection products (Scharpé, 1994). (Main basic legislative instruments)*

DEVELOPMENT | Directive 91/414/EEC

PRODUCTION
[including PACKAGING and LABELING]

Directive 67/548/EEC
Directive 74/464/EEC
Directive 80/1107/EEC**
Directive 82/501/EEC
Directive 90/394/EEC**

PLACING ON THE MARKET

Authorization	Prohibition	Export to third countries
Directive 91/414/EEC Directive 78/638/EEC	Directive 79/117/EEC	Reg(EEC) no 2455/92

DISTRIBUTION

USE

Regulatory	Insentives to reduce use	'Eco'-labelling
Directive 91/414/EEC	Reg. (EEC)no 2078/92	Reg. (EEC)no 2092/91

RESIDUES

Soil

Treated crops

Groundwater	Surface water
Directive 80/68/EEC	Directive 75/440/EEC

Directive 74/63/EEC
Directive 76/895/EEC
Directive 86/362/EEC
Directive 90/642/EEC
Directive 91/414/EEC

Drinking water
Directive 80/778/EEC

Animal products
Directive 86/363/EEC

•only basic text is mentioned, not amendments, not implementation measures
••worker protection aspects, may also concern use and distribution

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USING CATCHIS TO ASSESS THE RISK TO WATER RESOURCES FROM DIFFUSELY APPLIED PESTICIDES

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ABSTRACT

A knowledge of how the local risks to water resources vary within a catchment is vital if those resources are to be effectively monitored and managed. Any risk assessment thus needs to take into account the spatial and temporal variation of the factors which determine pesticide environmental fate. A methodology for such a risk assessment procedure is described, based on models which integrate the variation of climate, soil, hydrogeological and hydrological characteristics within the landscape with pesticide physico-chemical properties and usage patterns. The methodology has been implemented within a Geographical Information System using APIC systems software. A straightforward hierarchical series of menus allow the user to examine the vulnerability of and risk to water resources within the Severn Trent Water region as well as accessing basic data on the quality and supply of water at abstraction points. An overview of the resulting catchment information system, CatchIS, is given.

INTRODUCTION

The EC drinking water quality standard of 0.1 µg per litre for individual pesticide compounds (EC, 1980) has imposed stringent obligations on those responsible for the management and supply of water. Firstly, in order to monitor pesticide concentrations in raw water resources, regular and reliable analyses of pesticides, often at very low levels, are necessary. Secondly, many supply companies need to treat their raw waters with granular activated carbon and/or ozone to ensure that the quality standard is met. The combination of regular pesticide analysis and water treatment is very expensive. In some cases, treatment may eventually increase production costs by up to £8 million per year, whilst during 1993, Severn Trent Water spent over £1 million on pesticide analysis alone (Court *et al.*, 1995).

If such costs are to be reduced, it is imperative that pesticide analysis is effectively targeted on those areas where the combination of pesticide properties, local usage patterns and environmental characteristics are likely to give significant residual concentrations in water resources. In the long term, it is more important to minimise the reliance on treatment by developing management strategies that reduce the impact of pesticide usage on water resource quality. Both these solutions require an ability to integrate the many factors which determine pesticide fate in the environment, so that those areas and factors that give rise to the greatest environmental impact can be identified. A methodology for such an integrated approach to

assessing the risk to water resources from pesticide usage has been outlined by Hollis & Brown (1993).

This paper describes how the methodology has been implemented within a Geographical Information System (GIS) using software that links models with both spatial and parameter databases. The resulting Catchment Information System (CatchIS), developed by the Soil Survey and Land Research Centre and Severn Trent Water Ltd., enables the user to produce spatial assessments of both the vulnerability of water resources to a range of agriculturally applied pesticides and the subsequent risk to water quality associated with their use within the Severn Trent region.

CATCHIS OVERVIEW

A thematic overview of CatchIS is given in Fig. 1. It is operated on a powerful IBM/RS6000 RISC workstation running the AIX operating system, using the 'object based' APIC spatial application development environment developed by APIC Systems. This possesses powerful spatial object data modelling capabilities and is particularly appropriate for applications such as CatchIS which require high performance handling of large volumes of spatial and non-spatial data (Timms, 1992; Shore, 1992). CatchIS utilises a number of core databases derived from LandIS (Hallett *et al*, in press) comprising information on:

The spatial variation of agroclimatic characteristics describing the start and duration of the field capacity period and the volumes of excess winter rain (Jones & Thomasson, 1985) at 5 km x 5 km raster resolution.

The spatial variation of soil series as shown on the regional 1:250,000 scale soil maps of England and Wales (Soil Survey Staff, 1983), at 100 m x 100 m raster resolution.

Ordnance Survey 1:250,000 scale vector data describing the surface hydrological network, roads, railways, settlements and other features.

Ordnance Survey 1:50,000 scale raster data showing 'Landranger' map features as a passive backdrop.
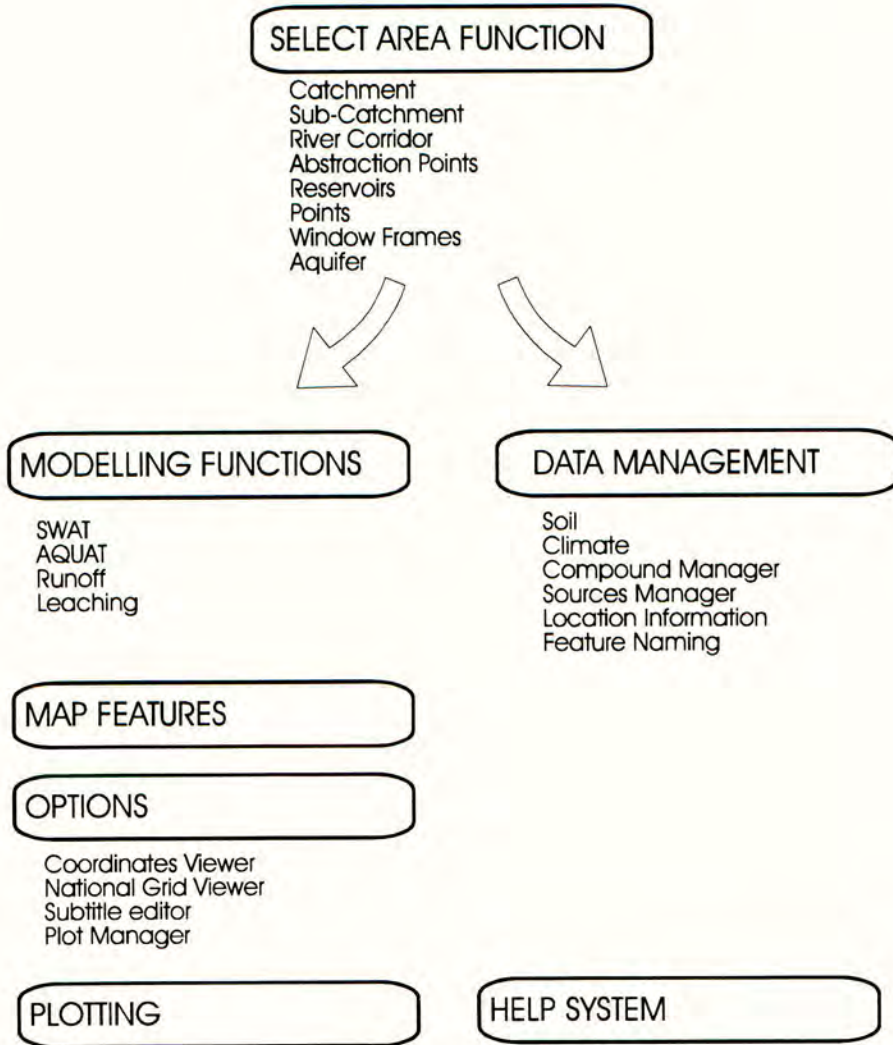
Vector data defining the boundaries of river catchments and subcatchments as standardised by the National Rivers Authority.

Vector data defining the boundaries of reservoir catchments.

Tabular data describing the physicochemical properties, average application rates, target crops, average application dates and estimated crop interception factors for over 100 of the most commonly used pesticide compounds within the Severn Trent region.

Tabular data for surface and groundwater abstraction points, including georeferences, licence details, abstraction rates and other important information.

Fig 1. Thematic overview of CatchIS

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┌─────────────────────────────────┐
│ SELECT AREA FUNCTION            │
└─────────────────────────────────┘
     Catchment
     Sub-Catchment
     River Corridor
     Abstraction Points
     Reservoirs
     Points
     Window Frames
     Aquifer
```

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┌─────────────────────────────┐      ┌─────────────────────────────┐
│ MODELLING FUNCTIONS         │      │ DATA MANAGEMENT             │
└─────────────────────────────┘      └─────────────────────────────┘
   SWAT                                  Soil
   AQUAT                                 Climate
   Runoff                                Compound Manager
   Leaching                              Sources Manager
                                         Location Information
                                         Feature Naming
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┌─────────────────────────────┐
│ MAP FEATURES                │
└─────────────────────────────┘
```

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┌─────────────────────────────┐
│ OPTIONS                     │
└─────────────────────────────┘
   Coordinates Viewer
   National Grid Viewer
   Subtitle editor
   Plot Manager
```

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┌─────────────────────────────┐      ┌─────────────────────────────┐
│ PLOTTING                    │      │ HELP SYSTEM                 │
└─────────────────────────────┘      └─────────────────────────────┘
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Tabular data relating soil series to run-off and leaching potential classes and, for each of these, describing the physical characteristics of each distinct soil and substrate layer from the soil surface to the estimated average upper surface of groundwater, for each of four different land uses, arable, short term rotational grass, long term grassland and 'other' land under semi-natural or recreational use.

Additional datasets describing the spatial variation of crop types at 2km x 2km resolution, derived from the Ministry of Agriculture Fisheries and Food parish agricultural census for

1993 and defining vector boundaries of aquifer resource and management units, will be added during 1995.

Using the APIC development environment, software routines have been written that enable the user to manipulate, interact and interrogate the databases using a series of functions initiated via a hierarchical system of menus. **Select area functions** enable the user to focus on an area of interest. This may be a surface water catchment, a subcatchment, a river corridor, a circular area of user-specified radius around a borehole abstraction point, or, eventually, an aquifer resource or management unit. Having selected the area of interest, **modelling functions** allow the user to map the distribution of different classes of run-off potential and leaching potential within the area, run models that assess the pesticide-specific vulnerability of, or risk to, local surface or ground waters and to map the results. **Map features functions** allow the addition of Ordnance Survey vector or raster map data as background to the mapped areas and a **plotting** function enables any generated map to be printed on an appropriate plotter. Other **options** can be used to facilitate identification of specific locations on the mapped areas, edit map titles or specify types of plotters, whereas **data management functions** enable the user to view, add or delete items in the pesticide compound and abstraction sources databases and to carry out location specific interrogation of the soil and climate databases. Finally, a context sensitive **help system** is available at all stages in the menu driven system.

USING CATCHIS FOR INTEGRATED RISK ASSESSMENT

Both surface and ground water risk assessments are made using models which integrate seasonally dynamic factors relating to pesticide usage, land management and weather, with more intrinsic but spatially variable factors relating to soil, hydrogeological and hydrological characteristics. The models, called SWAT (Surface Water ATtenuation) and AQUAT (AQUifer ATtenuation), have been described by Hollis (1991) and Brown & Hollis (in preparation). They are based on the attenuation factor concept developed by Rao *et al.* (1985) and Leonard & Knisel (1988) and also utilise the direct, empirically-derived link between soil types and stream flow, established during the Hydrology of Soil Types (HOST) project (Boorman & Hollis, 1990).

The way in which the models are used to make pesticide specific vulnerability assessments has been described by Hollis (1991) and Hollis & Brown (1993). These vulnerability assessments are converted into a risk assessment by integrating information on pesticide usage patterns and water quality criteria into the procedure. Using CatchIS, an area-specific risk assessment is initiated by choosing whether a surface or ground water assessment is required. The user is then asked to select the pesticide of interest and its target crop and the appropriate model is then run for each unique combination of climate, soil and hydrogeological or hydrological characteristics within the selected area. These unique combinations are defined by intersecting the spatial soil and climate datasets, variation in hydrogeological and hydrological characteristics being derived directly from the soil dataset using HOST criteria. For each unique soil and climate combination, relevant data are selected from the soil parameter and climate datasets and combined with appropriate data from the pesticide database to be used as input parameters for the models.

In order to take into account the uncertainty attached to measured values of pesticide adsorption coefficients and degradation rates, models are run for both 'best-case' environmental conditions (shortest half-life and greatest adsorption) and 'worst-case' ones (longest half-life and smallest adsorption). This gives a predicted maximum and minimum pesticide concentration likely to impact on any adjacent stream or top of the underlying groundwater body as a result of diffuse applications. Finally, it is necessary to take into account the decrease in these predicted pesticide concentrations resulting from dilution by waters reaching the water body from areas not treated with the specified pesticide. This is done by decreasing both maximum and minimum predicted concentrations by a factor determined from the percentage cover of the target crop. The resulting values represent the likely maximum and minimum predicted environmental concentrations for a given agricultural usage scenario. They are converted into a risk assessment by comparison with water quality or toxicological standards. Thus, where the predicted maximum environmental concentration is less than the standard, the risk assessment is *low* and where the predicted minimum environmental concentration is greater then the standard, it is *high*. All other results will be between these two and can be assigned to intermediate risk categories depending on the exact relationship between the predicted maximum and minimum concentrations and the standard comparison value.

For CatchIS, the standard for comparison is the EU drinking water quality standard of 0.1 µg per litre and the resulting assessments show the relative risks that local water resources will exceed this threshold as a result of agricultural pesticide usage.

CONCLUSIONS

Assessments of the risk to water resource quality posed by diffusely-applied pesticides must take into account a variety of environmental and agronomic factors, many of which vary both in space and time. The GIS object-based approach adopted in CatchIS allows the user to integrate many types of data covering all the main factors that determine the potential environmental impact of pesticides used in agriculture. The resulting spatial risk assessments enable water resource monitoring to be effectively targeted. In the longer term, effective protective measures can be developed and focused on those areas where they will have the greatest impact.

ACKNOWLEDGEMENTS

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USE OF A PESTICIDE MONITORING SYSTEM (PEMOSYS) FOR THE RISK ASSESSMENT OF PESTICIDE LEACHING POTENTIAL   -   CONCEPT FOR POST REGISTRATION ACTIVITIES

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ABSTRACT

According to a recommendation of the FAO and a guide-line of the EEC, post-registration activities to investigate long-term effects of pesticides should be carried out in all member countries. This includes both the assessment of the behaviour (chemical monitoring) and of side effects (biological monitoring). PEMOSYS was developed to facilitate a large-scale monitoring using a wide range of soils and climatic conditions (scenarios). Maps show soil classifications according to the German guideline and measured soil properties. They are the base for using simulation models and/or rule-based approaches for the assessment of potential risk of groundwater contamination. An intelligent data base of soil and pesticide properties and weather data delivers all information necessary for running the system. Examples are given to show the influence of horizontal variability of soil properties on the predicted results.

INTRODUCTION

Even when pesticides are applied properly and only for the intended purpose, a certain risk of environmental contamination remains. Therefore, in some justified cases post registration studies regarding the behaviour and persistence of pesticides are required according to a recommendation of the FAO and a guide-line of the EEC. In order to meet this demand as efficiently as possible, the expert system PEMOSYS has been developed (Pestemer & Günther, 1993). This system facilitates the simulation of the behaviour (degradation and leaching) of pesticides. The prototype includes three main parts (ANPROG, CHEMPROG and VARLEACH), which can use the same data base. ANPROG: long-term prediction of pesticide residues in the upper 10-cm-layer of soil after repeated applications; CHEMPROG: the assessment of groundwater contamination hazards using rule-based systems; VARLEACH: for prediction of the distribution of pesticides in the soil profile using the implemented simulation model (Walker, 1987). As a framework, a 'Geographical Information System' (GIS) has been chosen, which enables a clear presentation of stored data and simulated results imbedded in maps of the respective region. As reference areas, mainly the well investigated experimental sites of the Federal Biological Research Centre with a wide range of soil and climatic conditions will be included. Using PEMOSYS, possibly critical situations in certain ecosystems or regarding soil or climate conditions can be detected quickly, and if neccessary, further studies at the critical sites can be carried out.

This article describes the use of the PEMOSYS component VARLEACH to assess possible leaching hazards after herbicide use in a practical scenario with varying soil conditions. Examples are given to show the influence of horizontal variability of soil properties on the predicted results for selected pesticides. As a conclusion a proposal for environmental risk assessment of simulation results in cooperation with the registration authorities is given.

MATERIAL AND METHODS

Selection of a scenario

Topographic maps and maps of the experimental fields of the BBA including soil information according to the German guideline for soil classifications (Anon. 1982) and grid sampling data of measured soil properties are the base for using the simulation models and/or the rule-based approach for the assessment of potential risk of groundwater contamination. Selecting a site or a part of it in a map automatically delivers all available soil properties for the selected part to the chosen component of PEMOSYS. In this study, the model VARLEACH was used to simulate pesticide residue distribution in the top 30 cm of the soil in three layers of 10 cm each.

Pre-emergence herbicide treatments in winter wheat with Fenikan (62.5 g diflufenican + 500 g isoproturon/l) or with Tribunil (70% methabenzthiazuron) were simulated. Fenikan is applied at 3 l/ha (187.5 g/ha diflufenican + 1500 g/ha isoproturon), and Tribunil at 4 l/ha (2800 g/ha methabenzthiazuron). Application was set to 15.10.1994 and simulation was run for 9 months until 15.07.1995. In these cases long-term weather data (30-year average) are used. A site in Berlin-Dahlem with a sandy soil (loamy to silty sand) and low to average organic carbon content (0.72 to 3.03%) was selected. The variation of soil types and properties in the plough layer (top 30 cm) is shown in Table 1. The field, divided into 103 areas of 625 m² (25 m grid) each, clearly shows a variability in the organic carbon content which has a significant influence on the leaching behaviour of pesticides.

Table 1: Soil variability in the experimental field of the BBA in Berlin-Dahlem (103 soil samples; 0-30 cm);
Soil types according to the German guideline (Anon. 1982): S - Sand; Sl2, Sl3 - loamy Sand with different clay contents; Su - silty Sand; Ls - sandy Loam. Field capacity estimated according to the German guideline

Soil type	S	Sl2	Sl3	Su	Ls
Number of Samples	3	42	35	22	1
Clay (%)	4 - 5	5 - 8	8 - 14	1 - 5	22
pH	6.4 - 6.9	4.3 - 6.8	5.7 - 7.0	5.9 - 6.8	6.0
C_{org} (%)	1.47 - 3.03	1.10 - 2.70	0.72 - 2.61	0.87 - 2.74	1.22
Field Capacity (Vol.%), estimated	18	22	27	24	34

The influence of soil properties on modelling results with VARLEACH is mainly depending on the adsorption and degradation parameters and the field capacity used as input values. Therefore the selection of appropriate input parameters is very important.

Selection of input parameters

The intelligent data base of soil and pesticide properties and weather data automatically prepares all information stored about this site for model input. Missing data, e.g. field capacity, can be estimated using pedotransfer functions and other implemented relationships. Bulk density, because usually unknown, is set to 1.4 kg/l.

Very important in this respect is the selection and estimation of adsorption parameters. The database contains measured K_d-values together with the soil properties under which they were determined. They are selected automatically by matching the stored soil with the soil to be used in the simulation scenario. For the adsorption, the organic carbon content of the soil is the main determining factor. Therefore the difference in percentage of the organic carbon between the soil used for the simulation and the closest stored reference value must not exceed 0.2. If no suitable K_d-value is available it will be calculated from the K_{oc}-value stored in the database using the organic carbon content of the soil according to the formula : $K_d = K_{oc} \times C_{org}$ / 100. If even the K_{oc} is missing, K_{ow} or log K_{ow}-values which are readily available from literature for all pesticides are used to calculate K_{oc}-values. Many approaches have been used (e.g. Briggs, 1973, Karickhoff et al., 1979, Karickhoff, 1981, Matthess et al., 1985). The results of the calculations are quite different, e.g. for isoproturon (log K_{ow} = 2.48) from 82.7 (acc. to Briggs, 1973) to 228 (acc. to Matthess et al., 1985). Karickhoff's (1981) formula $K_{oc} = 0.411 * K_{ow}$ has frequently been used (e.g. Di Guardo et al., 1994) and was therefore chosen for the calculation in PEMOSYS.

Table 2: Characterization of input parameters used for the simulation of leaching and dissipation behaviour of Tribunil (methabenzthiazuron -MBT-) and Fenikan (diflufenican -DFF- + isoproturon -IPU-) in soil at the BBA experimental field in Berlin-Dahlem
all K_d-values derived from K_{oc} acc. to: $K_d = K_{oc} * C_{org}$ / 100

Soil type	S	Sl2	Sl3	Su	Ls
K_d (MBT) K_{oc}: 179.4	2.64 - 5.43	1.98 - 4.85	1.29 - 4.68	1.56 - 4.91	2.19
K_d (DFF) K_{oc}: 32647	480 - 989	361 - 883	235 - 852	285 - 894	399
K_d (IPU) K_{oc}: 124	1.82 - 3.76	1.37 - 3.35	0.89 - 3.24	1.08 - 3.40	1.51
A, B, E_a for IPU [% C_{org} / % clay]	330/1.22/47 [1.02/4.6]	330/1.22/47 [1.02/4.6]	130/0.8/42 [1.70/14]	330/1.22/47 [1.02/4.6]	59/0.3/45 [1.04/18.8]
(Gottesbüren 1991)		62/0.38/40 [0.46/7.1]	62/0.38/40 [0.46/7.1]	62/0.38/40 [0.46/7.1]	
DT_{50} (MBT)	146 d (16% Moisture, 20°C), from lab exp. (Bunte, 1991)				
DT_{50} (DFF)	160 d (15% Moisture, 12°C), from field exp. (Günther et al., 1994)				
DT_{50} (IPU)	17 d (14% Moisture, 20°C), from lab exp. (Pestemer, 1985, pers. com.)				

As degradation parameters, ABE-values describing moisture and temperature dependence according to Walker (1974) are used, if available. They are stored in the database with the soil properties and the temperature and moisture conditions for which they have been determined. Clay and organic carbon content are the determining factors for the selection here. If no ABE-values are stored for the chemical in question, laboratory half-lives will be used and ABE-values are estimated by the program. E_a (activation energy) is set to the average values 50 kJ/mol and B (slope of the soil moisture - half-life relationship) to 1 (Walker, 1994, pers. com.). The A-value (half-life at 1% moisture) can then be calculated according to the formula $H = A * M^{-B}$ where H is the half-life at moisture content M, and A and B are constants (Walker, 1974).

In this simulation scenario, measured ABE-values were only available for isoproturon. Since they are selected to match clay and organic carbon content, four different sets have been used for the different soil types. They are listed in Table 2. Half-lives (see also Table 2), on the other hand, are used for all soils. For isoproturon, both options were used for comparisons. K_d-values were estimated for all three compounds from K_{oc}-values, which were derived from K_{oc} (Karickhoff 1981). The range of calculated K_d-values used is also shown in Table 2.

RESULTS

For methabenzthiazuron residues were simulated in the top two layers for most of the samples (Table 3), but in all of them the main amount stayed in the top 10 cm. Residues in this layer were between 1089 and 1444 µg/kg or 54 and 72% of the initial application rate, resp. In the 10 to 20 cm layer, residues were between 0.2 and 123.5 µg/kg or 0.02 and 6.2% of the initial. Only for the two samples with the lowest organic carbon content (0.72 and 0.87%) leaching was down to the 20-30 cm layer, but only in very small quantities

Table 3: Leaching depth for 3 herbicides and all soil types, calculation using laboratory half-life (see Table 3), K_d from K_{oc} according to Karickhoff (1981, eq. 6)

	IPU	DFF	MBT
	number of samples		
- 10 cm	6	103	1
- 20 cm	96	-	100
- 30 cm	1	-	2

(0.9 and 0.1 µg/kg, resp.). The highest residues were found in the sandy soils with low field capacity, the lowest in the sandy loam which had the highest field capacity.

Diflufenican showed a slow degradation and very low leaching ability (Table 3). In all 103 samples, regardless of the varying soil properties, residues remained in the top 10 cm of the soil. They ranged from 56 to 80 µg/kg soil or 42 to 60% of the initial application rate, resp. As for methabenzthiazuron, residual concentration was related to field capacity.

The leaching behaviour of isoproturon was similar to methabenzthiazuron, although overall residues were much lower. Using half-life, in 96 of 103 (or 93%) samples leaching to the 10-20 cm layer was simulated (Table 3). Only for one sample with 0.72% organic carbon, simulated leaching was down to the 20-30 cm layer (0.1 µg/kg soil). Leaching depth was mainly depending on organic carbon content. From 0.87 to 2.53% C_{org} leaching was simulated to 20 cm depth, with higher organic carbon content only to 10 cm. Concentration in the top 10 cm was between 42.0 and 2.4 µg/kg (3.9 to 0.2% of the initial concentration). In the next layer (10-20 cm), the concentration did not exceed 4.0 µg/kg soil. As for the other two herbicides, the remaining overall concentration (0-30 cm) decreased with increasing field capacity.

Leaching depth of isoproturon calculated with ABE-values is shown in Table 4. With these input parameters leaching was even less and degradation faster. For about half of the samples, no leaching below 10 cm depth was simulated, with residues below 2 µg/kg soil. All simulations with deeper leaching used the ABE-value set "62/0.38/40" which was selected for 54 samples of the loamy and silty sand soils (SI2, SI3, Su). These simulations resulted in slightly higher residues than the other sets (2 to 5 µg/kg soil) which was probably the reason why quantifiable residues were found for 48 of them below 10 cm depth. The remaining six simulations with this set where no herbicide was found below 10 cm had a high organic carbon content.

Table 4: Leaching depth for Isoproturon, calculated with ABE-values (see Table 3), as distributed according to soil types and C_{org}-content. No herbicide was found below 20 cm depth.
K_d from K_{oc} according to Karickhoff (1981)

Soil Type	S	Sl2	Sl3	Su	Ls	Overall
Samples overall	3	42	35	22	1	103
- 10 cm	3	16	17	18	-	54
Kd (IPU)	1.82-3.76	1.37-3.35	1.59-3.24	1.43-3.40		1.37-3.76
- 20 cm	-	26	18	4	1	49
Kd (IPU)		1.46-2.47	0.89-2.52	1.08-2.21	1.51	0.89-2.52

DISCUSSION

Post-registration activities play an important role in the risk assessment procedure for environmental chemicals (including pesticides) according to the principles of the FAO (Anon., 1990). A part of this is the risk of pesticide leaching to the groundwater, which is in principle shown in Figure 1.
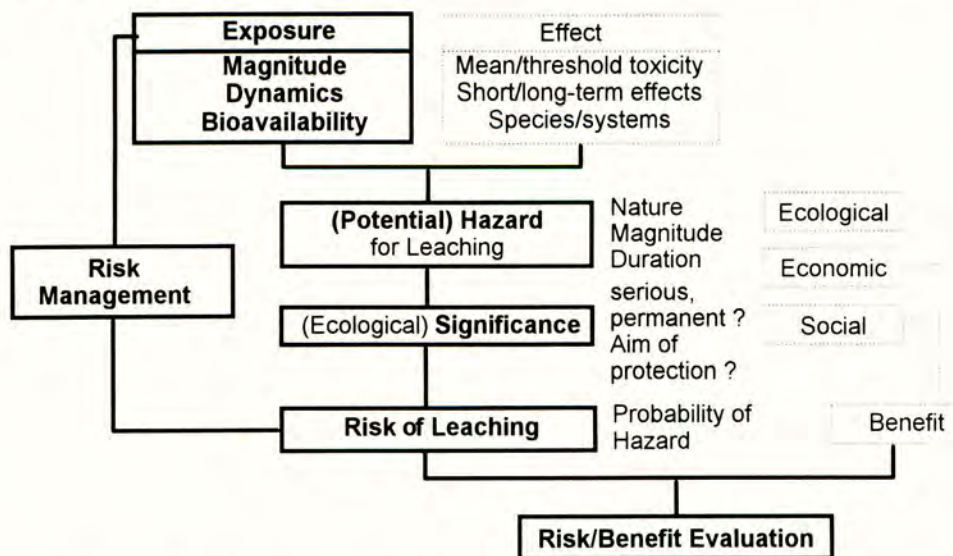
Fig 1: Risk evaluation and principles of environmental risk assessment of leaching potential as part of the post-registration process (according to FAO-principles of risk assessment, Anon., 1990)

The exposure is usually determined by sampling and analysis which is very expensive. But during this stage of pesticide use, informations on e.g. degradation and sorption in soil are usually available. They can be used as model input data and thus can provide us with a good estimation of possible environmental concentrations (magnitude) their dynamics (e.g. plant uptake, degradation) and bioavailability (using K_d-values). This knowledge in itself is

not sufficient for a risk assessment; only in relation to the potential environmental effects the potential leaching hazard can be estimated. The risk of leaching is then estimated taking into account the significance and probability of the potential hazard according to its seriousness and the importance of the aim of protection. Finally, risks and benefits of the pesticide under assessment have to be considered. If the leaching risk is too high, risk management has to reduce the exposure level. The resulting knowledge on exposure and/or effects provide the tools necessary for definite conclusions about the risks caused by pesticides in terrestrial or aquatic systems (Pflüger, 1994).

ACKNOWLEDGEMENTS

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SIMULATION MODELLING AND UK REGULATORY DECISION-MAKING:-
PERFECT PARTNERS OR WARRING FACTIONS?

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ABSTRACT

The use of modelling studies in regulatory submissions is currently of very limited value
since the models cannot be used in a predictive manner. This paper details a more
pragmatic approach to the use of simulation modelling in the regulatory process. Data
are presented to show how use can be made of an existing field study to compare
and/or calibrate the model outputs. This provides a degree of confidence in the output
of the model and with limited further extrapolation, meaningful results can be obtained
on the effect of different weather conditions from other countries or from different
years in the UK. The approach is amenable to use with soil or leachate concentrations
of pesticide depending on the model used. The limitations of the method are explored
and the possible uses are discussed in terms of current UK legislation and the
Authorisations Directive (91/414/EEC).

INTRODUCTION

Under the current Control of Pesticides Regulations (COPR, SI 1986/1510) and the
forthcoming implementation of the Authorisations Directive (91/414/EEC, Anon., 1991), data
must be submitted on the fate and behaviour of a pesticide in the environment in order to
attain a level of approval/authorisation. Only when this has been granted is commercial use of
the product allowed. These data have traditionally been obtained from the laboratory and the
field and together they help to predict the environmental fate of the pesticide.

Field studies are expensive to conduct and frequently have to be undertaken in the country
in which registration is sought. Often they provide results that are so specific for a particular
situation that they have limited value in the assessment of the fate of the pesticide at other
locations (both within a country and between countries). As a cheaper alternative, modelling
studies are sometimes used.

This discussion paper examines the ways in which models are currently used in the
regulatory system and seeks to suggest further ways in which their undoubted potential can be
channelled into providing better and more complete information on the environmental fate of
pesticides. It should be emphasised that these ideas do not constitute the present regulatory
position with respect to simulation modelling. Rather the intention is to move discussion
forward and to stimulate thought in both the industry and amongst regulators on how this
potentially powerful tool can be used to best enhance our knowledge on the fate and behaviour
of a given pesticide.

REGULATORY USE OF SIMULATION MODELLING

The number of simulation studies of pesticide behaviour in the environment has increased recently in regulatory submissions to the Pesticides Safety Directorate (PSD), the UK regulatory authority. These submissions are currently still made under national legislation but this will shortly be superseded by EC legislation. In the Uniform Principles (Anon., 1994) of this directive there are specified uses for models in obtaining Predicted Environmental Concentrations (PECs) of pesticides in soil, surface and ground water and air. Hence the use of modelling in regulatory submissions will continue to increase in the future.

Most modelling studies submitted to PSD to date concentrate on the likelihood of the pesticide of interest leaching through the soil profile into receiving waters (ground or surface) at levels which could breach the Drinking Water Directive (80/778/EEC, Anon., 1980) limit of 0.1 µg/l. Some studies modelling other processes such as surface run-off of pesticides have also been submitted but these will not be discussed further in this paper. Several different leaching models have been used in submitted regulatory studies due to the fact that, unlike some other regulatory authorities, it is PSD's policy not to specify the use of a particular model. However, it is the responsibility of the applicant to provide any information that will enable PSD to have confidence in the output of the chosen model.

Simulation studies currently submitted to PSD generally have a number of shortcomings which results in problems when regulatory decisions have to be made on the basis of their predictions. These shortcomings can be summarised in the following list:

1. The accuracy of the model is uncertain and when small differences in sensitive parameters have a large effect on the output data, there is no relevance in predictions of extremely small concentrations of pesticides in drainage waters.

2. Not all parameters used as inputs to the model can be measured and the assumptions made about their values are not always possible to assess (i.e. variation of degradation with depth, hold back factors etc.).

3. Very few of the current generation of models incorporate routines that can take account of macropore flow and since this can be a significant percentage of the flow in many soils (not just cracking clay soils) it is likely to have a major impact on the amount of pesticide transported to depth.

4. In some circumstances the submitted simulation studies have been conducted using a range of values for a given input parameter (i.e. adsorption coefficient and half life) and results given as a range of possible concentrations of pesticide in water below a depth of soil (often 1m). Hence it approaches a sensitivity analysis of the model rather than an evaluation of the fate of the pesticide and under these circumstances provides no useful information.

Most current modelling studies therefore result in an unsatisfactory substitution for real field data because the models cannot be used in a predictive manner. However, not to use models in the regulatory process would be an oversight as they are potentially very powerful tools for examining a wide range of scenarios. To overcome the problems that have been outlined above, co-submitted field study results could be used to provide a comparison with

model outputs. (This would be in addition to their current role in confirming the laboratory data.) The comparison of the models with field data would provide a greater degree of confidence in their subsequent output because they would already have been tested with real, and directly applicable, field results obtained using the compound of interest. Hence they can then be used with the same pesticide to investigate the effects of different climate scenarios.
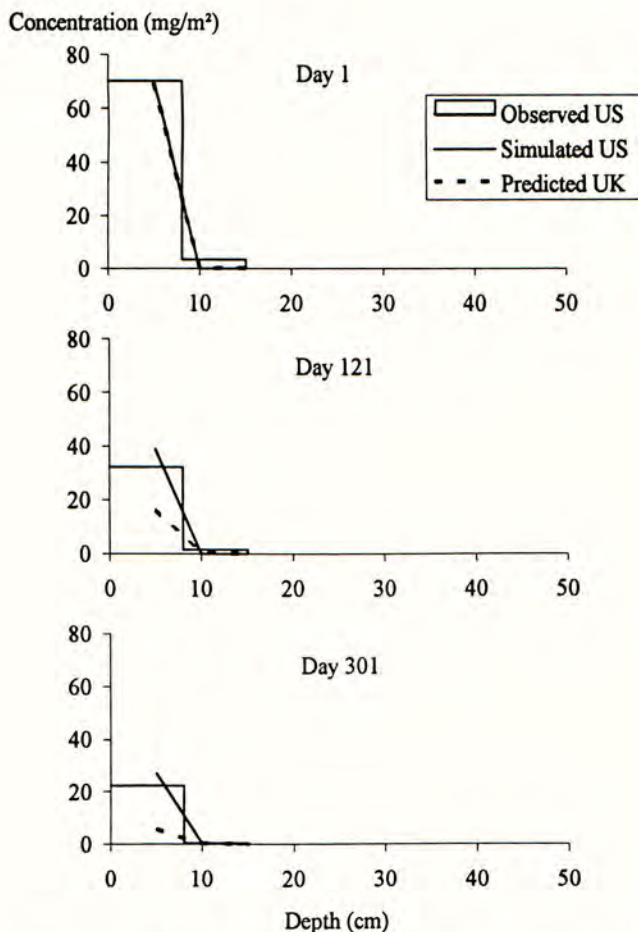

Figure 1. The observed and simulated concentrations of a non-mobile fungicide in soil in California and a prediction of the concentration of the same compound in the same soil in UK weather conditions.

RESULTS OF SIMULATION MODELLING

The use of field data to test models is demonstrated in the following two examples. In both cases the experimental data were taken from recent regulatory submissions.

Example 1

Data from a field study in a sandy loam soil in California on a non-mobile fungicide were used. These data showed gradual dissipation of the compound from the top (0-8 cm) soil layer and occasional residues above the limit of detection in the second soil layer (8-15 cm). Results at three dates after application (1, 121 and 301 days) are presented in fig 1.

The model PLM (Hall, 1994) was used initially to simulate this behaviour. Pesticide input parameters (half life, adsorption constant) were obtained from laboratory data and the daily climatic data from the Californian field site was obtained from the field study. Soil parameters typical of a sandy loam soil were taken from literature (Hall *et al.*, 1977) and the simulation was then undertaken using these inputs to ensure conditions were as close as possible to those of the field site.

The output of model simulated (fig. 1 solid line) the amounts of fungicide in the soil (in 5 cm segments) to be in reasonable agreement with the observed values. This provided a degree of confidence that the model gave sufficiently accurate results with this particular pesticide/soil/climate combination and the final stage of the modelling was then undertaken.

Using the same pesticide and soil input parameters as used for the previous simulation, a prediction was then undertaken with real UK weather data from a site in Eastern England and an application date within the timing of the proposed use in the UK. The final (broken) line in fig. 1 shows that in these weather conditions the model predicted that the fungicide degraded faster in UK conditions than in California.

Example 2

Leachate data were obtained from a lysimeter study in a sandy loam soil with a triazole fungicide. The data showed that no fungicide was leached from the soil core until day 260 and after this the cumulative amount leached increased slowly throughout the second year after application (fig. 2, crossed line).

The model PLM contains routines accounting for macropore flow and was used first to simulate the observed behaviour. The pesticide input parameters were laboratory values submitted by the applicant, soil data typical for a sandy loam soil were used (Hall *et al.*, 1977) and the daily weather data from the field site in Eastern England was provided. To ensure an acceptable fit (fig. 2 solid line) to the observed data one parameter was optimised. This parameter was the proportion of macropore flow, a value which cannot be measured directly.

Once the model was optimised for this scenario it was then used to predict the behaviour of the fungicide under different climatic conditions. The pesticide and soil input parameters (including the optimised hydrological input) were retained but the weather data from a different year were used. The results are shown as the dashed line in fig. 2.

In a different climatic situation where there was heavy rainfall shortly after application, the model predicts much faster breakthrough of the compound and a rather greater amount of the compound leached in total.
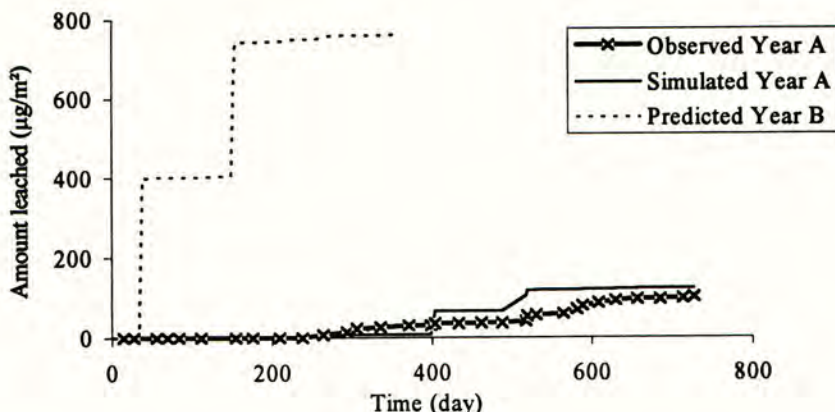
Figure 2. The observed and simulated losses of a triazole fungicide in leachate from a UK lysimeter study and a prediction of loss of the same compound from the same soil in different UK weather conditions.

DISCUSSION

The results presented above give two different examples of how simulation modelling can be used in an innovative manner to provide useful information for regulatory submissions. Example 1 details how a foreign field trial providing information on the concentration of pesticide in a soil profile can be compared to a simulation under the same conditions. Once the model output is shown to be in reasonable agreement with the field data, a different set of weather data can be substituted to provide a more reliable prediction of the behaviour of the pesticide in a relevant climate. Example 2 shows how the calibration of a model can be usefully undertaken for a given soil and pesticide combination. This can then be used to predict the behaviour of the pesticide in other weather conditions where rainfall or temperature patterns may lead to altered losses by leaching.

If these techniques are to be useful tools for simulation modelling in regulatory decision making a number of factors must be considered. First, the relevant model inputs should be easily obtainable (i.e. from the laboratory studies, literature etc.). It is not realistic to expect further detailed studies to be undertaken by registrants in order to obtain input data necessary to run the models. However, the level of detail of field study results must be sufficient to allow comparison with the modelled outputs.

Secondly, the calibration of a model must be undertaken with great care. It is essential that values such as the adsorption constant and the half life which are experimentally determined in the laboratory should not be altered during the calibration process. Only those inputs for which experimentally determined values are not available (e.g. the proportion of macropore flow) should be considered as changeable if any optimisation of the output is required.

Finally, the models that can be used in this manner depend largely on whether the accompanying field study provides data for soil or leachate concentrations of pesticide. Because the concentration of pesticide in the soil profile is not greatly affected, even when a significant amount of macropore flow is taking place, models used to simulate soil concentrations would not require macropore flow routines. However, models calibrated with the concentration of pesticide in drainage water, for instance from a lysimeter, would have to incorporate macropore flow routines since in non-chromatographic soils the solute concentration is extremely sensitive to this process. Models calibrated with concentrations of pesticide in soil would not be suitable to provide predictions of concentrations in leachate.

CONCLUSIONS

The use of models in the submission of regulatory packages is in its infancy even though their use in a research context is further advanced. Most current models are not of sufficient accuracy to be used in a purely predictive manner and therefore cannot be used as replacements for field studies in regulatory data submissions.

However, the potential for the use of models in regulation is great and at this stage there is scope for them to be used in a partially predictive manner alongside field data. As the aim of both industry and regulators is to construct an overall picture of the behaviour of a pesticide in the environment, this use of models should be seen as an advance that would provide useful data.

A justification for this partially predictive modelling could be made under the current UK national legislation for the extrapolation of foreign field data (which is often considered not applicable) to UK conditions. A similar role could be envisaged in the Authorisations Directive where it would also provide a firmer foundation for the calculation of PECs. Ultimately it is hoped that this method will result in a reduction in the number of field trials that applicants would need to perform to obtain widespread approval/authorisation.

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PESTICIDE SELECTION FOR MONITORING PRIVATE WATER SUPPLIES

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ABSTRACT

A method is described for selecting pesticides to include in monitoring programmes for private water supplies. Examples of results are presented. The assumptions made and the limitations of the data are discussed and some of their effects on the results are demonstrated.

INTRODUCTION

In England and Wales, the quality of private water supplies is regulated by The Private Water Supplies Regulations, 1991. These regulations prescribe standards of wholesomeness, including the maximum admissible concentrations (MAC's) for pesticides specified in the EC Drinking Water Directive. It is the duty of local authorities to sample and analyse private water supplies under these regulations. In the case of pesticides, local authorities are expected to select compounds for analysis according to the likelihood that they will be present in particular supplies. Department of the Environment guidance (DoE,1991) suggests this assessment can be made according to pesticide properties, pesticide usage, methods of use and local knowledge of crops grown in an area and by taking account of public water supply and NRA monitoring results. Accordingly a number of local authorities have approached ADAS seeking guidance on which pesticides should be included in their monitoring programmes.

At first sight this may seem a straightforward task. Guidance is not sought on whether pesticide MAC's will be exceeded, or even whether positive detections will be made. The objective is to prioritise the pesticides used in an area into an order of decreasing likelihood of being detected. However, to achieve this a number of major assumptions and estimates must be made which, as discussed in the following, greatly influence the final results achieved.

METHODOLOGY

The key parameters used in drawing up the priority listing are set out in Table 1. Pesticide usage is assessed by local knowledge of the crops grown in the area, the main pesticides used on those crops and the numbers and rates of applications. Non-crop and amenity pesticide usage is included if the relevant bodies make the data available. This gives the total weight used per year. Pesticide physicochemical properties, K_{oc} (distribution coefficient between soil organic carbon and water) and DT50 (time for 50%

loss under laboratory conditions), are obtained from published values, if available. If not, K_{oc} is calculated according to the formulae of Briggs (1981); DT50 is estimated from other, similar pesticides and persistence of efficacy.

TABLE 1. Parameters included in prioritising pesticides for analysis.

Parameter	Source
Pesticide usage (kg/y)	Local ADAS consultants
K_{oc}	Published values or calculation
DT50	Published values
Time of application	Local ADAS consultants

The parameters are combined to produce a numerical score. K_{oc} and DT50 are combined according to the formula of Gustafson, (1989):

$$GUS = lg (DT50) \times (4 - lg (K_{oc}).$$

The value obtained is multiplied by the weight used, (kg/year) and by a factor reflecting the time of year applied. Each month is attributed a number between one and ten, with late autumn and winter applications assumed to present the highest risk of water contamination and late spring and summer applications the lowest.

RESULTS

The result is a prioritised list, usually of 40 or 50 pesticides. Table 2 shows the top ten pesticides from one such list, prepared for a local authority in eastern England. Further guidance on selection for monitoring can be given according to specific concerns of the authority, such as mammalian toxicity.

TABLE 2. Pesticides judged most likely to be detected in water, for a local authority in eastern England.

1. Isoproturon	6. Carbendazim
2. Dimethoate	7. Mecoprop
3. Chlormequat	8. Chlorfenvinphos
4. Metamitron	9. Simazine
5. Aldicarb	10. Carbofuran

DISCUSSION

The reliability of the results depends on not only the accuracy of the data used but also the way in which these are combined. Consideration of the individual parameters identifies several weaknesses and some improvements are suggested.

Pesticide rate

Multiplying the GUS value by the weight of AI used per year assumes that the likelihood of reaching ground - or surface-water is directly proportional to the rate. This may not be the case, (Harris *et al.*, 1995), but in the absence of sufficient data to formulate a relationship other than a linear one, direct proportionality is assumed.

K_{OC} and DT50

The variability of these parameters is well recognised. Factors such as soil type and experimental conditions can have a major influence on the results obtained, yet these conditions are frequently not known when values from the literature are used. Further, it may not always be clear which formulation of a pesticide is being reported upon. For example, the esters of acidic herbicides will have higher K_{OC} and often lower DT50 values than the free acids, yet it is the free acids which are likely to be determined during water analysis. Calculating K_{OC} provides a useful check on reported values and the correction factor given by Nicholls and Evans, (1985), can be used to calculate an apparent K_{OC} for anions. However, this frequently leads to the dilemma of choosing between a single literature value with no background information and a contrasting calculated value.

Table 3 demonstrates the sort of variability encountered in the literature. The K_{OC} values for monolinuron show the range that can be obtained. The K_{OC} values for chlorthal-dimethyl and diclofop-methyl are high and would suggest these herbicides are non-mobile. In soil, the esters will hydrolise rapidly to the acids with much lower K_{OC} values. However, these latter values are not reported, nor even are the chemical data required to calculate the values. Table 3 also shows the difference in DT50 for fluazifop-butyl and fluazifop. Tomlin (1994) generally does not show such data for other esters.

TABLE 3. Examples of variability in reported values of K_{OC} and DT50.

Pesticide	K_{OC}	DT50
Monolinuron	250-500[1]	/
	71[2]	
Chlorthal-dimethyl	5000[3]	/
Diclofop-methyl	14000-24400[1]	
Fluazifop-butyl	/	< 1 week[1]
Fluazifop	/	< 3 weeks[1]

[1]Tomlin (1994); [2]Calculated (Briggs, 1981); [3]Wauchope *et al.* (1992).

GUS

The GUS index is widely used to combine K_{OC} and DT50. This may not be the best formula. It was devised to fit the pesticide monitoring results of the California Department of Food and Agriculture. Hence, it takes account of the rates and timings of pesticide use, soils, climate and other factors in California and is not necessarily a universal formula for combining K_{OC} and DT50.

Developing such a formula could be achieved in a lysimeter study by applying a range of pesticides with well-documented K_{OC} and DT50 values, at identical rates and under identical environmental conditions. A problem with this, mentioned by Gustafson, (1989), is the difference between laboratory and field DT50 values. This is particularly so for pesticides with significant losses by volatilisation: laboratory DT50 values will omit this pathway of dissipation. For the purposes of risk assessment, field values of DT50 would be better. However, other variables affecting DT50, in particular temperature and soil moisture content, must be standardised if K_{OC} and DT50 are to be combined in any simple formula. Inevitably this means laboratory values of DT50 will have to be used. A lysimeter study to investigate a "universal" formula for K_{OC} and DT50 should be devised with pesticides of negligible volatility, but the formula would carry the warning that it may not be appropriate for volatile compounds.

Time of application

It could be assumed that there will be no leaching of pesticides which are applied after soils have dropped below field capacity, because there is little or no drainage from the soil profile. This is unlikely to be correct. Storm events might lead to deep pesticide movement by preferential flow, even during summer. Such events might also move pesticides to sub-surface horizons, if not as far as ground or surface water, where their greater persistence may be sufficient to cause water contamination with later drainage. Persistence even in the top-soil may be sufficient for water contamination to occur in the following autumn. Such effects were found by Harris et al. (1994) with spring-applied isoproturon.

Hence some score, above zero, should be attributed to pesticides applied in summer. The problem is deciding what weighting should be attributed, according to time of year used and this part of the prioritisation method has least scientific basis. Multiplication of the score by between one and ten, according to time of use, may underestimate the effect. Traub-Eberhard et al. (1993) applying similar rates of isoproturon in November and chloridazon in April, (compounds with fairly similar K_{OC} and DT50 values) reported a peak isoproturon concentration in drainage water nearly four hundred-fold greater than for chloridazon. Perhaps, then, a 100-fold difference in weighting between summer and winter would be more appropriate. There is a dearth of information on which to decide, yet the results in Table 4 suggest the precise weighting may be of minor importance.

TABLE 4. Pesticides judged most likely to be detected in water, for a local authority in eastern England, a) weighted up to 100-fold or b) not weighted according to time of application.

a	b	a	b
1. Isoproturon	Isoproturon	6. Carbendazim	Mecoprop
2. Dimethoate	Metamitron	7. Mecoprop	Chlorothalonil
3. Chlormequat	Dimethoate	8. Chlorfenvinphos	Aldicarb
4. Metamitron	Chlormequat	9. Carbofuran	Chloridazon
5. Aldicarb	Carbendazim	10. Simazine	Chlorfenvinphos

In this table, the data for the catchment in Table 2 has been re-worked using either a maximum 100-fold weighting for winter versus summer use, or no weighting at all for time of year. Compared to Table 2, the results show that there was negligible difference in the ranking between a ten- and 100 -fold weighting. In contrast, a rather different list was produced if no weighting at all was used. Unless monitoring results are available, it is not possible to say which ranking is most accurate. A consideration of leaching processes suggests some weighting for time of application should be given, but the results above suggest the magnitude of this weighting is relatively unimportant.

CONCLUSION

The method described above is a very simple predictive model. It does not attempt to predict actual concentrations in water, only to bring some scientific basis into pesticide selection. Several additional factors could readily be taken into account. For example, no account is taken of soil type: it is assumed this is a constant for the relatively small catchments involved, though if pesticide usage varies with soil type in the catchment this may not be so. Accuracy would further be increased if individual private supplies were considered and pesticide use in the near-vicinity of springs and shallow wells given more weight. However, commercial pesticide analysis is offered in suites of compounds, (eg substituted ureas, triazines) and competition between laboratories is very strong. The point is soon reached when the cost of more accurate predictions is greater than analysis of readily available suites. Predictions are also likely to select a number of pesticides which cannot readily be analysed. Local authorities are then forced to drop these from their lists, perhaps substituting pesticides with a lower priority rating.

The method described would benefit from several refinements to improve its accuracy. Current and future research will, no doubt, permit this. The problem is, guidance is needed now and monitoring cannot wait until we have better data: decisions must be made on the knowledge and data available today.

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