

SESSION 7

POSTER SESSION B

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Volatilisation: an important route reducing pesticide leaching and persistence in soil

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ABSTRACT

Pesticide losses by volatilisation during and after application may represent an important dissipation factor. To assess the rate of volatilisation of malathion, ethoprophos and procymidone a field experiment was carried out using the *Theoretical Profile Shape* method and monitoring residues in the air continuously 2-3 weeks after the pesticide application. A bare silty loam soil was sprayed with the pesticides during Spring, Autumn and Winter. All pesticides volatilise as a function of air temperature and soil humidity, but solar energy during the day represents one of the main factors increasing the flux from the top soil to the atmosphere. In the winter experiment an estimated 0.2-15 % of the dose applied volatilised; during the autumn-spring experiment this rate increased enormously reaching the 60 % of the dose applied. The obvious consequence of this losses is a reduction in soil persistence and potential leaching of the pesticide studied.

INTRODUCTION

Pesticide dissipation via volatilisation from soil and plant surface as well as drift after the normal agricultural applications may be an important process. Most of the field measurements carried with different techniques report very intensive volatilisation sometime higher than 20 % from fallow soil (Willis G H *et al.*, 1972; Harper L A *et al.*, 1976; Glotfelty D E *et al.*, 1984; Glotfelty D E *et al.*, 1989). Volatilisation losses of this magnitude may influence the air quality and the pesticide persistence in field.

The rate and the nature of the pesticide which pass into the air are influenced by different factors such as the pesticide physico-chemical properties, the application techniques, the meteorological conditions and dissipation processes. The nature of the surface treated and the season of the application can also have an important impact. The volatilisation from soil surface may also be influenced by the soil organic matter and the mineralogical particles with which the pesticide is associated.

In this paper we report the results of the three field experiments carried out in different periods of the year where the volatilisation rate of three pesticides from fallow soil was monitored.

METHODS AND MATERIALS

Measurement of volatilization in the field

The experiment was conducted at the Rhône-Poulenc experimental station in the Emilia-Romagna region outside Bologna, lat. 44°31'N, long 11°17'E. The field is situated on a flat alluvial plain in the Po valley. Soil is silty loam with a 1.8 % content in organic matter and pH 7.8.

The volatilization rate from the soil surface is calculated according to:

$$V = \frac{[u(t)c(t)]}{\Omega} \Big|_{Z_{\text{inst}}}$$

where $u(t)$ is the wind speed and $c(t)$ is the pesticide concentration in the air at the sampling height Z_{inst} . The ratio of the horizontal to vertical flux Ω , can be obtained with the 'trajectory simulation method' (Wilson, 1982). This ratio depends on the surface roughness, Z_0 , and the upwind fetch distance (i.e. the radius of the treated surface). The roughness length was estimated by measurements of the wind speed at three heights two weeks prior to the sampling events. The roughness length was then obtained from the logarithmic wind profile where Z_0 is the intercept with the z axis. A value of 0.8 cm was obtained for both the sampling events (Capri *et al.*, 2000).

With the 'theoretical profile simulation', the hypothetical movement of the particles in the atmosphere are tracked from the source to the point of measurement. Since the height profiles of the theoretical position of the volatilised pesticides cross each other for stable and unstable atmospheric conditions, it is possible to identify a single height, Z_{inst} , where measurements can be performed for all atmospheric conditions. The value of Z_{inst} was calculated to be 67 cm with a corresponding value of 7.0 for Ω .

Pesticide application

Ethoprophos, Procymidone, Malathion were applied three times in December 1998, April and October 1999; Pyrimethalin was applied only in September 1999 (Table I). The pesticide application was performed with a hand carried sprayer with a boom of 5-m width in a quasi circle with 25 m diameter and an area of 495 m² (Figure 1). The air sampling started about 15 minutes after application and lasted 2 weeks in the experiment of December and April, 3 weeks in October.

The field measurements of volatilization in Bologna were performed with samplers consisting of a glass tube of 10 mm diameter containing a plug of polyurethane foam (PUF). These were connected with Teflon tubing to air sampling pumps (SKC LTD 224-PCX4) which were operated with an air flow of 2 l/min. The PUF sampling plugs were positioned at the centre of the circular plot at Z_{inst} height. Replicate samples were collected, but with differing sampling intervals. After exposure, the plugs were returned to their sample jars and kept frozen until analysis.

An automatic weather station on the field recorded hourly values of temperature, wind speed, wind direction, precipitation, air humidity, and solar radiation. Hourly values of soil surface temperature were also recorded with two sensors covered by a thin layer of soil and protected against direct sunshine.

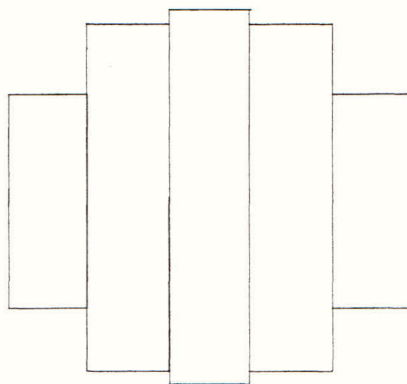


Figure 1. Representation of the pesticide treated area in Bologna. The pesticides were applied in 5 m segments (rectangles) with a total area of 495 m² reproducing a quasi-circle (dashed line) with an area of 491 m².

Validation of the air sampling procedure

For the measurement of airborne pesticide, the sampling equipment consisted of a glass tube of diameter 10 mm containing a plug of polyurethane foam (PUF), as described previously, which were operated with an air flow regulated at 2 L/min. The extraction procedure of PUF was carried using a triple extraction with acetone (50 mL for each extraction) by ultrasonic bath, followed by filtration with 10 g of anhydrous sodium sulphate. This was then concentrated under vacuum, and finally blown down to a volume of 1 mL under nitrogen flow. This 1 mL extract was used for the final GLC-ECD and HPLC analysis. Detection limit were 0.01 µg/L for ethoprophos, malathion and pyrimethalin and 0.1 µg/L for Procymidone.

The air sampling system adopted for the field study was developed by evaluating a number of different procedures following the air sampling methodology reported by the American Society for Testing Materials (ASTM, 1988). Recovery tests were also evaluated for each procedure as reported in Capri *et al.*, (1999).

RESULTS

The air temperature in December was on average 1.9 °C (−3.3 °C to 12.7 °C); in April 12 °C (3.5 °C ÷ 19 °C); in October was 15.0 (8.0 °C to 20.0 °C). Total rainfall was 34 mm and 35 mm in December and April respectively; in October we measured 57 mm between the 12 to 21 days after the pesticide application. On average the wind velocity was 0.6 m s^{−1} and 1.4 m s^{−1} in all the experiments.

Pesticide volatilisation showed a large variation between the night and morning in the first three days after the application, with the highest rate in the early afternoon where the temperature is high and lowest rate at night (Figure 2). The energy balance of the soil-atmosphere regulate the fluxes between the soil layer and volatilisation losses.

The total rate seems to follow a two-phase kinetic: the first short and fast where diffusion and convection are the most important processes; the second slow where the soil-water relationship, f.i. sorption and degradation, become important (Figure 3). However the

volatilisation correlated well with the pesticide vapour pressure ($\text{Pa m}^3 \text{mol}^{-1}$): the rate was Procymidone > Ethoprophos > Malathion $\cong$ Pyrimethalin where the Henry constants respectively are 20.46, 0.015, 0.00114 and 0.0036.

Increased soil moisture also increased the volatilisation, particularly when the soil was re-wetted. These results confirm that in fallow soil the climatic condition and the properties of the pesticide drive the rate of volatilisation: soil-pesticide processes such as adsorption and degradation becomes more important later.

The season had a strong effect as in Spring and Autumn the volatilisation was higher than in Winter due to the effect of the temperature.

Table 1. Total volatilisation in the experiments.

	Dose applied (g/m^2)			Amount volatilised (μg)		
	12/1998	04/1999	10/1999	12/1998	04/1999	10/1999
Ethoprophos	100	133	100	3.745	28.653	10.990
Malathion	64	82	64	1.386	22.770	6.611
Procymidone	75	77	75	1.87	14.20	9.99
Pyrimethalin			20			0.42

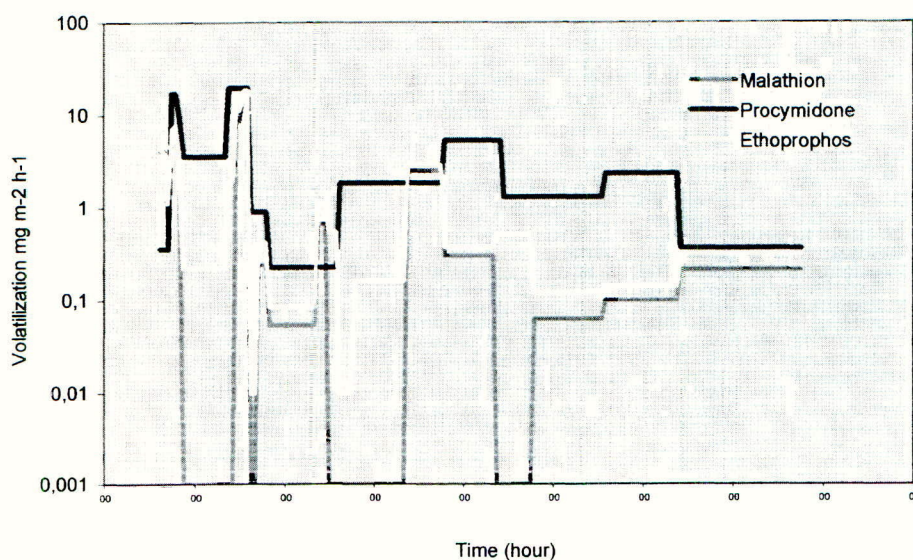


Figure 2. Pesticide in air ($\text{mg m}^{-2} \text{h}^{-1}$) in the week 12 to 19 in April 1999.

More than 90 % of the volatilisation is occurred out in the first few days after the pesticide application.

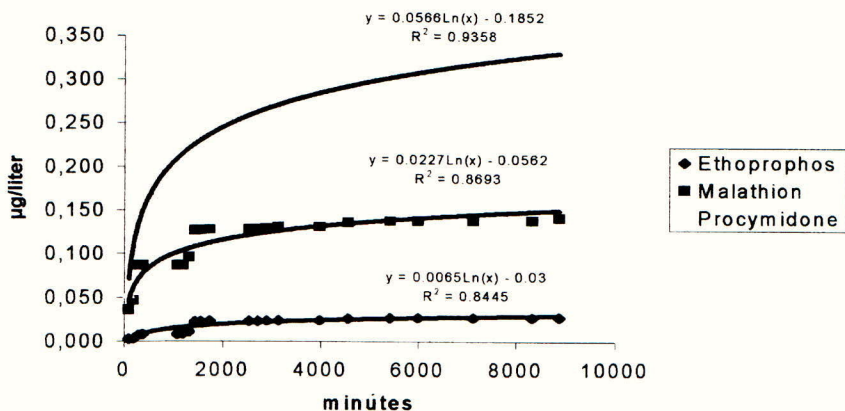


Figure 3. Cumulated volatilization of Ethoprophos, Malathion and Procymidone during the Spring experiment.

Total amount of pesticide in the air was 3.8 to 28.7 µg for Ethoprophos, 1.4 to 22.8 µg for Malathion, 1.9 to 14.2 µg for Procymidone, 0.4 µg for Pyrimethalin. The volatilisation rate calculated via TPS was very high and comprised between 0.5 to 60 % of the applied dose. If we exclude the leaching as a dissipation process (field capacity was never reached in the field measurement) and the transformation in the first week would be low for some of the pesticide studied (data not reported), we can argue that most of the pesticide dissipation in the experiment would be due to the volatilisation (Table 3).

These results confirm the need to measure the volatilisation in air for both pesticide leaching assessment in field and for the model validation. In fact as volatilisation reduces the pesticide dose available for leaching, this process represents a form of mitigation to be taken into the risk assessment procedure. Also field data sets used for model validation purposes should contain the measurement of this process to avoid over-estimation of the mobility in soil (Garratt *et al.*, 2001; Boesten *et al.*, 2000).

ACKNOWLEDGEMENTS

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REFERENCES

- Boesten J J T I; van der Pas L J T (2000). Movement of water, bromide and the pesticides ethoprophos and bentazone in a sandy soil: the Vredepeel data set. *Agricure, Water and Management*, **44**: 21-42.

- Capri E; Alberici R; Glass C R; Minuto G; Trevisan M (1999) Potential operator exposure to procymidone in greenhouses. *Journal of Agricultural and Food Chemistry*, **47**: 88:1123-1132.
- Capri E; Larsson M; Trevisan M; Nicelli M; Del Re A A M (2000). Studi di volatilizzazione di antiparassitari dal suolo: misure e previsioni. In: Atti XVII Convegno nazionale della Società Italiana di Chimica Agraria, 231-239.
- Garratt J A; Capri E; Trevisan M; Errera G; Wilkins R A (2001). Parameterisation, evaluation and comparison of pesticide leaching models in a Bologna field environment. Submitted to *Pesticide Science Management*.
- Glotfelty D E; Leech M M; Jersey J; Taylor A W (1989). Volatilization and wind erosion of soil surface applied atrazine, simazine, alachlor and toxaphene. *Journal of Agricultural Food Chemistry*, **37**: 546-551.
- Glotfelty D E; Taylor A W; Turner B C; Zoller W H (1984). Volatilization of surface-applied pesticides from fallow soil. *Journal of Agricultural Food Chemistry*, **32**: 638-643.
- Harper L A; White A W; Bruce R R; Thomas A W; Leonard R A (1976). Soil and microclimate effects on trifluralin volatilisation. *Journal Environmental Quality*, **1**, **3**: 236-242.
- Willis G H; Parr F; Smith S; Carroll B R (1972). Volatilization of dieldrin from fallow soil as affected by different soil water regimes. *Journal Environmental Quality*, **1**, **2**: 193-196.
- Wilson J D (1982) Turbulent dispersion in the atmospheric surface layer. *Boundary Layer Meteorology*, **22**: 399-420.

A spatially distributed assessment for pesticide exposure in surface waters via drainflow

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ABSTRACT

There is no consensus on the approach to estimating exposure at higher tiers of environmental assessment. Step 1 calculations conducted for a novel herbicide did not exclude the potential for the compound to exhibit effects on higher aquatic plants following transport in drainflow. In a higher tier approach, a model was first validated against field data and then used for distributed modelling for 15 environmental scenarios with 30-year simulations for each. Predicted concentrations of the herbicide for the 15 scenarios were weighted according to their relative abundance within wheat-growing areas. The resulting 450 model outputs were ranked to assess risk and the probability of impact at the national scale.

INTRODUCTION

A step 1 risk assessment for a winter wheat herbicide proposed for use in the UK indicated a potential for effects on higher aquatic plants following transport in drainflow. The compound is acidic, impersistent and relatively mobile. There is currently no consensus on the approach to estimating exposure at higher tiers of environmental assessment. Here, a deterministic model (MACRO) is applied in a distributed manner to predict concentrations of herbicide in a small ditch. The approach is a pragmatic attempt to assess the distribution of exposure concentrations within the limitations of current knowledge and tools. It ignores much of the uncertainty in modelling which may only be addressed through the further development of probabilistic procedures and, in the longer term, true stochastic models.

MATERIALS AND METHODS

Field drainflow study

A field drainflow study was carried out to investigate the potential for movement of the herbicide to drains and a receiving water body. The compound was applied on 16 May 2000 to a 7.7-ha winter wheat field situated in Northamptonshire in the UK. The effective drainage at the site (plastic pipes and mole drains), the texture of the soil (Hanslope series; clay loam over clay), its alkaline pH (7.1-8.5) and low organic carbon content (1.2% in the topsoil) made the field experiment a worst-case for the transfer of acidic compounds to drains. Transport of pesticides via preferential flow can be significant on such soils. Water collected by the drainage system left the field via a single outfall with water moving directly into a receiving ditch. The experimental site was monitored continuously following application, with water

samples collected from both the drain outfall and the receiving water body. Collection of water samples for analysis of herbicide concentrations was triggered in response to drainflow. An automatic weather station was erected on site to record rainfall, air and soil temperatures, wind speed, humidity and solar radiation.

Model selection and validation

The MACRO model (www.mv.slu.se/bgf/macrohtm/~macro.htm) was selected for the work as it simulates both drainflow and preferential flow. MACRO is a physically-based model with the soil porosity divided into two flow systems or domains (macropores and micropores), each characterised by a flow rate and solute concentration. Richards' equation and the convection-dispersion equation are used to simulate soil water flow and solute transport in the soil micropores, whilst a simplified capacitance-type approach is used to calculate fluxes in the macropores. Additional model assumptions include first-order kinetics for degradation in each of four 'pools' of pesticide in the soil (micro- and macropores, solid/liquid phases), together with an instantaneous sorption equilibrium and a Freundlich sorption isotherm in each pore domain. Version 4.1 of the model was used in this study.

In order to support the use of the model in predictive mode for the distributed assessment, data from the field drainflow study were simulated without any calibration ('blind simulation'). No site-specific data were available for DT50 or Koc, so mean data from a range of soil types were used for the blind simulation and predictive work.

Spatially distributed assessment

The first phase of the distributed assessment of herbicide entry into surface waters via drainflow was to divide England and Wales into environmental scenarios comprising discrete classes of soil type and climate. The study sought to cover the range of soil and climatic conditions within the major wheat cultivation areas of England and Wales. Just over 50% of the area cultivated with wheat in England and Wales is estimated to be artificially drained. The soil series making up the drained wheat area were divided into six broad classes (Figure 1) based on vulnerability for leaching of the acidic herbicide via drainflow (principally clay content and pH). A representative soil was selected for each class. Non-drained soils and those with peaty topsoils were considered to have no vulnerability for leaching via drainflow, so that five soil classes were considered by the modelling, each typified by a single soil profile.

Three weather datasets were taken from the SEISMIC database (Hollis *et al.*, 1993) to represent 'dry', 'medium' and 'wet' conditions (Figure 1). Average annual rainfall for the three classes was 588, 713 and 815 mm, respectively. Wheat rarely accounts for more than 5% of land in the parts of England and Wales with >850 mm rain per annum and no modelling was thus carried out for these areas. A 30-year run of weather data was compiled for each climate class.

The model was run for the 15 scenarios (i.e. 5 soil x 3 climate classes) assuming annual applications of the test compound in the spring of each of 30 years. A simple approximation of dilution within a small receiving water body was undertaken on the basis of drainflow from a 1-ha field entering a ditch 100 m long, 1 m wide and with a water depth of 30 cm (equivalent to 3 mm water distributed across 1 ha). The maximum daily concentration in the ditch for each of the 450 years simulated was extracted and ranked in a frequency distribution.

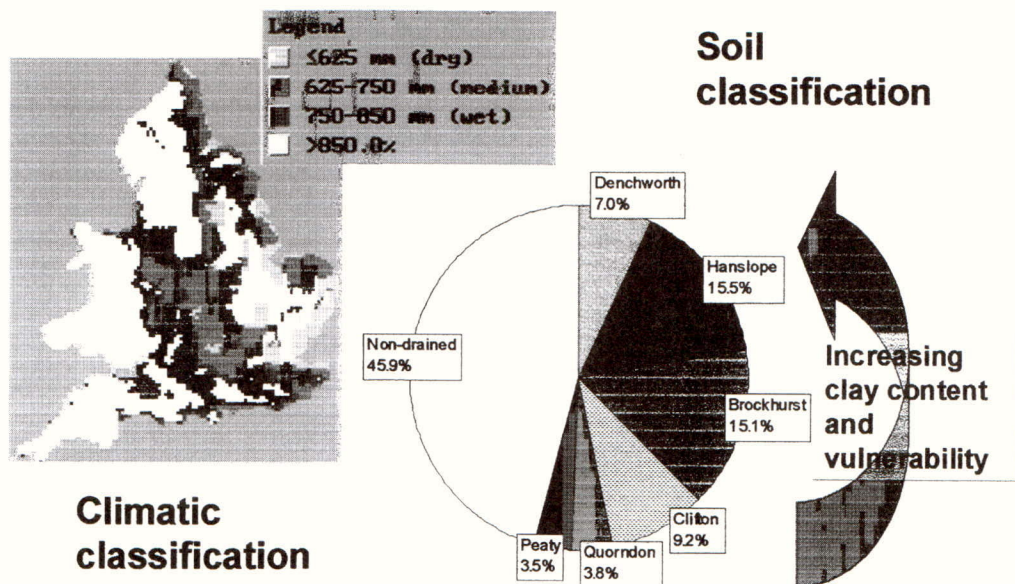


Figure 1. Division of the wheat growing areas into climatic and soil classes

RESULTS

Concentrations in field drainflow

Drainflow was measured on an hourly basis with the frequency of sampling for herbicide determined by the automatic sampling. Peak concentrations were short-lived, lasting only a few hours. Figure 2 shows drainflow and herbicide concentrations for an event commencing 10 days after treatment (DAT). The first sample collected in response to this drainflow contained the largest concentration of herbicide ($2.3 \mu\text{g l}^{-1}$), which is indicative of the importance of preferential flow phenomena for the transfer of pesticide to drains at the experimental site.

Flow and concentrations of herbicide were also monitored regularly in the ditch receiving drainflow from the field. Concentrations of the compound were <LOQ ($0.05 \mu\text{g l}^{-1}$) apart from a single sample collected 12 DAT which contained $0.06 \mu\text{g l}^{-1}$. This indicates a dilution factor for pesticide concentrations between raw drainflow and ditch water of approximately 100 or greater.

Model validation

Figure 2 also compares observed concentrations of herbicide in the first significant drainage event after application with values from the blind simulation by MACRO. The simulated peak concentration in drainflow was within 12% of that observed. The shape of the chemograph was well matched although the decline in concentrations from peak values was underestimated. This suggested that output from the model in predictive mode would be conservative with respect to actual concentrations under the conditions of use.

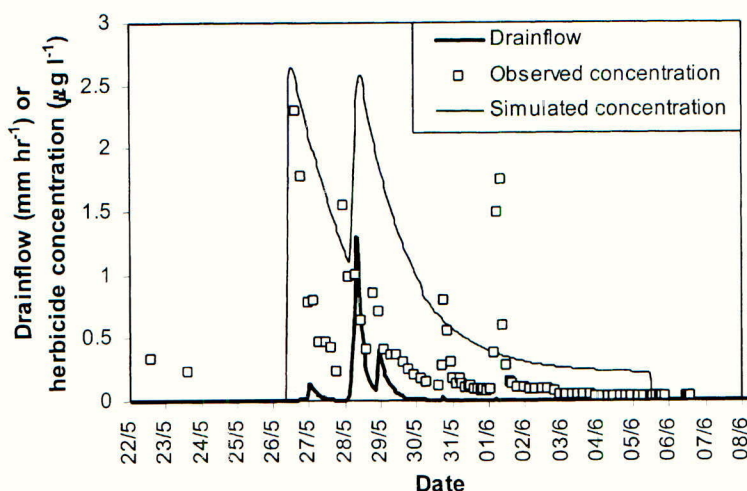


Figure 2. Flow for a drainage event commencing 10 DAT and comparison between observed concentrations of herbicide and those predicted by MACRO

Distributed risk assessment

The model was run for the 15 scenarios assuming annual applications of the test compound in each of 30 years. Daily concentrations of herbicide in the ditch are shown in Figure 3 for the worst-case scenario (heavy clay soil with high pH in the wet climatic region). Concentrations were again indicative of preferential flow with a transient pulse of the chemical predicted to move to surface water in the first significant drainflow event after application. Concentrations and losses were largest where drainflow was initiated soon after application in spring.

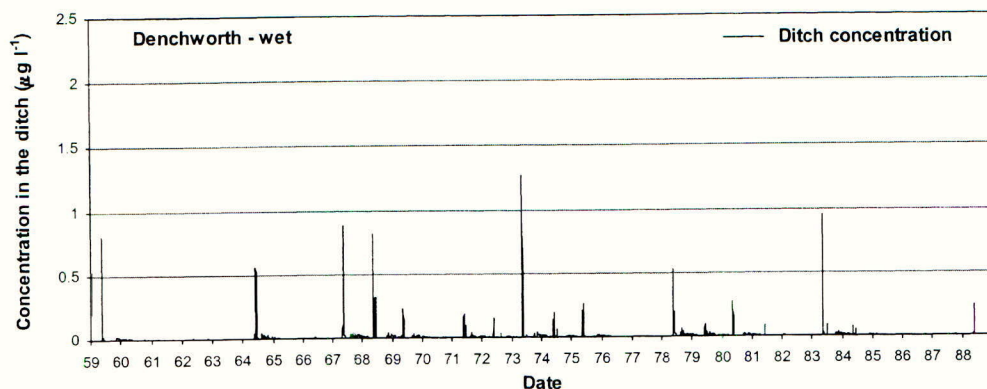


Figure 3. Herbicide concentrations in the receiving ditch predicted for a heavy clay soil in a wet climatic zone

The maximum daily ditch concentration for each of the 450 years simulated was extracted and ranked in a frequency distribution (Figure 4). A maximum daily concentration of $1.1 \mu\text{g l}^{-1}$ was derived for the field study by taking a flow-weighted average of residues in samples taken over each day. This maximum placed the field study on the 97th percentile of the distributed assessment, thereby confirming its worst-case character. Results for each scenario were weighted according to the abundance of the soil-climate combination. Maximum daily concentrations were then compared with deterministic effects endpoints for *Lemna gibba* (EC50 $1.0 \mu\text{g l}^{-1}$; recovery within 14 days for all concentrations up to $7.0 \mu\text{g l}^{-1}$ and exposure periods up to 4 days) to generate a semi-probabilistic risk assessment. *Lemna gibba* was previously shown to be the most sensitive from five species of higher aquatic plant (Davies *et al.*, 2001). Results summarised in Table 1 indicate that there will be no impact on *Lemna gibba* across 98.9% of the scenario/year combinations. There may be a potential for a temporary effect in 1.1% of instances, but recovery can be expected in all cases.

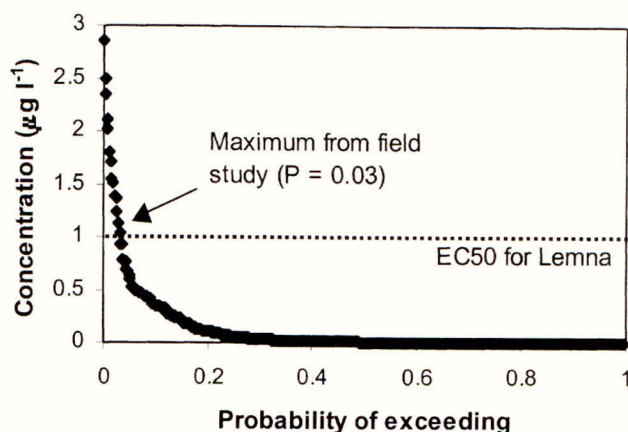


Figure 4. Frequency distribution for the annual maximum of daily concentrations of herbicide in the receiving ditch (based on 450 individual predictions)

Table 1. Summary statistics for the distributed assessment of risk to *Lemna gibba*

Maximum exposure concentration ($\mu\text{g l}^{-1}$)	Potential for effect	Potential for recovery	Relative abundance (% of wheat area)
<0.1	Negligible	-	91.8
0.1 - 1.0	Very unlikely	Very high	7.1
1.0 - 7.0	Possible	High	1.1
>7.0	Possible	Low	0

DISCUSSION

The approach adopted moves forward from a simple worst-case assessment to cover a realistic range of conditions under which the herbicide is proposed to be used. However, a number of worst-case assumptions are retained and provide an additional element of environmental protection. Most notably, dilution of drainflow concentrations within the standard EU ditch (almost always less than a factor of 2) was very much smaller than that observed in the field study (a factor of 100 or greater).

There are established procedures for exposure estimation for surface waters at lower tiers of environmental assessment and these will soon be strengthened by the introduction of the FOCUS surface water scenarios (Russell, 2000). However, there is no consensus on the approach to be adopted when a lower tier assessment indicates a potential for risk. The environment into which pesticides are released is inherently variable both spatially and temporally and techniques based on probabilistic modelling and/or landscape analysis offer the best potential for more realistic exposure assessment at higher tiers. The approach presented here is a pragmatic attempt to assess the distribution of exposure concentrations within the limitations of current knowledge and tools. The technique applies deterministic models in a distributed manner and has relatively low data and time requirements compared to more sophisticated approaches. As such, the methodology may prove useful whilst the research and development necessary to implement more sophisticated approaches is being undertaken.

The main shortcoming of the approach is that it ignores much of the uncertainty associated with the modelling process. This uncertainty may partially be addressed using probabilistic procedures currently under development, but eventually will require the development and adoption of true stochastic models such as those based on the transfer function approach (Grochulska and Kladvko, 1994; Jury *et al.*, 1996). In addition, the method described here takes no account of the intensity of occurrence of a particular scenario in a particular location. This could be overcome through the use of GIS technology to replace the national scenario statistics used here.

REFERENCES

- Davies J; Tencalla F G; Honnegger J L; Brain P; Newman J R; Pitchford H F (2001). Toxicity of sulfosulfuron, a novel sulfonylurea herbicide, to aquatic plants. In Abstracts of the SETAC Europe meeting, Madrid 6-10 May 2001, pp. 144-145.
- Grochulska J; Kladvko E J (1994). A two-region model of preferential flow of chemicals using a transfer function approach. *Journal of Environmental Quality* **23**: 498-507.
- Hollis J M; Hallett S H; Keay C A (1993). The development and application of an integrated database for modelling the environmental fate of herbicides. *Proceedings of the BCPC Conference - Weeds 1993*, **3**: 1355-1364.
- Jury W A; Sposito G; White R E (1996). A transfer function model of solute transport through soil. 1. Fundamental concepts. *Water Resources Research* **22**: 243-247.
- Russell M H (2000). Advances in surface water modelling in the USA and Europe. *Proceedings of the BCPC Conference - Pests and Diseases 2000*, **1**: 77-84.

Modelling pesticide behaviour at the catchment-scale – the TERRACE project

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ABSTRACT

This paper presents the work of the TERRACE project (Terrestrial Runoff modelling for Risk Assessment of Chemical Exposure). The project seeks to develop and test models for assessing the movement of pesticides at the catchment scale as part of the development of new pan-European risk assessment tools for the evaluation of the environmental fate of new chemicals (the GREAT-ER project). TERRACE seeks to adapt existing models of pesticide, and other diffuse source pollutants, to spatial scales larger than those presently covered by the FOCUS model scenarios. In parallel to the selection and adaptation of suitable models the project will apply these models to field data.

INTRODUCTION

The GREAT-ER project (Geography-referenced Regional Exposure Assessment Tools for European Rivers) is a pan-European project to develop risk assessment tools for new chemicals sponsored by CEFIC (European Chemicals Industry Federation) and ECETOC (European Centre for Ecotoxicology and Toxicology of Chemicals). The project is now in its second three-year phase. In the first three-year phase the project focused on the development of a modelling system of point-source pollution in the river environment, especially the release of detergent compounds from sewage treatment works (Feijtel *et al.*, 1998). This system incorporates spatially-distributed, steady-state models that produce distributions of predicted environmental concentration (PEC) via an Arcview interface, and was designed to work at the regional catchment scale across the whole of Europe. The package has been tested for catchments in the UK, Italy and Germany.

In the second three-year phase of the project the model is to be expanded to include chemical behaviour in three further environments – the atmosphere, estuaries and terrestrial runoff. These three components are to be combined to give predictions of chemical transport and persistence throughout the environment. The terrestrial runoff component of this model is being considered by the TERRACE project (TERrestrial Runoff modelling for

Risk Assessment of Chemical Exposure). TERRACE focuses on the modelling of diffuse source pollution in regional scale river catchments (i.e. at much larger scales than the FOCUS model scenarios). The first phase of the project is to review and select suitable existing models rather than create new model. The project will go on to evaluate selected models using catchment scale data.

The TERRACE project is examining a range of diffuse source pollutants, including pesticides. Pesticides reach water sources in either dissolved or bound form, posing health risks to human beings and aquatic species. The greatest contribution to the overall pesticide pollution of waters comes from agriculture (Bach *et al.*, 2001). Important risk and management decisions regarding control of such pollution are made based on rough estimates of agricultural pollution, which do not consider interaction between climate, crop soil and hydrology (Thorsen *et al.*, 1996). Collecting data and conducting field experiments to assess this kind of pollution is becoming prohibitively expensive and so there is a need for appropriate tools to predict this pollution. Accurate representation of the processes responsible for transport and transformation of pesticides is crucial for the tools to give desired results.

Numerous models have been developed to date to predict the environmental fate of pesticides. Some catchment scale hydrological models also have modules in them to predict pesticide runoff. The amount of pesticide loss via runoff water is a complex function of rainfall timing, the hydrologic and soil characteristics of the field and the chemistry, formulation and persistence of the chemical itself (Wauchope & Leonard, 1980).

In reviewing models for inclusion in the TERRACE project a number of criteria were considered:

1. the capability for application to large-scale catchments (> 100's km²).
2. the capability for interface with a GIS system.
3. a physically reasonable representation of hydrological and contaminant transport processes.
4. input data requirements that allow the model to be applied in a wide variety of European situations.
5. A readily available model that could be made available as part of a freely accessible package.
6. a model validated for pesticides, preferably in a European setting.

Initial review identified three models suitable for further exploration. ANSWERS 2000 (Bouraoui & Dillaha, 2000), SWATCATCH (Hollis *et al.*, 1996), and SWAT (Neitsch *et al.*, 2001). ANSWERS-2000 represents an event-based model with a high data requirement, and SWATCATCH an empirical model with little input data requirement. However, our first choice model is SWAT which represents a trade off between physical complexity and input data requirement that we believe could be achieved across Europe. As a first step in testing these models SWAT was applied to predict pesticide runoff for a catchment in Bedfordshire, UK.

THEORY

The Soil Water Assessment Tool (SWAT) is a basin scale model developed by the United States Department of Agriculture-Agricultural Research Service to predict the impact of land management practices on water, sediment and agricultural chemical yields. It is a distributed continuous simulation model. A number of earlier USDA models CREAMS (Chemicals, Runoff and Erosion from Agricultural Management Systems, Knisel, 1980), GLEAMS (Groundwater Loading Effects on Agricultural Management Systems, Leonard *et al.* 1987) and EPIC (Erosion-Productivity Impact Calculator, Williams *et al.*, 1983) contributed significantly to the development of SWAT.

Surface runoff

SWAT divides the catchment into Hydrologic Response Units (HRU) based on land use and soil type. Surface runoff is simulated by two methods. 1. Modified SCS curve number method and 2. Green & Ampt infiltration method.

Pesticide Degradation and Transport

The equations used to model movement of pesticides are adopted from GLEAMS. Simulated processes include wash-off, degradation, leaching and transport.

Wash-off

Wash-off of pesticides is estimated as a function of plant morphology, pesticide solubility and the timing and intensity of rainfall event.

Degradation

Pesticide degradation in each soil layer is governed by first order kinetics. SWAT allows different half-lives for foliar and soil degradation. Soil half-life is a lumped parameter, which takes care of the net effect of volatilization, photolysis, hydrolysis, biological degradation and chemical reactions in the soil.

Partitioning

Partitioning of pesticide between the solute and sorbed phases is defined by the soil adsorption coefficient for the pesticide (K_{oc}). This coefficient is calculated from the adsorption coefficient normalized for soil organic carbon content (K_{oc}) and the percentage of organic carbon in the soil.

Transport of pesticides in solution

The amount of pesticide removed in surface runoff is calculated as a function of concentration of pesticide in mobile water, the volume of surface runoff and a pesticide percolation coefficient.

Transport of sorbed pesticide

Sorbed pesticide attached to soil particles may be transported by surface runoff to the main channel. Sorbed transport rates are related to the concentration of pesticide sorbed onto sediment, HRU area, the pesticide enrichment ratio and the sediment yield on a given day.

Pesticide lag

SWAT has a storage feature to lag surface runoff and pesticide in surface runoff reaching the main channel for large basins.

GIS Interface

The interface takes a digital elevation model as input and delineates the catchment and sub-catchments automatically. Additional outlets can also be added manually to increase the number of sub-catchments. The interface then divides the sub-catchment into hydrological response units based on land use and soil information and parameters for routing water are derived simultaneously. Land management information supplied by the user is used to simulate crop growth and pesticide applications, based on the information available in the SWAT-Arc View Interface database. Weather input parameters entered by the user are coupled with other available information and flow and pesticide routing is carried out (Figure 1).

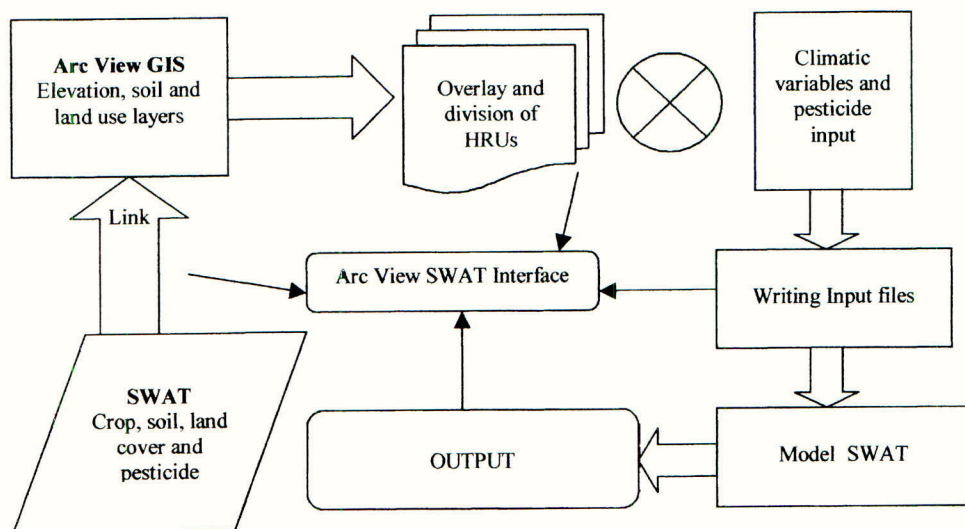


Figure 1. Methodology for modelling pesticide runoff.

STUDY AREA

The study area is located in Sharnbrook, Bedfordshire, UK (in an area bounded by National Grid References 495000,263000 and 499000,263000). The total area is about 140 ha. The predominant soil series is Hanslope, consisting of a clay loam soil over stony, calcareous clay. A group of eight fields forming approximately half of the catchment area is directly controlled by Unilever and a rotation of wheat, oil seed rape, grass, linseed, beans and peas is grown. All eight fields are underdrained by means of tile drains.

DATA COLLECTION AND PROGRESS

Runoff, and pesticide and nutrient concentrations in runoff have been monitored at the outlet of the catchment since October 1999. Using Arc View GIS, A Digital Elevation Model (DEM) of the study area was prepared by digitising the contours from Ordnance Survey maps and using Arcview GIS. Automatic delineation of the catchment and its sub-catchments was carried out using the tools available in the SWAT-Arcview Interface. Land use and soils maps were overlaid and the catchment was divided into HRUs (hydrological response units) Relevant soil, crop and pesticide data were obtained and appended to the existing database in SWAT. Calibration of the model is currently being carried out with one year of collected data with the coming year's data to be used for validation of the model.

CONCLUSIONS

The TERRACE project aims to provide risk assessment for new chemicals at the regional river basin scale (a spatial scale not previously considered in the risk assessment process). The project has identified three models with varying input requirements which have the potential for inclusion in the TERRACE system. The first choice model is SWAT which is currently being evaluated for pesticide and nutrient transport using data from a UK catchment.

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REFERENCES

- Bach M; Huber A; Frede H G (2001). Input pathways and river load of pesticides in Germany-a national scale modelling assessment. *Water Science and Technology* **43**: 261-268.
- Bouraoui F; Dillaha T A (2000). ANSWERS-2000: non-point source nutrient planning model. *J. Env. Eng.* **126**: 1045-1055.
- Feijtel T; Boije G; Matthies M; Young A; Morris G; Gandolfi C; Hansen B; Fox K; Matthijs E; Koch V; Schroder R; Cassani G; Schowanek D; Rosenblom J; Holt M (1998). Development of a geography-referenced regional exposure assessment tool for European rivers - GREAT-ER. *J. Hazardous Materials* **61**: 59-65.
- Hollis J M; Brown C D; Thanigasalam P (1996). SWATCATCH: A catchment scale model for predicting weekly river flows and pesticide concentrations. SSLRC Report to the Environment Agency, TAPS Centre, SSLRC, Silsoe, UK.
- Knisel W G (1980). CREAMS, a field scale model for chemicals, runoff and erosion from agricultural management systems. USDA, Research Report No. 26.
- Leonard R A; Knisel W G; Still D A (1987). GLEAMS: Groundwater Loading Effects of Agricultural Management Systems. *Trans. Amer. Soc. Agric Engrs.* **30**: 1403-1418.

- Neitsch S L; Arnold J G; Kiniry J R; Williams J R (2001). *Soil and Water Assessment Tool User's Manual*, Version 2000. Grassland, Soil and Water Research Laboratory, USDA Agricultural Research Service, Temple, Texas.
- Thorsen M; Feyen J; Styczen M (1996). *Agrochemical modelling, Chapter 7, Distributed Hydrological Modelling*. Kluwer Academic Publishers, The Netherlands.
- Wauchope R D; Leonard R A (1980). Maximum pesticide concentrations in agricultural runoff: a semi-empirical prediction formula. *J. Environ Qual* 9: 665-670.
- Williams J R; Renard K G; Dyke P T (1983). EPIC: a new method for assessing erosion's effect on productivity. *J. Soil and Water Cons.* 38: 381-383.