

Session 9C

**The Assessment and
Interpretation of the Fate
and Effects of Pesticides in
the Environment**

Session Organisers

Mr N D Simmons and
Dr F J Lewis

Poster Papers

9C-1 to 9C-17

A COMPARISON OF THE USE AND REGULATORY INTERPRETATION OF A PREDICTIVE MODEL, LYSIMETER AND FIELD STUDIES TO DETERMINE THE LEACHING POTENTIAL OF A SEED DRESSING

P. FOGG, ANDRÉE D. CARTER

Soil Survey and Land Research Centre, Cranfield University, Shardlow Hall, Shardlow, Derby, DE72 2GN

C.D. BROWN

Soil Survey and Land Research Centre, Cranfield University, Silsoe, Bedfordshire, MK45 4DT

ABSTRACT

There have been relatively few attempts to assess the comparability, validity and effectiveness of predictive modelling, lysimeter and field studies with respect to their use by regulatory agencies. A 'BBA compliant' lysimeter study and a 'realistic worse case' field study were established in the UK to investigate the leaching potential of a fungicide applied as a seed dressing at a low application rate (200g ha^{-1}). The model LEACHP was used to predict fate for both experiments. The lysimeter study showed that between 10 and 30% of the applied radioactivity leached in the first nine months of the study whereas the field study suggested that a maximum of 0.5% leached from the soil profile during the same period. LEACHP was unable to predict the magnitude of the leachate concentrations from the lysimeter but to date predictions for the field study are good. The interpretation of these results suggest that a different regulatory decision concerning the registration of this seed dressing would be made. The relative costs of carrying out these studies for this product, including analyses, show the lysimeter study was 20% more expensive than the field study and the modelling study was approximately 5% of the field or lysimeter study cost.

INTRODUCTION

Lysimeter studies are used by several regulatory authorities to determine whether a pesticide is likely to contaminate water sources. The BBA guidelines (Federal Biological Research Centre, 1990) assumes a worse casing for leaching scenario with a sandy soil of low organic carbon content of $<1.5\%$ and a requirement for 800mm of rainfall/irrigation over an annual period. This scenario may be too extreme and not necessarily representative of the majority of Western Europe. In the UK, only 1-2% of land is represented by this BBA soils/agroclimatic combination and therefore a more realistic worst case scenario was required in order to provide both a spatially representative and a field based assessment of the leaching behaviour when the product is used at the maximum recommended rate for winter cereals. Field leaching studies have also been requested by some regulatory

authorities as alternative second or third level studies following results from lysimeter studies in order to assess the impact on water quality under conditions of normal use. The two leaching studies were therefore established to compare the regulatory use and interpretation of the different study types. LEACHP (Hutson and Wagenet 1992) is a widely used mechanistic model which describes water movement by solution of the Richard's equation and thus should be particularly suitable for use with coarse textured soils where by-pass flow is limited. Modelling can be used to predict fate or to extrapolate the results of experiments to a range of conditions and as such can be an important and potentially powerful regulatory tool.

EXPERIMENTAL SITES

The field experimental site was located close to Lockington, south-east of Derby in the UK Midlands. The soil type for this study was chosen for its hydrological properties to represent a realistic and representative worst case scenario for leaching. A detailed profile description, physical, chemical and microbiological analyses were carried out to fully characterise the site as a gleyic brown earth, classified as an Arrow series (Clayden and Hollis 1984) and a gleyic cambisol, in the FAO system (FAO-UNESCO 1988). The soil is a permeable light loam having a slightly stony sandy loam topsoil, a similar textured uppersubsoil, overlying a weakly structured loamy sand and a topsoil organic carbon content of 1.1%. Soils for the lysimeters were taken near Biggleswade, Bedfordshire UK, and were classified as a typical brown earth of the Cuckney series (Clayden and Hollis 1984), a well drained sandy and ferruginous fine loamy soil overlying soft sandstone and classified as a luvic arenosol in the FAO system (FAO-UNESCO 1988). This soil is very permeable, well drained, with low water retention properties, an organic carbon content of 0.8% and prone to droughtiness unless irrigated or located in an area of high rainfall.

The field experimental plot consisted of a 55x31m plot with a 31x4m untreated control. The site was cultivated according to normal, good agricultural practice and the fungicide applied as a winter wheat seed dressing sown at the rate of 200 kg ha⁻¹ equivalent to 200g ha⁻¹ of active ingredient early in November 1993. Replicated soil water suction samplers (Clark *et al* 1990) were installed to 1000mm to enable the collection of soil water as it drained from the soil profile. Soil hydrology was monitored using septum sealed tensiometers and neutron probe access tubes to provide the necessary water flux information for targeted sampling. Annual average rainfall for the area is 635mm. Three lysimeters of 1.1m length with a surface area of approximately 0.5m² were collected in March 1993 and located at Silsoe near Bedford. The hydrological integrity of each lysimeter was established throughout the spring and summer of 1993 by the application of an inorganic bromide tracer and the breakthrough curves were compared to ensure uniformity. Each lysimeter was sown with ¹⁴C radiolabelled winter wheat seed at the rate equivalent to the field study and a total activity for each lysimeter of 60 MBq. Annual average rainfall for this area is 555mm, and artificial irrigation was applied to attain 800mm yr⁻¹.

SAMPLING AND MONITORING STRATEGIES

The field study site was monitored and sampled on a routine basis of at least twice per month for the first 6 weeks of the study and thereafter monthly until water sampling ceased.

The site was also monitored following rainfall, with trigger events being 10mm within a 24 hour period or 15mm over a 48 hour period. At each monitoring event the hydrological status of the site was monitored to establish periods when downward fluxes were dominant and water sampling was appropriate. The soil was sampled on 0, 1, 3, 7, 30, 90, 180 and 220 days after treatment (DAT) in 10cm layers to 30cm depth using a 30x14cm block sampler in order to determine a field dissipation rate. The sampler was positioned such that the line of drilled seeds fell centrally along the long axis of the sampler and such that approximately the same number of seeds or plants were incorporated within each block sample. Crop residues were removed from the soil samples, bagged separately and kept deep frozen with the soil until analysis took place. The soil profile was sampled on 220 DAT in 10cm increments down to 1 metre to establish the extent to which the fungicide had leached.

Leachate from the lysimeters was collected following rainfall and artificial irrigation. The irrigation was applied at times of low local levels of precipitation and also when necessary to maintain the long term monthly averages for the area. Aliquots of leachate following each sampling were measured for their total radioactivity using a liquid scintillation counter (LSC), any samples found to contain radioactivity equivalent to $0.05\mu\text{g l}^{-1}$ active ingredient or greater were subject to further analysis to determine the proportion of active ingredient as well as any metabolites. One of the lysimeters was destructively sampled at harvest to obtain soil from each 10cm layer. The remaining two lysimeters will remain intact until the end of the study period with one receiving a further application of ^{14}C fungicide to monitor the effects of a second application on leachate concentration. Samples of straw, grain and stubble have been taken to determine a radiochemical mass balance for the lysimeter study.

RESULTS AND DISCUSSION

Breakthrough of the active ingredient in the soil water at 1.0m depth at the field site occurred around 05/01/94, when the soil profile was close to saturation following a rainfall event of 22.2mm. Antecedent soil water conditions and time to breakthrough suggested that a chromatographic type flow was dominant. Concentrations continued to climb reaching a maximum of $0.91\mu\text{g l}^{-1}$ on 21/03/94. One month later this maximum had dropped to $0.66\mu\text{g l}^{-1}$ with concentrations at $0.22\mu\text{g l}^{-1}$ by 23/05/94. The main metabolite was observed at low concentrations near to the limit of detection of $0.1\mu\text{g l}^{-1}$ from 21/03/94 onwards. These concentrations remained until the end of the spring monitoring period. Suction samplers remove water from the larger soil pores which are only water filled when the soil is at or near saturation ie when gravity drainage or leaching is predominant. The sphere of influence of each suction sampler varies according to the soil water and physical conditions which are prevailing and therefore volumes obtained cannot be used to determine leaching losses. An estimate based on determination of drainage fluxes and the likely soil water sampling area can be made and for the field site was calculated to be approximately 0.5%.

The lysimeter study showed a slightly earlier breakthrough response relative to the field study with concentrations of $0.07\mu\text{g l}^{-1}$ being measured on 22/12/93. These residue levels rapidly climbed with maximum concentrations reaching $42\mu\text{g l}^{-1}$ on 24/03/94 in one

lysimeter. The confined hydrology and use of radiolabelled material within lysimeters enables a leaching load to be calculated, for example in lysimeter no. 2 total of 2782 μg of the active ingredient and metabolite had leached by the end of the monitoring period, equivalent to 28.04% of applied material. Figure 1 illustrates the difference between leachate concentrations in the two studies.

The significant differences in measured concentrations between the field and lysimeter results are thought to be attributable to several factors, primarily soil texture and organic carbon content and the actual lysimeter test system, which superimposes worst-case climatic conditions onto a worst-case for leaching soil type. The field topsoil has a higher silt and clay content and an organic carbon content of 1.1% compared to 0.8% in the lysimeter. Sorption of the fungicide at the field site is likely to be greater with less fungicide available for leaching. Preliminary laboratory data suggest a Koc range of 75-100 ml g^{-1} . Differences in texture/organic carbon content significantly affect the water retention and hydraulic conductivity properties of the two soils and drainage, hence leaching from the lysimeter soil is greater. Rainfall totals for each month were similar for both studies up until April 1994 when the lysimeters required 45mm of additional irrigation to supplement rainfall thus maintaining the field capacity status and therefore water available for leaching. Pore water pressures and water content data for the field study show that after 21/04/94 evapotranspiration increased and the dominant downward flux of soil water ceased.

An analytical detection limit of 0.05 mg kg^{-1} was originally established for the field soils, but due to dissipation within the profile this was found to be insufficiently sensitive to determine a field degradation rate (the application rate was equivalent to 0.841 mg kg^{-1} in the top 0-10cm of soil). Samples from the 220 DAT for each 0.1m layer to 1.0m depth were analysed with a detection limit of 0.5 $\mu\text{g kg}^{-1}$ and provided an estimated field half life of 159 days. The average measured quantity of fungicide remaining within the profile at 220 DAT totalled 308 μg , equivalent to 36.6% of the applied, with peak concentrations of 26 $\mu\text{g kg}^{-1}$ and 22 $\mu\text{g kg}^{-1}$ being measured in the 10-20cm and 20-30cm layers respectively. Soils data for the lysimeter study is not yet available for comparison.

The leaching model, LEACHP was used to predict the distribution of the total fungicide in the soil profile and also in soil water at 1.0m depth for both the field and lysimeter study. Predictions for the field study were also extended to investigate the impact on soil water concentrations at 1.0m depth during subsequent seasons. Model input parameters were derived from site-specific soil and weather data ie a field measured topsoil half-life of 159 days, an estimated 320 days for the subsoil and a Koc of 100 ml g^{-1} . A laboratory measured half-life of 640days for the topsoil and subsoil and an artificially low Koc value of 30 ml g^{-1} were used for the lysimeter study.

The simulated profile distribution of the fungicide on 220 DAT correlated very well with the measured data giving a very similar distribution of residues down the profile to those predicted. Figure 2 plots the mean field study data and the model predictions of soil water concentration at 1.0m depth. Model predictions show the fungicide breaks through at a similar time to the field study but peak concentrations occur one month later at approximately 0.5 $\mu\text{g l}^{-1}$ then increase to a maximum of almost 2 $\mu\text{g l}^{-1}$ in the second season after application. The earlier breakthrough in the field may have been caused by some preferential movement in the profile and the decrease in spring 1994 concentrations

attributed to increased sub-soil degradation, upward flux of pesticide in water due to the effects of evapotranspiration or the diluting influence of the shallow water table. Comparison between measured concentrations in lysimeter leachate and predicted values differed significantly. Figure 3 shows concentrations of the fungicide appear in lysimeter leachate at the end of December and a peak concentration of $37\mu\text{g l}^{-1}$ occurs in March. Less leaching of the fungicide is predicted from the lysimeter by LEACHP despite the use of 'worst case' half-life and sorption input parameters.

CONCLUSION

Data suggest that for this active ingredient and for the first nine months of the study, leaching from the lysimeter study was 20-60 times greater than the field study. The field study was able to provide more comprehensive information on soil dissipation and a site specific rate was determined. The derivation of the data did however require time consuming sampling to 1m depth and the development of an improved analytical detection limit. The analytical component of this field study was 29% greater than that of the lysimeter due to the number of soil and water samples generated and the 'cold' extraction procedures. The lysimeter facility and method is capital intensive and the sampling, installation, application and monitoring components of the study were 65% more expensive than the establishment of the field site. The modelling study represented approximately 5-6% of the cost of a field or lysimeter study, however monitoring may be required to give confidence in any predictions. The amount of fungicide leaching from the lysimeter indicates that no level of regulatory approval for use could be given on the basis of this data alone. Data would suggest that under conditions of normal usage, leaching to ground and surface water would occur at levels of concern. The field data, to date, suggests that the amount of chemical leaching might be acceptable and is less likely to cause significant contamination of water sources. Modelling predictions for the field site simulate well the observed behaviour of the chemical but are unable to simulate the lysimeter results. This research suggests that lysimeter data should not be evaluated in isolation from other field or modelling data when evaluating the potential for a chemical to contaminate water sources.

ACKNOWLEDGEMENTS

Analytical work by Hazleton Europe, and in particular Andy Burden and Chris Lewis.

REFERENCES

- Clayden, B. and Hollis, J. M. (1984) Criteria for differentiating soil series. Soil Survey Technical Monograph 17, Harpenden UK.
- Clark, L., Gomme, J., Carter, A., Harris, R. C. (1990) WRC/Soil Survey inert suction sampler. *BCPC Pests and Diseases* 1011-1016.
- FAO-Unesco (1988) Soil map of the world. Revised legend Food and Agriculture Organisation of the United Nations. Rome.
- Hutson, J. L. and Wagenet, R. J. (1992) LEACHM : Leaching Estimation and Chemistry Model, Version 3. Dept. of Soil, Crop and Atmospheric Sciences, Research Series No. 92-3. Cornell University, New York.

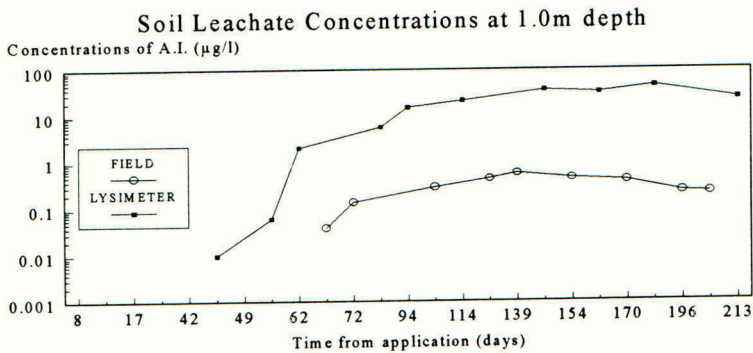


Figure 1

Observed concentrations of A.I. in soil water at 1.0m depth compared to predicted concentrations by LEACHP (half-life = 159 d; $K_{oc} = 100$)

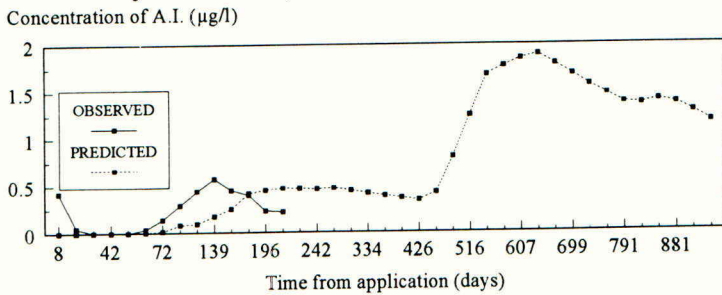


Figure 2

Observed concentrations of A.I. in lysimeter leachate compared to predicted concentrations by LEACHP (half-life= 640d; $K_{oc} = 30$)

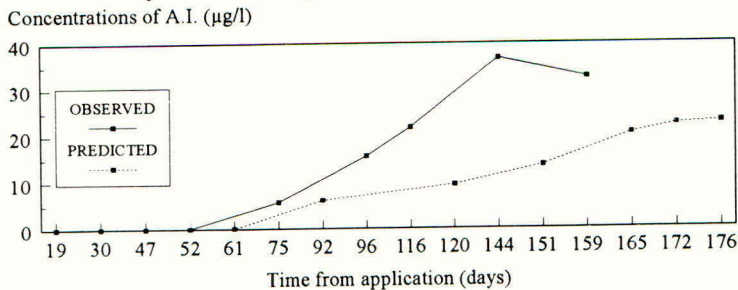


Figure 3

EFFECTS ON EARTHWORM POPULATIONS OF REDUCING PESTICIDE USE: PART OF THE SCARAB PROJECT

K. A. TARRANT, S. A. FIELD, A. JONES, C. McCOY

Central Science Laboratory, Ministry of Agriculture, Fisheries and Food, London Road, Slough, SL3 7HJ

S. D. LANGTON, A. D. M. HART

Central Science Laboratory, Ministry of Agriculture, Fisheries and Food, Tangley Place, Worplesdon, Guildford, Surrey, GU3 3LQ

ABSTRACT

The SCARAB project is a major, long-term investigation of the effects of pesticide use on invertebrates and soil microflora in UK arable cropping systems. Two pesticide regimes are being compared: Current Farm Practice (CFP) which represents typical levels of use, and Reduced Input Approach (RIA) which consists of substantially reduced inputs (especially of insecticides). The treatments began at three farms in 1990, and effects on the overall abundance and diversity of earthworms have been monitored twice yearly since Spring 1993. Results up to Spring 1994 showed that although some differences existed between earthworm populations in RIA and CFP plots they lacked consistency between the pairs of plots, and were of negligible magnitude compared to overall differences between the farms. It was concluded that the two regimes of pesticide use caused no ecologically-significant differences in earthworm populations at this stage of the project. Preliminary results from additional sampling for selected pesticides detected no mortality of earthworms after applications of omethoate and dimethoate. Residues of dimethoate in soil and earthworm samples were close to the predictions used in risk assessment, but no residues were detected for omethoate which degrades more rapidly.

INTRODUCTION

The SCARAB project is a field-scale, long-term investigation of the effects of pesticide use on invertebrates and soil microflora in arable cropping systems (Bowerman 1993). Two pesticide regimes are being compared: Current Farm Practice (CFP), which represents typical levels of use, and Reduced Input Approach (RIA), which consists of substantially reduced inputs, especially of insecticides. The intensification of modern agriculture and reliance on the use of pesticides presents potential hazards to earthworm populations. Earthworms are important because of their role in maintaining soil fertility and structure (Edwards and Lofty 1977). Furthermore, in some cases there may be significant hazards to birds and other vertebrates from ingesting earthworms which contain pesticide residues (Cooke et al. 1992). Both these types of hazard are considered in risk assessment of pesticides for regulatory

purposes in the UK (Greig-Smith 1992). Effects on earthworms are therefore being investigated as part of the SCARAB project.

The primary objective of the earthworm studies is to monitor effects of the SCARAB treatments on earthworm populations by means of twice-yearly sampling. Monitoring began in Spring 1993, in the third year of the CFP and RIA treatments, and will continue until 1996. Changes will be interpreted in relation to the overall contrast between CFP and RIA levels of pesticide use, and in relation to cropping changes and cultivations during the rotation cycles. Further sampling is being carried out to monitor the immediate effects of particular pesticides thought likely to present a particular hazard to earthworms, in order to assist in understanding longer-term changes. This requires analyses of pesticide residues, which will provide the additional benefit of increasing understanding of hazards to animals which feed on contaminated earthworms. This paper outlines the results obtained so far.

METHODS

Study sites and treatments

The two treatments are being compared at three separate experimental farms in England: High Mowthorpe in North Yorkshire, Drayton in Warwickshire and Gleadthorpe in Nottinghamshire. The three farms include a representative range of conditions in terms of climate, altitude and soil types. The 6-year crop rotations at each site are typical of the surrounding areas (Bowerman 1993). The rotation at Drayton comprises 4 years of grass ley and 2 of winter wheat. The rotation at Gleadthorpe includes potatoes, beans, beet, wheat and barley, whereas at High Mowthorpe the rotation includes rape, beans, wheat and barley. The experiment is based on a split-field design, including 2 fields each at High Mowthorpe and Drayton, and 3 at Gleadthorpe. For sampling, the northern and southern parts of one field at High Mowthorpe are treated as separate fields, in effect giving a total of 8 fields. Each field is split into 2 roughly equal halves, one treated with CFP and one with RIA.

Current Farm Practice (CFP) is designed to represent typical pesticide use by technically competent, financially-aware farmers. Reduced Input Approach (RIA) is intended to contrast with CFP in its severity on non-target invertebrates. It includes minimal use of fungicides and herbicides, which are applied at half rate or less. No insecticides, nematicides or molluscicides are used on RIA plots unless a severe threat of crop loss is evident. The treatments began in 1990-91 after a one-year baseline period in which CFP and RIA plots in each field received the same treatment. Overall, less than 50% of the pesticides applied to CFP were used on RIA in 1991, 36% in 1992 and 35% in 1993. The mean number of pesticide applications per crop was 4.9 for CFP, and 2.0 for RIA (half rate applications counted as 0.5). No insecticides were applied to any RIA plots.

Population monitoring

The overall abundance and diversity of earthworms is monitored biannually, in Spring and Autumn when earthworm activity is expected to be the highest. Three samples are collected in each half-field using a 50 cm x 50 cm quadrat, dropped at random at 10-20m intervals. Preliminary comparison of the formalin and hand-dug methods indicated that a combination of

both was required to obtain fully representative samples of earthworms. This involved hand-digging to the plough layer, followed by extraction of additional worms from below the plough layer using 1.14 litres of a 0.2 % formalin solution spread evenly in the base of the hole to bring up any deep-burrowing species that might be below the plough layer (Edwards & Lofty 1977). Any earthworms emerging in the base of the hole were collected for twenty minutes after the formalin solution was applied. Each sample was subsequently sorted according to species and age classes. The full scientific names of species mentioned in this paper are as follows: *Allolobophora chlorotica*, *Aporrectodea caliginosa*, *Aporrectodea rosea*, *Aporrectodea longa*, *Lumbricus terrestris*, *Octolasion cyaneum*.

Sampling after selected pesticide applications

The occurrence of gross short-term mortality was monitored by searching four 1m x 100m transects of field surface in both the CFP and RIA areas. Samples of worms were collected from the top 50mm of soil using a corer of diameter 150mm. At least 15 cores were taken at 2m intervals, to provide a pooled sample of at least 5g of earthworms which were stored frozen for residue analysis. In addition, a 0.5kg subsample of the soil from the cores was taken for residue analysis. The core depth was chosen to be consistent with that used for estimating exposure of earthworms to pesticides in risk assessment (EPPO/CoE, 1993).

RESULTS

Population monitoring

The density and biomass of earthworms recorded in the first three sampling periods are shown in Figure 1. There were very large differences between farms. By comparison, there were only minor differences between fields within farms, and between CFP and RIA areas in the same field. There was a general tendency for both numbers and biomass to increase over time. None of the samples collected from South field at Gleadthorpe contained any earthworms at all. Data for South field were therefore excluded from all statistical analyses. There was a marked difference between the northern and southern parts of the split field at High Mowthorpe.

Earthworm biomass was highly correlated with density ($r = 0.91$). Split-plot analysis of variance (ANOVA) was conducted separately for each of the three sampling periods, on the square roots of earthworm numbers and on $\log(\text{mass}+1)$, taking the mean of the three samples from each half-field to avoid pseudo-replication. The results confirmed the predominance of differences between farms, which were highly significant ($P < 0.05$) in every case except for biomass in Spring 1994, when an increase in variability between fields reduced the significance level to $P = 0.08$. Only for earthworm numbers in Autumn 1993 was there a significant difference between the CFP and RIA treatments ($F_{1,4} = 8.81$, $P < 0.05$), reflecting higher numbers for RIA than CFP at Drayton and High Mowthorpe, although the reverse was true at Gleadthorpe. In Spring 1993 there was a significant interaction between farm and treatment ($F_{2,4} = 10.1$, $P < 0.05$), reflecting the fact that while at Drayton higher numbers occurred for CFP than RIA, the reverse was true at the other two farms. It can be concluded that those differences which related to the treatments were relatively small, and were not consistent between farms or over time.

Differences between farms were again the main feature when species and age composition were examined. Mean numbers for each farm are shown in Tables 1 and 2. The populations at Drayton were dominated by juveniles, and by the species *A. chlorotica* and *A. caliginosa*, whereas there was a much more even distribution of worms amongst age classes and species at High Mowthorpe. *A. rosea* was rare at both sites. There were so few worms at Gleadthorpe that meaningful comparisons of population composition with the other sites were not possible. Statistical analysis (Tarrant et al. in prep.) confirmed the predominance of differences between farms, and showed that there were no consistent differences in age and species composition between the RIA and CFP treatments. However, there were some significant shifts in species and age composition over time.

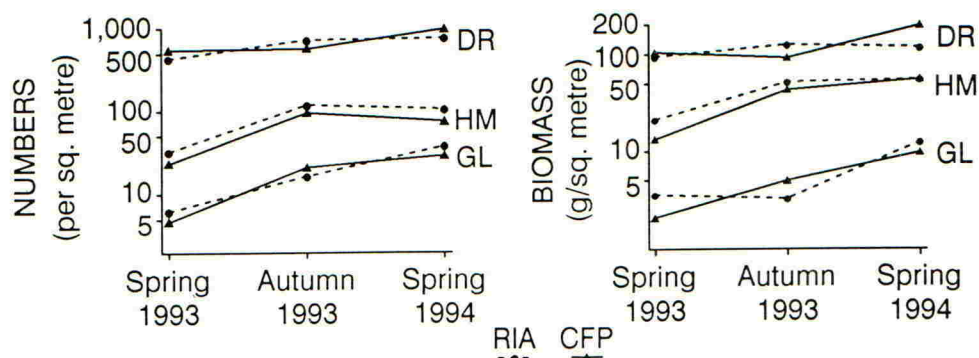


FIGURE 1. Earthworm densities and biomass in the SCARAB plots. DR = Drayton, HM = High Mowthorpe, GL = Gleadthorpe.

TABLE 1. Mean numbers of earthworms per square metre by species, based on data pooled over three sampling periods. Each value is the mean of 36 samples (DR and GL) or 54 (HM).

	Drayton	High Mowthorpe	Gleadthorpe
<i>Lumbricus terrestris</i>	35	13	1
<i>Aporrectodea longa</i>	26	20	0
<i>Allolobophora chlorotica</i>	378	13	1
<i>Aporrectodea caliginosa</i>	233	36	21
<i>Octolasion cyaneum</i>	8	4	0
<i>Aporrectodea rosea</i>	3	0.4	0
Unidentified	1	1	0

TABLE 2. Mean numbers of earthworms per square metre by age class, based on data pooled over three sampling periods. Totals differ slightly from Table 1 due to rounding.

	Drayton	High Mowthorpe	Gleadthorpe
Juvenile	532	47	9
Sub-adult	83	22	5
Adult	70	18	8

Sampling after selected pesticide applications

Sampling was carried out on two occasions in June 1993, to assess the practicality of the methods. Worms and soil collected on the fifth day after an application of omethoate at Drayton were found to contain no detectable residues of omethoate (detection limit 0.02 mg/kg). Sampling on the second day after an application of dimethoate at Drayton produced positive results. The soil sample contained 0.22 mg/kg dimethoate, while the worms contained 0.15 mg/kg. Both worm samples were obtained by taking 150 mm cores, which proved extremely difficult in the dry conditions which prevailed. For neither pesticide were any worms found on the soil surface.

DISCUSSION

Population monitoring

The results showed that although some differences existed between earthworm populations in RIA and CFP plots they lacked consistency between the pairs of plots, and were of negligible magnitude compared to overall differences between the farms. This was true both for the analyses of overall numbers and biomass, and for age and species composition. It can therefore be concluded that, at this stage of the project, the two regimes of pesticide use caused no ecologically-significant differences in earthworm populations.

The substantial differences in earthworm populations between farms were largely consistent with the expected effects of differences in climate, soil types, crop types and cultivations (Edwards and Loftly 1977). Drayton had the highest earthworm populations, perhaps because of the predominance of pasture there in previous years. High earthworm densities are common in pasture, partly because of reduced frequency of cultivations and manuring by livestock. Overall densities and biomass at High Mowthorpe were rather low for arable fields. The loamy soil over chalk should be favourable for earthworms, but prolonged low temperatures will inhibit reproduction and freezing conditions will kill immature juvenile stages unable to burrow deep enough to escape temperatures below 0° C. The very low numbers of earthworms found at Gleadthorpe are probably attributable to the sandy nature of the soil and the growing of root crops in earlier years. Sandy soil is often unfavourable for earthworms due to low moisture content and low pH. Root crops involve more frequent and deeper cultivations than other crops.

Effects of selected pesticide applications

Omethoate and dimethoate are both organophosphorus insecticides which are likely to be of some toxicity to earthworms (dimethoate is described as 'slightly toxic' by Edwards and Bohlen (1992)). However, no dead earthworms were found on the soil surface in searches 5 days after omethoate application, and 2 days after dimethoate. The residues found after the application of dimethoate may be compared with the estimates which would be used in the preliminary stages of risk assessment. Given the application rate of 336 g active ingredient (ai)/ha, and assuming all the pesticide remains in the top 5 cm of soil, and soil density of 1.4 g/cm³, the predicted maximum residue in our samples would be 0.48 mg/kg (EPPO/CoE 1993), compared to the observed value of 0.22 mg/kg. Given that the prediction is

intentionally worst-case, the agreement is reasonable. Predicted residues in earthworms are sometimes based on the simple assumption that the earthworm contains 30% soil, and does not accumulate the chemical in its tissues. This would give an expected concentration in the worms of 0.14 mg/kg (based on predicted soil concentration) or 0.07 mg/kg (based on actual soil concentration). The observed value of 0.15 mg/kg is high enough to suggest that the method of prediction may be unconservative for at least some chemicals.

For omethoate applied at 630 g ai/ha, predicted concentrations would be 0.9 mg/kg in soil and 0.27 mg/kg in worms, but no residues were detected. This may be due to a number of differences between pesticides which are ignored in making the predictions. The samples for omethoate were taken later after application than those for dimethoate; omethoate is more susceptible to hydrolysis (Worthing and Walker 1983); omethoate is slightly more volatile; and preliminary experiments showed that more omethoate became bound in soil. In the light of these points it is not surprising that soil residues of omethoate were well below the worst-case prediction.

ACKNOWLEDGEMENTS

This work was funded by MAFF Pesticides Safety Directorate. We are very grateful to ADAS staff for their cooperation, and to J R Lofty for advice on earthworm identification.

REFERENCES

- Bowerman, P. (1993) Sequels to the Boxworth Project - studies of environmental, agronomic and economic effects of reduced crop inputs. *Journal of the Royal Agricultural Society, England* **154**, 45-60.
- Cooke, A.S.; Greig, Smith, P.W. & Jones, S.A. (1992) Consequences for vertebrate wildlife of toxic residues in earthworm prey. In: *Ecotoxicology of earthworms*. eds. P.W. Greig-Smith, H. Becker, P.J. Edwards & F. Heimbach. Intercept Ltd, Andover. pp. 159-168.
- Edwards, C.A. & Bohlen, P.J. (1992) The effects of toxic chemicals on earthworms. *Reviews of Environmental Contamination and Toxicology* **125**, 23-99.
- Edwards, C.A. & Lofty, J.R. (1977) *Biology of earthworms*. Chapman & Hall, London.
- EPPO/CoE (1993) Decision-making scheme for the environmental risk assessment of plant protection products. Chapter 8. Earthworms. *EPPO Bulletin* **23**, 131-149.
- Greig-Smith, P.W. (1992) Risk assessment approaches in the UK for the side-effects of pesticides on earthworms. *Ecotoxicology of earthworms*. eds. P.W. Greig-Smith, H. Becker, P.J. Edwards & F. Heimbach. Intercept Ltd, Andover. pp. 159-168.
- Worthing C.R. & Walker, S.B. (1983) *The pesticide manual* - 7th edition. British Crop Protection Council, Croydon, UK.

MONITORING AND MODELLING PESTICIDE OCCURRENCES IN A RURAL SOURCE OF DRINKING WATER

M. FIELDING, D.B. OAKES, C. CABLE, K. MOORE AND J. WEDDEPOHL
WRc, Henley Road, Medmenham, Marlow, SL7 2HD

ABSTRACT

Around four hundred pesticides are approved for use in the UK and some of these have the potential to reach drinking water sources. The UK has incorporated into national regulations the requirement of the EC Directive on Water Intended for Human Consumption that the concentrations of individual pesticides in drinking water supplies must not exceed the maximum allowable concentration (MAC) of 0.1 µg/l.

Multi-residue methods of analysis for selected pesticides were developed and these were applied to a rural catchment, used as a source of drinking water. Many pesticides, from both agricultural and non-agricultural usage, were detected at concentrations above the MAC in the main river and its tributary.

The factors that govern the occurrence of pesticides in water sources, such as usage, seasonal effects and pesticide properties, and models to predict their occurrence were investigated. A predictive model was developed to simulate pesticide transport and fate through the catchment into the water. The model was able to simulate concentrations similar to those detected in the river for the major contaminant pesticides used for agricultural purposes.

INTRODUCTION

Approximately four hundred pesticides are approved for use in the UK and some of these have the potential to reach water sources used for drinking water supplies. As pesticides concentrations above the MAC have been detected in some of these water sources a study was undertaken to investigate the occurrence and sources of pesticides in water. The study was undertaken on a surface water source catchment. This paper covers some techniques and observations resulting from the study on surface water sources of drinking water. More details are given in Cable *et al.* (1994).

CATCHMENT SELECTION

The River Leam catchment in Warwickshire and Northamptonshire (English Midlands) was selected for study. The River Leam flows into the Warwickshire Avon between the towns of Leamington and Warwick and water, for treatment at Campion Hills Drinking Water Treatment Works, is abstracted just upstream of Leamington. The catchment covers an area of 36 547 hectares and is predominantly rural. Over 80% of the catchment is farmed with cereals

and grass being the main crops. Many roads as well as a railway line cross the catchment implying the likely extensive use of non-agricultural herbicides.

The soils are principally of the Denchworth, Evesham and Whimple associations, heavy clays with permeabilities declining rapidly with depth which result in the generation of surface runoff in the top metre or less.

PESTICIDE USAGE AND OCCURRENCE

Pesticide applications were obtained from specialist surveys conducted annually in England and Wales, and those for the River Leam catchment are given in Table 1 and Table 2 (Cable *et al.*, 1994).

TABLE 1. Major agricultural pesticide applications (Active Ingredient) in the River Leam catchment in 1992.

Pesticide	Use (kg)	Pesticide	Use (kg)	Pesticide	Use (kg)
Atrazine	106	Fenpropimorph	2290	Prochloraz	1057
Chlormequat	9204	Glyphosate	3399	Propiconazole	975
Chlorothalonil	3476	Isoproturon	15312	Simazine	710
Chlorortoluron	1322	Mancozeb	1267	Thiabendazole	1593
Chlorpyrifos	981	Mecoprop	2771	Tri-allate	1807
Diquat	1002	Pendimethalin	1470	Trifluralin	1311

TABLE 2. Major non-agricultural pesticide applications (Active Ingredient) in the River Leam catchment in 1992.

Pesticide	Use (kg)	Pesticide	Use (kg)
Atrazine	1.5	Iprodione	45.0
Carbaryl	26.3	Maleic hydrazide	84.0
2,4-D	96.5	Mecoprop	51.5
Dichlobenil	48.9	Thiabendazole	35.6
Diuron	68.9	Thiophanate-methyl	38.0
Glyphosate	97.6	Triclopyr	73.0

In order to collect data for the study a sampling programme was carried out over 1991-1992. Grab samples of river water were taken from various points along the river using twin Winchester bottles with the bottle necks a few inches below the water surface. During sampling, the water temperature was measured and additional samples were taken for determination of total organic carbon, nitrate and suspended solids. The pH of the samples was measured before storing them at 5°C while awaiting three multi-residue pesticide determinations. Results for the major contaminant pesticides are given in Table 3 (Cable *et al.*, 1994).

TABLE 3. Occurrence of pesticides in the River Leam catchment in 1991-1992.

Pesticide	Max. conc. ($\mu\text{g/l}$)	Pesticide	Max. conc. ($\mu\text{g/l}$)
Atrazine	0.58	Isoproturon	7.45 * (1.52)
Carbendazim	0.17	Linuron	1.94
Chlorotoluron	0.41	Mecoprop	110.00 * (0.93)
2,4-D	0.25	MCPA	86.40 * (1.16)
Diuron	0.47	Simazine	0.40
Flutriafol	0.22	Trietazine	0.17

*transient peaks in the River Itchen tributary. The next highest concentration observed is given in brackets.

There appeared to be no obvious correlation of pesticide concentrations with rainfall and river flow, although such relationships may have been obscured by trends in pesticide applications. Due to uniform cropping patterns throughout the catchment, there was no correlation between pesticide use and the occurrence of pesticides at different sites. Triazines were detected at levels above $0.1 \mu\text{g/l}$ but apart from trietazine, which had little usage in the catchment, their presence could be explained by their mobility, persistence and pattern of usage. There was evidence from monitoring over three years, by Severn Trent Water plc, that atrazine levels have declined recently due, no doubt, to reduced usage brought about by new legislation covering non-agricultural use.

Several urons were detected, especially isoproturon which was the pesticide detected most frequently and most consistently at high levels. The results for isoproturon were consistent with its mobility, persistence and pattern of use. Levels of diuron were increasing probably because of its use as an alternative to atrazine.

Mecoprop, which is used in high quantities, occurs at relatively high levels, but less frequently than isoproturon. This probably reflects the fact that mecoprop degradation in soil is faster than that for isoproturon.

Very high levels of mecoprop and MCPA, and to a lesser extent, isoproturon and linuron, detected at one sampling point, strongly indicated a point-source, probably related to pesticide misuse. Such point-sources of contamination could be fairly common, but are probably short term, and consequently, may be of more significance to local aquatic life than drinking water quality.

It should be noted that the final treated water for public supply from the River Leam contained levels of pesticides consistently below the limit of detection.

PREDICTIVE MODELLING

In order to be able to predict and understand the spatial and temporal variations in pesticide occurrences some form of mathematical modelling is required. Mathematical models allow the factors that govern the occurrence of pesticides in water, such as usage, seasonal

effects, meteorology, and pesticide physico-chemical properties to be investigated. Following validation of the models by comparing predictions with measured concentrations, they may be used as relatively low cost tools to assess various options for catchment control of contaminant pesticides, as well as optimising the cost effectiveness of monitoring strategies. Models may also be used in filling information gaps caused by the financial limitations imposed upon sampling frequency.

It should be borne in mind that modelling cannot be used as a surrogate for monitoring as most models require measured data on which to base their predictive ability. Water companies are required by law to monitor water supplies to ensure compliance with current legislation.

DEVELOPMENT OF A PREDICTIVE MODEL

The predictive model needed to be easy to use and to require minimal, and easily obtained, data while describing the physical processes of pesticide fate and transport to an acceptable level of accuracy.

Whether a pesticide can be found in a water source depends on the use of the pesticide (site of application, amount applied, time applied, method of application) and on its properties as they relate to its mobility and persistence in the environment. Of prime importance also is the mechanism of transport of the pesticide from the site of application to the water courses. This transport mechanism in a surface water catchment is the surface runoff and interflow.

The runoff flow paths through the catchment will depend on the topography, and to allow the model to simulate the runoff process a Digital Terrain Model (DTM) was used to generate topographic heights on a 250 m grid covering the catchment. The DTM also produced the river network and the watershed boundary to define the catchment area. A flow route to the river system was thereby provided for each 250 m grid square in the catchment. It became apparent however that a 250 m grid was inadequate to describe the retardation and degradation processes which demanded a finer spatial resolution. The 250 m model for the Leam catchment required 5900 mesh points which is a practical size for modelling purposes, however a 2 m grid would require over 90 million mesh points which is impractical for the DTM and the pesticide transport model. An alternative approach was therefore used in which the catchment is conceptualised as a set of flowpaths running from topographic highs down to the river system. Each flowpath may be considered as independent of other flowpaths, and pesticide behaviour may then be simulated by modelling 1-D flow down each flow path and summing the inputs to the river. It has been demonstrated with the model, however, that predictions of pesticide transport through the soil are essentially independent of flowpath length and so the catchment may be accurately modelled by a single average length flowpath. This was the approach taken here. As pesticide usage is conceptually evenly distributed over the catchment, the input of water and pesticides to the river may be equated to concentration in the river. The assumptions underlying the model may be summarised:

- water and pesticides move through the upper zone of the soil under hydraulic gradients resulting from catchment topography and rainfall recharge;
- the catchment may be represented by a typical flowpath of length 1350 m, starting on high ground and terminating at the river;

- during movement through the soil the processes of pesticide adsorption onto organic carbon, and chemical and biochemical degradation can occur;
- at the river boundary, water and dissolved pesticides flowing out of the soil are multiplied by the total length of the river and equated to the flow and mass of the pesticide in the river.

Sediment transport of pesticides was not included. Underdrainage was not modelled explicitly, but assumed to be included implicitly in the model formulation.

The flowpath model was based on the method described by Haith (1980) and adapted by subdividing the flowpath into 1 m length cells with a Haith type calculation applied to each cell. The runoff (with dissolved pesticide) from one cell becomes an input to the next downgradient and the concentration in the river is equated to that in the runoff from the final cell in the flowpath. The model used a 5-day timestep.

Runoff was generated from 5-day totals of effective rainfall (rainfall-evaporation \pm soil moisture deficit) derived from a 50-year synthetic rainfall sequence. This sequence was based on the statistical features of actual rainfall in the English Midlands and used to allow the effect of climatic variations on pesticide concentrations to be considered. Runoff was scaled to give an average effective rainfall of 180 mm/yr, valid for the Leam catchment.

Other model parameters included: soil depth, soil bulk density, soil organic carbon, soil water content, pesticide Koc (partition coefficient between water and organic carbon) and T $\frac{1}{2}$ (pesticide half life due to biochemical decay). Results for the major pesticides are given in Table 4.

TABLE 4. Measured and simulated maximum concentrations ($\mu\text{g/l}$) in the Leam catchment at Campion Hill water treatment works.

Pesticide	Koc (ml/g)	T $\frac{1}{2}$ (d)	Measured	Simulated
Isoproturon	107	20	2.40	2.63
Chlorotoluron	175	135	0.30	0.25
Mecoprop	127	28	0.68	0.44
Diuron	288	64	0.65	0.66
Flutriafol	1200	600	0.22	0.02
Carbendazim	129	52	0.07	0.04

In most cases the model predictions were good. For Flutriafol the physico-chemical properties database is very limited and must be considered suspect. Plots of measured against simulated concentrations showed good agreement. Variations in predicted annual peak concentrations were seen to be due to annual variations in rainfall recharge, particularly the incidence of runoff immediately after pesticide application. Low peak concentration result when there is little runoff at the time of application so that biochemical decay significantly reduces the loading on the catchment prior to transport into the river.

CONCLUSIONS

A monitoring programme to sample for pesticides in the surface waters of the River Leam catchment has been described. A wide range of pesticides, mainly herbicides and a few fungicides, were detected. Many occurred at levels in excess of 0.1 µg/l. Monitoring showed that pesticides used in non-agricultural situations showed the most tendency to reach river water.

Triazine herbicides were detected at significant levels due to their chemical properties and usage patterns. Urons, especially isoproturon, were consistently detected at all sampling sites. This can be explained by high mobility and persistence and, particularly in the case of isoproturon, high agricultural usage. Isoproturon was the pesticide detected most consistently at significant levels during this study. Mecoprop, which is applied in large amounts, also occurred at relatively high levels but less consistently than isoproturon, probably due to lower usage and persistence. Some anomalies occurred in that pesticides with high usage, mobility and persistence were not detected at the expected high levels. Some pesticides that would be expected to be detected at high concentrations were excluded from the study due to difficulties with the analytical detection methods. Extremely high concentrations of pesticides at one of the locations indicated possible misuse of pesticides (i.e. a virtual point-source).

A model was developed to simulate pesticide concentrations in the River Leam resulting from pesticide applications in agricultural situations only. The model was validated against measured data and appears to be capable of providing reasonably accurate predictions of pesticide concentrations. Timing (not amount) of rainfall after pesticide application was seen to be the major factor controlling the severity of pesticide contamination to surface waters.

ACKNOWLEDGEMENTS

This paper is based on work funded by the Department of the Environment under the supervision of the Drinking Water Inspectorate, and their permission to publish is gratefully acknowledged. The co-operation of Severn Trent Water plc is also acknowledged.

REFERENCES

- Cable, C.J.; Fielding, M.; Gibby, S.; Hegarty, B.F.; Moore, K.M.; Oakes, D.B.; Watts, C.D. (1994) Pesticides in drinking water sources. WRc report to the Department of the Environment. WRc Report No. DoE 3376(P).
- Haith, D.A. (1980) A mathematical model for estimating pesticide losses in runoff. *Journal of Environmental Quality*, **9**, 428-433.

A MICROCOSM SYSTEM FOR EVALUATING THE EFFECTS OF PESTICIDES ON DYNAMIC SOIL PROCESSES AND SOIL ORGANISMS

CLIVE A. EDWARDS, SCOTT SUBLER, SHU-KANG CHEN

The Ohio State University, Department of Entomology, Columbus, Ohio, 43210, U.S.A.

ABSTRACT

Residues of many pesticides reach soil, affect populations of soil-inhabiting invertebrates and soil microorganisms, and influence dynamic soil processes that facilitate the release of plant nutrients from organic matter. Pesticide residues may also be taken up into plants or leached into groundwater. There have been many techniques used to assess the effects of pesticides on individual components of soil ecosystems, but few holistic methodologies which investigate the effects of pesticides on dynamic soil processes and soil organisms and simultaneously assess their leaching and uptake into plants.

We describe a laboratory soil microcosm technique with plants grown in soil treated with pesticides. Effects of the pesticides on rates of breakdown of organic matter, transformations of soil NH_4 and NO_3 , soil microbial biomass N, soil respiration, soil enzyme activity (dehydrogenase, urease, phosphatase and cellulase) and plant uptake of N were assessed at frequent intervals after treatment with the pesticide. Data on the effects of benomyl and captan on soil microbial and nutrient cycling processes are presented.

INTRODUCTION

The maintenance of soil quality, fertility, and structure is essential to the protection and maintenance of the biodiversity and integrity of terrestrial ecosystems. Critical to achieving this aim is understanding the potential effects of pesticides on the structure and function of soil ecosystems. Pesticides can affect soil organisms, species interactions, nutrient cycling and soil food webs (Tu & Miles, 1976; Parmelee *et al.*, 1993a; Edwards, 1994).

Most of the single-species or single-process tests that have been used to date, in soil ecotoxicological research and for environmental risk assessment, fall short of providing data which can predict the environmental consequences of chemical contamination in the field adequately (Van Voris *et al.*, 1985). Field studies, although perhaps providing realistic conditions for ecotoxicological assessment, are usually limited severely by soil variability, inadequate controls, poor reproducibility, and exorbitant costs (Edwards, 1992).

In recent years, terrestrial ecologists have been using simplified model ecosystems, or microcosms, as tools to investigate species interactions and ecosystem processes, and to elucidate relationships between soil microorganisms and micro- and macro-invertebrates (Anderson & Ineson, 1984), as well as the effects of soil and litter-dwelling organisms on organic matter decomposition and nutrient cycling processes (Tueben, 1991).

An integrated microcosm approach, in which a suite of organismal and process-level measurements, involving different levels of ecological organization, are made can provide a much broader understanding of the mechanisms by which chemicals affect the structure and function of soil ecosystems, resulting in a much more flexible and widely-applicable predictive capability. Such an approach combines measurements of soil organism populations, soil processes, and plant growth, as well as the bioaccumulation and persistence of chemical contaminants into a single testing system. This approach can offer great possibilities as a widely applicable and cost-effective means of assessing the possible effects of chemicals on soil ecosystems and environmental quality.

Key parameters of the function of ecosystems include: the size of microbial and invertebrate populations, the rates of organic matter decomposition and the rates of release of plant nutrients. Major components of these soil processes are rates of soil respiration and the level of activity of free enzymes released into soil by microorganisms. In addition to assessing the effects of pesticides on soil ecosystems, it is also important to assess the persistence of pesticides in soils, their leaching and volatilization from soils and their uptake into plants.

In recent years, interest has begun to develop in the use of microcosm techniques for ecotoxicological assays (Sheppard, 1994; Van Voris *et al.*, 1985). Microcosms used have consisted of soil units containing several biotic species and have ranged in size from a few grams of soil to units as large as up to a metre in diameter. They have consisted of mixed cultures of organisms and artificial substrates (Ausmus *et al.*, 1979), mixed soil containing organisms (Lichtenstein, 1980; Edwards & Bohlen, 1992) or intact cores from the soil ecosystem that they represent (Van Voris, 1985). The attraction of such microcosm tests is that they can assess the impact of a contaminant at different levels of biological organization and produce data that is much more relevant to the field situation.

The size of microcosms used in tests have ranged from as small as 4 g soil to much larger systems involving intact cores 17.5 cm diam x 60 cm deep. Kuehle (1988) described an even larger system which consisted of undisturbed soil cores 72 cm diam x 43 cm deep planted with four different crops and Kappers and van Estoroek (1987) and Kappers and Manger (1990) used similar-sized cores to assess the effects of chemicals on nematodes. Nearly all of the microcosms described in the literature to date are large and use intact soil cores. Although these can simulate field conditions well, and may be especially useful for leaching studies, they create major problems in reproducibility, because of: soil variability, particularly for large microcosms, the lack of contact between soil organisms and the contaminant, and the relatively short time-span of many tests. We describe here a much smaller, inexpensive and cost-effective technique which yields extensive data. Because of the small size and relative simplicity of the soil microcosms, large numbers of replicates can be handled in individual experiments.

METHODS

We used soil microcosms in a laboratory investigation of the effects of two pesticides on soil microbial processes and nutrient dynamics. Each soil microcosm consisted of a core of freshly collected field soil, sieved, mixed and packed gently into a plastic cylinder. Wheat seedlings were planted into the soil (Figure 1). The cylinder was 5 cm (inside diam) x 15 cm high made of commercially-available high density polyethylene (HDPE) pipe. The pesticides tested were benomyl and captan. Soils were treated with the chemicals at concentrations

equivalent to recommended field rates (51 ppm a.i. for benomyl and 125 ppm a.i. for captan). This is based on the assumption that surface-applied chemicals are concentrated into the upper 2 cm of soil at a bulk density of 1.2 g/cm^3 . A small quantity of organic material (chopped wheat straw) contained within a small cylinder of fiberglass screen material ($1.6 \times 1.8 \text{ mm}$ mesh) was inserted into the surface of the microcosm soil to measure the rates of decomposition of the organic material.

SOIL MICROCOSM

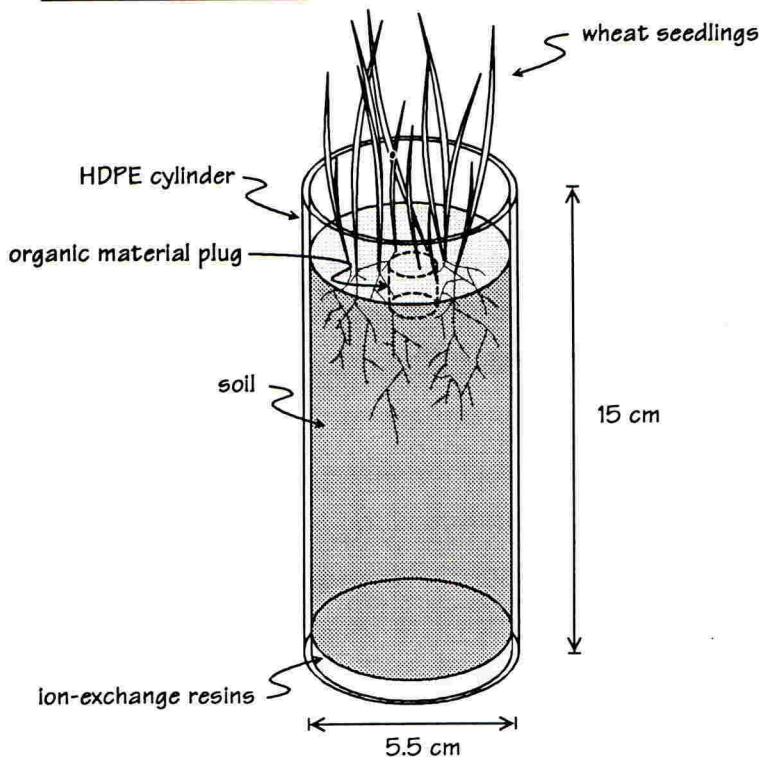


Figure 1. Schematic diagram of the soil microcosm

At the bottom of each microcosm cylinder there was a layer of mixed-bed ion-exchange resins separated from the soil core by a thin layer of nylon stocking material. This allowed free passage of soil leachate from the microcosms, and acted as a partial barrier to prevent root growth out of the core bottom, while collecting nutrient ions leaching from the microcosms. Water was added two or three times a week to maintain a soil moisture content between 30-40% (dry weight basis)

Six wheat seeds were planted in the surface 0.5 cm of the microcosm soil. After one week, germination success was recorded for each microcosm. At regular intervals, soil from each microcosm sampled was removed, mixed gently and subsampled to determine amounts of soil respiration, microbial biomass, soil enzyme activity (dehydrogenase, urease and

phosphatase), rates of organic matter decomposition, and nitrogen dynamics. Ion-exchange resins were analyzed to determine cumulative leaching losses of inorganic N, and plant shoots and roots were separated and analyzed for biomass and tissue nutrient concentrations. By repeating these measurements at regular intervals, on microcosms incubated for different periods over a total of 56 days, an integrated view of the dynamic effects of the chemicals on soil organisms, soil processes, and plant growth could be obtained.

The microcosms can be readily adapted for additional measurements of the influence of chemicals on soil fauna and of the fate and transport of pesticides. In addition to the soil microarthropods and nematodes that are normally present in fresh, field-collected soil, small earthworms can be added to the microcosms. These represent macrofaunal integrators of the effects of chemicals on soil microbial and food web processes, and as biomarkers of the bioaccumulation and toxicity of contaminants. Earthworm biomass, tissue C and N concentrations, and tissue contaminant concentrations can be determined at the termination of microcosm experiments or at intermediate intervals. Concentrations of chemical contaminant residues in the soil and in plant tissues can also be measured at the end of experiments or at intermediate intervals to assess contaminant bioaccumulation and persistence.

RESULTS

Soil Variable	Chemical Treatment		
	Control	Benomyl	Captan
	Day 7		
SIR (mg CO ₂ /kg soil/hour)	0.80±0.39 ^a	10.97±1.13 ^a	7.71±0.25 ^b
DHA (mg TTF/kg soil/hour)	10.38±1.06 ^a	7.34±1.80 ^a	1.88±0.45 ^b
NH ₄ -N (mg/kg soil)	1.59±0.35 ^b	1.81±0.23 ^b	10.04±0.57 ^a
NO ₃ -N (mg/kg soil)	10.68±1.47 ^a	11.90±1.19 ^a	10.93±1.92 ^a
Net nitrification (mg/kg soil/d)	-0.69±0.37 ^a	-1.00±0.30 ^a	-3.23±0.48 ^b
Net N-mineralization (mg/kg soil/d)	-1.26±0.34 ^a	-1.73±0.30 ^a	-5.38±0.55 ^b
	Day 28		
SIR (mg CO ₂ /kg soil/hour)	30.83±12.86 ^a	14.70±2.45 ^a	7.37±1.65 ^a
DHA (mg TTF/kg soil/hour)	3.26±0.96 ^a	4.53±1.78 ^a	2.85±0.86 ^a
NH ₄ -N (mg/kg soil)	2.08±0.26 ^b	1.85±0.18 ^b	16.30±4.75 ^a
NO ₃ -N (mg/kg soil)	3.83±0.28 ^a	6.22±1.98 ^a	4.51±1.05 ^a
Net nitrification (mg/kg soil/d)	-0.15±0.007 ^a	0.22±0.17 ^a	0.05±0.09 ^a
Net N-mineralization (mg/kg soil/d)	0.03±0.03 ^b	0.10±0.02 ^b	0.87±0.30 ^a

Table 1. Mean values of substrate induced respiration (SIR), dehydrogenase enzyme activity (DHA), inorganic N concentrations, and rates of net nitrification and N mineralization in soil sampled from microcosms 7 and 28 days after treatment with pesticides (Mean±SE). For each variable, means with different letters are significantly different ($P < 0.05$), as determined by Tukey's multiple comparisons test following single classification ANOVA.

Preliminary data are presented to illustrate the utility of this approach for investigating the effects of chemicals on soil systems. Seven days after chemical treatment, substrate induced respiration (SIR), as determined by CO₂ production of the soil following amendment with a glucose solution, and soil dehydrogenase activity (DHA), an index of the respiratory activity of soil microorganisms, were both significantly lower in soils treated with captan than in untreated (control) soils (Table 1). Benomyl had no significant effect on these variables. Conversely, NH₄-N concentrations in soils treated with captan were significantly higher than in benomyl-treated or control soils. Rates of net nitrification and net N mineralization between three and seven days following chemical treatment were negative in all soil treatments (indicating net reduction in nitrate concentrations and net immobilization of inorganic N). Captan-treated soils showed greater reductions in nitrate concentrations and greater net N immobilization than benomyl-treated and control soils.

Twenty-eight days after chemical treatments, no significant effects of captan or benomyl on SIR or DHA were detected. However, NH₄-N concentrations in captan-treated soils were significantly higher than in other soils. Rates of net N mineralization after 28 days were positive in all soil treatments, with captan-treated soil having significantly greater rates than the other soils.

Reduced microbial activity in captan-treated soils, indicated by short-term reductions in SIR and DHA, is consistent with lower initial rates of net nitrification and net N mineralization, since both of these processes are mediated microbially. Significant NH₄ accumulation over 28 days in the captan-treated soil appeared to result from a combination of lower initial nitrification rates, and subsequent higher rates of net N mineralization, than in the other soils.

Using the integrated microcosm approach, the conclusion that captan can increase short-term inorganic N availability in soils is supported both by direct measurements of NH₄-N and NO₃-N concentrations, and also by mechanistic explanations derived from corresponding measurements of microbial activity and N-cycling processes.

REFERENCES

- Anderson, J.M.; Ineson, P. (1984) Interactions between micro-organisms and soil invertebrates in nutrient flux pathways of forest ecosystems. In: *Invertebrate-Microbial Interactions*, J.M. Anderson, A.D.M. Rayner & D.W.H. Walton (Eds.), Cambridge University Press, pp. 59-88.
- Ausmus, B.S.; Kimbrough, S.; Jackson, D.R.; Lindberg, S. (1979) The behavior of hexachlorobenzene organic soil pollutant in pin Pinus forest microcosms: transport and effects on soil processes. *Environmental Pollution*, 20(2), 103-111.
- Edwards, C.A. (1994) Pesticides as environmental pollutants. In: *World Directory of Pesticide Control Organizations*, 2nd Edition, E. Ekstrom (Ed.), Crop Protection Publications. Royal Society of Chemistry, pp. 1-24.

- Edwards, C.A. (1992) Testing the Effects of Chemicals on Earthworms: The Advantages and Limitations of Field Tests. In *Ecotoxicology of Earthworms*. P.W. Greig-Smith, H. Becker, P.J. Edwards and F. Heimbach (Eds). Intercept, Andover, U.K. 75-84.
- Edwards, C.A.; Bohlen, P.J. (1992) The assessment of the effects of toxic chemicals upon earthworms. *Reviews of Environmental Contamination and Toxicology*, **125**, 23-99.
- Kappers, F.I.; van Esbroek, M.L.P. (1987) Use of soil organisms in experiment on vulnerability to soil pollutants. *Verslagen en Mededelingen*, Commissie voor Hydrologisch Onderzoek TNO, **38**, 161-164.
- Kappers, F.I.; Manger, R. (1990) Population dynamics of free-living nematodes in oil contaminated soil during the clean-up with a microbiological restoration technique. *Nematologica*, **36**, pp. 363.
- Kuehle, J.C. (1988) Radioecological studies on earthworms and their value for ecotoxicological risk assessment. In *Earthworms in Waste and Environmental Management*. C.A. Edwards and E.F. Neuhauser (Eds). The Hague, The Netherlands, SPB Academic Publishing, 377-388.
- Lichtenstein, E.P. (1980) Fate and behavior of pesticides in a compartmentalized microcosm. In: *Microcosms in Ecological Research*, J.P. Giesy (Ed.), J.P. Technical Information Center, U.S. Department of Energy, DOE Symposium Series 52 CONF-781101, pp. 954-970.
- Parmelee, R.W.; Wentzel, R.S., Phillips, C.T., Simini, M.; Checkai, R.T. (1993) Soil microcosm for testing the effects of chemical pollutants on soil fauna communities and trophic structure. *Environmental Toxicology and Chemistry*, **12**, 1477-1486.
- Sheppard, S.C. (1994) Toxicity testing using microcosms. In: *Soil Ecotoxicology* G. Bitton, J. Tarradellas and D. Rossel (Eds.), Michigan, Lewis Publishers (in press).
- Tueben, A. (1991) Nutrient availability and interactions between soil arthropods and microorganisms during decomposition of coniferous litter: a mesocosm study. *Biology and Fertility of Soils*, **10**, 256-266.
- Tu, C.M.; Miles, J.R.W. (1976) Interactions between insecticides and soil microbes. *Residue Reviews*, **64**, 17-65.
- Van Voris, P.; Tolle, D.A.; Arthur, M.F.; Chesson, J. (1985) Terrestrial microcosms: applications, validation and cost-benefit analysis. In: *Multispecies toxicity testing*, J. Cairns, Jr. (Ed.), New York: Pergamon Press, 117-142.

THE QUANTACOUNT: QUANTUM YIELDS AND MODELLING DIRECT AQUEOUS PHOTOLYSIS

F. MOFFATT, A. WADLEY

Environmental Sciences Department, Zeneca Agrochemicals, Jealotts Hill Research Station, Bracknell, Berks RG12 6EY

ABSTRACT

This paper outlines an approach to meeting new regulatory requirements for Germany and the European Union to determine quantum yields and environmental half-lives for direct photolysis of pesticides in water. Practical issues addressed include low solubility in water, weak absorption in the sunlight region and multiple chromophores. Quantum yields were determined using a QuantaCount (Amko GmbH). Calibration using chemical actinometers and a modification of the QuantaCount are described. A streamlined procedure was devised to generate results rapidly. The model for calculation of environmental half-lives used sunlight intensities but took each month in isolation and so was extended to take account of light changes throughout the year giving a more meaningful interpretation.

INTRODUCTION

ECETOC work (1981 and 1984) led to Umweltbundesamt guidelines (1990) for direct aqueous photolysis studies. It was argued that 70% of new chemicals reach the aquatic environment and photolysis may be the only degradation pathway. The rate of photolysis is governed by the quantum yield, a parameter that is independent of the light source. A study is triggered when enough sunlight is absorbed ($\epsilon > 10$ at a wavelength ≥ 295 nm, where ϵ is the extinction coefficient in $l \text{ mol}^{-1} \text{ cm}^{-1}$).

Quantum yields for photolysis (Φ) may be derived experimentally as the ratio of moles degraded to Einsteins of light (Avogadro's number of photons) absorbed. A convenient method is to irradiate a solution of the chemical in a cuvette by means of a QuantaCount, which acts as an electronic actinometer, "counting" the amount of light absorbed. The "counts" can be converted to Einsteins by calibration using a chemical actinometer. The decrease in concentration through photolysis can be determined by chemical analysis.

Computer programs (Zepp & Cline, 1977; Frank & Klöpffer, 1989) use experimental ϵ and Φ values to calculate environmental half-lives ($t_{1/2}$). Environmental parameters are sunlight intensity values as a function of wavelength for particular latitudes and attenuation values for light passing through natural water bodies. The model gives a table of $t_{1/2}$ values for each month for a particular depth of water. This provides a range of degradation rates in a range of environmental conditions. $t_{1/2}$ derives from the pseudo first order rate constant for direct photolysis, k , where $k \propto \sum \Phi(\lambda) \epsilon(\lambda) \Delta\lambda I_0(\lambda)$ (where $I_0(\lambda)$ is the photon irradiance in $\text{einstein cm}^{-2} \text{ s}^{-1}$)

METHODS AND MATERIALS

UV/visible absorption spectra were determined on a Perkin Elmer Lambda 2 spectrophotometer. This established whether a study was triggered; provided ϵ data; and enabled selection of a wavelength for irradiation.

Quantum yields were determined by irradiation with light from a 1000W Xenon arc lamp in a QuantaCount. A monochromator provided light of the chosen wavelength range. Silicon solar cell photodetectors produced electrical signals which were converted into "counts" of the amount of light absorbed during irradiation.

Two chemical actinometers were used to calibrate the QuantaCount, Actinochrome IR (Brauer & Schmidt, 1983) and potassium ferrioxalate (Parker, 1953; Hatchard & Parker, 1956). The former is thermally stable and reversible. The ferrioxalate system is well established and useful over a large range of wavelengths but care must be exercised in its use (Bowman & Demas, 1976).

Aqueous solutions (3.5 ml) of the chemicals (with acetonitrile co-solvent if needed) were irradiated in 1.00 cm quartz cuvettes at a set wavelength range and time e.g. 290-310 nm for 3 h. Initial concentrations were 0.1-50 mg l⁻¹ (ca 10⁻⁶-10⁻⁴ M). Losses of 1-12% were determined directly by reverse phase HPLC. Stability to hydrolysis and the absence of acid/base dissociation at environmental pH ranges had been established.

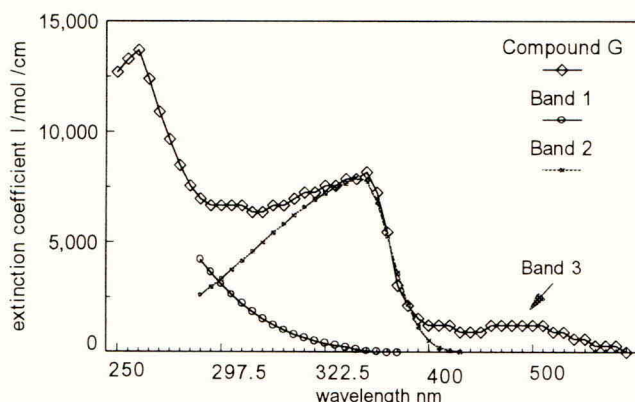
The Frank & Klöpffer model was chosen to estimate $t_{1/2}$ of the chemicals in water with photolysis as the only theoretical loss route. A set of data for river water described light attenuation with depth and other water quality parameters for each month. This gave $t_{1/2}$ for each month based on the average monthly sunlight intensities measured over 10 years. Two closed systems were considered: a 5cm depth surface layer and a 30cm 'pond'. These $t_{1/2}$ values assume constant conditions, therefore any predicted half-life longer than one month will not take account of different sets of conditions during ensuing months. The model output was processed to integrate the monthly outputs and produce half-lives for a theoretical release in any month of the year.

RESULTS & DISCUSSION

Calibration of the QuantaCount using Actinochrome IR was particularly convenient. A few seconds irradiation was enough, enabling calibration to be completed within minutes. However, the wavelength range for calibration is limited to 248-334 nm so for longer wavelengths ferrioxalate was used. This was much more time consuming and tricky because normal fluorescent lighting caused decomposition at 0.13% per minute.

Six compounds, A-G, were studied. Compounds C-F had insufficient water solubilities (< 0.1 mg l⁻¹) for both UV spectroscopy and quantum yield measurements so acetonitrile was added (Table 1). For example, at the trigger value of $\epsilon = 10$ and a concentration of 10⁻³ M the absorbance is 0.01, at which level the specified accuracy of our spectrophotometer is $\pm 50\%$ (± 0.005). The QuantaCount gave best reproducibility when absorbances were $\geq 5\%$. Compound G had three absorption bands above 290 nm (Figure 1) with large differences in susceptibility to photolysis (Table 1).

FIGURE 1 Plots of extinction coefficient data points for compound G and Gaussian components for bands 1 and 2



Only absorption bands 1 and 2 contribute to photolysis but they overlap in the high energy region where relative sunlight intensities differ greatly from season to season. To account for this the two major peaks were resolved into component Gaussian curves using the PROC NLIN procedure of SAS (Statistical Analysis System, Version 6.08) according to the equation:

$$\epsilon = a_1 \theta^{b_1(\lambda - u_1)} + a_2 \theta^{b_2(\lambda - u_2)}$$

where $a_{1,2}$ are the peak heights, $b_{1,2}$ are related to peak widths and $u_{1,2}$ are the positions of the peak maxima.

To estimate the impact of the high energy Band 1 weighted means, Φ_{mean} were calculated:

$$\Phi_{\text{mean}} = \frac{\Phi_1 \epsilon_1}{\epsilon_1 + \epsilon_2} + \frac{\Phi_2 \epsilon_2}{\epsilon_1 + \epsilon_2}$$

where $\Phi_{1,2}$ are the quantum yields and $\epsilon_{1,2}$ are the extinction coefficients for band 1 and 2.

Finally, Φ_{mean} and ϵ values were used to compute $t_{1/2}$.

Compounds C-F had very low absorption of sunlight even at the higher concentrations achieved using a co-solvent (Figure 2, Table 1). Therefore irradiations were carried out at wavelengths below those of sunlight (270-290 nm). This is justified because Φ is constant within the same absorption band. The wide bandwidth (20 nm) maximised the light input to the photolysis cell.

FIGURE 2 Plots of extinction coefficient data points for compounds A-F

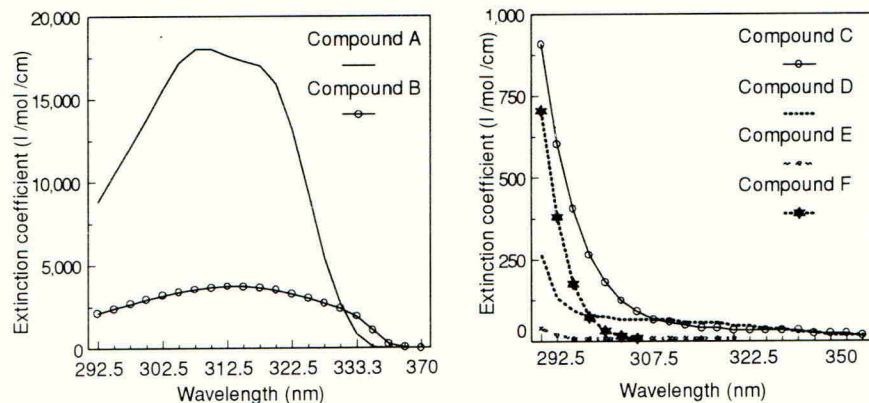


TABLE 1 Conditions and results of irradiation of compounds A-G

Compound	% water in solvent	Wavelength of light (nm)	Irradiation time	milli einsteins absorbed	m mol degraded	Quantum yield
A	100	303-323	1 h	2×10^{-2}	8×10^{-6}	4×10^{-4}
B	100	307-319	2 h	10^{-3}	10^{-5}	10^{-2}
C	50	270-290	4 h	4×10^{-2}	2×10^{-4}	5×10^{-3}
		290-310	4 h	6×10^{-3}	3×10^{-5}	5×10^{-3}
D	50	270-290	15 min	2×10^{-4}	2×10^{-5}	10^{-1}
E	50	270-290	15 min	10^{-4}	7×10^{-6}	7×10^{-2}
F	50	270-290	2 min	6×10^{-5}	2×10^{-5}	3×10^{-1}
G	75	255-275	1.5 h	3×10^{-4}	3×10^{-7}	10^{-3}
		336-356	2 h	9×10^{-3}	4×10^{-7}	4×10^{-5}
		470-490	5 h	6×10^{-3}	0	0

While compounds A,C and G have low quantum yields (Table 2), high absorption of light compensated for this in compounds A and G. Compound C (and the low energy band of compound G) required 4-5 h to produce significant degradation. Since the QuantaCount requires 1h to warm up it was difficult to conclude an experiment within one working day. To speed things up the window area of the cuvette holder was increased from 133 to 300 mm², more than doubling the light falling on the solution. This raised productivity gave significant degradations in minutes in some cases (Table 1).

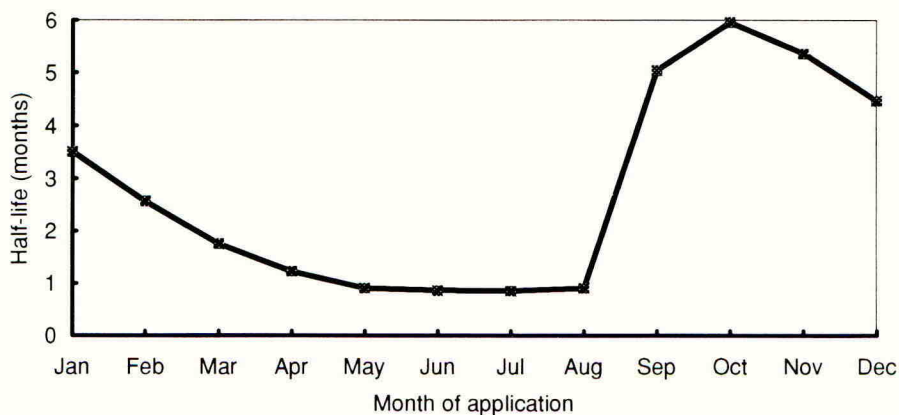
TABLE 2 Environmental half-lives of Compounds A-G due to direct photolysis, calculated using the standard and extended Frank & Klöpffer model

	Light absorption	quantum yield	Standard model half-lives		Extended model half-lives	
			5 cm deep water	30 cm deep water	5 cm deep water	30 cm deep water
A	HIGH	LOW	5 h - 5 d	12 h - 12 d	5 h - 5 d	12 h - 12 d
B	HIGH	HIGH	2 d - 2 m	8 d - 9 m	2 d - 2 m	8 d - 3 m
C	LOW	LOW	11 d - 7 m	1 - 16 m	11 d - 3 m	1 - 5 m
D	LOW	HIGH	1 - 12 d	2 d - 1 m	1 - 12 d	2 d - 1 m
E	LOW	HIGH	1 m - 3 y	3 m - 8 y	1 - 6 m	3 - 8 m
F	LOW	HIGH	2 m - 58 y	6 m - 189 y	2 - 8 m	7 - 12 m
G	HIGH	LOW	3 d - 2 m	9 d - 4 m	3 d - 2 m	9 d - 3 m

Note: Values are arbitrarily classed as HIGH for ϵ values > 1000 and $\Phi \geq 10^{-2}$; or otherwise LOW.

The ranges are based upon mean sunlight intensities in June and December. The influences of ϵ and Φ and environmental variables are shown in $t_{1/2}$ values (Table 2). Where light absorption is low and tails off rapidly in the sunlight region $t_{1/2}$ in the winter are un-realistically prolonged. A spreadsheet was used to calculate $t_{1/2}$ starting from any month but incorporating the effect of variation in conditions with time. Figure 3 shows the predicted $t_{1/2}$ values for Compound E in surface layers.

FIGURE 3 Compound E: predicted half-lives for direct photolysis in 5cm deep water



CONCLUSIONS

Quantum yields can be determined quickly using the QuantaCount.

The susceptibility of a compound to direct photolysis can be established by modelling using its intrinsic properties coupled with environmental variables. This gives rise to a wide range of "possible" half-lives according to the season, depth of water and whether average or extreme sunlight intensities are used. The model clearly shows that the rate of direct photolysis may vary hugely under variable environmental conditions, especially of sunlight intensity.

Estimated half-lives can be drastically reduced by extending the standard model to take account of the variation of conditions over time, especially in cases of very low light absorption (and high quantum yield) under winter conditions. The behaviour of compound F is particularly dramatic, with a half-life falling from 189 years to 12 months (for a simulated 30 cm deep waterbody).

ACKNOWLEDGEMENTS

E McIndoe for fitting the Gaussian distributions. C Wollerton, R Husband & G Walter for providing ϵ data. J P Leahey for technical discussions and suggestions.

REFERENCES

- Bowman, W.D.; Demas, J.N. (1976) Ferrioxalate actinometry. A warning on its correct use. *Journal of Physical Chemistry*, **80**, 2434-2435.
- Brauer, H.D.; Schmidt, R. (1983) A new reusable chemical actinometer for uv irradiation in the 248-334 range, *Photochemistry and Photobiology*, **37**, 587-591.
- ECETOC (1981) An assessment of test methods for photodegradation of chemicals in the environment, *Technical Report No 3*.
- ECETOC (1984) The phototransformation of chemicals in water: Results of a ring - test, *Technical Report No 12*.
- Frank, R.; Klöpffer, W. (1989) A Convenient Model and Program for the Assessment of Abiotic Degradation of Chemicals in Natural Waters. *Ecotoxicology and Environmental Safety*, **17**, 323-332.
- Hatchard, C. G.; Parker, C.A. (1956) A new sensitive chemical actinometer II. Potassium ferrioxalate as a standard chemical actinometer, *Proceedings of the Royal Society A*, **235**, 518-536.
- Parker, C.A. (1953) A new sensitive chemical actinometer I. Some trials with potassium ferrioxalate, *Proceedings of the Royal Society A*, **220**, 104-116.
- Zepp, R.G.; Cline, D. M. (1977) Rates of direct photolysis in aquatic environment, *Environmental Science & Technology*, **11**, 359-366.
- Umweltbundesamt (1990) *Test Guideline: phototransformation of chemical in water: Part A: Direct Phototransformation*, Berlin.

BIOLOGICAL EFFECTS OF THE PESTICIDE SAN 527 I 240 EW IN FRESHWATER PONDS

M. CRANE*, P. WHITEHOUSE

WRc plc, Henley Road, Medmenham, Buckinghamshire, SL7 2HD

* Current address: Department of Biology, Royal Holloway University of London, Egham, Surrey, TW20 0EX

B. LEFEBVRE

Sandoz Agro, PO Box Building 210, CH-4002 Basle, Switzerland.

A. BURDEN

Hazleton UK, Otley Road, Harrogate, North Yorkshire, HG3 1PY

K.C. BROWN

Ecotox Ltd, PO Box 1, Tavistock, Devon, PL19 0YU

ABSTRACT

SAN 527 I 240 EW (MAVRIK® AQUAFLOW) is a product containing the synthetic pyrethroid tau-fluvalinate which may be used for controlling a broad range of arthropod pests. Laboratory studies suggest that there may be significant effects on non-target aquatic organisms. A study was therefore performed to assess the impact of SAN 527 I 240 EW on freshwater ponds.

Detrimental effects on the survival of *Cyprinus carpio* were evident only at an application rate of 48 g ai/ha. Total zooplankton abundance and populations of benthic organisms were not significantly affected by applications of SAN 527 I 240 EW. However, densities of cladocerans, copepods and winged insects declined and rotifers became more abundant in response to the pesticide. These effects were generally short-lived, reflecting the low persistence of tau-fluvalinate in water and sediment.

The results with SAN 527 I 240 EW are consistent with similar studies on other pyrethroid insecticides, with acute effects on certain aquatic taxa followed by rapid recovery.

INTRODUCTION

Sandoz Agro has developed a new product, SAN 527 I 240 EW, for the control of insect pests and mites in a variety of crops. The active ingredient is tau-fluvalinate ((RS)- α -cyano-3-phenoxybenzyl-N-(2-chloro- $\alpha\alpha\alpha$ -trifluoro-*p*-tolyl)-D-valinate). Laboratory studies show that tau-fluvalinate is highly toxic to certain aquatic taxa. However, the exposure of aquatic organisms to this substance in natural systems may be lower than that

experienced in laboratory systems where losses of chemical are prevented. Because of this, a study of the fate and biological effects of SAN 527 I 240 EW was undertaken in experimental freshwater ponds. The study was performed to Good Laboratory Practice and according to recent guidance on pesticide testing in mesocosms (SETAC 1991).

MATERIALS AND METHODS

Site description

Six experimental ponds at WRC Medmenham, in the Thames Valley, UK, were used in the study. Each pond was approximately 5 m x 5 m at the surface and 1 m deep. The ponds were lined with butyl rubber leached in river water before use. All of the ponds were filled with River Thames water and a layer of sediment, approximately 10 cm deep, obtained from a Nature Reserve pond.

During the two-month period before pesticide application, steps were taken to promote both biological richness within and homogeneity between the ponds. Measures included supplementing the indigenous biota with samples of macroinvertebrates from uncontaminated local sources, the reciprocal transfer of invertebrates attached to Standard Colonisation Units (SCA 1983), and the redistribution of water, sediment and vegetation samples.

Assessments of chemical and biological homogeneity shortly before the first pesticide application revealed some differences in physical and chemical parameters (suspended solids, some metals and phosphorus), and in the abundance of some biological taxa. However, the ponds showed similar taxonomic richness and similar abundances of dipteran and zooplankton taxa - groups of particular interest in a study with a pyrethroid.

Experimental design

A regression design was adopted, with a different rate of application (reflecting normal application rates) to each of four ponds: 6, 12, 24 and 48 g ai/ha. The two remaining ponds were used as undosed controls. Two separate applications of pesticide were made to each of the dosed ponds, with a time interval between applications of 21 days. The pesticide was delivered using an Azo boom and nozzle sprayer calibrated to deliver 200 l/ha. The three month study ended 86 days after the first application.

Physical and chemical sampling

Samples for residue analyses of water, sediment and biota were taken at regular intervals after each spray application. Samples were also taken for the analysis of total hardness, total phosphorus and chlorophyll *a* concentrations. Dissolved oxygen concentrations, turbidity, pH, barometric pressure, relative humidity, temperature, rainfall and light intensity were monitored electronically on site.

Invertebrate sampling

Zooplankton were sampled with a plexiglass device similar to that described by Crossland (1988). Three randomly selected samples (2-4 litres) were taken from each pond

on each occasion and sieved through a 63- μm mesh. The zooplankton retained on the mesh were preserved in 100 ml of 5% buffered formaldehyde. Subsamples of 2 or 5 ml were taken, after thorough mixing, for enumeration and taxonomic identification.

Macroinvertebrates in the water column were sampled with a Freshwater Biological Association sweep net (1 mm^2). The net was swept through the water column for 30 seconds at each of three randomly selected co-ordinates on each sampling occasion. Samples obtained in this way were immediately preserved in 70% industrial alcohol. Invertebrates were then sorted from the detritus, identified and counted.

Benthic macroinvertebrates were sampled with an airlift device similar to that described by Pearson *et al.* (1973). Sampling was undertaken at three randomly selected co-ordinates in each pond for 30 seconds. Sorting was carried out within 24 h and the isolated invertebrates preserved in 70% industrial alcohol.

Emergence traps designed at WRc Medmenham were used to sample emerging insects. These traps consisted of a perspex and nylon mesh box, with an open base covering an area of 20 cm x 20 cm. A removable cover could be slotted into the base when removing the traps. A polystyrene float provided buoyancy. Three traps per pond were tethered at randomly selected co-ordinates over a 24 h period on each sampling occasion. At the end of this period the bases were inserted, and the traps removed and frozen at -18 °C to stun winged insects. These were then preserved in 70% industrial alcohol for identification and enumeration.

Fish mortality and growth

The natural biota in each pond were supplemented by the addition of 50 caged carp (*Cyprinus carpio* L.). These fish measured <5 cm at the start of the study and were checked regularly for mortalities during the experiment. The 500-l enclosures containing the fish allowed the passage of water and small invertebrates, and full contact between fish and pond sediment. Supplementary food (No. 2 trout chow; approximately 4% of initial body weight) was added to each enclosure every other day and therefore only direct effects of the insecticide on growth were assessed. On day 86 of the study the surviving fish were removed, killed with MS222 anaesthetic and weighed.

RESULTS AND DISCUSSION

Fate

Tau-fluvalinate passed rapidly from the water (DT_{50} in water approximately 1 day) into the sediment, where it dissipated rapidly (DT_{50} in sediment 3 to 14 days).

Phytoplankton

There were no significant differences in algal density (measured by chlorophyll *a* concentration) between treatments and controls at any application rate.

Invertebrate abundance

The absence of a linear response in dosed ponds meant that useful regressions could not usually be obtained. Therefore, a factorial model was applied in which variability between and within ponds was compared, followed by identification of significant differences between dosed ponds and both control ponds.

Results for total zooplankton densities showed no dose-related effects, but there were some significant effects on individual zooplankton taxa. SAN 527 I 240 EW significantly reduced the abundance of cladoceran zooplankters such as *Daphnia hyalina* Leydig, *Alonella nana* Baird and *Alona rectangula* Sars after the second application, but recovery to control levels was observed within 35 days at the most, depending upon application rate (Figure 1). Copepod abundances were also reduced significantly (Figure 2), with consistent, but incomplete, recovery by the end of the study at the highest application rate. In contrast with cladocerans and copepods, rotifers such as *Polyarthra* spp. and *Keratella* spp. tended to increase in abundance in dosed ponds, probably because of a reduction in predation from pesticide-sensitive fauna (Figure 3).

Hemipterans in dosed ponds showed signs of unnatural swimming behaviour and knockdown, but we were unable to sample the small populations precisely enough to detect significant differences. This was a general difficulty with patchily distributed macroinvertebrates in the benthos and water column. However, alates of a range of insect species were significantly reduced in abundance for up to 12 days in samples taken from emergence traps after the first spray application, although not after the second application (Figure 4). Macroinvertebrate species that are likely to be affected by pyrethroid pesticides, such as mayflies and surface-dwelling insects, were found in all of the dosed ponds by the end of the study.

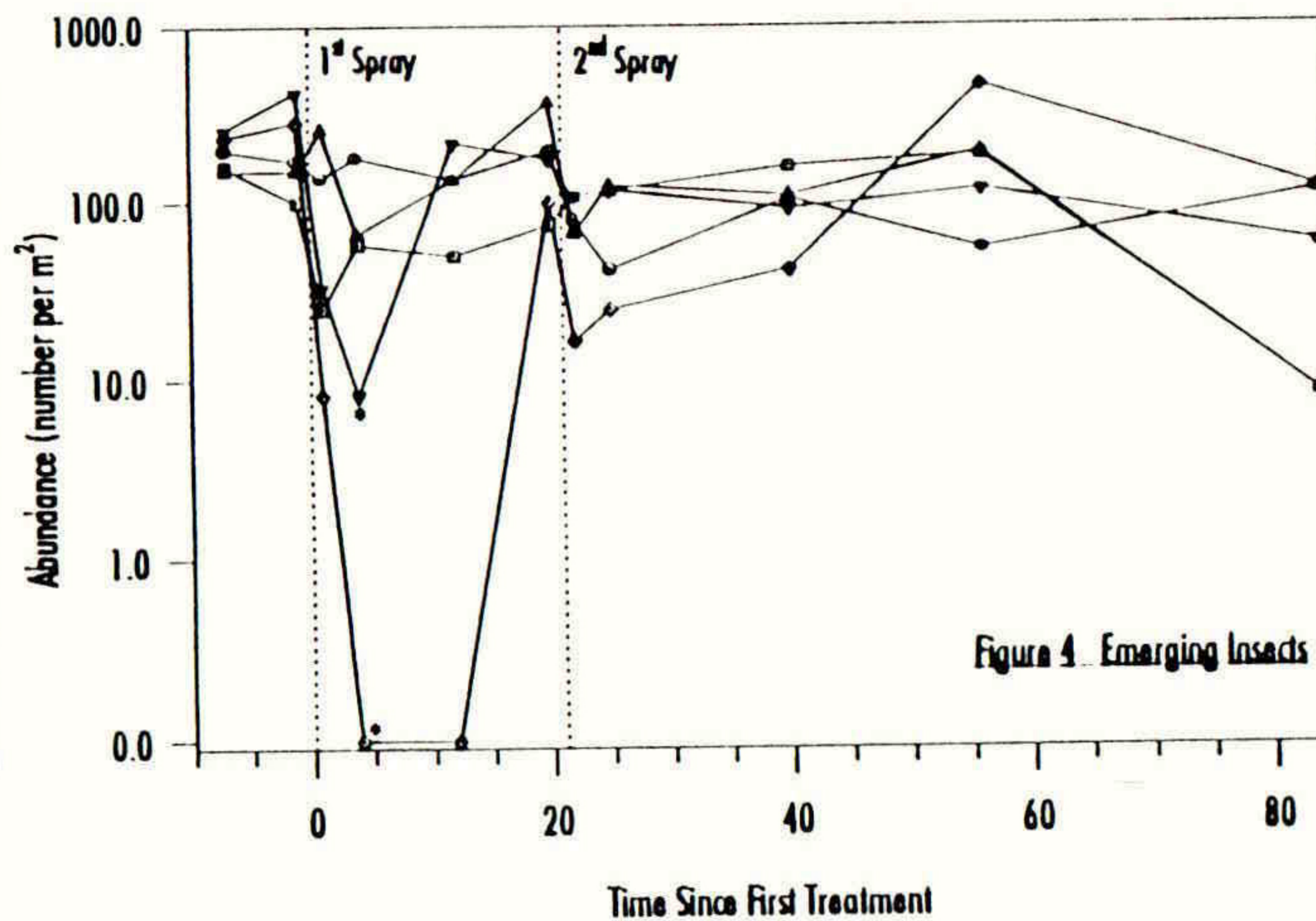
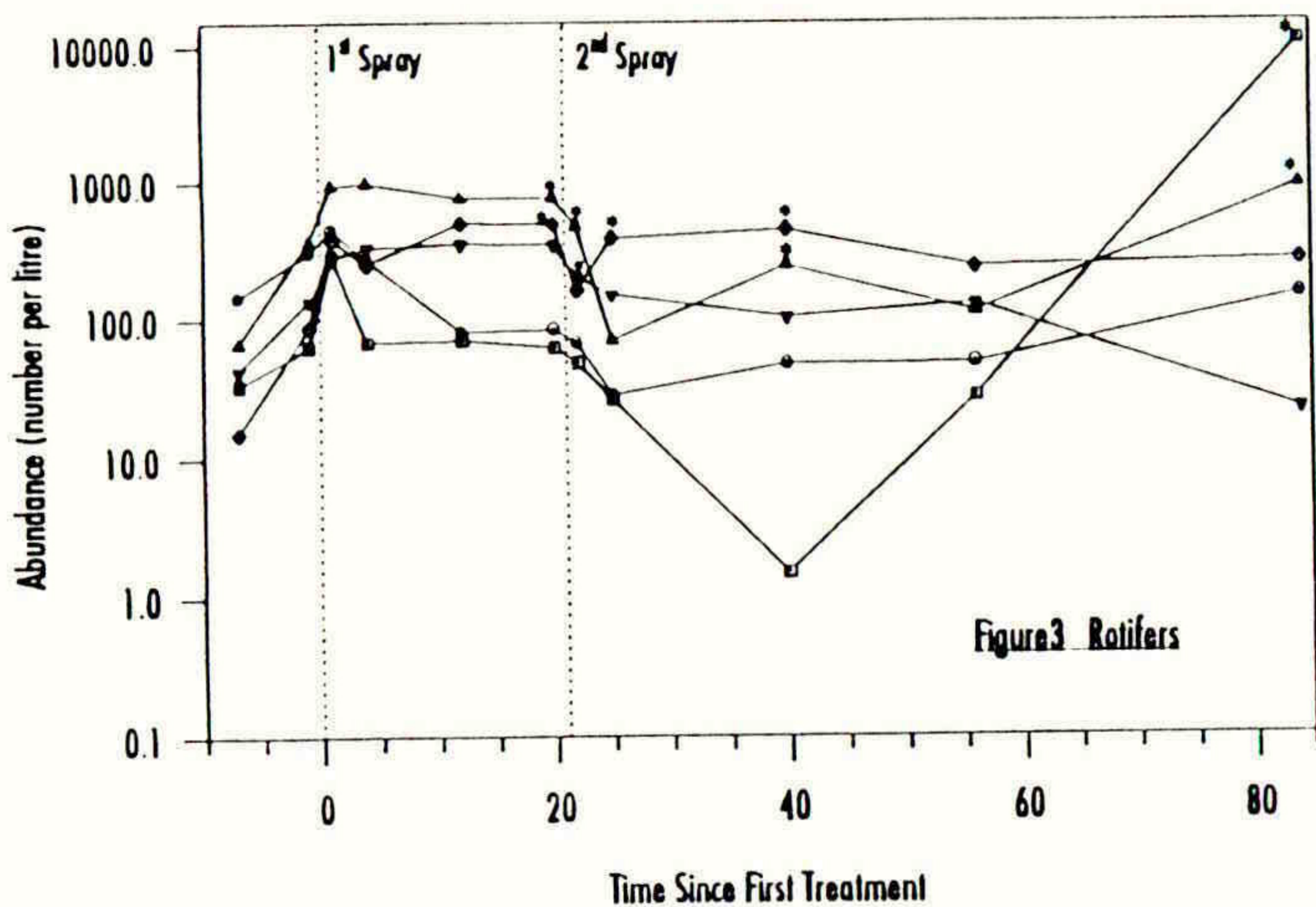
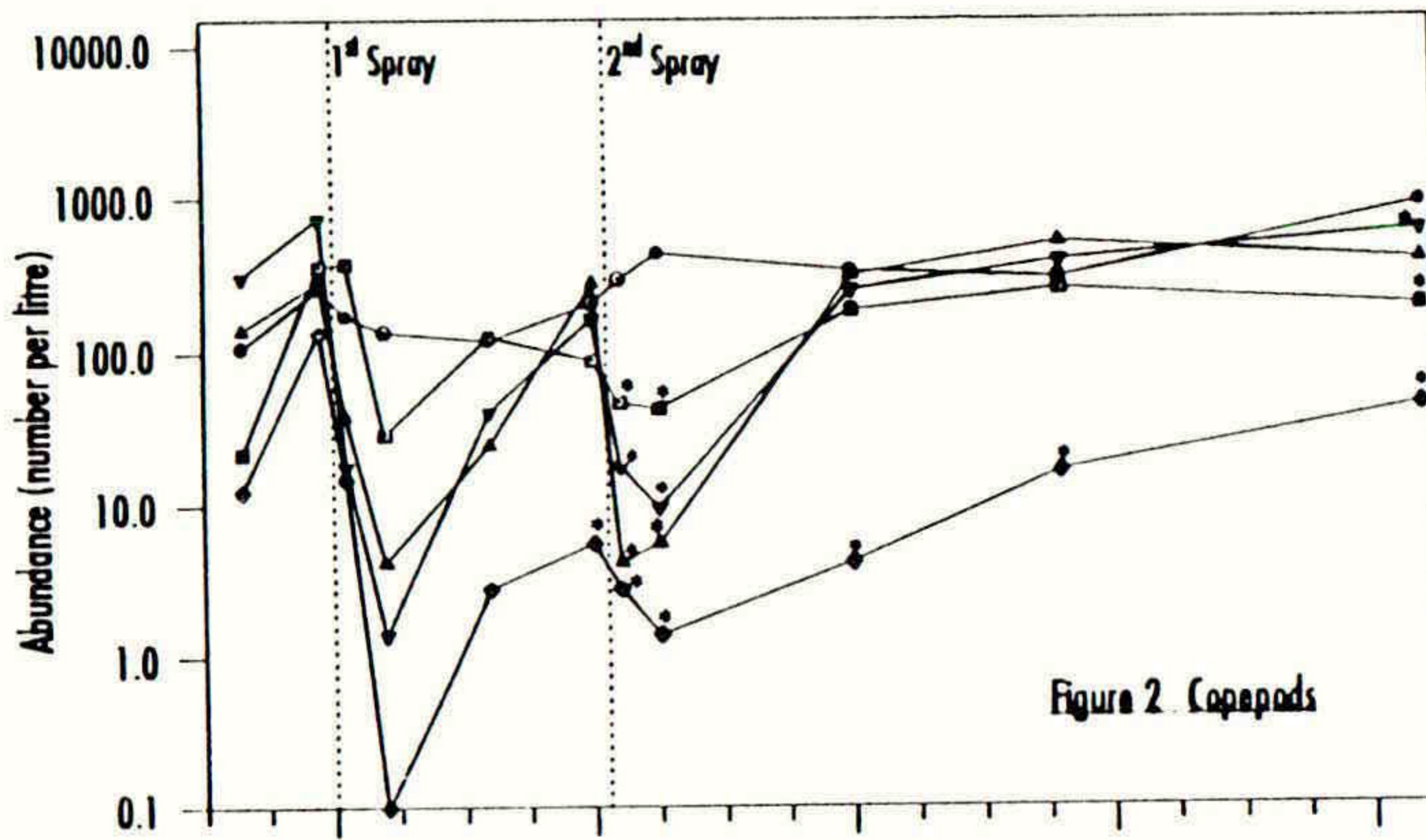
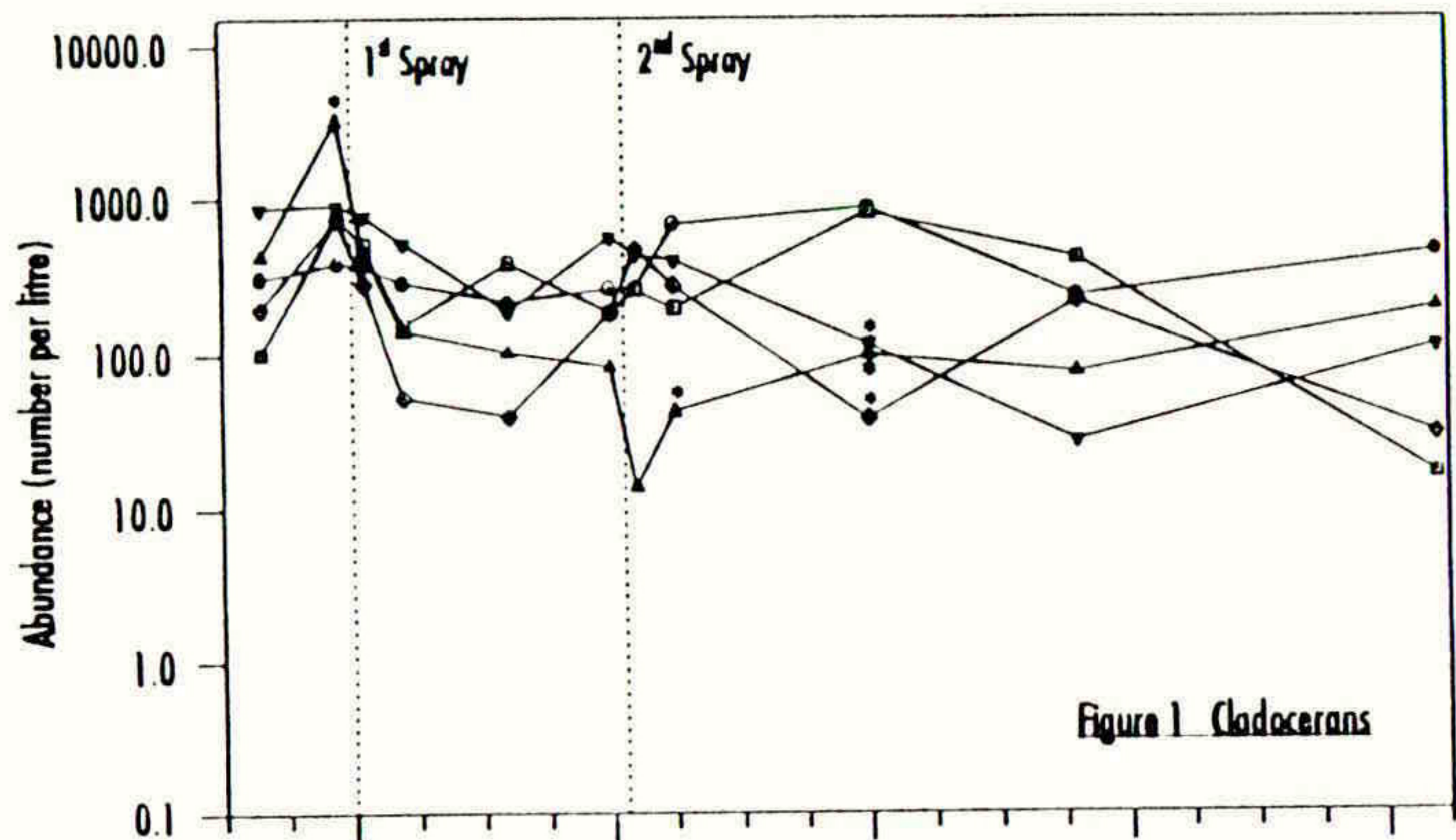
Fish mortality and growth

Significant carp mortalities were observed only after applications of SAN 527 I 240 EW at the highest rate of 48 g ai ha⁻¹. Thirty percent of the fish died after the first application, and the total cumulative mortality during the study was 48%. There were no significant direct effects of the insecticide on the growth of surviving fish.

CONCLUSIONS

The effects of SAN 527 I 240 EW on fish, crustacean zooplankton, and some insect taxa, and the subsequent recovery of the invertebrate populations, are similar to those found in several other model ecosystem studies with pyrethroid pesticides (Crossland 1982, Hill 1985, Day *et al.* 1987, Fairchild *et al.* 1992). The biological effects of pyrethroids, such as SAN 527 I 240 EW in semi-field tests tend to be less than those predicted from laboratory experiments because:

1. Differences in exposure conditions render some of the chemical unavailable to biota, for example by adsorption to dissolved organic carbon or sediment.
2. Diverse natural populations of microorganisms in ponds may optimise biotic degradation.



Figures 1 - 4 Abundance of invertebrates in ponds treated with SAN 527 I 240 EW. Asterisks mark treatments that are significantly different from both controls ($p < 0.05$).

—●— 0 g a.i. ha⁻¹ —□— 6 g a.i. ha⁻¹ —▲— 12 g a.i. ha⁻¹ —▼— 24 g a.i. ha⁻¹ —◇— 48 g a.i. ha⁻¹

SAN 527 I 240 EW does cause adverse effects on some non-target species, but these effects are relatively small and short-lived.

ACKNOWLEDGEMENTS

We should like to thank Paul Delaney, Ian Sims, Peter van Dijk and Alan Winnard for their assistance and advice.

REFERENCES

- Crossland, N.O. (1982) Aquatic toxicology of cypermethrin. II. Fate and biological effects in pond experiments. *Aquatic Toxicology*, **2**, 205-222.
- Crossland, N.O. (1988) A method for evaluating effects of toxic chemicals on the productivity of freshwater ecosystems. *Ecotoxicology and Environmental Safety*, **16**, 279-292.
- Day, K.E., Kaushik, N.K. and Solomon, K.R. (1987) Impact of fenvalerate on enclosed freshwater planktonic communities and on *in situ* rates of filtration of zooplankton. *Canadian Journal of Fisheries and Aquatic Sciences*, **44**, 1714-1728.
- Fairchild, J.F., La Point, T.W., Zajicek, J.L., Nelson, M.K., Dwyer, F.J. and Lovely, P.A. (1992) Population-, community- and ecosystem-level responses of aquatic mesocosms to pulsed doses of a pyrethroid insecticide. *Environmental Toxicology and Chemistry*, **11**, 115-129.
- Hill, I.R. (1985) Effects on non-target organisms in terrestrial and aquatic environments. In: *The Pyrethroid Insecticides*, edited by J.P. Leahey, Taylor and Francis Ltd, p 151-262.
- Pearson, R.G., Litterick, M.R. and Jones, N.V. (1973) An air-lift for quantitative sampling of the benthos. *Freshwater Biology*, **3**, 309-315.
- SCA (1983) Methods of Biological Sampling. A Colonization Sampler for Collecting Macro-invertebrate Indicators of Water Quality in Lowland Rivers. Methods for the Examination of Waters and Associated Materials, Standing Committee of Analysts, Her Majesty's Stationery Office, London.
- SETAC (1991) Guidance Document on Testing Procedures for Pesticides in Freshwater Mesocosms. SETAC-Europe, Brussels.

IMPACT ON NON-TARGET AQUATIC ECOSYSTEMS BY PESTICIDES

W. KÖRDEL, H. KLÖPPEL, I. RÖNNEFAHRT, M. KLEIN

Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, 57392 Schmallenberg, Germany

ABSTRACT

In order to calculate realistic and reliable predicted environmental concentrations (PEC) for a given scenario, different processes have to be interpreted with respect to probability of the occurrence, time scale of occurrence, concentration profiles and physical status. Small and large plot simulation experiments and large scale field experiments were carried out to investigate the importance of spray drift, surface runoff and agricultural draining systems for the impact on aquatic ecosystems and their dependence on complex environmental and compound properties. The results indicate that runoff events and discharge by drainages may have a comparable impact on aquatic ecosystems. Highest concentrations were found by rain events within 2 weeks after application. Water soluble and slightly soluble pesticides may reach concentrations of 50 - 200 µg/l in drain-effluents as well as runoff water.

INTRODUCTION

Pesticides can reach non target areas by spray drift during application, by volatilisation and subsequent deposition, by runoff events and by transport via subsurface drains.

For a realistic risk assessment for aquatic ecosystems it is essential to know the highest pesticide concentrations which may enter aquatic systems, the duration of the respective events, and the dependence on the time interval between application of the pesticides and the first discharge, which is especially important for runoff events.

Each discharge process is governed by a number of factors, as e.g. soil type and climate, which may also influence each other. Therefore plot trials and field experiments were carried out under different pedologic and climatic conditions in Germany to obtain an appropriate and valid data base. Pesticides with different physico-chemical properties and half-lives were used as model compounds.

For predicting environmental concentrations in aquatic ecosystems the sequence of discharge events and possible simultaneous occurrence of pesticides discharge by runoff and drains have to be considered. Therefore the results have been evaluated taking into account all relevant aspects.

DISCHARGE OF PESTICIDES BY DRAINS

Description of the experiments

The field monitoring was conducted at two sites in the „Soester Börde“, a typical crop growing area in Germany, where 25 to 35 % of the cropland is drained.

The field plots (plot 1: 5 ha; plot 2: 1.1 ha; plot 4: 0.7 ha) have surface slopes of less than 1 %. They are characterized as loamy silt soils (orthic luvisol) with an organic carbon content of 1.2 % in the 0-30 cm soil layer. The soil characteristics of all three plots are very similar. Subsurface drains (6.5 and 10.0 cm diameter) were installed at spacings of 5 to 9 m and at an average depth of 80 to 110 cm more than 12 years ago. The monitoring was also performed for a sandy soil in Brandenburg, which is typical for large areas in Northern Germany.

Herbicides with different water solubilities and soil sorption coefficients were chosen as test substances to obtain information on the dominant leaching processes. The herbicides were applied as formulated products according to agricultural practice. Total drainage from each plot area was sampled and measured in a central collection pipe. The total drain flow was continuously measured, samples were collected automatically on a time-related basis and analysed for all applied herbicides. A detailed description of the experiments is given by Traub-Eberhard et al., 1993 and 1994.

Results

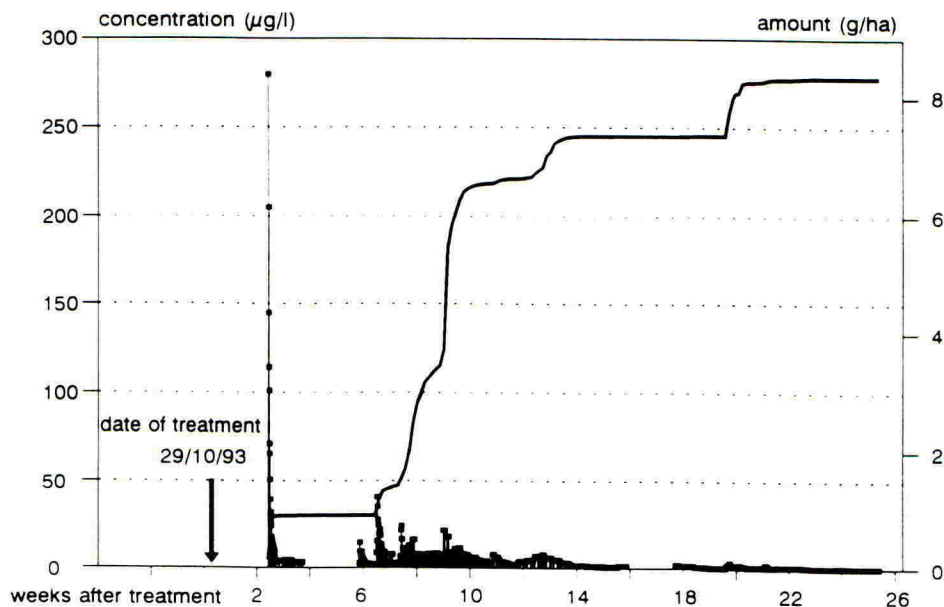
In the loamy silt soil, total drain flow of all three plots was very similar and reached about 35 % of the total precipitation in winter. Only isolated drain events occurred in spring and summer (May to October) as a result of low precipitation and higher evapotranspiration during the growing season. In the sandy soil the maximum amount of water removed by the drains was only about 6 % of the total precipitation. The completely different amounts of drain water (% of precipitation), which were collected at the sites with the loamy silt and the sandy soil on the one hand are due to the different soil types, however the results may also be influenced by the slightly different drain systems.

Fall application on a loamy silt soil caused high concentrations in drain effluent. Maximum concentrations of about 62 µg/l (1993) and 280 µg/l (1994) were measured for isoproturon shortly after the beginning of drainflows. Within 24 h, the concentration had already declined significantly, but always increased when the drain flow started again, e.g. after a frosty period. Comparable results were obtained for chlortoluron (fig. 1) The importance of macropore flux is indicated by the Pendimethalin concentrations in drain effluent. The concentration profile of Pendimethalin is identical with that of Isoproturon in the outflow of the drains, however the concentration were much lower, reaching a maximum of 0.34 µg/l. The importance of preferential flow for drains is also supported by the results obtained from the experiments on the sandy soil. Only one minor peak of isoproturon (max. 1.4 µg/l) was obtained, which indicates that in sandy soils preferential flow can be neglected.

The highest mass flow of pesticides is in winter time for fall application when drain flow reaches about 35 % of the precipitation. The total discharge rates for isoproturon and chlortoluron may reach 1 % of the applied amounts (tab. 1). It may be concluded that water soluble and slightly soluble pesticides are rapidly transported to subsurface drains after rainfalls initiating drainflow. Concentrations within the first 6 hours can reach values of 100 µg/l. Upon fall application losses of pesticides by subsurface drains may occur over longer periods of time (up to three months) with concentrations of 5 - 15 µg/l. The total loss of pesticides by subsurface drains may reach 1 % of the applied amount for compounds of K_{oc} values up to 200.

Fig. 1 Drainage - ISOPROTURON DISCHARGE

fall application, 1.5 kg/ha, loamy silt



RUNOFF

Description of the experiments

Field plot rainfall simulation studies were carried out to investigate the importance of factors influencing surface runoff. The following variations were tested:

- intensity of irrigation
- soil properties, slope, cultivation and plant cover
- start of irrigation after application (2h to 14d)
- size of the plots (small 7m² and large 1200m² plots)
- herbicides with different physico-chemical properties

During irrigation runoff samples were taken; the amount of runoff water and transported soil, concentrations of pesticides in runoff water and in the sediment phase as well as vertical migration of the pesticides were measured. A detailed description of the experiments is given by Klöppel et al., 1994 and Kördel and Klöppel, 1993.

Tab. 1.

SUMMARY OF DRAINAGE EXPERIMENTS

pesticide	K _{oc}	application	field	rate (kg/ha)	discharge concentration		
					(µg/ha)	max. (µg/l)	o (µg/l)
Bentazon	63	Apr. '1993	loamy silt	1,0	132	0,45	< 0,001
Chloridazon	33	Apr. '1992	loamy silt	1,3	372	0,15	0,001
Dichlorprop-p	23	Apr. '1993	loamy silt	0,7	n.d.	n.d.(< 0,05)	n.d.
Isoproturon	130	Nov. '1992	loamy silt	1,0	3,50E+06	62	4,4
		Nov. '1992	loamy silt	1,0	8,40E+05	26	1,5
		Nov. '1992	sand	1,5	531	1,4	0,02
		Oct. '1993	loamy silt	1,5	8,30E+06	279,76	6,957
Chlortoluron	190	Oct. '1993	loamy silt	2,5	1,70E+07	371,21	14,214
MCPA	110	May '1993	loamy silt	0,8	n.d.	n.d.(< 0,05)	n.d.
Metamitron	40	May '1992	loamy silt	2,5	18	0,02	0,001
Metolachlor	261	Jun. '1992	sand	1,7	33	0,05	0,001
		Mai '1993	sand	2,0	2,50E+04	0,46	0,3
Pendimethalin	4010	May '1992	loamy silt	1,6	n.d.	n.d.(< 0,01)	n.d.
		May '1992	sand	1,6	n.d.	n.d.(< 0,01)	n.d.
		Nov. '1992	loamy silt	0,8	1810	0,7	0,003
		Nov. '1992	loamy silt	0,8	1,00E+04	0,3	0,01
		Nov. '1992	sand	0,8	n.d.	n.d.(< 0,01)	n.d.
Terbutylazin	186	Jun. '1992	sand	0,8	462	1,4	0,01
		May '1993	sand	1,0	n.d.	n.d.(< 0,03)	n.d.

Results

Runoff events are strongly supported under conditions favouring a start of runoff shortly after beginning rainfall. This e.g. applies for silty soils with a sparse plant cover which tend to clogging; soils with a relatively high water content also contribute to increased runoff. The small plot experiments with different intensities of irrigation demonstrate that the infiltration capacity of the soil is exhausted after an irrigation period of 35 min (50 mm/h), whereas runoff started after 12 min with an intensity of 99 mm/h (extreme rainfall) (fig. 2). Using a realistic rainfall scenario and the above mentioned soil conditions runoff will start upon cumulative rainfall of 20 to 30 mm leading to pesticide concentrations of 50 - 200 µg/l in the runoff water and a total export of up to 5 % of the applied pesticide (fig.3). The pesticide concentration in the runoff (water phase) decrease significantly within the first hour. Mobile pesticides which are transported by the water phase disappears from the soil surface either by vertical or horizontal transport. The results clearly show that pesticides with similar or higher mobility than IPU are mainly transported dissolved in the water phase and can reach aquatic ecosystems during "normal" rainfall after applications.

CONCLUSIONS

The processes of spraydrift, runoff and drainage can contribute to the exposure of aquatic ecosystems to pesticides. The intensity of the pesticides export depends on the crop, spraying techniques, soil types, topology, chemical properties and climatic conditions.

Pollution by spraydrift can occur directly during application while runoff and drainage events may follow after intensive rainfall. These processes are favoured by silty soils of a relative high water content. Runoff is important for fields with a slope of > 5 %, contrary to fields with a slope < 5 % where drains may be used.

ACKNOWLEDGEMENT

The studies were supported by the Umweltbundesamt, Berlin. The authors appreciate the scientific input of the monitors of the sponsor for the project Dr. J. Goedicke, Dr. R. Winkler and Dr. B. Stein.

REFERENCES

- Klöppel, H., Haider J. & Kördel W, Herbicides in Surface Runoff: A rainfall simulation study on small plots in the field, *Chemosphere* **28**(4), 649-662, 1994
- Kördel, W. & Klöppel H, Contamination of Aquatic Ecosystems by Runoff Events - Comparison of Small and Large Plot Experiments, *Proceedings of the BCPC*, 835-842, 1993.
- Kördel, W. & Klöppel H, Herbicides in Surface Runoff, UBA Report 126 050 87, 1994
- Traub-Eberhard, U., Kördel W & Klein W, Pesticide Movement into Subsurface Drains on a Loamy Silt Soil, *Chemosphere* **28**(2), 273-284, 1994
- Traub-Eberhard, U., Kördel W & Klein W, Monitoring Pesticide Movement into Subsurface Drains, *Proceedings of the BCPC*, 885-892, 1993

Fig.2 RUNOFF - DEPENDENCE ON THE INTENSITY OF RAINFALL
 small plot experiment, sandy loam
 start of irrigation 24 h after application

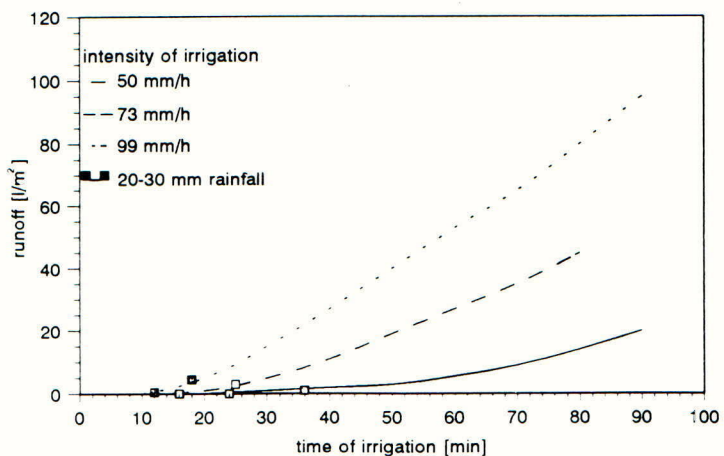
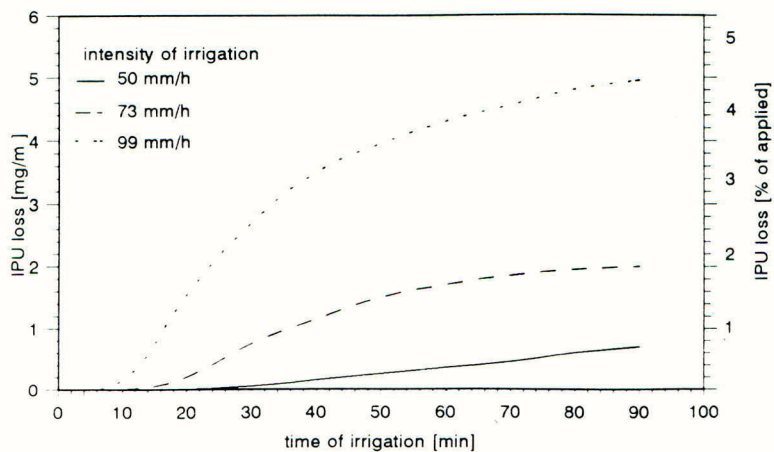


Fig.3 RUNOFF OF ISOPROTURON
 small plot experiment, sandy loam
 start of irrigation 24 h after application



LEACHING PATTERNS OF PESTICIDES AS RELATED TO SORPTION AND POROSITY PROPERTIES OF SOILS

L. COX, R. CELIS, M.C. HERMOSIN and J. CORNEJO

Instituto de Recursos Naturales y Agrobiología de Sevilla, C.S.I.C. P.O. BOX 1052, 41080 Sevilla, Spain

ABSTRACT

The influence of adsorption-desorption phenomena and distribution of pore sizes on the leaching behaviour of two herbicides, thiazafurion (highly polar, nonionic) and clopyralid (anionic) in three soils has been studied. Adsorption data, obtained by batch equilibrium, were fitted to Freundlich equation and Kf values calculated. Pore size distribution of the soils was studied by mercury porosimetry. Mobility has been studied by leaching in handpacked soil columns and the retardation factor (Rf) calculated as the pore volumes required for leaching 50 % of the applied herbicide. Rf and Kf values correlated directly in the case of thiazafurion. Rf and mean pore radius were inversely related in both cases.

INTRODUCTION

The study of pesticide movement throughout the soil profile is of great interest as far as biological performance and groundwater contamination are concerned (Bowman, 1989; Beck et al., 1993). Adsorption and mobility, in general, have been shown to be inversely related (Bilkert & Rao, 1985; Beck et al., 1993). Pore size distribution, as accounting for different pore water velocity, is also related to the transport of solute in soils (Ping et al., 1975).

The aim of this study was to compare the leaching patterns of two different adsorbing herbicides in three different soils with special attention to the influence of their adsorption capacity and pore size distribution.

MATERIALS AND METHODS

The herbicide thiazafurion (1,3-dimethyl-1-(5-trifluoromethyl-1,3,4-thiadiazol-2-yl)urea) used in this study was the high purity compound supplied by Ciba-Geigy. Thiazafurion is a non-selective herbicide used for industrial weed control and active mainly through plants roots. The herbicide clopyralid (3,6-dichloropicolinic acid) used was the high purity compound supplied by DOW Chemicals. Clopyralid is an herbicide of selective use in cereal crops, rangeland, grass pastures and turf (Worthing & Hance, 1991).

Soils were sampled, air dried, sieved to pass a 2 mm mesh and stored in a refrigerator. Their physico-chemical properties were determined by the usual methodology (Hermosin et al., 1987) and are given in Table 1.

Duplicate samples of 2.5 g of each soil sample were treated with 10 ml of thiazafurion and clopyralid initial solution concentrations (Ci) 0.05, 0.1, 0.3, 0.5, 0.8, 1, 1.5 and 1.8 mM using 0.01 M CaCl₂ as solvent. The suspensions were shaken at 20 ± 2 °C for 24 hours and then centrifuged at 12000 r.p.m. at the same temperature. Equilibrium concentration (Ce) was determined in the supernatant by UV spectroscopy (absorption maximum, 266 nm for thiazafurion and 280 nm for clopyralid). Previously, it was checked that equilibrium was reached before 24 hours and no significant degradation occurred during this period. Differences between Ci and Ce were assumed

to be adsorbed. Desorption was measured after adsorption using the 1 mM and 1.8 initial solution concentrations. After the samples were shaken and centrifuged, 5 ml of supernatant were removed and analyzed and 5 ml of 0.01 M CaCl₂ added to the centrifuge tubes. The samples were resuspended, shaken for other 24 hours and centrifuged and equilibrium concentration in the supernatant was determined. Desorption procedure was conducted three times for each soil sample.

Table 1. Physicochemical properties of the soils.

Soil property	Soil 1	Soil 2	Soil 3
% Organic Matter	0.99	2.24	2.54
pH	7.9	7.7	7.6
% Sand	70.7	12.1	11.9
% Silt	8.9	43.6	35.8
% Clay	20.4	44.3	52.3

The distribution of pore radii of soil samples from $4 \cdot 10^4$ to 3.7 nm was determined using a Carlo Erba 2000 mercury depression and intrusion porosimeter. The measurements were carried out on soils packed in the same way as the columns used for leaching experiments.

Leaching has been studied in 30 cm long metacrilate soil columns of 5 cm inner diameter. The first ring was filled with sea sand and the last ring was filled with sea sand and glass wool. The other four rings were handpacked with the soils. Leaching experiments were run in triplicates, and for every soil a blank column (without herbicide) was used. The amount of thiazafururon and clopyralid corresponding to the maximum application rate in soils (12 Kg/Ha and 100 g/Ha, respectively) was applied to the top of the columns. 50 ml of 0.01 M CaCl₂ were applied daily. In this way, water flow rates were 0.8 ml/min for soil 1 and 0.3 ml/min for soil 2 and 3. The total amount of CaCl₂ applied was 2,5 L. Leachates containing the herbicides were collected daily, filtered and analyzed by HPLC.

RESULTS AND DISCUSSION

Thiazafururon adsorption isotherms in the soils studied are shown in Figure 1. Adsorption coefficients, K_f and n_f , obtained by fitting adsorption isotherms to Freundlich equation, are given in Table 2, together with desorption percentages after three successive dilutions. Higher adsorption was found for soil sample 3, of higher organic matter and clay content. The last has been shown to be the most important single factor affecting the adsorption of this highly polar herbicide in soils (Cox et al., 1994-a,b). Desorption percentages indicate that only a small amount of the herbicide adsorbed is released after three desorption cycles. This has been attributed to irreversible binding of thiazafururon molecules to soil clay (Cox et al., 1994-b). The herbicide clopyralid did not adsorb on the soils studied. Adsorption studies at the μ M range gave the same results. This could be due to the low pKa of the herbicide (pKa= 2.33), which indicates that at the pH of the soils (Table 1) the molecule would be in the anionic form. The low content of the soils in organic matter, which has been shown to adsorb this herbicide (Pik et al. 1977), would also contribute to these results.

Cumulative and differential mercury porosimetry curves of the three soils are shown in Figure 2. The volume of greater pores ($r > 1 \mu$ m) for soil samples 1 and 2 are nearly the same, but soil 1 has a lower volume of smaller pores ($r < 1 \mu$ m). Pore size distribution of soil 3 is characterized

by a great volume of pores in the lower limit of pore radius studied (about 0.03 μm). Thus, the mean pore radius, r_m , for the three soil samples decreases in the order $r_m(3) < r_m(2) < r_m(1)$.

Table 2. Thiazafururon adsorption coefficients (K_f and n_f) calculated from Freundlich equation and desorption percentages (D) calculated at 1 mM and 1.8 mM thiazafururon initial solution concentrations after three desorption cycles.

Soil	K_f	n_f	r	% D
1	0.41	0.73	0.97	14.5
2	1.00	0.76	1.00	14.5
3	1.33	0.80	1.00	10.5

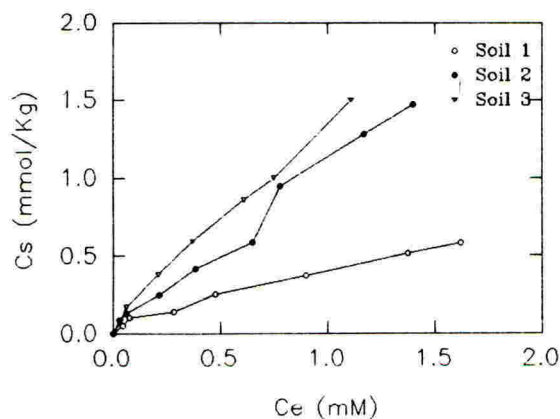


Figure 1. Thiazafururon adsorption isotherms on soils studied.

Figure 3a shows thiazafururon BTCs in the three soils studied. Recovery percentages of the applied thiazafururon were 88.4, 67.7 and 65.1 % for soils 1, 2 and 3, respectively. Thiazafururon BTC in soil 1 has a higher concentration peak when compared with the curves for soils 2 and 3, indicating that thiazafururon moves more rapidly in this soil. All BTCs showed solute concentration peaks to the right of one pore volume, which result from solute adsorption (Beck et al., 1993). Although BTCs for thiazafururon were not symmetrical, a retardation factor R_f was calculated as the pore volumes required to leach 50 % of the applied herbicide (Brusseau and Rao, 1989). R_f values (Table 3) correlated directly with adsorption coefficients K_f , indicating that adsorption and mobility of thiazafururon in soils are inversely related and that the different shape of thiazafururon BTCs can be explained considering the different adsorption capacity of the soils. The asymmetry ("tailing effect") observed in the BTCs can also be attributed to the low desorption rate of thiazafururon found in batch studies, as shown in Table 2.

Figure 3b shows clopyralid BTCs in the three soils studied. Recovery percentages were higher than 80 % for the three soils. Although no adsorption of clopyralid had been detected, differences in clopyralid BTCs for the three soils studied were observed. R_f values for clopyralid (Table 3) were found around one pore volume, indicating the low influence of adsorption in leaching of this herbicide. Differences between the BTCs and R_f values for the different soils can

be explained considering the different pore size distribution of the soils. Clopyralid BTC in soil 1 showed higher concentration peak than in soils 2 and 3 and, thus, lower retardation factor R_f . Soil 1, as mentioned above, has the highest mean pore radius (r_m) and, consequently, water flow rate, which can give rise to earlier breakthrough (Van Genuchten et al., 1990). Broadening of the leaching curves observed in soils 2 and 3 during flow reflects the combined influence of diffusion and hydrodynamic dispersion processes (Biggar & Nielsen, 1962), the first more likely to occur in these heavier soils of lower mean pore radius and water flow rate. In soil 3, of a higher clay content and higher volume of small pores than the others, there would be a greater tendency for clopyralid to diffuse into stagnant or relatively non-conducting pores causing the BTCs to become more diffused and broadened and to have lower peak concentrations. The different porosity of the soils should also contribute to the extend of adsorption processes in the case of thiazafurion.

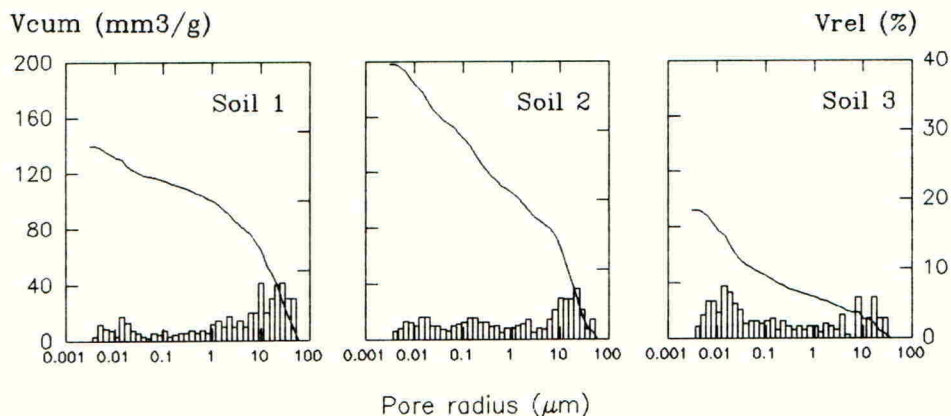


Figure 2. Differential and cumulative mercury pore volume for the three soil samples as a function of calculated pore radius.

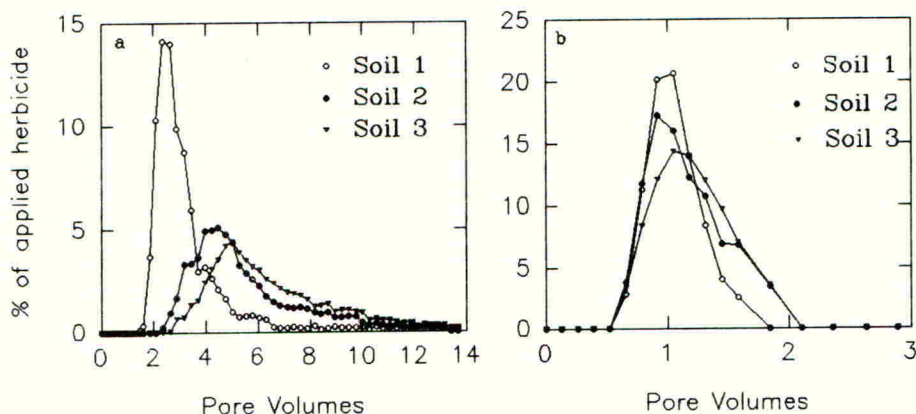


Figure 3. a) Thiazafurion BTCs. b) Clopyralid BTCs

Table 3. Retardation factors, R_f (pore volumes) calculated from thiazafururon and clopyralid BTCs.

Soil	$R_{f_{\text{Thiazafururon}}}$	$R_{f_{\text{Clopyralid}}}$
1	4.7	0.9
2	6.3	1.0
3	7.9	1.2

CONCLUSIONS

The herbicide thiazafururon moves more slowly in soils than clopyralid, due to adsorption of thiazafururon on soil clay, as confirmed by previous studies. The different porosity of the soils affects the leaching of these herbicides in soil columns, since it controls water movement. This different porosity might also affect adsorption processes by determining the permanence of the herbicide in the column in contact with soil components.

ACKNOWLEDGEMENTS

This work has been partially supported by CICYT in Project AMB 93-81, and Junta de Andalucía through research group 4092. L. Cox and R. Celis also thank the Spanish Ministry of Education and Science for P.F.P.I. and P.F.P.U. fellowships, respectively.

REFERENCES

- Beck, A. J.; Johnston, A.E.J.; Jones, K.C. (1993). Movement of nonionic organic chemicals in agricultural soils. *Critical Reviews in Environmental Science and Technology*, **23**, 219-248.
- Biggar, J.W.; Nielsen, D.R. (1962). Miscible displacement: II. Behaviour of tracers. *Soil Science Society of America Proceedings*, **26**, 125-128.
- Bilkert, J.N.; Rao, P.S.C. (1985). Sorption and leaching of three non-fumigant nematicides in soils. *Journal of Environmental Science and Health*, **B20**, 1-26.
- Bowman, B.T. (1989). Mobility and persistence of the herbicides atrazine, metolachlor and terbuthylazine in plainfield sand determined using field lysimeters. *Environmental Toxicology and Chemistry*, **8**, 485-491.
- Brusseau, M.L.; Rao, P.S.C. (1989) Sorption nonideality during organic contaminant transport in porous media. *Critical Reviews in Environmental Control*, **19**, 33-99.
- Cox, L.; Hermosín, M.C.; Cornejo, J. (1994a). Retention of thiazafururon by surface horizons of some Spanish soils. *Fresenius Environmental Bulletin*, **3**, 129-134.
- Cox, L.; Hermosín, M.C.; J. Cornejo (1994b). Adsorption and desorption of thiazafururon by soils. *International Journal of Environmental Analytical Chemistry* (in press). *Proceedings*, **36**, 257-261.
- Hermosín, M.C.; Cornejo, J.; Pérez-Rodríguez, J.L. (1987) Adsorption and desorption of maleic hidrazide as a function of soil properties. *Soil Science* **144**, 250-256.

- Pik, A.J.; Peake, E.; Strosher, M.T.; Hodgson, G.W. (1977). Fate of 3,6-dichloropicolinic acid in soils. Journal of Agricultural Food and Chemistry 25, 1054-1061.
- Ping, C.L.; Cheng, H.H.; McNeal, B.L. (1975) Variation in picloram leaching patterns for several soil. Soil Science Society of America Proceedings 39, 470-474.
- Van Genuchten, M.Th.; Ralston, D.E.; Germann, P.F. (1990). Transport of water and solutes in macropores. Geoderma Special edition, p. 46.
- Worthing, C.R.; Hance, R.J. (1991). The Pesticide Manual. BCPC, Surrey, U.K..

RELATIONSHIPS BETWEEN SEDIMENT HANDLING TECHNIQUES AND EMERGENCE SUCCESS FOR THE MIDGE *CHIRONOMUS RIPARIUS*

K.M. THIRKETTLE, K.L. BARRETT

AgrEvo UK Limited, Chesterford Park, Saffron Walden, Essex, CB10 1XL

ABSTRACT

Methods for assessing the toxicity of pesticides to sediment-dwelling organisms are currently under development. A proposed test using *Chironomus riparius* involves exposure from first instar larvae to adult emergence, in a sediment water system, for up to twenty eight days.

This test system contains a number of variable parameters including the handling of the sediment matrix. Sediment samples taken from the environment will contain a diverse range of naturally occurring fauna. These fauna could interact with the test organism, confounding test results.

In this study we demonstrate that freezing the sediment at -18° C for a minimum of two weeks is an effective method of removing indigenous fauna from natural sediments, and is more effective than sieving the sediment through a 0.5 mm mesh

INTRODUCTION

The use of agrochemical products creates the risk of contamination of surface waters by drift or runoff, and sediment contamination by the more lipophilic persistent compounds.

For risk assessments of lipophilic chemicals on aquatic benthic communities, a laboratory-based toxicity test for prediction of potential effects in the environment is required. One such method for testing the impact of persistent pesticides has been proposed (Barrett and Dohmen, 1992) using *Chironomus riparius* as the test organism. This is a benthic invertebrate selected by criteria such as the life-cycle, size and availability.

Standardisation from the initial stage of culture through to experimental end points is desirable if valid comparisons are to be made from data generated in different laboratories. The sediment matrix incorporated into the test system is often collected from the field and could contain not only a diverse range of species but disproportionate numbers of any particular organism. If additional fauna are present in the test system, effects may include predation, and competition, altering the subsequent emergence rates (Reynoldson *et al*, 1994). As the presence of indigenous organisms can influence the interpretation of chronic end points, removal is essential.

MATERIALS

Test species

First instar Chironomid larvae were obtained from established laboratory cultures. These were maintained as described by Barrett and Dohmen, (1992). A number of egg ropes laid on the same day were held in small vessels of culture water. Larvae hatching 3 days after collection of the eggs were pooled for use in the study. Active larvae were selected under a binocular microscope using a blunt wide bore pipette.

Sediment collection

Two natural sediments were studied, Mill Stream Pond and Iron Hatch. The physical and chemical properties are detailed in Table 1. These were obtained from uncontaminated sites in Wareham, Dorset. They were collected using a drag net of 25 cm cross section and 100 mesh. Surficial sediment to a depth of ca. 5 cm was collected, and sieved through a stainless steel 2 mm sieve.

TABLE 1: Physical and chemical properties of the test sediments.

Parameter	Mill Stream Pond Sediment	Iron Hatch Sediment
pH	7.9	8.2
Cation Exchange Capacity Me/100 g	37.0	3.0
Particle size distribution:		
2000-600 μm %	1.0	24
600-212 μm %	2	70
212-63 μm %	12	3
63-20 μm %	24	0
20-2 μm %	27	1
<2 μm %	34	2
Calcium carbonate %	20.9	0.6
Organic matter %	14.2	0.30
Organic carbon %	8.24	0.17
Biomass C ($\mu\text{gC g}^{-1}$)	1674.41	118.29

METHODS

Two treatments were applied to both sediments. Firstly the effects on emergence success by altering the duration of freezing was investigated. Samples were frozen at -18°C , and removed for testing after 24, 48 and 96 hours, 1 week, 2 weeks and 1 month. Secondly the effects of sieving were investigated by comparing emergence success in vessels containing 2 mm sieved sediment, and 0.5 mm sieved sediment.

One hundred grams of Mill Stream Pond sediment or 130 g of Iron Hatch sediment were added to 400 ml beakers to create a substrate depth of approximately 2 cm. To each beaker 300 ml of a reconstituted water, M4 (Elendt and Bias, 1990) was added, the mixing between the substrate and medium minimised. A pump provided aeration to the system. Once prepared the units were left to acclimate for 7 days.

Twenty five first instar chironomid larvae, less than 24 hours old, were added to each test vessel after which the aeration was stopped for a 24 hour period. The larvae were fed daily with a fine suspension of Tetra-Min®, at a rate of 10 mg / vessel / day for the first nine days, and 15 mg / vessel / day thereafter.

Five replicates of each treatment were arranged in a completely randomised design. The study was run in a constant environment room at a temperature of $20^{\circ}\text{C} \pm 2^{\circ}\text{C}$ and a 16 h light (ca. 940 lux), 8 h dark photoperiod. Each day the vessels were checked for the presence of additional fauna, and chironomid emergence. Water quality parameters including temperature, pH, conductivity and oxygen content were monitored at the start of the investigation, and weekly thereafter.

Emergence data was arcsine transformed before analysis by ANOVA. Where significant differences between treatments were identified ($p < 0.05$), Tukey multiple range tests were performed.

RESULTS

Overall, for both sediment types, total emergence increased with length of storage period of the sediment, while sieving through a 0.5 mm mesh also appeared to increase the total emergence in the Mill Stream Pond sediment (Table 2).

TABLE 2. Total emergence success in the frozen sediment and sieved sediment treatments

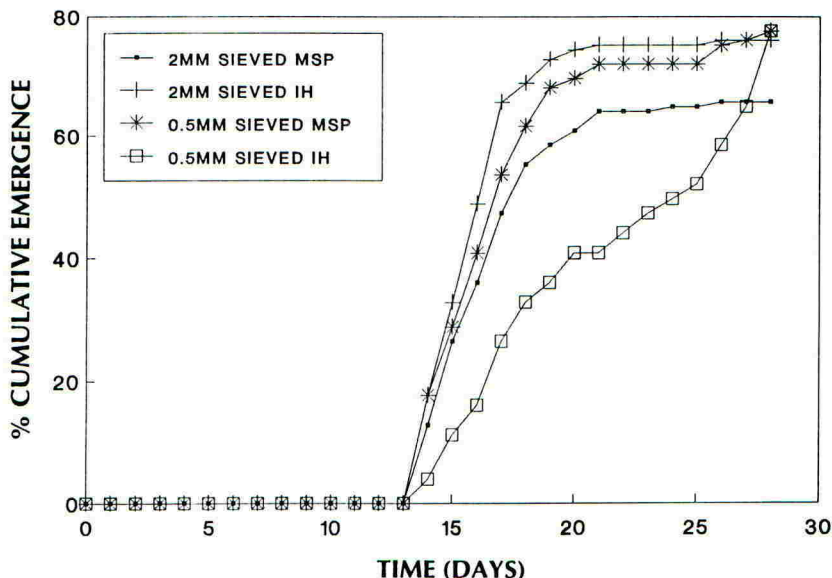
Treatment	Mill Stream Pond Sediment		Iron Hatch Sediment	
	mean % total emergence	standard deviation	mean % total emergence	standard deviation
Duration of freezing:				
24 hours	44.8	23.7	74.4	15.7
48 hours	66.4	10.8	74.4	4.6
96 hours	64.0	16.0	75.2	6.6
1 week	72.0	18.8	76.0	6.3
2 weeks	89.6	11.5	95.2	5.2
1 month	93.6	7.3	94.4	4.6
Sieving :				
2 mm sieved	65.6	20.1	76.8	19.1
0.5 mm sieved	82.4	12.8	77.6	7.3

For the Mill Stream Pond sediment, there was a highly significant difference in total emergence with increasing freezing duration ($p < 0.05$), the 24 hour treatment resulting in significantly lower emergence than the 2 week and 1 month treatments. Also for the Mill Stream Pond sediment there was greater emergence in the 0.5 mm sieved sediment compared to the 2 mm sieved sediment, although this was not statistically significant.

For the Iron Hatch sediment there was also a highly significant difference in total emergence with prolonged freezing ($p < 0.05$), the 24 hour treatment again resulting in significantly lower emergence compared to the 2 week treatment. However for the Iron Hatch sediment no statistically significant differences were found in emergence success between sieving treatments, or between sieved and frozen samples. However sieving did affect the rate of emergence, which decreased when the sediment was sieved at 0.5 mm (Figure 1).

Overall, for both sediment types greatest emergence success was found in samples frozen for 2 weeks and 1 month. The emergence success from the other treatments were not significantly different.

FIGURE 2. Cumulative emergence success of chironomids in sieved Mill Stream Pond (MSP) and Iron Hatch (IH) sediments.



The water quality parameters measured in all treatments did not differ significantly over time, the oxygen content and temperature remaining approximately the same, pH showed a slight decrease and conductivity exhibited a small increase.

Indigenous organisms identified in both sediments are summarised in Table 3. Both sediments contained a wide range of live indigenous organisms in samples frozen for up to 1 week, the numbers becoming proportionally less with increasing freezing period.

Species found included Psychodidae and Lonchopteridae larvae, Ephemeropteran nymphs and imagos, and numerous Ostracoda. No species survived in the 2 week or 1 month freezing treatment samples. In the Iron Hatch sediment the species consisted mainly of Dipteran larvae, and Ephemeroptera.

TABLE 3. Species diversity in the Mill Stream Pond and Iron Hatch sediments

Class	Subclass/Order	Genus/Family	Stages Present
Clitella	Oligochaeta	Tubifex	Immature to adult
Crustacea	Ostracoda	Cypria	Immature to adult
Crustacea	Copepoda	Cyclops	Immature to adult
Insecta	Exopterygota	Ephemeroptera: <i>Ephemerella</i> <i>Ignita</i>	Nymph
Insecta	Diptera: Nematocera	Ephemeroptera: <i>Ephemera</i> <i>Danica</i>	Nymph, sub- imago, imago
Insecta	Diptera: Nematocera	Psychodidae	Larva + adult
Insecta	Diptera: Nematocera	Chironomidae	Larva + adult

Both sieving treatments had larger proportions of and a greater diversity of species compared to the frozen sediment samples. The 2 mm sieved Mill Stream Pond samples contained a high proportion of the Oligochaete *Tubifex tubifex*, which were greatly reduced in the 0.5 mm sieved sediment. However, the 0.5 mm sediment contained a much greater diversity of species, possibly due to less competition from the *Tubifex* worms. These included numerous Ostracods, Cyclops, Mayfly nymphs (*Ephemera* and *Ephemerella*) which reached emergence, and the Dipteran *Lonchoptera lutea*.

The Iron Hatch sediment contained significantly fewer species than the Mill Stream Pond, the 2 mm sieved samples containing only a few *Tubifex* worms, Ephemeropteran and Lonchopteran species. In the 0.5 mm sieved samples no indigenous species were found, but chironomid emergence success was still lower than in the 2mm samples.

DISCUSSION

The use of laboratory-based bioassays relying on interpretation of chronic end points require an exceptional level of standardisation, due to the considerably high potential variation in biological systems.

If natural sediments are to be incorporated into the experimental design, the fauna present in the sediment must be eliminated as they are a source of variation.

As the test species *Chironomus riparius* can be found in naturally occurring sediment, it is reasonable to expect multispecies community relationships do exist, incorporating competitive and predatory factors. Therefore when natural sediment is utilised in bioassays, there is a high risk of these interactions affecting the chironomid emergence success.

Both sediments investigated in this study contained a wide diversity of species with variable abundance which altered the emergence success of introduced chironomids. The freezing treatments revealed interactions with the chironomids occurred in samples frozen for up to 1 week, the emergence success being lower than that in samples frozen for at least 2 weeks where no organisms were found. These interactions were proportional to abundance, the greater the abundance, the higher the competition for food, the slower the growth which subsequently reduced the emergence of the chironomids.

Similar interactions were observed in the sieved treatments for the Mill Stream Pond sediment. Sieving at 0.5 mm removed some of the fauna present, so emergence success improved slightly compared to 2 mm sieved samples. In the Iron Hatch sediment no organisms were found in the 0.5 mm sieved samples but the rate of chironomid emergence was still much slower than in the 2 mm sieved samples, suggesting that extensive disruption of the sediment (e.g. selection of smaller particle sizes) was also an important factor in determining survival and emergence of introduced chironomids.

The data from this study shows that freezing at -18°C for a minimum of 2 weeks is an effective method of removing fauna from natural sediments to be used in laboratory toxicity assessments. This eliminates biological variables creating a more standardised approach to testing. However it is recognised that the microbial viability of the sediments is likely to be significantly affected by such a treatment.

REFERENCES

- Barrett, K.L.; Dohmen, G.P. (1992) A proposed test method for the assessment of pesticide impact on sediment dwelling larvae of the midge *Chironomus riparius*. *Brighton Crop Protection Conference - Pests and Diseases 1992-2*, 769-774.
- Elendt, B.-P.; Bias, W.-R. (1990) Trace nutrient deficiency in *Daphnia magna* cultured in standard medium for toxicity testing. Effect of the optimisation of culture conditions on life history parameters of *D. magna*. *Water Research*, **24** (9), 1157-1167.
- Reynoldson, T.B.; Day, K.E.; Clarke, C.; Milani, D. (1994) Effect of indigenous animals on chronic end points in freshwater sediment toxicity tests. *Environmental Toxicology and Chemistry*, **13** (6), 973-977.

'PHYSICO-CHEMICAL EVALUATION: THE ENVIRONMENT' AN EXPERT SYSTEM FOR PESTICIDE PREREGISTRATION ASSESSMENT

P.H. NICHOLLS

Institute of Arable Crops Research, Rothamsted Experimental Station, Harpenden, Herts, AL5 2JQ

ABSTRACT

The first version of an expert system, called "Physicochemical Evaluation: The Environment", is described. The system is Windows-based for use on a PC, and calculates redistribution of organic compounds in the environment from basic physicochemical properties. Data on physical chemistry, sorption and mobility in soils and sediments, translocation in plants, bioconcentration, volatilisation, biodegradation and leaching to ground and surface waters are produced. The first version is customised to the needs of the MAFF Pesticide Safety Directorate. The main aim is to give a broad theoretical prediction of the behaviour of a compound against which scientific data provided by applicants for registration can be interpreted. Firstly, the system is of direct interest to PSD departments working on fate and behaviour, residues in food, efficacy and wildlife. Secondly, the system enables rapid transfer to PSD of the results of our research on the movement of pesticides in soils and plants. Thirdly, the programme is a training aid for those requiring quantitative knowledge of factors influencing the fate of crop protection agents in the environment. Innovative features include predictive routines for ionisable compounds and an empirical method to estimate trace concentrations of compounds in lysimeter leachates.

INTRODUCTION

Applicants for registration provide a data package, covering the fate and behaviour of the compound in the environment, which usually contains much information. Many aspects of the fate and behaviour can be predicted from a few physicochemical properties, and such predictions give a useful scientific perspective which aids the evaluation of the data package. The system described makes predictions from the physicochemical properties of the compound of the factors which influence redistribution in the environment. The system calculates information on physical chemistry, sorption and mobility in soils and sediments, translocation in plants, bioconcentration, volatilisation, biodegradation and leaching to ground and surface water. Important information is given for consultation on perhaps more esoteric topics, such as volatilisation from water, about which the evaluator might be less familiar. Understanding developed from using the system can help the evaluator to make more constructive contribution to the consideration of topics such as residues in foods, efficacy and the effects on wildlife.

SYSTEM REQUIREMENTS

An IBM-compatible PC running Microsoft Windows 3.1 is required. The graphics in the programme are quite demanding and so a fast machine is recommended. The software was developed on a 486 DX 33 MHz machine with 8 MB RAM. The option in Windows Setup was: 800 x 600 256 color (small Font). The database of pesticide physicochemical properties was prepared in Microsoft Access 1.1 format.

INPUT DATA

The structure of the system is given in Figure 1. Input data required include values of: $\text{Log } K_{ow}$ (where K_{ow} is the 1-octanol/water partition coefficient), half-life in soil, $\text{p}K_a$ (if ionisable at environmental pH values), melting point, vapour pressure and molecular weight. Thus, only six items are needed and these are usually provided at the beginning of the data package. Input data for over 400 compounds can be provided automatically from the database. Users will usually be of two types. Firstly, those interested in commercial compounds for whom compound properties will usually be in the database and, secondly, synthetic chemists who usually have the resources to calculate values of lipophilicity and $\text{p}K_a$ of experimental compounds.

OUTPUT DATA

Soils and sediments. Values of organic carbon/water and organic matter/water partition coefficients (K_{oc} and K_{om} respectively) and the Rf value on soil thin-layer chromatographic plates are calculated from the physical properties of the compound, using the methods of Briggs (1981) for non-ionised compounds and Nicholls and Evans (1991) for ionised compounds. A measured value of K_{oc} can also be entered. An Rf value for leaching in a soil column is calculated from K_{oc} using the method of Hamaker (1975). K_{oc} for acids and bases is termed 'Pseudo K_{oc} ' because it is a function of soil pH and is calculated for soil of pH 6.5. Three classifications (viz. Soil Survey and Land Research Centre (SSLRC), Helling & Turner (1968) and McCall *et al* (1980)) of soil-mobility derived from K_{oc} values are displayed. Sorption and mobility properties are initially calculated for a soil of pH 6.5 and organic carbon content of 1% but are recalculated when other values of soil properties are entered. Values of K_{oc} are saved for use in later estimations of leaching through soils and for distribution within a mesocosm.

Translocation within plants. Factors that indicate systemicity are calculated. The root concentration factor (RCF), transpiration stream concentration factor (TSCF), the TSCF value adjusted for a plant growing in moist soil and the stem concentration factor (SCF) are calculated using the equations given by Bromilow & Chamberlain (1989). The macerated-stem/water partition coefficient is calculated and may be used to estimate uptake from water by the submerged foliage of aquatic plants such as *Hydrilla*. Translocation in *Lemna* species may, perhaps, be better estimated by the TSCF value given for plants grown in hydroponic solution. The translocation of organic acids in phloem and xylem is not numerically quantified but is indicated graphically by methods similar to those given in Bromilow & Chamberlain (1989). Further work on translocation of polyions such as glyphosate is required before their systemicity can be incorporated into future versions of the system.

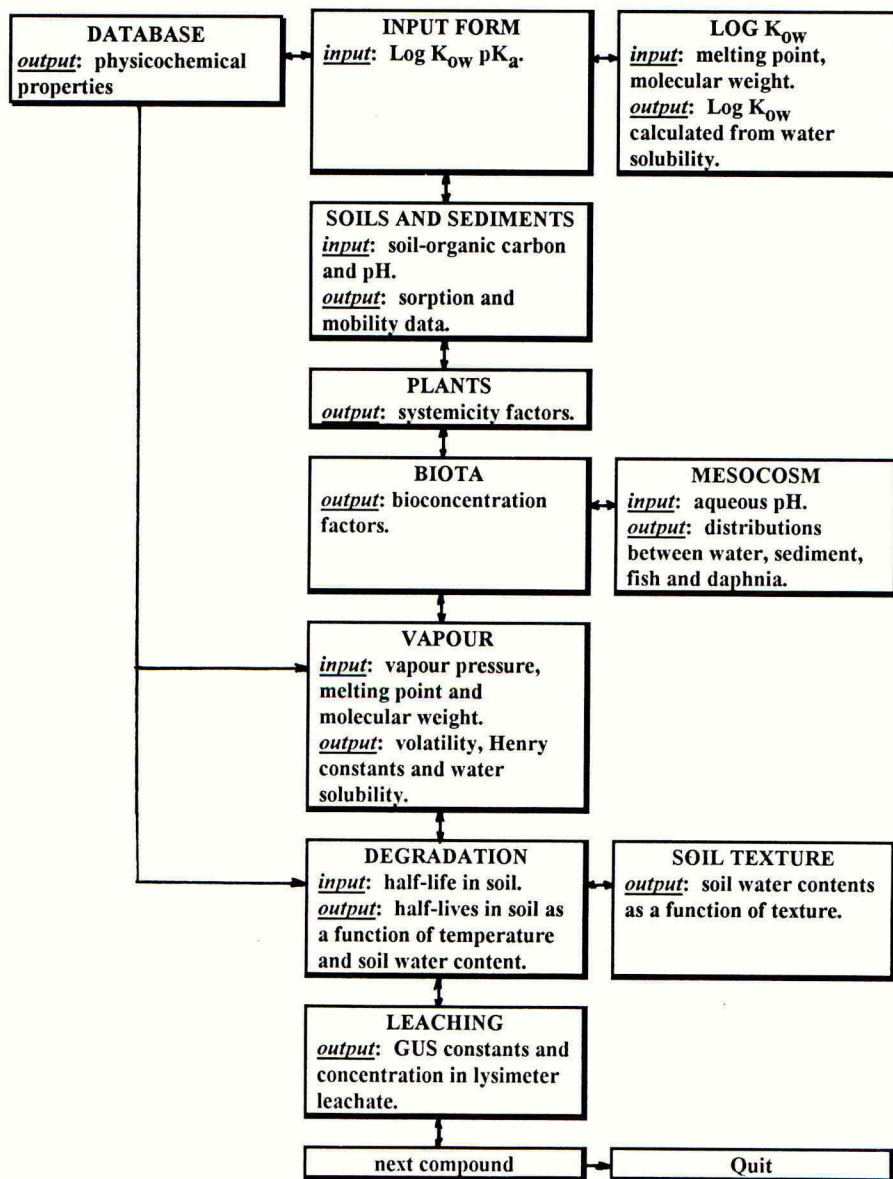


Figure 1. Structure of the system "Physicochemical Evaluation: The Environment".

Biota. A range of bioconcentration factors (viz. for protein, lipids, fish muscle, earthworms, whole organisms [e.g. fish] and *Daphnia pulex*) are calculated (Briggs, 1981; Lyman *et al.*, 1982; Isnard & Lambert, 1988). Values are calculated for acids and bases, as a function of the pH of the water, using the Henderson-Hasselbalch equation and assuming that the value of $\text{Log } K_{ow}$ for the ion is 3.4 units less than that of the non-ionised form (Bromilow, R.H. & Chamberlain, K., 1991). The distribution and concentrations of the compound in a mesocosm are calculated for a system consisting of water, sediment, fish and *Daphnia pulex*. The mesocosm is assumed to be at equilibrium with no dissipation by degradation, metabolism or volatilisation. The pH of the water in the mesocosm can be changed for ionisable compounds. The following parameters which are used in the mesocosm calculation can also be adjusted: application rate of the compound, depth of water, weight of fish and the following properties of sediment: depth, organic carbon content and bulk density. In general, toxicity cannot be predicted from the physical properties of a compound and so toxicological end-points are not given.

Vapour. A number of properties are calculated that influence the dissipation by volatilisation of the compound. Vapour pressure values are adjusted to 20°C and Henry's constant is given in three commonly quoted units. Henry's constant, being an air/water partition coefficient, is a measure of the potential of the compound to volatilise from water. The rate of volatilisation from river water is calculated using methods of Lyman *et al.* (1982). A partition coefficient for the compound between air and moist-soil is given, such a value being useful when considering lipophilic soil-acting herbicides such as triallate and insecticides such as tefluthrin. The rate of volatilisation of the compound from leaf-surfaces in still air at 20°C or from field soil are estimated using empirical methods (G.G. Briggs, personal communication). Water solubility, which is used to calculate Henry's constant, is also calculated if a measured value is not given.

Biodegradation in soils. Rates of degradation cannot usually be predicted from simple physical properties and so an appropriate value of the half-life in soil of the compound must be entered. The half-life can then be calculated for different values of temperature and soil-water content using the equations given by Walker (1976). Different units of soil-water content tend to be used in the different circumstances of laboratory measurement, calculation of degradation, soil physics and the simulation of leaching. Routines are given to convert to a range of units of soil water content. The units of soil-water content used in laboratory studies of degradation, as submitted to PSD, are often in units of water holding capacity (WHC %) or field capacity (FC %). Comparison of studies in different soils requires knowledge of soil texture. Routines are given to calculate soil water content, given in units of WHC% or FC%, and in a range of other units for soils of 11 different textures. Rates of degradation, for soils of different texture at a given temperature, are likely to be similar for soils at the same soil-water pressure. Thus, comparison can be made of the water content of soils of different texture at the same soil-water pressure. Some planned European protocols may require soil-water pressure in units of pF and so pressure is given in units of kPa and pF.

Some compounds are degraded slowly largely because they are strongly sorbed, and this can be explored by estimating the rate of degradation in the soil-water phase.

Empirical estimations of the half-life of the compound in mammals, plants and stored grain are displayed with the SSLRC category of persistence in soil.

Leaching through soils. The potential of a compound to leach is assessed from its K_{oc} value and its half-life in soil by calculating the GUS index (groundwater ubiquity score; Gustafson, 1982). The position of the compound is shown on a graphical representation of the GUS plot and compared with benchmark compounds. Values of K_{oc} and half-life can be varied by entering new data.

The GUS index takes no account of the rate of application of the compound. For example, metsulfuron methyl is applied at such low rates that, although it is classified as a leacher by its GUS index, it may not reach high concentrations in drainage water. The consideration of rate of application is timely because, for example, all but one of the new herbicides announced at the BCPC Conference - Weeds 1993 are applied at less than 100 g/ha.

TABLE 1. Quantities of herbicide predicted to leach through a lysimeter.

	Isoproturon	Pendimethalin	Metsulfuron methyl	Mecoprop	
<u>Input</u>					
Log K_{ow}/pK_a	2.24/-	5.18/-	1.64/3.64	3.2/3.18	
Half-life (day)	25	50	60	4	
Application rate (g/ha)	2500	1000	12	2500	
<u>Output</u>					
Amount leached in one year below 1 m (% of applied)	struct.*	0.05	<0.005	0.99	0.02
	chrom.*	<0.005	<0.005	0.01	<0.005
Average concentration in leachate over 1 year ($\mu\text{g/l}$)	struct.	0.3	<0.005	0.04	0.13
	chrom.	<0.005	<0.005	<0.005	<0.005

*Predictions for a structured soil and for chromatographic flow in a non-structured soil.

Therefore, an empirical method of assessing risk of leaching through a lysimeter of 1 metre depth was devised. The method assumes that for a non-ionised compound with half-life (days) = $t_{1/2}$ in a structured U.K. soil:

$$\% \text{ leached} = (t_{1/2}/40) \times 10^{-0.5 \text{ Log } K_{ow}}$$

If measured $t_{1/2} > 100$ then $t_{1/2}$ is put in as 100. For chromatographic soil, % leached = 0.01 x (% leached for structured soil). If % leached is predicted > 1 then % leached is taken to have a maximum value of 1.

Examples of results for herbicides are given in Table 1. When the application rate is entered, the amounts and concentrations of the compound in leachate from a fallow lysimeter, exposed to UK weather for 1 year, can be estimated. Results are consistent with our own lysimeter experiments, with observations at Brimstone farm and with the

compounds found in drainage waters in East Anglia, and this indicates that the method assesses the risk of leaching in a realistic way.

CONCLUSIONS

Although simulation models are able to predict results of specific events, the input data they require and the time required to learn their operation often takes from several hours to many days. The operation of the present system is fast and can be learnt in a few seconds whilst a run takes about 20 minutes for each compound. A database, assembled from the literature and containing most of the properties of over 400 compounds can speed the preparation of input data. Additional information, such as soil texture diagrams, can be stored in the context-sensitive Windows Help system.

Expert systems of this type make it possible to transfer the results of research from the bench to the PC of the user within 24 hours and to present such results in an attractive and digestible form. For example, the new compounds announced at this conference have already been included in the database. The system may be of particular use during the initial "sifting" of applications by PSD. Future versions will include extended databases and context-sensitive help systems, together with additional sections on uptake through cuticles of plants and the influence of different European climates.

ACKNOWLEDGEMENTS

I am grateful to MAFF for funding commissioned projects on movement of pesticides in soils and plants. Thanks are due to Dr T D Jarvis and his colleagues in MAFF PSD for testing and commenting constructively on development versions of the system.

REFERENCES

- Briggs, G.G. (1981) Theoretical and experimental relationships between soil adsorption, octanol-water partition coefficient, water solubilities, bioconcentration factors and the paracher. *J. Agric. Food Sci.*, **29**, 1050-1059.
- Bromilow, R.H.; Chamberlain, K. (1991) Pathways and mechanisms of transport of herbicides in plants. In: *Target Sites for Herbicide Action*, R.C. Kirkwood (Ed.), Plenum, New York. 245-284.
- Gustafson, D.I. (1989) Groundwater ubiquity score. *Env. Tox. Chem.* **8**, 339-357.
- Hamaker, J.W. (1975) The interpretation of soil leaching experiments. In: *Environmental Dynamics of Pesticides*, R. Haque; V.H. Freed, (Eds.), Plenum, New York.
- Helling, C.S.; Turner, B.C. (1968) *Science (Washington D.C.)* **162**, 562-563.
- Isnard, P.; Lambert, S. (1988) Estimating bioconcentration factors. *Chemosphere*, **17**, 21-34.
- Lyman, W.J.; Reehl, W.F.; Rosenblatt, D.H. (1982) *Handbook of Chemical Property Estimation Methods*, McGraw Hill, New York.
- McCall, P.J.; Swann, R.L.; Laskowski, D.A.; Unger, S.M.; Vrona, S.A.; Dishburger, H.J. (1980) *Bull. Env. Contam. and Toxicol.* **24**, 190-195.
- Nicholls, P.H.; Evans, A.E. (1991) Sorption of ionisable organic compounds by field soils. *Pestic. Sci.*, **33**, 319-345.
- Walker, A. (1976) Simulation of herbicide persistence in soil. *Pestic. Sci.*, **7**, 41-49.

DISSIPATION OF CHLORPYRIFOS AND 3,5,6-TRICHLOROPYRIDIN-2-OL IN GERMAN SOILS

A. KHOSHAB, A. NICHOLSON

DowElanco Europe, Letcombe Laboratories, Letcombe Regis, Wantage, Oxon, OX12 9JT

ABSTRACT

Four trials were carried out at different locations in Germany during 1991-1993 to determine the dissipation of chlorpyrifos and concentrations of its major metabolite, 3,5,6-trichloropyridin-2-ol (TCP) in different soil types following autumn application of DURSIBAN® FLUESSIG to bare soil. Soil cores were taken to a depth of 1 metre at various intervals from pre-application to one year post application. Cores were segmented and each horizon was analysed for residues of chlorpyrifos and TCP to a lowest validated level of 0.01 mg/kg. Chlorpyrifos declined according to square root 1st order function in three trials and 1.5 order function in one trial. The half lives (DT50) ranged from 10 to 22 days, and the time required for 90% degradation (DT90) ranged from 97 to 248 days. Residues of TCP in the 0-10cm horizon ranged from <0.01 mg/kg to 0.02 mg/kg. Chlorpyrifos or TCP residues were detected in the 10-20cm horizons at a few sampling times and ranged from <0.01 mg/kg to 0.01 mg/kg. In the light of these results no samples from lower horizons were analysed. The data shows that under the field conditions there is no indication of vertical mobility and leaching potential of the residues in soil, and also accumulation of residues in soil is unlikely to occur.

INTRODUCTION

Chlorpyrifos [0,0-diethyl 0-3,5,6-trichloro-2-pyridyl phosphorothioate] is an organophosphorous insecticide effective against a wide range of insect pests on crops of commercial importance. It is effective by contact, ingestion and vapour action. The degradation and leaching of chlorpyrifos and TCP in the soil environment has been extensively investigated and documented (Racke, 1993). Chlorpyrifos and TCP exhibits many different half-lives depending on soil type as well as mode of application and environmental variables. Prediction of leaching based on sorption affinity and modelling, as well as actual results obtained with soil columns or under field use conditions have demonstrated the negligible leaching potential of chlorpyrifos. Theoretically, chlorpyrifos movement would be limited to the upper 30cm of all soil profiles, but greater mobility of TCP is predicted, at trace levels, to 30-185cm, based on a model assuming 11.2 kg/ha surface broadcast application and maximum predicted rainfall from 10 years data (Racke, 1993).

In this paper we report actual field data sets on chlorpyrifos dissipation and the fate of TCP obtained in four field trials carried out at different locations with three different soil types.

EXPERIMENTAL

Field

Four trials were conducted at different locations representing typical agricultural soils in Germany during 1991-1993. Locations of trials, soil type and soil characterisation details are given in Table 1.

Table 1. Trial locations, soil type and soil characterisation data.

Location	Trial A Adelshausen (Bayern)	Trial B Grebien (Schleswig- Holstein)	Trial C Herford (Nordrhein- Westfalen)	Trial D Lauter (Hessen)
Soil type	sandy loam	sandy silt loam	loamy silt	loamy silt
pH	6.2	5.3	5.7	6.0
C (%)	3.3	1.22	1.30	1.20
Clay (%)	9.4	12	12	19
Silt (%)	14.3	38	84	77
Sand (%)	76.3	50	4	4
Total cation exchange (mval/100g soil)	14.4	10.8	10.1	14.3
Max. water capacity (%)	-	-	50.4	49.8

DURSBAN® FLUESSIG, an EC formulation containing 480g chlorpyrifos per litre was applied in autumn to bare soil plots (plot layout shown in Figure 1) at a rate of 400 L/ha, equivalent to 720g ai/ha using a plot sprayer with Teejet 8003 nozzles at a pressure of 2 bar. Twenty soil cores (5 cores per replicate) were taken at each sampling time; a 'Coremaster' soil corer (5.0cm diameter, 20cm deep) was used for 0-15 days sampling points and 'Humax' or 'Raupe' soil corers (4.7cm diameter, 100 cm deep) for 30-385 days sampling points. Samples were deep frozen immediately after sampling. Weather data (maximum and minimum air temperature and rainfall) were recorded throughout the duration of trials.

Analytical

Each core was split into 0-10, 10-20, 20-40, 40-60, 60-80 and 80-100cm horizons. Replicate horizons were bulked and these bulk wet samples were mixed, sieved through a 4mm mesh sieve and immediately deep frozen until analysis. Residues of chlorpyrifos and TCP were determined in duplicate with batch recoveries by using DowElanco Analytical Method (Khoshab, 1990 and Khoshab *et al.*, 1993 respectively) with a lowest validated level of 0.01 mg/kg. Chlorpyrifos was extracted from soil with an acetone/water solvent mixture, additional water was added and chlorpyrifos partitioned into hexane. The chlorpyrifos in the hexane solution was quantified by gas chromatography with flame photometric detection. Residues of TCP were extracted from soil using acidified acetone. An aliquot of the acetone extract was evaporated and the aqueous acid diluted with water. The TCP was partitioned into toluene. The toluene extract was purified using high resolution gel permeation chromatography with toluene as the elution solvent. The TCP fraction was collected and derivatised with

N,O-bis(trimethyl-silyl)-trifluoroacetamide (BSTFA) to the TCP trimethyl silyl derivative. The derivative was quantified by gas chromatography using electron capture detection.

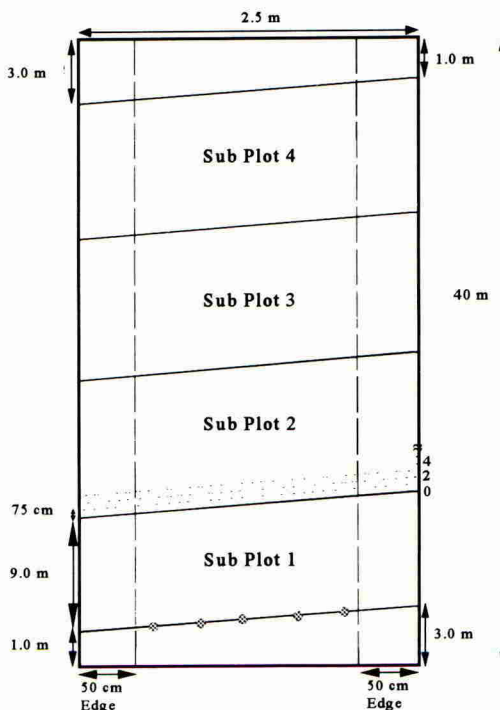


FIGURE 1. Plot layout,
Diagram not to scale

● = Core (5 cores per sub plot, 20 cores per sampling time)

CALCULATION OF HALF LIFE (DT_{50}) AND DEGRADATION TIME FOR 90% (DT_{90}) OF CHLORPYRIFOS IN SOIL

In many cases the decline of pesticide residues cannot be described mathematically as a reaction of 1st order. The residues may decline at a considerably faster rate shortly after application than during the subsequent course of the study. Several researchers have reported the inadequacy of simple 1st order kinetic assumptions in describing the degradation of chlorpyrifos in soil (Racke, 1993). It has been reported that the apparent 1st order rate constant decreased with time, and thus overall degradation represented a significant deviation from 1st order kinetics. For this reason the decline may be described as a 1.5 or 2nd order reaction, or with the time axis compressed using the square roots of the time data for the scale. DT_{50} and DT_{90} reported in this paper, were calculated using PC Evaluation Programs (Etwin, 1992) for the evaluation of residue degradation studies, which were based on the mathematical process described by Timme et al., 1980 and Timme et al., 1986. These programs utilise the degree of fit to assign the most appropriate kinetic function to describe the DT_{50} and DT_{90} .

RESULTS AND DISCUSSION

The residues of chlorpyrifos and TCP in soil are summarised in Tables 3-6. All residue results are quoted on a dry weight basis and are not corrected for recovery. Procedural recovery for chlorpyrifos and TCP were in the range 83-117% (mean 101%) and 68-99% (mean 86%) respectively. Given an application rate of 720g chlorpyrifos/ha, an assumed soil density of 1.5 kg/dm³ and sampling depth of 10cm, the theoretical initial concentration of chlorpyrifos can be calculated as 0.48 mg/kg. The values actually obtained for the day of application in the top 10cm of the soil ranged from 0.35 to 0.58 mg/kg chlorpyrifos. There was good agreement between the residues determined and the theoretical values. Residues of TCP in the 0-10cm horizon ranged from <0.01 to 0.02 mg/kg. Chlorpyrifos or TCP residues were detected in the 10-20cm horizons at a few sampling times and ranged from <0.01 to 0.01 mg/kg. In the light of these results no samples from lower horizons were analysed. The chlorpyrifos residue data from the 0-10cm horizons was used for calculation of DT₅₀ and DT₉₀ using the best fit option of the PC Evaluation programs (Etwin, 1992). The DT₅₀ and DT₉₀ of chlorpyrifos in soil are summarised in Table 2.

Table 2. DT₅₀ and DT₉₀ of chlorpyrifos in soil and mathematical functions used.

	Trial A	Trial B	Trial C	Trial D
DT ₅₀	13	22	19	10
DT ₉₀	148	248	97	112
Mathematical Function	SRF 1st order	SRF 1st order	1.5 order	SRF 1st order

SRF = Square Root Function

In trial B, the programme automatically selected the 1st order function giving a DT₅₀ and DT₉₀ of 68 and 224 days respectively. An outlier result at day 30 of trial B which fell well outside the band of plotted points was omitted and the data re-analysed. The square root 1st order function was selected and a good curve fit with better confidence interval achieved with a DT₅₀ and DT₉₀ of 22 and 248 days respectively. Figure 2 shows a representative decline curve of chlorpyrifos. The data shows that under the field conditions following autumn application there is no indication that mobility, leaching or accumulation of residues of both chlorpyrifos and TCP in soil is likely to occur.

Table 3. Residues of chlorpyrifos and TCP in soil, Trial A, Adelshausen (sandy loam).

Days After Application	Chlorpyrifos residues found (mg/kg)		TCP residues found (mg/kg)	
	Soil horizon (cm)		Soil horizon (cm)	
	0 - 10	10 - 20	0 - 10	10 - 20
0	0.58	ND	0.01	ND
3	0.28	ND	0.01	ND
7	0.31	0.01	0.01	ND
14	0.35	ND	0.01	ND
143	0.11	ND	0.02	ND
213	0.02	ND	<0.01	ND

ND = Not Detected or < 0.002 mg/kg

Table 4. Residues of chlorpyrifos and TCP in soil, Trial B, Grebin (sandy silt loam).

Days After Application	Chlorpyrifos residues found (mg/kg)		TCP residues found (mg/kg)	
	Soil horizon (cm)		Soil horizon (cm)	
	0 - 10	10 - 20	0 - 10	10 - 20
0	0.35	ND	<0.01	ND
3	0.32	ND	<0.01	ND
9	0.24	ND	<0.01	ND
15	0.26	ND	<0.01	ND
30	0.37	ND	0.02	ND
58	0.14	<0.01	<0.01	ND
128	0.14	<0.01	0.01	ND
214	0.03	ND	0.02	ND

Table 5. Residues of chlorpyrifos and TCP in soil, Trial C, Herford (loamy silt).

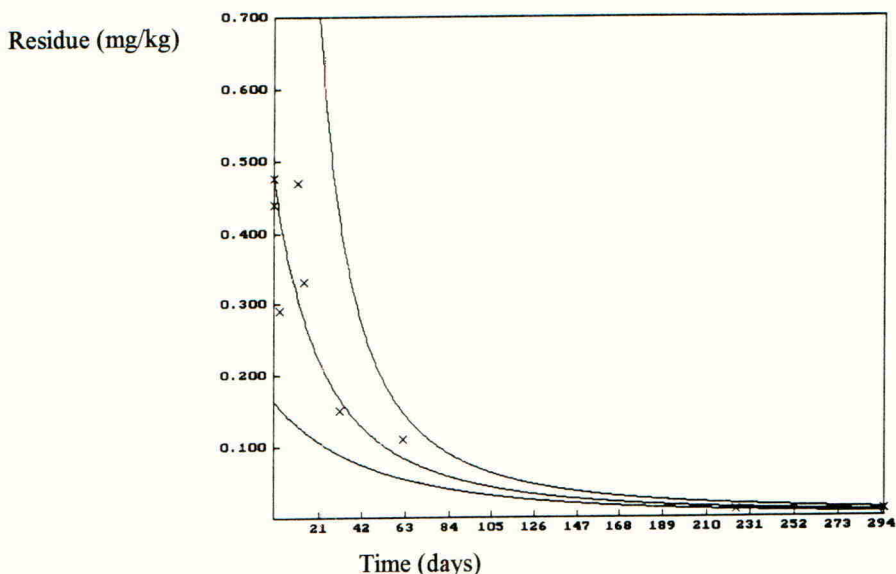
Days After Application	Chlorpyrifos residues found (mg/kg)		TCP residues found (mg/kg)	
	Soil horizon (cm)		Soil horizon (cm)	
	0 - 10	10 - 20	0 - 10	10 - 20
0	0.44	<0.01	0.01	ND
3	0.29	ND	<0.01	ND
11	0.47	ND	0.01	ND
14	0.33	ND	0.01	ND
31	0.15	0.02	<0.01	ND
62	0.11	0.01	0.01	<0.01
224	0.01	ND	<0.01	ND
295	0.01	ND	<0.01	NA

NA = Not Analysed

Table 6. Residues of chlorpyrifos and TCP in soil, Trial D, Lauter (loamy silt).

Days After Application	Chlorpyrifos residues found (mg/kg)		TCP residues found (mg/kg)	
	Soil horizon (cm)		Soil horizon (cm)	
	0 - 10	10 - 20	0 - 10	10 - 20
0	0.41	<0.01	<0.01	ND
3	0.31	<0.01	0.01	ND
7	0.28	<0.01	0.01	ND
14	0.32	0.01	0.01	ND
37	0.05	<0.01	<0.01	ND
76	0.09	<0.01	<0.01	ND
128	0.04	<0.01	<0.01	ND
223	ND	ND	ND	ND

FIGURE 2. Decay curve for chlorpyrifos, trial C, 1.5 order decay curve



ACKNOWLEDGEMENTS

The authors thank members of DowElanco GmbH, Munich field trials personnel, P. Kinzel, C. Hecht, E. Schmolke, J. Schroeder, H. Lempke, R. Weiher, for their support and contribution on this work. The authors also wishes to thank R.Dutton, J. Perkins, R. Maycock and A. Sisson for comments on drafts of this paper.

REFERENCES

- Etwein, F. Models for describing the decline of pesticide residues, PC Evaluation Programme Version 2.0 (IVA), BAYER AG, 30 Nov 1992.
- Khoshab, A. Determination of chlorpyrifos in soil, DowElanco Analytical Method ERC 90.13. An unpublished method of DowElanco Europe.
- Khoshab, A.; Nicholson, A. Determination of 3,5,6-trichloropyridin-2-ol in soil, DowElanco Analytical Method ERC 92.40. An unpublished method of DowElanco Europe.
- Racke, K. D. (1993) The environmental fate of chlorpyrifos, *Rev. Environ. Contam. Toxicol.*, **131**, 1993.
- Timme, G. ; Frehse, H. (1980) Statistical interpretation and graphic representation of the degradational behaviour of pesticide residues I, *Pflanzenschutz-Nachrichten Bayer*, **33**, 47-60.
- Timme, G. ; Frehse, H.; Laska, V. (1986) Statistical interpretation and graphic representation of the degradational behaviour of pesticide residues II, *Pflanzenschutz-Nachrichten Bayer*, **39**, 187-203.

THE USE OF A COMPARTMENT MODEL FOR EVALUATING THE FATE OF PESTICIDES IN SEDIMENT/WATER SYSTEMS

R.R. CARLTON, R. ALLEN

AgrEvo UK Limited, Chesterford Park, Saffron Walden, Essex, CB10 1XL

ABSTRACT

The need to predict environmental concentrations of pesticides and their environmentally significant degradation products in surface water, and how these concentrations decline with time, is now an integral part of hazard evaluation procedures. This paper outlines an approach to the evaluation of results from two laboratory sediment/water studies with pesticides and its application in the calculation of PEC's in surface water and sediment with time. Through the use of a compartment model, rate constants for degradation and adsorption/desorption processes of parent compound and metabolites were calculated using an iterative computer program (TOPFIT version 1.1). The derived rate constants can be used to simulate behaviour in ponds following loadings of a pesticide as a result of drift, run-off and erosion.

INTRODUCTION

Sediment/water systems, such as ditches and ponds, are parts of the environment which, although not directly targeted by the farmer, may be contaminated by pesticides through run-off or spray drift. This is of concern due to the impact such an event may have on non-target organisms. The effect on the population of a non-target organism in a sediment/water system will depend upon the initial concentration of the pesticide, its fate within the ecosystem, the sensitivity of the organism to the pesticide and its degradation products, and the ecology of the species in question.

In this paper we address the second of these factors by demonstrating how environmental fate data generated by laboratory sediment/water studies can be evaluated by a computer model. We also demonstrate that this model can then be used to simulate how the pesticide and its degradation products move between the compartments of the ecosystem and how their respective concentrations vary with time. The results of such computer predictions can be evaluated with ecotoxicology data to assess the potential environmental impact of run-off and spraydrift events.

Data for two pesticides, a fungicide and an acaricide, are used here to demonstrate how TOPFIT (Heinzel *et al.*, 1992), an iterative computer program for linear compartment modelling used widely in the area of pharmacokinetics, can simulate the fate of pesticides in simple (single event) and complex (multiple event) scenarios.

EVALUATION OF SEDIMENT/WATER STUDIES

Model definition

The evaluation process consists of two stages. Initially the user defines a compartment model based on a broad understanding of the pesticide's behaviour. The model structure is inputted into the program together with information concerning the quantity and location of the 'dose application' (i.e. whether the compound was applied to water or directly to sediment). Information concerning the nature of each compartment (entry (parent compound in water), transient (degradation product) or terminal (CO_2) compartment) is required. Initial estimates for the rate constants for each of the processes are also required together with an upper and lower boundary for each. Finally the data sets presenting the concentration of each component in water and sediment at a number of timepoints (standard output from sediment/water studies) are inputted.

Once completed an iteration process is initiated which determines the 'best-fit' rate constants for the experimental data according to the defined model. The iteration systematically varies all of the rate constants within the defined boundaries to achieve a best-fit. If a best-fit is achieved with rate constants at or near the boundary conditions then these can be widened in subsequent iterations in order to improve the fit. The model assumes that all individual processes (e.g. degradation of A to B in water or movement of A in water to A in sediment) follow first order kinetics. The goodness of fit can be assessed by reference to the 'fitting criterion' which is essentially equivalent to an r^2 value in a multiple regression. This value can be used to compare a range of proposed models describing the dissipation processes although a prior understanding of the behaviour of the compound is invaluable.

Once an iteration has been successfully run using real data from a study the model can be used to simulate the pesticide fate beyond the end of the study period and to simulate pesticide fate during a number of sequential contamination events.

Details of pesticides

Fungicide F is readily hydrolysed at pH7 to product G ($t_{1/2} = 22$ days). It is also lipophilic and hence strongly adsorbs to organic matter. Adsorption appears to significantly reduce the rate of hydrolysis. A model describing the fate of this compound in sediment/water systems is proposed in Figure 1. Here following application of F to water it can either degrade to product G or be adsorbed to sediment. Once in sediment it can either desorb back into the water column or also degrade to G in sediment. The adsorption/desorption rate constants result in an equilibrium which is disturbed by degradation of F in the two compartments.

Acaricide A is rapidly hydrolysed in water to two products B and C ($t_{1/2} < 1$ day). Like fungicide F, Acaricide A is lipophilic and strongly adsorbed to organic matter. However this process does not significantly reduce hydrolysis. Product B is also degraded to C. A more complex model describing the fate of A in sediment/water systems is presented in Figure 2. Experimental data showed that C was the major product in the sediment/water system and in turn in terms of concentration is most likely to be the compound of environmental concern.

In Figure 2 the model assumes that product C can be formed from hydrolysis of both the active ingredient A and product B. The model allows for a partition between water and sediment and degradation in both phases.

FIGURE 1. Compartment model describing the fate of Fungicide F in water and sediment.

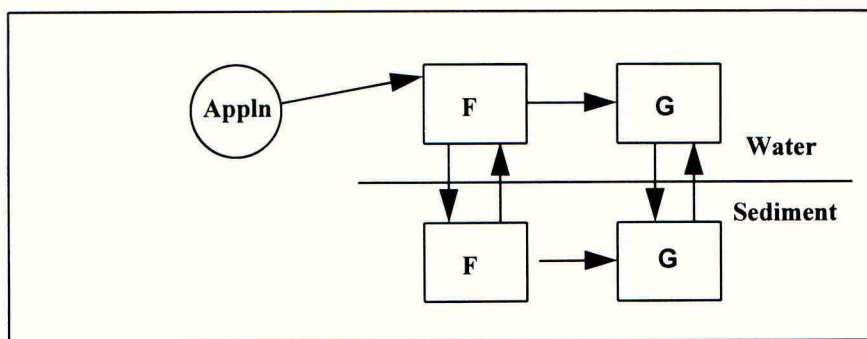
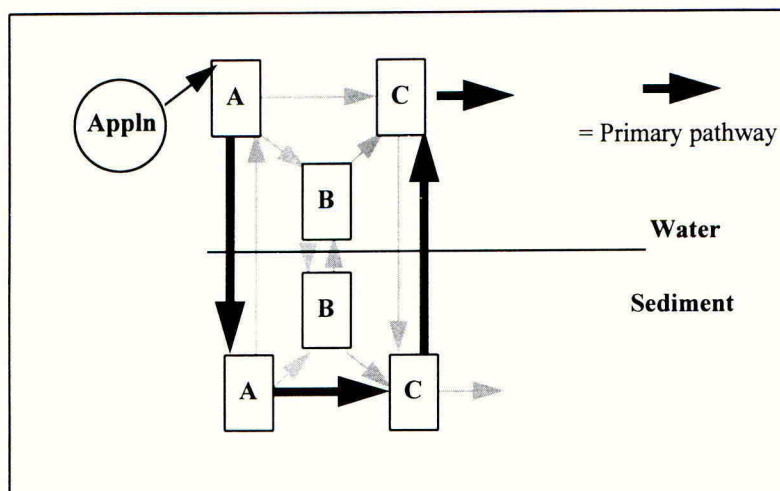


FIGURE 2. Compartment model describing the fate of Acaricide A in water and sediment.



RESULTS OF EVALUATIONS

Following iteration, results are presented in tabular and graphical form. These compare the actual data values against those calculated using the best-fit rate constants. The best-fit rate constants and corresponding 'half-life' times are also presented. Graphical representations of the model curves against data sets are also available, examples of which are presented in Figures 3 and 4.

Fungicide F

Figure 3 presents the data sets and best-fit curves for the concentrations of F in water and sediment phases. The fitting criterion for this evaluation was 0.97 indicating that there is a good fit between the experimental data and the the proposed model (perfect fit = 1.0). Review of the best-fit rate constants (or corresponding half-life times) enables conclusions to be drawn as to the likely fate of the compound in the system. In this case hydrolysis of F in water ($F_w \rightarrow G_w$) was calculated to be more rapid than the rate of adsorption to sediment ($F_w \rightarrow F_s$) (respective half-lives = 4.8 days and 22 days). Desorption from sediment to water ($F_s \rightarrow F_w$) is slow ($t_{1/2} = 91$ days) and will be controlled in part by degradation of F in the water column. Hydrolysis of F in sediment ($F_s \rightarrow G_s$) is slowest ($t_{1/2} = 138$ days), suggesting this is an insignificant route of loss.

Acaricide A

Figure 4 presents the data sets and best-fit curves for the concentrations of degradate C in water and sediment following application of acaricide A. The overall fitting criterion was 0.89 and was considered a good fit in view of the complexity of the model. Review of the rate constants allows for a primary route to be identified for the formation and degradation of C in sediment/water microcosms (bold arrows in Figure 2). Adsorption of A to sediment is rapid ($t_{1/2} = 0.07$ days) as is hydrolysis in sediment ($t_{1/2} = 1.3$ days). Product C is very polar and the model suggests rapid desorption into the water column ($t_{1/2} = 0.04$ days) where it is further degraded ($t_{1/2} = 8$ days).

FIGURE 3. Fate of Fungicide F in water (solid line) and sediment (dashed line) following application to water.

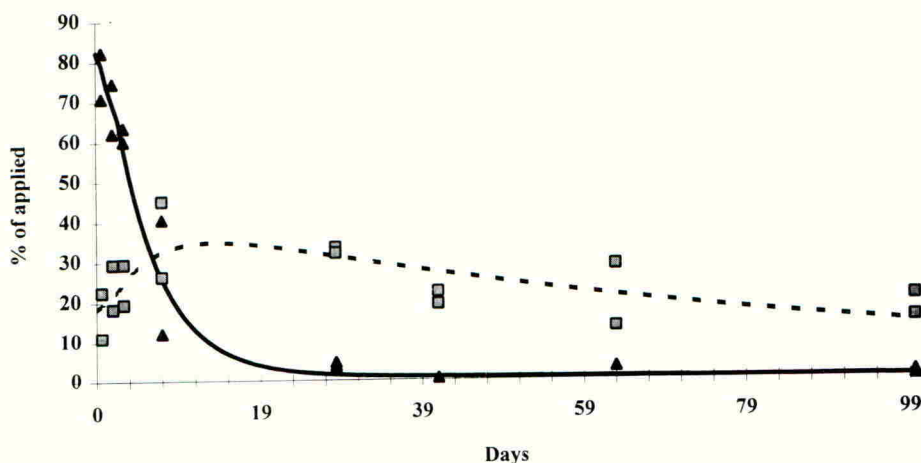
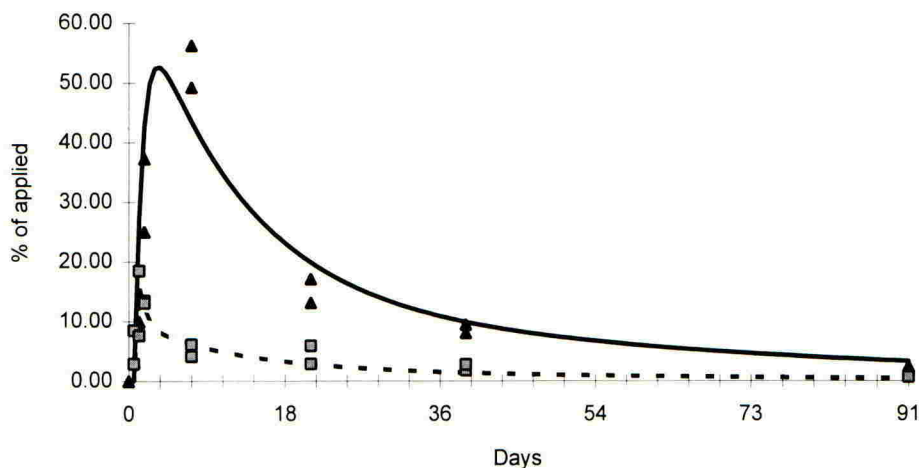


FIGURE 4. Fate of product C in water (solid line) and sediment (dashed line) following application of Acaricide A to water



SIMULATION OF FATE AND PREDICTION OF ENVIRONMENTAL CONCENTRATIONS IN SEDIMENTS AND WATER

Three run-off events to a sediment/water system from soil following application of fungicide E

Figure 5 shows how the concentration of F would vary in the sediment and the water following emissions to water via run-off on three occasions. The simulation indicates that contamination of water is relatively transitory but that there is the potential for F to accumulate in sediment. This may be of concern regarding potential hazard to sediment organisms.

Spray drift of acaricide A followed by two run-off events to a sediment/water system

Figure 6 shows how the concentrations of C, the degradation product of A, would vary in the sediment and the water following sequential emissions resulting from spray drift and two run-off events. Due to the short half life of A the run-off is assumed to contain C but not A. In this simulation there is no indication of accumulation although the persistence of C at concentrations of 10 ppb or above in water may be of concern regarding fresh water organisms.

CONCLUSIONS

In both cases the models are supported by the fitting criteria and calculate half lives which enhance our understanding of the fate of both molecules in sediment/water systems. The results indicate that TOPFIT can be an extremely useful aid for predicting concentrations of pesticides and their degradation products in sediment and water during complex series of events. The value of the model would be enhanced if confidence limits for the rate constants

were calculated at the iteration stage allowing subsequent simulations to be presented in terms of a frequency distribution rather than as a single decline curve.

FIGURE 5. Simulation of the PEC of Fungicide F in a static body of water and sediment following three run-off events resulting in an initial loading of 10 ppb to water 28 days apart.

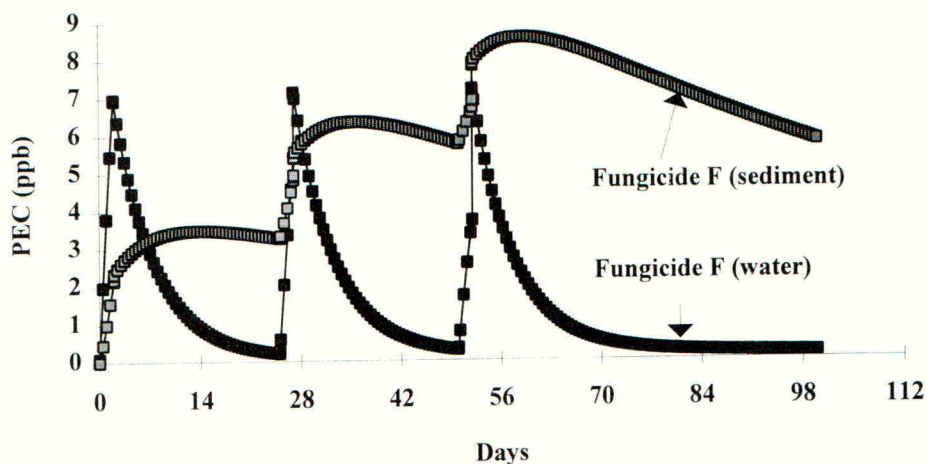
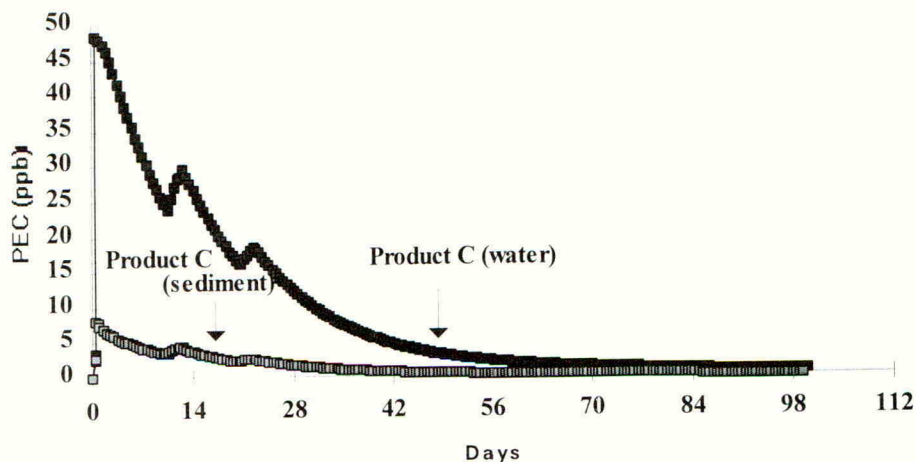


FIGURE 6. Simulation of the PEC of product C in a static body of water and sediment following a spray drift event resulting in a 50ppb loading of acaricide A to water and two subsequent run-off events (10 and 20 days) resulting in loadings of 10ppb and 5ppb of product C to water.



REFERENCES

Heinzel, G.; Woloszczak, R.; Thomann, P. (1992) TOPFIT Version 1.1 Pharmacokinetic and Pharmacodynamik Data Analysis System. Godecke, Schering, Thomae.

AQUATIC MICROCOSMS AS A TOOL FOR ASSESSING FATE AND EFFECTS OF PESTICIDES

I. RÖNNEFAHRT, A. FLIEDNER, A. REMDE, U. TRAUB-EBERHARD, R. DEBUS

Fraunhofer-Institut für Umweltchemie und Ökotoxikologie, 57392 Schmallenberg, Germany

ABSTRACT

Fate and effects of the herbicide isoproturon were investigated in newly developed aquatic microcosms. Isoproturon was applied to six microcosms (initial water concentrations: 10, 30 and 90 µg/l). During the post-treatment phase of 5 months the water phases, top sediment layers and leachates were analysed regularly for isoproturon and metabolites. The effects of isoproturon were investigated on plankton and sediment organisms. The concentration/time profiles of isoproturon in water and leachate were very similar in all microcosms. The mean DT50 and DT90 values in water were 23 and 77 days, respectively. Plankton organisms were not directly affected by isoproturon at any tested concentration. However, four weeks after treatment with 90 µg/l the *Cladocera* population started to decline and no recovery was observed until the end of the study. No effects were observed on anaerobic microbial degradation activity in the sediments and on abundance of sediment-dwelling nematodes.

INTRODUCTION

Various processes like run-off or spray-drift may cause the dissipation of pesticides into natural ditches or ponds. Environmentally relevant information on the fate of pesticides in aquatic ecosystems as well as on their ecotoxicological effects can be obtained from microcosm studies simulating selected environmental conditions. A new microcosm system containing undisturbed sediment cores and natural water was developed for simulating a pond system. (Traub-Eberhard, Schäfer et. al., 1994) The system can be operated with radiolabelled test substances, which allows the assessment of effects as well as a precise fate study and analysis of metabolites in water, sediment and leachate.

The aim of the present study was to assess fate and effects of the widely used phenyl-urea herbicide isoproturon which is mainly transported into surface water via aqueous run-off or drainage systems (Klöppel et. al., 1994, Traub-Eberhard et.al., 1994). The practicability and sensitivity of this integrated approach was demonstrated.

MATERIAL AND METHODS

Experimental design

The microcosms consisted of a cubic water column of about 800 l and a sediment layer (approx. 12 cm high) including an undisturbed sediment core of 60 cm diameter and about 60 cm depth (Traub-Eberhard, Schäfer et. al., 1994). Both sediment and water were taken from a mesotrophic pond and contained natural plankton and benthic communities. The physico-chemical data of sediment and water are given in Table 1.

TABLE 1. Sediment and water characteristics

sample	sediment (0-12 cm)	water
particle-size: sand	98 %	
silt	1 %	
clay	1 %	
CEC (me/100g)	29.9	
pH	8.8	7.7
organic carbon	0.6 %	16.4 mg/l
total nitrogen	200 mg/kg	4.2 mg/l
total phosphorus	2.3 mg/kg	0.02 mg/l

The microcosms were installed in a temperature-controlled greenhouse at $20 \pm 4^\circ\text{C}$. The sediment cores were below the ground of the greenhouse. Additional illumination was provided (approx. 14000 lux, light/dark cycle 14:10h). The water was aerated slightly. Removed water (leachate, evaporation etc.) was regularly replaced by deionised water. During the pre-treatment phase of 7 months the water columns were connected to each other. Water leaching through the sediment core was regulated by a valve (about 3.7 l per day) and collected at the bottom.

Treatment and fate studies

After an adaptation phase of 7 months the herbicide isoproturon (N-(4-isopropylphenyl)-N',N'-dimethylurea) was applied to six of the systems: three microcosms were treated with ^{14}C -labelled isoproturon the other three received unlabelled isoproturon to obtain initial water concentrations of 10 $\mu\text{g/l}$, 30 $\mu\text{g/l}$ and 90 $\mu\text{g/l}$, respectively. Isoproturon was applied as an aqueous solution to the water column simulating drainage or aqueous run-off as possible entry routes. The water phase, the leachate and the top sediment layer (about 0-12 cm) were regularly analysed for isoproturon and its metabolites. At the end of the investigation period (160 days after treatment) the sediment core was divided into 10 cm layers, which were analysed separately.

Microcosm water quality

Temperature, pH, dissolved oxygen, conductivity, and concentrations of nitrate, ammonium, and phosphate were measured weekly. Twice per month total water hardness, concentrations of silicon, manganese, and iron were determined.

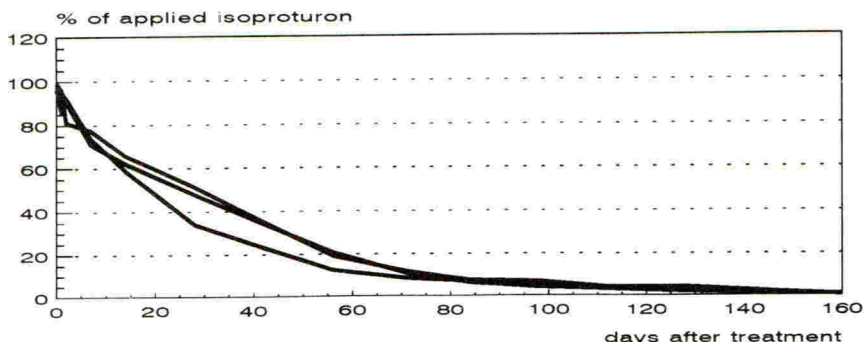


Fig. 3: Isoproturon in the water column of the microcosms 1 - 3 (initial water concentrations: 90 $\mu\text{g/l}$, 30 $\mu\text{g/l}$, 10 $\mu\text{g/l}$)

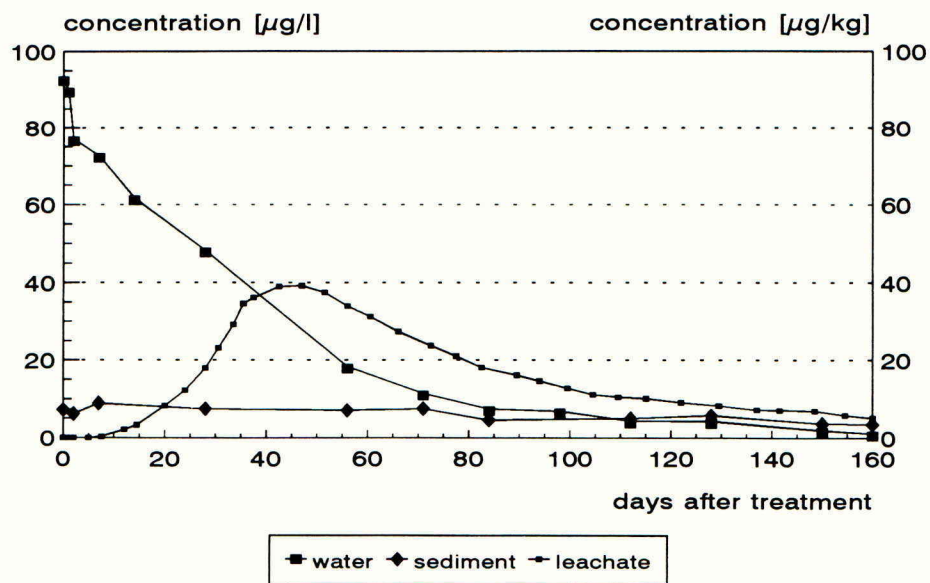


Fig.1 Isoproturon in water, leachate and sediment (mic.1)

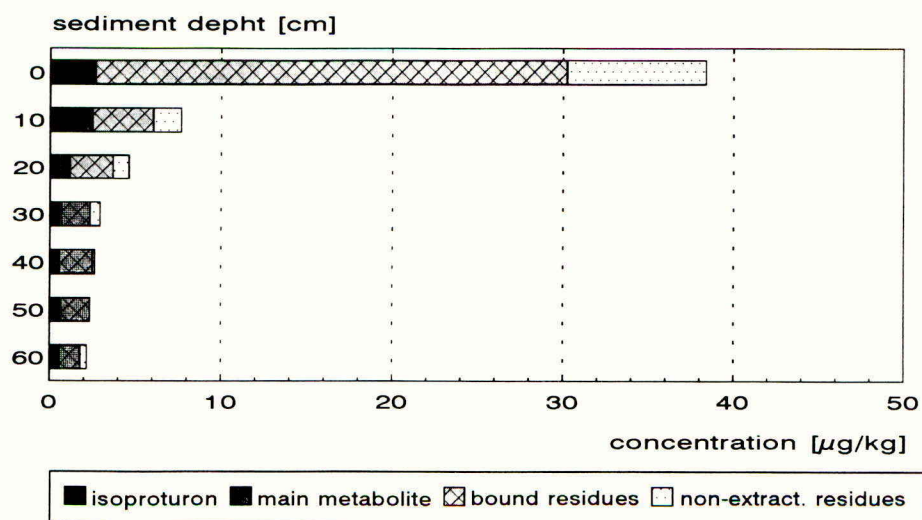


Fig.2 Isoproturon and residues in the sediment core (mic.1)

Effect studies

Zooplankton was sampled regularly by filtering 10 litres of water. The zooplankton-free filtrate was returned to the microcosms. Phytoplankton samples of 250 ml each were drawn simultaneously. Samples were fixed and analysed with respect to zoo- and phytoplankton community structure. Statistical analysis of the results was based on relative abundances (% of day -1 in the respective microcosm), i.e. changes in abundances following treatment were analysed. The data of the two replicates were pooled and compared with the controls using Student's t-test and Mann-Whitney U-test. In the sediments anaerobic microbial degradation activity was determined according to Remde and Traunspurger, 1994. Sediment was sampled regularly with a sediment corer and nematodes were extracted according to Uhlig et al., 1973. The samples were analysed with respect to nematode abundance and feeding type composition. The toxicity of leachate samples was determined with single-species tests using *Scenedesmus subspicatus* and *Daphnia magna*.

RESULTS

Fate studies:

In Fig. 1 a typical concentration/time profile for the fate of isoproturon in the microcosm with an initial water concentration of 90 µg/l is given (water and leachate). For these test conditions a relatively fast disappearance of isoproturon in the water column was observed. The DT50 and DT90 values were about 24 days and 79 days, respectively. The early appearance of isoproturon in the leachate about 6 days after treatment was a result of low sediment sorption and relatively high water solubility of the test substance. In the leachate the concentrations of isoproturon increased up to about 39 µg/l (approx. 45 days after application), declined gradually thereafter, but remained higher than the concentrations in the water column until the end of the study. This indicates that nearly no degradation of isoproturon occurred in deeper layers of the sediment core. This finding was confirmed by the analytical results of the sediment core, which was divided into layers at the end of the incubation period (Fig. 2). Significant amounts of non-extractable residues occurred only in the upper sediment layer, which was probably due to the higher organic carbon content. During the whole incubation period only 3-5 % of the applied isoproturon were detected in the 0-12 cm top sediment layer. An accumulation was not observed. The main metabolite of the herbicide isoproturon (N'-(4-isopropylphenyl)-N,N-methylurea) was found in the water as well as in the leachate in concentrations up to 3 µg/l. Traces of the second degradation product (N'-(4-isopropylphenyl)urea) were detected only in a few water samples.

The concentration/time profiles for isoproturon in water and leachate of the three microcosms were very similar (Fig. 3). The different concentrations had no effects on the DT50 values. At the end of the study an average of 0.8 % of the applied isoproturon was determined in the water column, and in total about 12.6 % was found in the leachate water.

Effects studies

Pre-treatment phase: Microcosm water quality did not differ significantly between the systems during the whole study. Phytoplankton in all microcosms was dominated by *Chlorophyceae* and microalgae (< 5 µm) whereas *Cladocera* and *Copepoda nauplii* were the most abundant groups of the zooplankton accounting for 49 ± 8 % and 33 ± 8 % respectively of the total zooplankton community. Counts of phyto- and zooplankton differed between the microcosms at the day of application.

Exposure and post-treatment phase: Direct effects of isotoproturon on phyto- and zooplankton structure were not observed, although pre-studies with algae had indicated clear effects at these concentrations. However, in the course of the study total zooplankton abundance decreased considerably at the highest treatment level (reduction to 8 % of the initial value) but increased in the controls by more than 500 %. In the microcosm treated with 90 $\mu\text{g/l}$ a breakdown of *Cladocera* was observed 4 weeks post treatment and no recovery to control levels occurred until the end of the study (Fig. 4). These effects can not be clearly attributed to direct effects of isotoproturon which had by that time decreased to approx. 50 % of the initial concentrations. Delayed effects as a result of bioaccumulation are unlikely because isotoproturon is readily water soluble with a logPow of 2.5. Furthermore, indirect effects by nutrient limitation for zooplankton can be excluded, since decreases in phytoplankton density or major shifts in phytoplankton composition were not observed.

Microbial activity in the nutrient poor sediment (9 % sand) was low with a release rate of 3.1 - 16.3 nmol carbon dioxide/h-g sediment dry weight. Methane production was below the detection limit. 56 days after application carbon dioxide release rate was stimulated in the untreated microcosms following a decrease (and sedimentation) of microplankton (< 5 μm). However, isotoproturon did not affect anaerobic mineralisation at any tested concentration. No effects of isotoproturon on abundance and diversity of sediment-dwelling nematodes were observed at any treatment level. Total abundance was high (100 to 700 ind./10 ccm, the variation being within natural ranges). The dominant feeding-types were deposit- and epistrate feeders.

Toxicity of leachate: Leachate with concentrations of isotoproturon ranging from 5.8 to 39 $\mu\text{g/l}$ had effects on algae but not on daphnids although strict concentration-effect relationships were not found. These results are in accordance with data obtained in single-species tests with isotoproturon, i.e. EC50-values of 39.5 $\mu\text{g/l}$ for *Chlamydomonas reinhardi* and *Scenedesmus subspicatus* (test system including sediment), and >1000 $\mu\text{g/l}$ for *Daphnia spec...*

Abundance of Cladocera

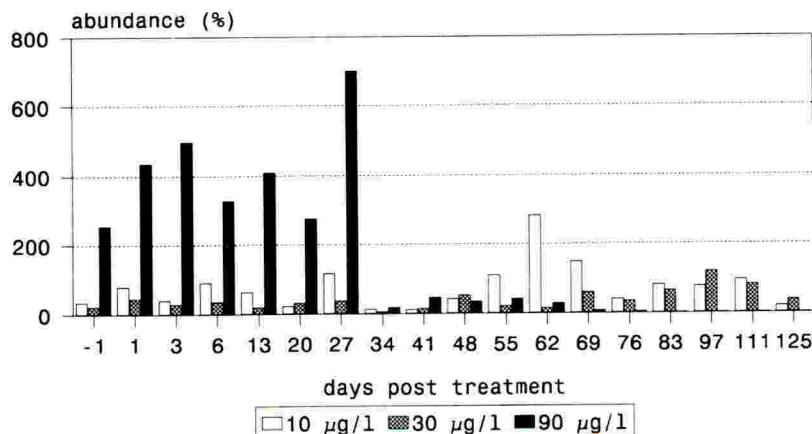


Fig. 4: Abundance of Cladocera in microcosms treated with isotoproturon (relative abundance referring to control on the respective day; treatment with isotoproturon on day 0). Given are mean values of two replicates per concentration.

CONCLUSIONS

(1) The indoor microcosms presented here are sensitive test systems which give ecosystem-relevant information on the behaviour of chemicals in aquatic systems. They allow cost-effective handling and standardization to a degree that enables performance of studies throughout the year.

(2) The design of our aquatic microcosms seems to be suitable for a simultaneous study of fate and effects including interactions between compartments and biota. The experimental results clearly demonstrate a high inter-microcosm similarity considering the fate of isoproturon in the compartments water, sediment and leachate. This reproducibility of the fate data indicates that for fate studies alone, replication and multiple rates may be unnecessary or very limited, whilst still producing reliable results. With respect to effect studies, however, a regression design may be more appropriate. Otherwise more replicates are needed to account for the high inter-microcosm variability in the planktonic community.

ACKNOWLEDGEMENTS

The work described in this report was funded by the Umweltbundesamt Berlin (Research Contract No. 126 05 105 - Verbleib und Wirkung von Pflanzenschutzmitteln in Oberflächengewässern - Freilandsimulation stehender Gewässer). The investigation of nematodes was performed by Dr. W. Traunspurger, University of Munich. The authors wish to thank J. Greve, U. Boshof, B. Otto and G. Wodtke for their excellent technical assistance and helpful discussions.

REFERENCES

- Klöppel, H., Haider, J., Kördel, W. (1994) Herbicides in surface runoff: A rainfall study on small plots in the field. *Chemosphere*, **28**, no. 4, 649-662
- Traub-Eberhard, U., Kördel, W., Klein, W. (1994): Pesticide movement into subsurface drains on a loamy silt soil. *Chemosphere*, **28**, no. 2, 273-284
- Traub-Eberhard, U., Schäfer, H., Debus, R (1994): New experimental approach to aquatic microcosm systems. *Chemosphere*, **28**, no. 3, 501-510
- Remde, A., Traunspurger, W. (1994): A method to assess the toxicity of pollutants on anaerobic microbial degradation activity in sediments. *Environ. Toxicol. Water Quality* **9**, no. 4, in press.
- Uhlig, G., Thiel, H., Gray, J.S. (1973): The quantitative separation of meiofauna. *Helgoländer wiss. Meeresunters.*, **25**, 173-195.

THE EFFECT OF A POLYMERIC ADJUVANT ON THE OFF-TARGET MOVEMENT OF A PESTICIDE SPRAY

J.R.M. THACKER, R.D.F. YOUNG, I. ALLEN AND D.J. CURTIS

Department of Biological Sciences, University of Paisley, Paisley, Scotland PA1 2BE

ABSTRACT

Field experiments were carried out in order to assess the ability of a commercially available polymeric adjuvant (Headland Guard: WBC Technology Ltd.) to modify pesticide spray drift. The experimental design, which adopted a bioassay approach comprised a field-rate application of the insecticide chlorpyrifos formulated with and without the adjuvant. For each of the chemical treatments, a single cabbage plant, a tray of soil, and a water-sensitive paper were placed, in four replicate lines, at a series of downwind distances (0 - 20 metres) at right angles to the path of the sprayer. Bioassays of foliar toxicity used the cabbage white butterfly *Pieris brassicae* while the bioassays of soil toxicity used the ground beetle *Nebria brevicollis*. The results demonstrated a significant reduction in spray drift for the insecticide plus adjuvant treatment in comparison to the insecticide alone. The control of spray drift by utilising chemical adjuvants is discussed in comparison to other options (i.e. physical devices or the implementation of buffer zones) that have so far been suggested.

INTRODUCTION

Despite the critical role that insecticides play within modern food production the efficiency of usage of these products has consistently been documented at less than one percent (Graham-Bryce, 1977; Adams & Hall, 1990). One source of this inefficiency results from wind-induced off-target movement of the chemical or spray drift (Miller, 1993). In addition to compromising the efficiency of usage of the chemical, spray drift can also result in more immediate adverse effects such as damage to neighbouring crops (Maybank *et al.*, 1978; Gilbert *et al.*, 1988) and the contamination of rivers, lakes and ponds.

It has been shown that the drift potential of spray droplets is inversely related to their diameters and that a rapid increase in drift occurs for droplets that are less than 150 - 200 μm in diameter (Reichard *et al.* 1992). However, although the elimination of droplets that are less than 200 μm in diameter from a spray proffers a possible solution to spray drift, achieving this aim has been problematic, not least because a typical hydraulic sprayer produces droplets in the diameter size range 30 - 500 μm (Matthews, 1979).

To date, methods for ameliorating spray drift include (1) the use of mechanical devices such as knockdown bars or shrouds (Pfalzer, 1993), (2) the implementation of buffer zones (Sinha *et al.*, 1990; Davis *et al.*, 1993), and (3) the use of chemical adjuvants (Ozkan *et al.*, 1993). In this paper we consider the last of these methods and present the results of initial experiments on the ability of a commercially available polymeric adjuvant to control insecticide drift under field conditions.

MATERIALS AND METHODS

Experimental Design

The field experiments were carried out in a field of stubble on Faulds farm in Renfrewshire, Scotland during December 1993 and April 1994. On each occasion the experimental design consisted of four replicate lines, laid out at 10 metre intervals, at right angles to the wind direction. Along each line samples were taken at 0, 1, 5, 10 and 20 metres. To sample the drifting aerial spray cloud greenhouse grown cabbage plants (cv Durham Early) were used. To sample the fraction out the drifting spray cloud that deposited on the soil surface, 23 x 13 cm plastic trays containing 2 cm of field-collected soil were used. To obtain a visual record of the soil deposit of the drifting spray cloud, water-sensitive papers were placed at each sampling position in addition to the tray of soil and the cabbage plant. The design on each occasion was repeated for the insecticide alone and for the insecticide plus adjuvant treatment.

Chemicals and Application Details

The insecticide and adjuvant used were chlorpyrifos (Dursban 4, Dow Elanco Ltd.) and Headland Guard (WBC Technology Ltd.), respectively. The insecticide and the insecticide/adjuvant combination were diluted with water and were used at recommended rates for field application (5.6 ml/l plus 1 ml/l, respectively: AI = 480g in 180 l/ha). Each treatment was applied through flat fan nozzles operating at 30 p.s.i. on a tractor mounted boom at a height of 1 metre above the soil surface.

Wind Speed Measurements

Throughout the course of all experiments windspeed was recorded continuously using a digital anemometer (AM-4201, Lutron Ltd.).

Laboratory Bioassays

Following treatment application the cabbage plants, trays of soil and water-sensitive papers were returned to the laboratory. To assay the toxicity of the plants laboratory-reared third instar cabbage white (*Pieris brassicae*) larvae were used while to assay soil toxicity field-collected adult *Nebria brevicollis* were used. For both the plants and the soil 10 insects were used per sampling position. The butterfly larvae were confined in 23 x 13 cm plastic containers with leaves from the field-exposed plants while the carabid beetles were placed directly onto the treated trays of soil. Both beetles and butterfly larvae were maintained in a constant environment room (21 °C:80% r.h.) throughout the course of the assessment. Mortality assessments were made at 24, 48, 72 and 96 hours. Beetles and butterfly larvae were scored as being either dead (no response to gentle prodding), knocked-down (visibly twitching) or alive (moving and feeding normally).

Water-Sensitive Paper Analysis

The water-sensitive papers at each position were simply scored for the presence or absence of any deposit. Because adjuvants change the physico-chemical properties of sprays it is not possible to accurately calculate droplet sizes using these papers (Thacker & Hall, 1991).

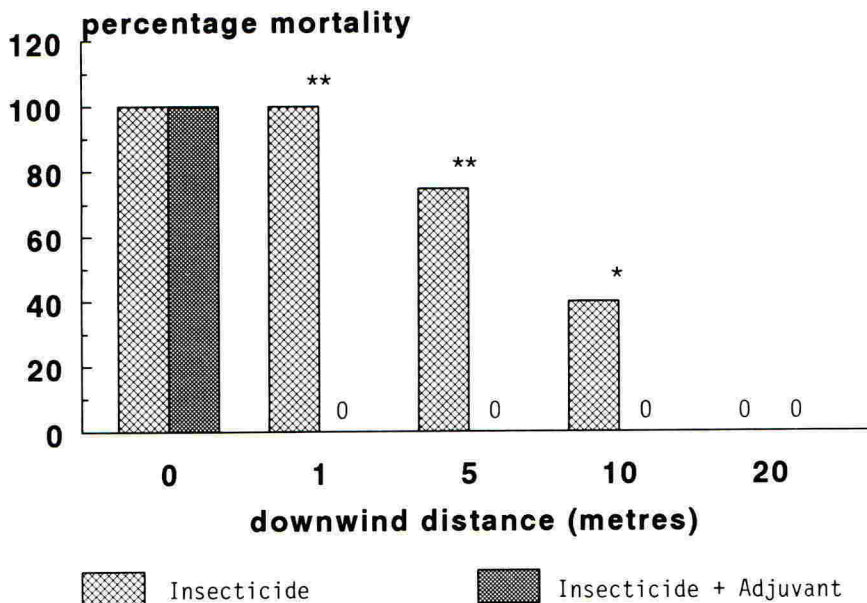
Data Analyses

The percentage mortality data that were derived from the field experiment bioassays were transformed using an arcsine square-root transformation (Sokal & Rohlf, 1981) for subsequent ANOVA analyses.

RESULTS

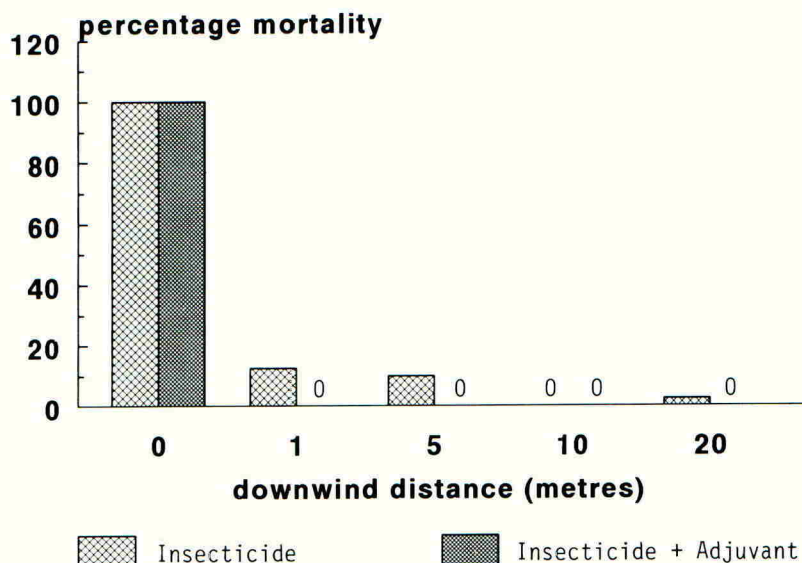
The results in both the December and April bioassay experiments were similar and showed that a significant decrease in insecticide drift could be realised by combining the insecticide with the adjuvant. The results from the data collected at 96 hours from the plant and soil bioassays from the December experiment are given in Figures 1 and 2. These data displayed the most dramatic effects of adding the adjuvant to the insecticide spray.

FIGURE 1. The percent mortality of third instar *Pieris brassicae* larvae fed leaves from the cabbage plants that were exposed to insecticide and insecticide plus adjuvant at different downwind distances. Asterisks indicate whether the mortality levels at each downwind distance were statistically significant (* = $P < 0.05$, ** = $P < 0.01$).



The results shown in Figure 1 indicate that the downwind deposits on cabbage plants (and hence the resulting mortality) were significantly greater for the insecticide treatment alone. The mortality of the butterfly species did not reach zero until a distance of 20 metres downwind was realised. In comparison, with the insecticide plus adjuvant combination the recorded mortality was zero from 1 metre downwind.

FIGURE 2. The percent mortality of third instar *Nebria brevicollis* placed on soil that was exposed to insecticide and insecticide plus adjuvant at different downwind distances.



Soil toxicity, with the exception of soil directly under the sprayer, gave the percentage mortality at less than 20% at all downwind distances for both treatments (Figure 2). However, as with the *Pieris* results the data indicate that some spray drift induced mortality may be controlled by the addition of the adjuvant.

The presence or absence of deposits, as recorded on the water-sensitive papers, at each position for each treatment is shown in Table 1. The results support the bioassay data. For the insecticide alone treatment deposits were recorded at all downwind sampling positions. For the insecticide plus adjuvant treatment deposits were only recorded over 0 to 5 metres downwind.

TABLE 1. The presence or absence of deposits on water-sensitive papers placed on the soil at the downwind distances assayed for the two treatments ('+' = deposits present, '-' = deposits absent). ('I' = Insecticide, 'A' = Adjuvant)

Treatment	Downwind distance																			
	0 m				1 m				5 m				10 m				20 m			
Replicate	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
'I' Only	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
'I' plus 'A'	+	+	+	+	+	+	+	+	+	+	+	+	-	-	-	-	-	-	-	-

DISCUSSION

The data presented in this paper concern the effects upon spray drift of adding a polymeric adjuvant to an organophosphate insecticide spray. The bioassay data show that the adjuvant has the potential to substantially reduce spray drift under field application conditions. These reductions were most dramatic in the December experiment in which the windspeed was the lowest (3.74 ms^{-1} vs 5.16 ms^{-1} in April). Significant reductions in drift were recorded from 1, 5, 10 and 20 metres downwind in December in comparison to significant reductions at 10 and 20 metres downwind in the April experiment. Overall therefore, the data show that the adjuvant can reduce spray drift over a range of windspeeds although the greatest reductions will be accrued at light to moderate windspeeds.

The control of spray drift by the addition of adjuvants to pesticide sprays represents a comparatively new technology. For example, of the 228 adjuvants that were listed in the *Farm Chemicals Handbook* (Meister Publishing Company, Ohio, USA) in 1970 none were described as being for drift control. However, of the 228 adjuvants that were listed in the 1990 handbook, 14 were described as drift control agents (Hall *et al.*, 1993a). Adjuvants for use within the UK are currently categorised in more general terms as being either extenders, stickers or wetters (*The Pesticide Manual* 1993, BCPC Publications Ltd.). The adjuvant used in the present work (Headland Guard) is, at present, listed in the UK as a sticker/spreader.

Since spray drift results from the off-target movement of droplets that are typically $< 150 \mu\text{m}$ in diameter it has been suggested that adjuvants might lessen this process by reducing the number of small droplets that are produced during spray atomization (Ozkan *et al.*, 1993). Indeed, Hall *et al.* (1993a) in a lab-based analyses of spray droplet size spectra report that the addition of 'Direct' (a putative drift control agent) to a water spray causes a 4.5% reduction in the volume of liquid in droplets that are $< 100 \mu\text{m}$ in diameter and a 19% increase in the volume of droplets that between 600 and $700 \mu\text{m}$ in diameter.

The use of adjuvants for the control of spray drift offers a number of advantages over alternative methods that have been suggested. For example, in comparison to the use of buffer zones (Rands & Sotherton, 1986; Davis *et al.*, 1983) the use of adjuvants does not require that a proportion of the crop is left untreated by the agrochemical. In comparison to physical devices such as 'shrouds' adjuvants may be a far simpler and cheaper option for applicators and they also do not suffer from the disadvantage of covering the boom which makes it difficult for the operator to check if nozzles have become blocked (Ozkan, 1991).

In conclusion, we believe that the data presented in this paper show that spray drift can be controlled under field conditions by the addition of an adjuvant to a spray. We believe the data to be robust in that the replicated experimental protocol was repeated in two field experiments both of which yielded similar results. At present, further work is underway with other adjuvants and to test the effects of varying the adjuvant concentration on drift control potential. We are also attempting to confirm our bioassay data on downwind deposits by labelling the spray with a fluorescent dye (a cheaper and simpler procedure than residue analysis which would also assist with the confirmation of our results). By linking these drift deposit data with measurements of physicochemical features of the spray such as its viscosity and surface tension it is envisaged that optimum recommendations might be produced for the adjuvants that are most able to ameliorate the undesirable effects of off-target spray movement (Hall *et al.*, 1993b).

ACKNOWLEDGEMENTS

Many thanks to Mr. J. Holmes of Faulds Farm for applying the chemicals. Funding and Technical support were provided by the Department of Biological Sciences, University of Paisley.

REFERENCES

- Adams, A.J.; Hall, F.R. (1990) Initial behavioural responses of *Aphis gossypii* to defined deposits of bifenthrin on chrysanthemum. *Crop Protection*, **9**, 39-43.
- Davis, B.N.K.; Lakhani, K.H.; Yates, T.J.; Frost, A.J.; Plant, R.A. (1993) Insecticide drift from ground-based hydraulic spraying of peas and brussel sprouts: bioassays for determining buffer zones. *Agriculture, Ecosystems and Environment*, **43**, 93-108.
- Gilbert, A.J.; Bell, G.J. (1988) Evaluation of the drift hazards arising from pesticides spray application. *Aspects of Applied Biology*, **17**, 363-376.
- Graham-Bryce, I.J. (1977) Crop protection: a consideration of the effectiveness and disadvantages of current methods and of the scope for improvement. *Philosophical Transactions of the Royal Society of London Series B*, **28**, 163-179.
- Hall, F.R.; Chapple, A.C.; Downer, R.A.; Kirchner, L.M.; Thacker, J.R.M. (1993a) Pesticide application as affected by spray modifiers. *Pesticide Science*, **38**, 123-133.
- Hall, F.R.; Thacker, J.R.M.; Downer, R.A. (1993b) Physico-chemical properties, in-flight evaporation and the spread of spray droplets containing pesticide adjuvants. In: *Pesticide Formulations and Application Systems, 13th Volume, ASTM STP 1183*, P.D. Berger, B.N. Devisetty and F.R. Hall (Eds), ASTM, Philadelphia, pp. 95-108.
- Matthews, G.A. (1979) Droplets. In: *Pesticide Application Methods*, Longman, London, pp. 57-74.
- Maybank, J.; Yoshida, K.; Gover, R. (1978) Spray drift from agricultural pesticide applications. *Journal of the Air Pollution Control Association*, **28**, 1001-1014.
- Miller, P.C.H. (1993) Spray drift and its measurement. In: *Application Technology for Crop Protection*, G.A. Matthews and E.C. Hislop (Eds), CAB International, pp. 101-122.
- Ozkan, H.E. (1991) *Reducing Spray Drift*. Technical publication, The Ohio State University, USA, pp. 17.
- Ozkan, H.E.; Reichard, D.L.; Zhu, H.; Akerman, K.D. (1993) Effect of drift retardant chemicals on spray drift, droplet size and spray pattern. In: *Pesticide Formulations and Application Systems, 13th Volume, ASTM STP 1183*, P.D. Berger, B.N. Devisetty and F.R. Hall (Eds), ASTM, Philadelphia, pp. 173-190.
- Pfalzer, H. (1993) Safety aspects and legislation trends. In: *Application Technology for Crop Protection*, G.A. Matthews and E.C. Hislop (Eds), CAB International, pp. 13-33.
- Rands, M.R.W.; Sotherton, N.W. (1986) Pesticide use on cereal crops and changes in abundance of butterflies on arable farmland in England. *Biological Conservation*, **36**, 71-82.
- Reichard, D.L.; Zhu, H.; Fox, R.D.; Brazee, R.D. (1992) Computer simulation of variables that influence spray drift. *Transactions of the ASAE*, **35**, 1401-1407.
- Sinha, S.N.; Lakhani, K.H.; Davis, B.N.K. (1990) Studies on the toxicity of insecticidal spray drift to the first instar larvae of the large white butterfly *Pieris brassicae* (Lepidoptera: Pieridae). *Annals of Applied Biology* **116**, 27-41.
- Sokal, R.R.; Rohlf, F.J. (1981) *Biometry*. W.H. Freeman & Co.
- Thacker, J.R.M.; Hall, F.R. (1991) The effects of drop size and formulation upon the spread of pesticide droplets impacting on water-sensitive papers. *Journal of Environmental Science and Health*, **B26**, 631-651.

EFFECTS OF CHLORPYRIFOS ON AQUATIC MICROCOSMS OVER A RANGE OF OFF-TARGET SPRAY DRIFT EXPOSURE LEVELS

RONALD C. BIEVER, JEFFREY M. GIDDINGS, MARIA KIAMOS, MARIA F. ANNUNZIATO

Springborn Laboratories, Wareham, MA 02571, USA

ROGER MEYERHOFF

Eli Lilly and Co., Indianapolis, IN, USA

KENNETH RACKE

DowElanco, Indianapolis, IN, USA.

ABSTRACT

To effectively assess the potential impacts of crop protection chemicals, it is important to determine the gradient of ecological responses over a range of possible exposure scenarios. Outdoor aquatic microcosms were sprayed with the organophosphorus insecticide chlorpyrifos to simulate off-target drift of 0.05% to 5% of a 1.12 kg AI/ha application rate (nominal water concentrations between 0.03 and 3 $\mu\text{g/L}$). The exposure-response relationships for plants, invertebrates, and fish were determined. Few significant ecological effects occurred at treatment levels corresponding to nominal chlorpyrifos concentrations of 0.03 or 0.1 $\mu\text{g/L}$. Treatment at 0.3 $\mu\text{g/L}$ caused temporary reductions in many groups of invertebrates, but fish were unaffected. Treatment at 1 $\mu\text{g/L}$ caused temporary, but longer-lasting effects on invertebrates; slight decreases in fish mean length and total biomass were noted, whereas no impact on fish survival, mean weight, and biomass increase occurred. The 3 $\mu\text{g/L}$ treatment caused persistent effects on nearly all invertebrate taxa and significantly reduced fish survival.

INTRODUCTION

Microcosms are commonly thought of as bridging the gap between simple laboratory test systems and full-scale field studies. In the context of environmental assessment of pesticides, microcosms are used to integrate, corroborate and extend the information derived from conventional laboratory toxicity tests and environmental fate studies. The value of microcosm data depends on the ability of the microcosms to simulate the exposure regimes and ecological responses to exposure that might occur when a product is used in actual agricultural practice. Microcosms are therefore most useful when studies are designed to take into account the specific environmental profile and agricultural applications of the product being tested (SETAC-RESOLVE, 1992, Crossland *et al.*, 1994). These considerations are different for each product, and there is no single standard microcosm design. The major objective of this microcosm study was to measure the fate and effects of chlorpyrifos in aquatic ecosystems over a range of off-target spray exposure scenarios. Since chlorpyrifos is a broad spectrum insecticide, this study focused on the direct effects on aquatic insects and other invertebrates and on direct and indirect effects on the predatory bluegill sunfish (*Lepomis macrochirus*).

STUDY METHODS

Microcosm design and construction

The study was conducted in northeastern Kansas, USA, latitude 40°N and longitude 95°W. Eighteen cylindrical fiberglass microcosms with bottoms were submersed in a flat-bottomed, water-filled basin. Each microcosm was 3.2 m in diameter and 1.5 m deep. When filled to nominal operating depth of 1.4 m, each microcosm contained 11.2 m³ of water.

Uncontaminated sediment and water from nearby ponds were added to the microcosms at the end of May 1991. The sediment and water contained native plankton, macroinvertebrate and macrophyte communities. The addition of sediment and water are described in detail in Giddings *et al.* (1994).

Forty juvenile bluegill sunfish were stocked into each microcosm. The total biomass of bluegill stocked into each microcosm ranged between 31 g and 58 g. A two-sided Dunnett's test was performed on the total biomass and no significant differences were observed.

Treatment with chlorpyrifos

The test material used in this study was the formulation 'Lorsban® 4E' chlorpyrifos, 41.2% AI. The design for spray treatment was intended to allow for determination of a no-effect concentration based on one spray application. The application rates corresponded to nominal concentrations in water of 0.03, 0.1, 0.3, 1, and 3 µg/L, equivalent to 0.049% to 4.9% drift from a 1.2 kg AI/ha application deposited on a 2 m water column (or 0.014% to 1.4% drift from a 4.2 kg AI/ha application).

The microcosms were treated on 10 July 1991 with a simulated spray drift, with three replicates at each treatment level. The application was made with a hand-held CO₂-pressurized sprayer and spray boom. The solution was sprayed onto the water surface from a height of approximately 10 cm.

Sampling and analysis

Temperature, dissolved oxygen, pH, alkalinity, hardness, conductivity and phytoplankton were sampled at two week intervals. Zooplankton were collected every two weeks until the application and weekly thereafter. Macroinvertebrates were collected at least once before treatment and every two weeks after. Two types of macroinvertebrate samples were taken: artificial benthic substrates (ABS) and emergent insects. Artificial substrates consisted of cylindrical (3.8 cm diameter x 5.1 cm high) sinking plastic surface enhancers arranged in groups of seven. They were colonized for 4-week periods. Emergent insects were collected using semisubmerged floating emergent insect traps, which were deployed for 4 days. Water quality and biota sampling began in early June 1991 and was concluded at the end of September 1991. Water and sediment for chlorpyrifos residue analysis were sampled periodically after the treatment. All of the sampling methods are described in detail by Giddings *et al.* (1994).

During the first week of October 1991 the microcosms were drained and subsamples of the macrophytes were removed, separated by species and weighed. All fish were weighed, measured for total length and examined for gross abnormalities.

Statistical Analysis

Biotic data were tested for univariate linear assumptions using graphical techniques. Data were transformed as necessary to conform to these assumptions before analysis of variance.

A one-sided Dunnett's test ($\alpha = 0.05$) was performed on each sample event for each taxonomic group where a variance in the dependent variable amongst treatment levels was observed. The test hypothesis of interest was:

$H_0: \mu_{\text{control}} \leq \mu_{\text{level}}$ $H_A: \mu_{\text{control}} > \mu_{\text{level}}$
where μ_{control} and μ_{level} were the mean transformed values for the control group and for each treatment level, respectively.

RESULTS

Chlorpyrifos residues

Chlorpyrifos concentrations in water samples taken approximately 2 hours after treatment averaged 0.030, 0.088, 0.25, 0.83, and 2.7 $\mu\text{g/L}$, in the five treatments respectively. Chlorpyrifos disappeared from the water with an apparent half-life averaging 3.6 days (S.D. = 0.61 days).

Measured chlorpyrifos concentrations in most sediment samples from the 0.03 $\mu\text{g/L}$ to 0.3 $\mu\text{g/L}$ microcosms were less than 2 $\mu\text{g/kg}$, with only 20% of the samples having quantifiable residues. In the 1 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$ microcosms, chlorpyrifos concentrations were typically less than 10 $\mu\text{g/kg}$, with several samples at concentrations as high as 14 $\mu\text{g/kg}$, 70% of the samples having quantifiable residues.

Water quality

Water temperature ranged between 23°C and 28°C through early September and dropped to 17°C to 18°C late in September. Dissolved oxygen never dropped below 7 mg/L and generally remained above 10 mg/L. pH was generally between 8 and 9 through mid-July and 9 to 10 for the remainder of the study. Total alkalinity, hardness, and conductivity were similar between all microcosms throughout the entire study period.

Zooplankton

The zooplankton community in the microcosms was comprised of 23 genera of rotifers and 16 genera of crustaceans. Rotifers dominated the zooplankton population (by numbers) and were unaffected by the chlorpyrifos spray treatments. Rotifers were typically present in densities of 300 to 400 individuals/L, while crustaceans were present at densities of 100 to 250 individuals/L. Taxonomic richness generally increased early in the study. Taxonomic richness in the spray-treated microcosm was significantly reduced at the 0.3 $\mu\text{g/L}$, 1 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$ treatment levels, two to four weeks after the chlorpyrifos application.

Crustaceans were much more sensitive to chlorpyrifos than rotifers, with significant effects in the spray-treated microcosms at the 0.3 $\mu\text{g/L}$ through 3 $\mu\text{g/L}$ treatments. Copepod and cladoceran abundances were significantly reduced at the three highest treatment levels for up to four weeks after the chlorpyrifos application. All treatment levels recovered to densities similar to the control before end of the study. Ostracoda were not affected by the chlorpyrifos spray treatment.

Macroinvertebrates

Sixty-three taxa of macroinvertebrates were collected from the ABS and emergent insect samples. The macroinvertebrates represented 13 orders, 34 families and at least 35 genera. The macroinvertebrate assemblages were dominated by insects. Taxonomic richness generally increased throughout the study period. Average taxonomic richness from the control microcosms over the entire study period from ABS samples was 22 taxa and from emergent insect samples was 18 taxa.

The macroinvertebrates identified in the ABS samples consisted mainly of Diptera and Ephemeroptera in approximately equal proportions. The Ephemeroptera were almost all from the genus *Caenis*, while the Diptera were predominantly represented by the family Chironomidae. The responses of the two orders to chlorpyrifos spray addition were similar: reductions in numbers at 3 $\mu\text{g/L}$ for four to six weeks, shorter reductions at 0.1 $\mu\text{g/L}$ and 0.3 $\mu\text{g/L}$, and no effect at 0.03 $\mu\text{g/L}$.

The total abundance of insects on artificial benthic substrates reflected the additive effects on the individual taxa. There were no major increases in any taxon to offset the decreases that occurred in others. Consequently, total insect abundance was significantly reduced at most treatment levels. The reduction at 0.03 $\mu\text{g/L}$ was brief and of questionable relationship to chlorpyrifos. At treatments of 0.3 $\mu\text{g/L}$ through 3 $\mu\text{g/L}$, the exposure-response trend was clear and consistent.

Most of the emergent insects collected were Diptera from the family Chironomidae. There were no significant reductions of Chironomidae emergence through the 1 $\mu\text{g/L}$ treatment. The only significant reductions in Chironomidae emergence occurred at the 3 $\mu\text{g/L}$ treatment, near the end of the study period. Emergence rates recovered by the end of the study.

The tribe Chironomini (Family: Chironomidae, Subfamily: Chironominae) was the most sensitive macroinvertebrate taxon to the chlorpyrifos addition. The Chironomini were significantly affected at 0.1 $\mu\text{g/L}$ through 3 $\mu\text{g/L}$ in the ABS samples. At 3 $\mu\text{g/L}$, the reduction was still significant at the end of the study. Two weeks after the chlorpyrifos addition, Chironomini emergence increased in the control microcosms but failed to increase in any of the treated microcosms, resulting in a statistically significant difference at all treatment levels. The difference disappeared before the next sample event, although emergence rates at the 3 $\mu\text{g/L}$ treatment remained below controls for the rest of the study period. It was interesting to note that the other dominant Chironominae tribe, Tanytarsini, was unaffected by the chlorpyrifos addition.

Fish

Survival was significantly affected at the 3 $\mu\text{g/L}$ treatment. The average number of fish surviving in the controls and the 0.03 $\mu\text{g/L}$ through 1 $\mu\text{g/L}$ treatments ranged from 36.0 to 38.3. The average number of fish surviving at 3 $\mu\text{g/L}$ was 26.7. The average total

biomass of the controls and 0.03 $\mu\text{g/L}$ through 0.3 $\mu\text{g/L}$ ranged from 105.0 g to 115.8 g. At the 1 $\mu\text{g/L}$ and 3 $\mu\text{g/L}$ treatments, the average total biomass was 94.6 g and 77.5 g, respectively. The bluegill at the 1 $\mu\text{g/L}$ treatment did not suffer survival effects from the chlorpyrifos spray addition, but were significantly smaller than the controls. Mean weight of the bluegills from the 1 $\mu\text{g/L}$ treatment was 2.63 g, while the mean weights from the remaining treatment levels ranged from 2.81 g to 3.08 g. The mean length of the bluegills from the 1 $\mu\text{g/L}$ treatment was 5.77 cm, with the mean length from the remaining treatment levels ranging from 5.86 cm to 6.02 cm. Although individual weight and length at the 3 $\mu\text{g/L}$ treatment were not included in the statistical analysis, the fish which survived the chlorpyrifos exposure at this level were able to grow at a rate similar to the controls and 0.03 $\mu\text{g/L}$ through 0.3 $\mu\text{g/L}$ treatments. This was likely a result of the decreased competition for the available food. The 30% reduction in fish population in the 3 $\mu\text{g/L}$ treatment allowed the surviving fish at this level to grow nearly as well as the controls.

DISCUSSION

To assess aquatic risks associated with the use of a crop protection product, one needs to have an array of data including but not limited to agricultural usage, environmental fate of the material in soil and water, and direct and indirect effects of the product on aquatic organisms. When laboratory data suggest there is a potential for environmental effects, a microcosm study can help resolve the uncertainty. This microcosm study provides a risk manager with information on an ecosystem comprised of over 100 zooplankton and macroinvertebrate taxa, and their interactions with their environment, habitat and the predacious bluegill sunfish. The algae and macrophyte communities were generally unaffected in this study and were not intensively monitored. However, in the case of an herbicide, this same experiment could have provided an additional level in the food chain, with the identification of probably 50 to 100 taxa of phytoplankton, periphyton, and macrophytes. Moreover this study provided valuable information on the environmental fate of chlorpyrifos in an aquatic system. This study demonstrated that chlorpyrifos had an environmental half-life of less than 4 days, which should be rapid enough to prevent a substantial build-up of chlorpyrifos in water after repeated spray drift events. This study also demonstrated that chlorpyrifos will partition into the sediment. Chlorpyrifos residues of 1 to 8 $\mu\text{g/kg}$ (dry weight) were measured in the sediment samples from the two highest treatment levels at the end of the study. The sediment residue data were too variable to calculate an accurate half-life for chlorpyrifos in sediment.

By measuring effects across a broad but realistic range of exposure regimes, microcosms can provide risk managers with a gradient of effects on aquatic ecosystems. This gradient of effects, when used in conjunction with probabilistic environmental fate modeling, allows the assessment of potential aquatic risks associated with different application scenarios. For example, it may be determined that 0.5% spray drift occurs once in a hundred applications. If that were so, one out of a hundred applications of 1.2 kg Al/ha would be expected to produce the effects observed in the 0.3 $\mu\text{g/L}$ microcosms: temporary reductions in many groups of invertebrates, but no effects on fish (Table 1). One out of a hundred applications of 4.2 kg Al/ha would produce the effects observed in the 1 $\mu\text{g/L}$ microcosms: temporary, but longer lasting, effects on invertebrates and slight decreases in fish mean length and total biomass (Table 1).

Table 1. Summary of chlorpyrifos effects in microcosms. Values shown represent the percent of sampling events following the chlorpyrifos application in which each taxon was significantly less than the controls ($P \leq 0.5$). X = significant effect on fish at the end of the study.

Taxon	% of Significant Effects at the Nominal Treatment Level				
	0.03 $\mu\text{g/L}$	0.1 $\mu\text{g/L}$	0.3 $\mu\text{g/L}$	1 $\mu\text{g/L}$	3 $\mu\text{g/L}$
Zooplankton					
Crustacea			20	30	50
Copepoda			20	40	50
Cladocera			10	40	40
Taxonomic Richness			20	20	20
Macroinvertebrates					
Diptera			10	10	50
Ceratopogonidae	10			20	10
Chironomidae			10	10	40
Chironominae			20	10	20
Chironomini	10	20	20	30	40
Podonominae					20
Orthoclaadiinae				30	40
Tanypodinae	10		10	10	30
Ephemeroptera	10	10	20	30	20
Total Insects	10		20	20	50
Taxonomic Richness			10	20	50
Fish					
Survival					x
Biomass				x	x
Growth				x	

The results of this simplified exposure scenario (single spray drift event) provided the basis for further experiments using simulated surface runoff, spray-runoff combinations, and pulsed exposure regimes.

REFERENCES

- Crossland, N.O.; Heimbach, F.; Hill, I.R.; Boudou, A.; Leeuwangh, P.; Matthiessen, P.; Persoone, G. (1994) Summary and recommendations of the European workshop on freshwater field tests (EWOFFT). In: *Freshwater Field Tests for Hazard Assessment of Chemicals*, I.R. Hill, F. Heimbach, R. Leeuwangh, P. Matthiessen (Eds.), Florida: Lewis Publishers, pp. XXV-XXXVII.
- Giddings, J.M.; Helm, R.L.; deNoyelles, F.J. Jr. (1994) Large-scale outdoor microcosms: tools for ecological assessment of pesticides. In: *Freshwater Field Tests for Hazard Assessment of Chemicals*, I.R. Hill, F. Heimbach, R. Leeuwangh, P. Matthiessen (Eds.), Florida: Lewis Publishers, pp. 191-198.
- SETAC-RESOLVE (1992) *Proceedings of a Workshop on Aquatic Microcosms for Ecological Assessment of Pesticides*. SETAC Foundation for Environmental Education and the RESOLVE Program of the World Wildlife Fund, Wintergreen, Virginia USA, 56 pp.

FIELD METHODS TO ASSESS THE EFFECTS OF PESTICIDES ON BENEFICIAL ARTHROPODS

J.N. REBOULET

ACTA Association de Coordination Technique Agricole - 149, rue de Bercy - 75595 PARIS CEDEX 12

ABSTRACT

The proposed field methodology is designed to assess in orchards the medium-term practical side-effects of pesticides on predatory insects of the European red mite and of the pear psyllid, as well as on the parasitism of pear leaf blister moth (leaf borer) and aphids.

The method used since 1988 provide the information necessary to incorporate the investigated product into an integrated pest management strategie, while preserving efficiency and selectivity.

Further studies have been pursued in order to develop methods based on the same principles and applicable to other "pest/auxiliaries" complexes as well as to other crops.

INTRODUCTION

Field implementation of the integrated pest management concept implies a precise knowledge of the impact of pesticides on the beneficial organisms, whether naturally present or introduced.

The proposed method is designed to assess the medium-term practical side-effects of pesticides on beneficial insects active on two types of pests generally kept under control by predators in orchards : the European red mite *Panonychus ulmi* Koch and the pear psyllid *Psylla pyri* L. In addition, the method provides information regarding the impact of the investigated products on the parasitism of pear leaf blister moth (leaf borer *Leucoptera scitella*) or aphids possibly present in the test orchard.

EXPERIMENTAL CONDITIONS

Treatments are applied in accordance with the frequency and time periods corresponding to the practical utilisation of the products under study.

Two references are required :

- one neutral reference, generally left untreated during the trials,
- one toxic reference, treated with an insecticide active on beneficial insects and without any known effect on the pest. The following toxic references are currently used :
 - . dimethoate at a concentration of 50 g a.i./hl, or deltamethrine at 1,75 g a.i./hl, for trials on predators of the red mite;
 - . fluvalinate at a concentration of 14,4 g a.i./hl, for trials on predators of the pear psyllid.

The treatments are applied with portable spray devices routinely used in the field, based on an application rate of 800 to 1 200 liters of mixture per hectare, depending on the vegetation density.

OBSERVATIONS

The following main variables are observed :

- number of pests (preys or hosts) with one variable per pest,
- number of predators of mites or pear psyllids (with one variable per predator or predator stage),
- if needed, number of parasitized pests (leaf borers or aphids).

Sampling method

Observations are carried out along the central row of each plot. In order to check for intraplot homogeneity in the arthropod populations, each observation row is subdivided into three equal sections in order to obtain a minimum of three samples.

For predatory insects of pear psyllid and mites, beating of the shoots as described by FAUVEL *et al* (1981) is carried out in each observation zone. Sample size is previously defined by preliminary sampling of the neutral reference : 25 shoots for an average number equal to or greater than one active predator per shoot, and 50 shoots for a number lower than one predator per shoot.

For the red mite, 10 leaves are collected from 5 trees scattered throughout each observation zone. Sample size is increased to 20 leaves for population densities under 5 mobile forms per leaf.

For the pear psyllid and eggs of the predatory heteropter *Anthocoris* sp., 10 shoots in the growing stage are collected throughout the observation zone.

For assessment of parasitism on leaf borer, the sample consists of 100 boreholes located over a minimum of 20 leaves collected throughout each observation zone.

For assessment of parasitism on aphids, 10 infested shoots per sample are randomly collected in each observation zone.

Counting

For predatory insects collected by beating, counts are performed under a binocular. The identification concerns mainly the predators active on the pest studied : red mite, pear psyllid (REBOULET, 1991).

For the red mite, counts of eggs and mobile forms are performed following brushing of the leaves (TOUZEAU, 1968).

For the pear psyllid, counts of eggs and larvae are performed on the three tip leaves and on the apex of each 5 shoots.

A count of *Anthocoris* sp. eggs is carried out as well on 5 shoots. This count should however be extended to all 10 collected shoots if the average egg number per shoot is under 3.

Assessment of the parasitism on leaf borer consists in counting, out of the 100 collected boreholes, the number of :

- boreholes with a live borer larva,
- boreholes with a dead borer larva (non-parasitized) or empty boreholes,
- boreholes with a parasitized borer larva.

The boreholes are inspected under a binocular, after lifting out the section of the epidermis corresponding to each borehole.

Assessment of the parasitism on aphids consists in counting in each sample of 10 infested shoots :

- the number of live and apparently healthy aphids,
- the number of aphids metamorphosed into "mummies" under the influence of the parasitoid hymenopter.

Mummies presenting the emergence hole of an adult hymenopter are not included in the count since it is impossible in such cases to determine whether the aphid was attacked prior to or after the test treatments.

Times and frequency of observations

For studies relative to the "predator-prey" complexes, observations are carried out every 15 days at least, making sure that one observation is performed prior to each test treatment.

Weekly sampling is however recommended for detection of any quantitative or qualitative changes in the populations of mites, pear psyllid or beneficial insects, which would require an additional observation of the entire system.

Observations are pursued until such time that no significant difference is found any longer between the neutral reference and the toxic reference.

For trials initiated in springtime on a population of predatory insects still relatively low, observations should start over the entire system as soon as an average of one active predator per shoot is detected after beating in the neutral reference. Thereafter, observations are performed every 15 days. This frequency may be shortened to 7 days in the event that any quantitative or qualitative changes occur in the pest or predator populations.

For the study of the impact of pesticides on the parasitism of leaf borer and aphids, a single observation is proposed for the time being, taking place approximately 2 weeks after the treatment. This observation is of interest only if parasitism is present in the neutral reference.

ANALYSIS OF VARIABLES AND INTERPRETATION OF RESULTS

In order to assess the impact of pesticides on predators, the analysis takes into account the following variables :

- (P), preys corresponding to a combination of the pest at all stages (pear psyllid eggs + larvae or red mite eggs + mobil forms), likely to be consumed by existing predators,
- (A), stages of the various predators active on the pest.

The variables corresponding to each predator or each active predator stage are analysed separately if the count is equal to or greater than 10 individuals per sample in the neutral reference. For lower counts, an analysis of combined variables is possible.

The definition of the variables to be investigated represents a significant phase in the interpretation of the results. It requires thorough knowledge of the potential efficiency of the beneficial insects according to the predators (REBOULET, 1992).

For each variable thus defined, the treatments may be classified on the basis of a calculation of the mean standard deviation of the samples.

For predators, the effects of the toxic reference and of the tested products are expressed as a reduction ratio (RR) as compared with the neutral reference :

$$RR (\%) = (1 - \frac{P_t}{P_n}) \times 100$$

where P_t is the mean population of the toxic reference and of each tested product, and P_n is the mean population of the neutral reference.

For each observation date following the test treatments, the effect of the tested product on the beneficial insects may be assessed, provided that :

- the population of the neutral reference is significantly higher than the population of the toxic reference,
- the reduction ratio (RR) of the toxic reference is higher than 50 %.

The tested product may then be regarded as :

- * non selective if $RR \geq 80 \%$
- * moderately selective if $80 \% > RR \geq 40 \%$
- * selective if $RR \leq 40 \%$.

Accounting for the "prey effect"

In the presence of an infestation of red mite or pear psyllid, the data should be expressed in the form of the following ratio :

$$R = \frac{A}{P}$$

Where A is the number of predators, P is the number of preys (mites or pear psyllid).

Following interpretation in accordance with the method described earlier, the above ratio should then be taken into account when calculating the reduction ratio (RR).

When assessing the effects of pesticides on the parasitism of leaf borer or aphids, the analysis takes into consideration the percentage of parasitized individuals. For each sample, this parasitism percentage (PP) is calculated according to the following formula :

$$PP \% = \frac{PI}{PI+LI} \times 100$$

Where PI is the number of parasitized individuals and LI is the number of live individuals.

CONCLUSION

This method presents the major advantage of providing information regarding the selectivity of the pesticides. Such data are essential in order to incorporate the investigated products into the integrated pest management program applied in the orchard, while preserving efficiency and selectivity.

The resulting knowledge acquired on methodology has already proved most useful for researchers faced with problems of field assessment of the impact of pesticides on beneficial insects.

The proposed method concerns the predatory insects of the European red mite and of the pear psyllid, as well as the parasitism on pear leaf blister moth and aphids although to a lesser experimental extent. Further studies relative to aphid predators in orchards and grain crops (GROS, 1985) have shown that the general principles of this method may be usefully applied to other "predator-prey" complexes.

BIBLIOGRAPHY

- A.C.T.A., 1991. *Les auxiliaires, ennemis naturels des ravageurs des cultures (Deuxième édition)*, Brochure A.C.T.A., 64 p.
- Fauvel G., Rambier A., Balduque-Martin R., 1981. *La technique du battage pour la surveillance des ravageurs en cultures fruitières et florales*. *Agronomie*, 1 (2), 105-113.
- Gros V., 1985. *Actions secondaires à moyen terme des traitements sur les ravageurs et les auxiliaires*. Mémoire E.N.S.A. Montpellier - A.C.T.A., 28 p.
- Reboulet J.N., 1988. *Produits agrosanitaires et faune auxiliaire*. *Défense des Végétaux*, 253, 19-24.
- Reboulet J.N., 1992. *Intérêt pratique de la faune auxiliaire en verger*. *Fruits et Légumes*, 94, 22-25.
- Touzeau J., 1968. *Utilisation de la machine à broser les feuilles pour le dénombrement des acaréens*. S.P.V., Note interne, 2 p.

A FIELD AND EXPERIMENTAL STUDY OF THE COMPOSITION OF SURFACE CRUSTS AND LYSIMETER LEACHATES AS A MEANS OF ASSESSING PESTICIDE TRANSPORT BY SUSPENDED AND COLLOIDAL MATTER IN BY-PASS FLOW

F.WORRALL, A.PARKER and J.E.RAE

Postgraduate Research Institute for Sedimentology, The University, Whiteknights, Reading, RG6 2AB

A.C.JOHNSON

Institute of Hydrology, Wallingford, Oxon., OX10 8BB

ABSTRACT

The composition of material carried in bypass flow has been investigated by a field and laboratory study, as part of a larger project on the role of suspended and colloidal matter in the transport of pesticides through and across soils.

The soil crusts from various locations (e.g. bare soil and tramlines) across a sloping field at ADAS Rosemaund (Hereford and Worcester, U.K.) were analysed for total and water-soluble organic carbon contents, clay mineralogy, and free iron-oxide, and particle-size distributions were also determined for each sample. An array of mini-lysimeters was set up using soil taken from the top 20 cm of the same field and the sediment released into the leachate was analysed during the winter period (Dec 93 - Mar 94). At the end of this experiment, samples of the surface crust formed were analysed to assess its change in composition. Results show that:

- (i) enrichment ratios of up to 1.9 are possible between the total organic carbon content of the crusts on the slope of the field and those at its foot;
- (ii) water-soluble carbon is always depleted in the surface layers, implying that it is washed off the site or moved vertically into the profile;
- (iii) clay mineralogy shows a tendency to be enriched in expandable minerals down the slope;
- (iv) sediment leached from the mini-lysimeters is enriched in organic carbon whilst the surfaces of the mini-lysimeter are depleted; and
- (v) there is down-slope transport of the silt-sized fraction of the soil.

These results suggest that bypass flow in the unsaturated zone, carries a particulate and colloidal phase that, by virtue of its increased surface area, and increased organic and expandable mineral contents, would have an enhanced potential for transporting pesticide over and above that which could be carried by sediment representative of the top-soil. The influence of these factors on pesticide transport will depend greatly on the adsorptive properties of the pesticide.

INTRODUCTION

It has long been realised that the occurrence of pesticides in streams of agricultural catchments can be attributed in part to compounds being transported directly to the water courses by overland flow - for reviews see Wauchope (1978) and Leonard (1990). The pesticide transported in this manner may either be in solution or carried adsorbed to a particulate or colloidal phase. The partition between an adsorbed and a dissolved phase is dependent on both the nature of the pesticide and the nature of the particulate/colloidal phase. The sediment eroded in runoff events may have properties different from those of the topsoil. Enrichment in the proportion of clay (Avinmelech and McHenry, 1984) and organic content (Avinmelech and McHenry, 1984; Sharpley, 1985; Harrod *et al.* 1991; and Ghadiri and Rose, 1991) have all been demonstrated for the sediment carried in runoff. It is suggested that these enhance the potential of eroded soil to transport pesticide and indeed Sievers *et al.* (1970) found an enrichment of insecticide on the particulate phase over that found in solution.

This study is concerned with the properties of the surface crust developed over a range of types of surface within a sloping field at ADAS Rosemaund (Hereford and Worcester, U.K.), where the soil is a typical brown earth of the Bromyard series (silt loam; 16% clay, 66% silt, 18% sand). It was hoped that by studying these surfaces over a period of a year, accumulation/depletion behaviour would become apparent, showing when material is being eroded, transported and deposited during runoff events. In addition to the field study an array of mini-lysimeters was set up using top-soil from the same field to explore the nature of the particulate phase carried in vertical bypass flow, i.e. flow down macropores.

METHODOLOGY

From May 1993 until May 1994 surface crusts were collected from a number of different types of site across the study field. Collection of samples was on a three-monthly basis (May 93, August 93, November 93, February 94 and May 94). The surface crust was defined as the top 1-2 mm of soil and sampled using a knife-blade. In August 1993 this crust was very well developed and could be picked off the surface by hand. The types of site sampled were: bare soil that was never under crop at any time during the study period, although it was cultivated; soil that was under crop; a slope-aligned tramline; a slope-perpendicular tramline; and an overland flow deposit at the down-slope end of the slope-aligned tramline used in the study. For each sample collected the following were measured: total organic carbon content (TOC), the clay mineralogy, the free-iron content (FIO), the dissolved organic carbon content (DOC) and the particle-size distribution (PSD). The TOC was measured using a titration method (Gaudette *et al.* 1974). The < 20 μm fraction of the soil was separated by sedimentation and its clay mineralogy determined by x-ray diffraction. The FIO was measured by extracting the iron using a citrate-dithionite solution as described by Olson and Ellis (1982) and then analysing the resultant solution by inductively-coupled plasma atomic emission spectroscopy (ICP-AES). The DOC was extracted by adding 0.02 M calcium chloride solution to a known amount of crust sample and shaking overnight. The mixture was then centrifuged and the supernatant analysed in a Astro T2001 carbon analyser. Samples of the crusts were treated with hydrogen peroxide so as to remove their

organic carbon content, then with a citrate-dithionite solution (as above) to remove the iron-oxide component, the resulting residue being dispersed with 1% sodium metaphosphate and the PSD then measured by laser granulometry. From the particle-size distribution it is possible to determine the % clay, % silt or % sand as well as the mean grain size and the skewness and kurtosis of the distribution.

During February 1994 samples were taken from three slope-aligned tramlines and their respective overland flow deposits. This allowed for direct comparison of the properties determined above between the crusts formed on the slope and those formed at its foot and so allowing enrichment ratios to be calculated. The enrichment ratio is the ratio of the value of a particular property in the overland flow deposit to the value of the same property in the crusts on the tramline.

An array of eight mini-lysimeters were set up in Reading using the top 20 cm of the soil from the Rosemaund field. The mini-lysimeter design is described in Worrall *et al.* (1993). These mini-lysimeters were allowed to operate outside over the winter of 93/94 (December to March) during which time the leachate was collected regularly and the sediment separated out by filtration. For the purpose of this study sediment is defined as that material that does not pass through a 0.45 μm filter. The material that does pass through a 0.45 μm filter is defined as colloidal and it is assumed that this is all organic and thus can be measured by an Astro T2001 carbon analyser. When the amount of the sediment collected was sufficient, its clay mineralogy, TOC, FIO and PSD were measured as above. At the end of this period the surface crust on each of the lysimeters was sampled and analysed for clay mineralogy, TOC, FIO, PSD and DOC, along with samples from the matrix of each mini-lysimeter. On one of the mini-lysimeters a thin covering of china clay was applied 31 days after the start of the experiment. This material has a clay mineralogy easily distinguishable from the clay mineralogy of the top soil and in this way it was hoped that an assessment of the source of material in the leachate could be made.

RESULTS

The data from the three monthly surface crust study were used to test two hypotheses:

I) Lateral transport down the slope of the field is the dominant process and the erosional mechanism is rainsplash. Surfaces under a crop, therefore, will appear less depleted than those of bare soil by virtue of interception. The value of a particular property in the different types of surface collected should follow the order: overland flow deposit > slope-perpendicular tramline > slope-aligned tramline > top-soil > soil under a crop > bare soil.

II) The top-soil value is always the highest. This hypothesis allows for lateral down-slope transport, but suggests that it may be subordinate to either vertical movement into the profile or complete removal from the site. The value of a particular property from the chosen types of site would, therefore, follow the same order as above, save for the fact that top-soil values are greater than those for all other surfaces.

This approach may neglect much of the fine detail, but by setting hypothetical ranking schemes it is possible quantitatively to compare the collected data with a model

by means of the Spearman's rank correlation coefficient. Those results that tested as being significant are given in Table 1.

Table 1. Properties of the sampled surface crusts that showed a significant correlation ($r^2 > 0.7$) with one or other of the alternative hypotheses set out above. * indicates a significant negative correlation.

Date of sampling	Property	Significant hypothesis
1/9/93	DOC	I*
1/9/93	%silt	I
1/9/93	skewedness	I
1/9/93	kurtosis	I
30/11/93	TOC	I and II
30/11/93	FIO	I
30/11/93	DOC	I* and II*
28/2/94	TOC	I
28/2/94	FIO	II
25/5/93	%exp	II

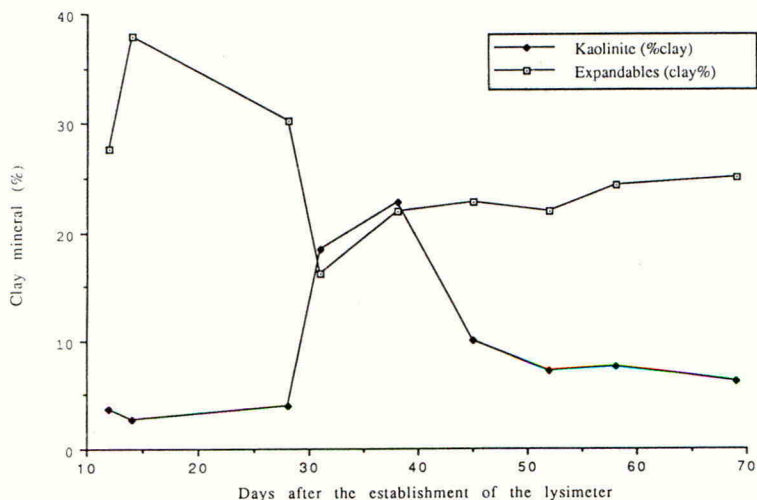


Figure 1. The clay mineralogy of the suspended sediment released from a lysimeter which was treated with china clay (china clay is approximately 100% kaolinite) on the 31st day of the experiment.

The comparison between the crusts on the slope-aligned tramlines and their respective overland flow deposits is given in Table 2. It should be noted that the errors involved in quantitative clay mineralogy are normally +/- 5% even with repeated sampling, and that this makes clear assertions difficult.

The study of the leachates from the mini-lysimeters has shown that the sediment had properties outlined in Table 3. The TOC and the clay mineralogy did not show any significant trends over the period of the experiment. The DOC, however, showed an abrupt decline subsequent to the initial sample. Values of DOC in the initial samples were as high as 400 ppm, but dropped to background levels of less than 20 ppm within 30 days.

From the occurrence of the china clay tracer in the leachate of one of the lysimeters (Figure 1) and a knowledge of the background levels of kaolinite it is possible, by means of linear combination, to estimate the proportion of material in the leachate that is sourced from the surface: at least 50%. The levels of kaolinite in the leachate decreased as successive bypass flow events used up the reservoir of available china clay, assuming that the leaching of sediment is independent of rainfall intensity once bypass flow is initiated.

Table 2. Comparison of the measured properties of tramlines and their respective overland flow deposits. The enrichment ratio for the mean grain size is the reciprocal of the normal value so as to represent the movement of the finer size fraction down the slope. All figures are quoted to the number of significant figures appropriate for the error involved in their measurement.

Property	tramline	overland flow deposit	enrichment ratio
TOC (%)	1.31	2.51	1.92
	1.48	1.94	1.31
	1.36	1.87	1.38
Expandable clay mineral content (%)	26	25	0.96
	11	32	2.91
	19	14	0.74
FIO (mg/kg)	0.025	0.055	2.2
	0.035	0.033	0.94
	0.022	0.042	1.91
Mean grain size (μm)	32.6	21.0	1.55
	40.1	12.4	3.23
	32.6	24.1	1.35

Results from the surface crusts formed upon the lysimeters are summarised in Table 3. Whereas the leachates were, in general, enriched in TOC and DOC, the surface crusts were depleted relative to the top soil. The mean grain size suggests the movement of the smaller-sized fractions from the surface into the leachate. The picture for the clay minerals is less clear because the errors involved are too large, but the general trend does support the idea that the smaller expandable minerals may be preferentially removed. With the FIO the surface appears depleted, but the suspended material in the leachate does not appear enriched. This cannot, as yet, be adequately explained.

Table 3. Comparison of the top-soil with the sediment collected from the lysimeter leachates and the surface crusts developed on those lysimeters. * indicates values which are not significantly different from the top-soil value at the 95% level.

Property	leachate	surface crust	top-soil
%exp	24%*	14%*	20%
FIO	0.07 ppm	0.037 ppm	0.125 ppm
TOC	3.37%	1.4%	1.64%
Mean grain size	-	33.0 μm	23.7 μm
DOC	0 - 400 ppm	-	-

DISCUSSION AND CONCLUSIONS

Agreement between Hypothesis I and the observed properties is good evidence for the movement across the soil surface and down-slope, and likewise a high correlation with Hypothesis II would lead to the conclusion that there was a significant component of vertical transport alongside lateral transport. It is possible, therefore, to conclude that there is good evidence for the movement of TOC, FIO, WSOC and fines down-slope and down-profile leading to enrichment ratios greater than 1. Worrall *et al.* (1993) have suggested that the expandable mineral content is enriched in bypass flow, but the data from this study are statistically unclear and cannot be taken as conclusive evidence of enrichment. The TOC seems to follow Hypothesis I whilst the DOC appears to follow the reverse of these hypotheses the best. So while insoluble carbon is moved and deposited down-slope the dissolved fraction is entirely removed from the site or moved vertically into the profile away from its source where levels remain high. For the TOC there is very poor correlation with either hypotheses in the summer months. This is due to the observable stagnation of the surfaces and the development of algal growths that bind the crust. This does not mean that organic matter is not preferentially transported during summer storms, merely that surface crusts cease to be good indicators of the process owing to the influence of a second factor controlling their composition.

It has been assumed in this study that vertical and horizontal bypass flow are equivalent, i.e. that overland flow, generated once the soil matrix infiltration capacity has been exceeded, will flow across the soil until it reaches a macropore down which

it will flow unless that macropore is already saturated (Beven and Germann, 1982). The vertical bypass flow then interacts little with the walls of the macropore - this is borne out by the china clay tracer experiment where the surface could be seen as the major source of material. This assumption will hold well for the lysimeters where all surface water generated must flow downwards as there is no slope and there is a lip to the lysimeter. Because of this assumption and, therefore, by analogy, it is possible to say that what we observe for overland flow will be true for macropore flow, a situation for which fewer data are available.

The observed properties of the particulate phase present in bypass flow will enhance the capacity to carry pesticide of both the flow in total, and of the sediment phase, in proportion to the total carried. An increased TOC will increase adsorption for all pesticides, and increased surface area and expandable mineral content will be especially significant for ionic pesticides where the cation exchange capacity is important. The pesticides which will be most affected are those with a low solubility and a high K_{oc} such as the pyrethroid insecticides.

The occurrence of DOC in the bypass flow appears related to soil disturbance, in this case by the setting up of the lysimeters, but in the field this could be by mechanical cultivation. If this is indeed so then DOC may only be high (that is above a background level due to turnover of organic matter levels) in the bypass flow for one or two runoff events after autumn cultivation.

The predictions of the amounts of pesticide in runoff would be of widespread importance and indeed approaches have been put forward for adsorbed pesticide by Leonard (1990) and for the total pesticide in runoff by Wauchop (1978). Both authors use the properties of the compound as a means of predicting its behaviour and indeed they have some success. This study shows that more complex approaches must be taken because bypass flow is a tri-phase system (sediment, colloid and pure solution) and each of the phases behaves differently in both time and space. For example, the sediment phase is deposited at the bottom of a slope whilst pesticide in pure solution or colloiddally bound passes off the site entirely.

It should also be noted that by examining the surface crusts it is possible to investigate properties of the surface that interacts with bypass flow. Whilst pesticide adsorbed to sediment may be physically removed from the flow as it is deposited, pesticide colloiddally-bound or in pure solution may adsorb to the surface crust. Thus overland flow fans, by virtue of their high TOC, may be good sites for pesticide deposition and adsorption from the solution.

ACKNOWLEDGEMENTS

The authors would like to thank the staff of ADAS Rosemaund, especially Dr.C.Hack and Mr.R.Edwards, for their support in carrying out fieldwork. Fred Worrall is supported by a NERC CASE award.

REFERENCES

- Avinmelech, Y.; McHenry, J.R. (1984) Enrichment of transported sediments with organic carbon, nutrients and clay. *Jour. Soil Sci.Soc.Amer.*, **48**, 259-266.
- Beven, K.J.; Germann, P. (1982) Macropores and water flow in soils. *Water Resources Research*, **18**, 1311-1325.
- Gaudette, H.; Flight, W.R.; Toner, J.; Folger, D.W. (1974) An inexpensive method for the determination of organic carbon in recent sediments. *Jour.Sediment.Pet.*, **44**, 249-253.
- Ghadiri, H.; Rose, C.W. (1991) Sorbed chemical transport in overland flow I. A nutrient and pesticide enrichment mechanism. *Jour.Environ.Qual.*, **20**(3), 628-633.
- Harrod, T.R.; Carter, A.D.; Hollis, J.M. (1991) The role of soil organic matter in pesticide movement via runoff, soil erosion and leaching. In *Advances in soil organic matter research*, Wilson (Ed.), Royal Society of Chemistry.
- Leonard, R.A. (1990) Movement of pesticides in surface water. In *Pesticides in the soil environment: processes, impacts, and modeling*, Cheng (Ed.). SSSA book series:2, Madison, WI. pp. 303-350.
- Olson, R.V.; Ellis, R. (1982) Iron. In *Methods of soil analysis*, Agronomy 9(2), ASA, Madison, WI, pp.301-312.
- Sharpley, A.N. (1985) The selective erosion of plant nutrients in runoff. *Jour.Soil.Sci.Soc.Amer.*, **49**, 1527-1534.
- Sievers, D.M.; Lentz, G.L.; Beasley, R.P. (1970) Movement of agricultural fertilisers and organic insecticides in surface run-off. *Trans.Amer.Soc.Agric.Eng.*, **13**, 323-325.
- Wauchope, R.D. (1978) The pesticide content of surface water draining from agricultural fields - a review. *Jour.Environ.Qual.*, **7**, 459-472.
- Worrall, F.; Parker, A.; Rae, J.E.; Johnson, A.C. (1993) Suspended and colloidal matter in the leachate from lysimeters: implications for pesticide transport and lysimeters studies. *Brighton Crop Protection Conference - Weeds 1993*, **2**, 899-904.