

SESSION 9

HERBICIDES IN THE ENVIRONMENT: EXPOSURE, CONSEQUENCES AND RISK ASSESSMENT – PART 1

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FOCUS surface water scenario development

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On behalf of FOCUS Working Group on Surface Water Scenarios (under the auspices of European Commission's DG Health and Consumer Protection).

ABSTRACT

The Authorisations Directive, 91/414/EC for the placing of Plant Protection Products on the market came into force in July 1993. In the Annexes, which give substance to the Directive, there is a clear need to provide Predicted Environmental Concentrations (PECs) as part of the process for assessing the risk to non-target organisms. In the specific context of organisms dwelling in surface water, the Annexes are also clear in the need to consider all appropriate input routes into surface water bodies. In the dossier preparation for the first list compounds most of the Agrochemical Industry concentrated on spray drift as the main route of entry into water bodies as this was readily quantified through the use of simple "models" based on empirical "drift tables", several sets of which exist at the National level. Little emphasis was put on the entry of pesticides into surface water via surface run-off/erosion and sub-soil drainflow and what work was done was carried out in an uncoordinated and unguided manner. In 1997 the fifth FOCUS (**FO**rum for the **C**oordination of pesticide fate models and their **U**Se) workgroup was created with the remit to define "standard scenarios" for surface water exposure. This paper records the advances made by the group since then and gives an overall appraisal of the timeline for the completion of the work.

INTRODUCTION

In 1992 an ad-hoc group of regulatory, industry and academic "experts" met in Brussels to lay the foundations for the FOCUS (**FO**rum for the **C**oordination of pesticide fate models and their **U**Se) groups. One of the remits of these groups has been to provide guidance to the Member States, the European Commission and the Agrochemical Industry on the role of modelling in the EU registratory process. The third of the FOCUS groups met to deal with surface water models and produced a report (DOC.6476/VI/96) which included an extensive review of available models and also proposed a "stepped" approach to exposure assessment, starting with simple "back of the envelope" calculations and increasing in complexity to sophisticated mechanistic modelling. The report also highlighted the importance of run-off/erosion and drainflow as entry routes into surface waters and the need for their inclusion in exposure calculations.

In 1997 the fifth FOCUS workgroup was created with the remit to define a limited number of "standard scenarios" for surface water exposure (not more than 10), representative of

commercial agriculture across the EU. The workgroup of "expert scientists" numbering 16 in total (14 at any one time) have been drawn from Regulatory, Academic and Industrial backgrounds and have relevant expertise in modelling surface water issues. They represent 8 Member State Nations as well as the European Commission.

REVISED REMIT

Whilst the original remit of the workgroup was interpreted as the need to create up to 10 standard scenarios for modelling surface water exposure ("step 3" in a four step process defined by the first FOCUS Surface water workgroup, see Figure 2), it quickly became apparent that this could not be done without reference to the two preceding steps in order to ensure that the correct level of conservatism and realism was used at each step. Consequently, as these two more conservative assessment steps had not been defined in detail, the workgroup undertook this additional task. It was agreed that the assessments should be most conservative (least realistic, highest safety margins) at step 1 and become less conservative (more realistic) through the steps. Furthermore, the range of possible predicted exposure concentrations gets wider as the user proceeds through the steps, reflective of the wider range of climates, soils and agronomic practices in the "real world". The perceived ranges of predicted exposure concentrations for the different steps, compared to "reality" are shown in Figure 1. As part of the definition of the step 1 and 2 calculations the workgroup also recognised the need to provide guidance for the calculation of exposure concentrations in sediment (PEC_{sed}).

SPRAY DRIFT

Spray drift had been perceived as the most significant entry route to surface waters for the compounds evaluated under list 1 and, therefore, was an important consideration for the workgroup. From the list 1 experiences, however, a number of shortcomings were identified; overspray was an unacceptable and illegal practice and should not be considered a realistic exposure route, drift deposition at the 95th percentile was too conservative, drift deposition for multiple applications each at the 95th percentile was extremely conservative and drift data for S. European agricultural practices (e.g. aerial application) was absent. The workgroup also agreed that all relevant published spray drift data should be considered for use in the new drift tables, however, when the data were evaluated only the work of Ganzelmeier *et al*, (1995) and the US Spray Drift Task Force (SDTF) AgDRIFT v 1.11 Model met the publication criteria and were used. After debate (and following the example of the FOCUS groundwater scenarios workgroup) the workgroup adopted the 90th percentile as a "realistic worst case" exposure level for drift events. The group also agreed that for multiple applications in a season, the total exposure from drift should be at the 90th percentile. To this end the drift data of Ganzelmeier *et al* were recalculated to provide 90th percentile drift values for single spray events and appropriate percentiles such that 2 to 15 sequential applications resulted in a cumulative probability of 90th percentile. Data for aerial applications were also taken from the SDTF and were included in the drift tables. However, after presentation of the workgroup concepts at a workshop held in Bilthoven in 1998 and discussions between workgroup members and scientists of the Federal Institute of the Ministry of Agriculture, Forestry and Fisheries (BBA), new official drift tables were released by BBA (2000) which included drift data for 5 crop classes (arable, vines, orchard fruit, hops and vegetables with vines and orchards further differentiated according to early and late growth stage and vegetables differentiated according to crop height) for distances of up to 250 m from the edge of the crop. Drift data were

calculated at the 90th percentile for single applications and also for up to 7 sequential applications such that the cumulative probability of 90th percentile was achieved. The workgroup agreed to adopt these data rather than to create another slightly different data set based on the earlier drift data.

The final product used for estimating drift loadings within the FOCUS surface water process was an Excel spreadsheet calculator based on a regression analysis of the various drift data sets, such that the drift at user defined distances from the edge of the field can be calculated. Drift loadings for up to 25 sequential applications can be calculated (after 7 the loadings are the same) for up to 28 crops plus a no-drift option. The calculator also allows the integration of spray drift over various widths of water body as required by surface water models (eg. EXAMS or TOXSWA) and will give appropriate "width averaged" loadings. The calculator has also been included as an integral part of the scenario management tool SWASH (see later).

STEP 1 AND 2

The conceptual starting point for the step 1 and 2 calculations was the standard "EU" ditch that was used for the surface water assessments for the compounds on the first list and was a static ditch (no dilution from flowing water) of 30 cm depth. In order to allow an estimate of exposure concentrations in sediment, a 5 cm deep sediment layer was added and after much discussion the organic carbon content and bulk density of this layer was set to 5 % and 1.5 g.l⁻¹. These values cover both the requirements for the sediment used in the sediment dwelling ecotoxicology tests and the laboratory water/sediment studies. A 5:1 field scaling factor was also applied for the area of treated field impacting on the water body. These constraints were applied at both steps 1 and 2.

At step 1 the application rate was the maximum season's usage applied as single dose. One exception to this was agreed when the DT₅₀ in water for the compound is less than a third of the interval between treatments. In this case a single application should be assessed because there is no possibility of accumulation of residues in the ditch. As described above, spray drift was considered at the 90th percentile for a single application and varied with crop. No-spray zones between the edge of the crop and the water body were fixed at 1m for row crops and 3 m for tall crops. Run-off/erosion and/or drainflow were also considered as a single non-specific loading and was fixed at a value of 10% for all calculations. The loading to the ditch also occurred on the day of application. Clearly this reflects a very "worst case" situation! All of the compound is in the water phase for the first 24 hours and is then partitioned between the water and sediment phases. This is driven by the average soil K_{oc} value. Degradation subsequently occurs in both the water and sediment phases. For step 2 calculations a number of refinements were included. Applications were made sequentially at rates and intervals representative of real use. This allowed degradation and partitioning to occur between applications, thus reducing the exposure in the water column. Spray drift was considered separately for each treatment but the sum of the spray drift represents the 90th percentile loading. No spray zones were still fixed as before. Four days after the last treatment, a percentage of the residue remaining on the treated field is then added to the ditch as a run-off/erosion or drainage input and is added directly to the sediment layer of the ditch. The magnitude of this loss is dependant on season and zone (North EU or South EU) of use and was set by expert judgement plus some calibration based on the results of the step 3

calculations. As with step 1, partitioning to sediment occurred after 24 hours and degradation occurred in both sediment and water phases.

The original versions of the step 1 and 2 calculators were Excel spreadsheets. It soon became apparent that these fell foul of the users PC operating system and version of MS Windows/Excel being used and, therefore, the decision was made to encode the tool in Visual Basic and this has made it much more system independent. The new tool is windows driven with drop down menus for selecting different options. Both the step 1 and 2 calculations have been encoded and both calculations can be conducted automatically and, therefore, because of the ease of conducting the more sophisticated step 2 calculations, the step 1 calculations are almost redundant. Output from the calculator is presented in tabular and graphical form which capture the input values and assumptions, calculate initial exposure concentrations as well as "time weighted average" concentrations for both water and sediment and finally present graphs of the exposure concentration with time.

STEP 3 "STANDARD SCENARIOS"

The step 3 scenarios were developed following a number of basic principles; there should be no more than 10 and these should be broadly representative of EU agriculture, the scenarios should take into account all relevant entry routes, target crops, surface water bodies, topography, soils and climates, the scenarios should reflect realistic combinations of run-off/erosion and drainage and wherever possible the scenarios should include conditions representative of a field test site with monitoring data to allow validation of scenarios. Digitised data characterising landscape, land use, climate and soils were collected together to allow a pragmatic approach to scenario selection based on available data and scientific judgement. Only arable agricultural areas were considered and land was broadly characterised into drainage (by recharge) and run-off/erosion (based on spring daily rainfall) areas. Appropriate soil type, slopes and crops were then obtained for these areas. In the absence of digitised data, dominant water bodies (ponds, ditches or streams) associated with the scenarios were determined from detailed topographic maps. At the end of this process 6 drainage and 4 run-off/erosion scenarios had been identified. The broad characteristics of the scenarios are shown in Table 1. The extent of the scenarios in European agriculture has been evaluated and found to vary between 1 and 12% of total EU agricultural land with all scenarios representing a total of 42%.

The approach to defining the water bodies was equally pragmatic given the absence of hard data and was governed in part by expert judgement, available literature references and some practical requirements from the models. The characteristics and scenario associations of the various water bodies are shown in Table 2.

Weather data associated with the scenarios was taken from Meteorology stations located near the representative field sites. Daily data for 20 years periods were obtained from the EU sponsored MARS project (Vossen & Meyer-Roux, 1995). The data were evaluated and weather years were selected which were representative of 50th percentile run-off and drainage years.

MODEL SELECTION AND PARAMETERISATION

Having defined the characteristics of the scenarios and associated water bodies, the workgroup was faced with the prospect of parameterising a wide range of possible models (*eg.* PELMO and PRZM for run-off, TOXSWA and EXAMS for surface water fate *etc.*). After much deliberation it was decided to parameterise only three models, MACRO for drainage, PRZM-3 for run-off/erosion and TOXSWA for surface water fate. This was not to state that other models were not equally applicable but rather a practical consideration to limit the workload.

The scenarios for MACRO and PRZM were parameterised based on actual field sites broadly representative of the scenarios. The field sites also generally represented national notional worst case examples for surface water exposure and included such locations as Brimstone (UK, DEFRA site), Lanna (Sweden, Swedish Land University site), Skousbo (Denmark, DEPA site), Vredepeel (Netherlands) and Roujan (France, INRA site). Data for soil properties, slope, drainage systems, cropping *etc.* were taken from these sites. For surface water fate, a new version of the TOXSWA model has been developed which has dynamic hydrology and is capable of simulating a water body of fluctuating height. This has particular importance for fast moving and seasonally dry streams associated with the run-off/erosion scenarios and also some of the drainage scenarios. This model uses the run-off and drainage losses as the driver for the water height in the water body. It also simulates an "upstream catchment" that feeds water into the water body of interest and which contains a percentage of untreated field, thus providing diluting water. The sizes of the "upstream catchments" vary between the scenarios.

All of the models are DOS based and have "user friendly" shells to improve ease of use and to present interfaces with similar styles. The shells for MACRO and PRZM were developed to select a crop first, this dictates the available scenarios which can then be run individually or in batch mode after entry of pesticide properties, use rates and timings. Output from these models can be visualised from the model shells but the most important output files are those which subsequently become input files for the TOXSWA model and these are automatically formatted. Links between PRZM, MACRO and TOXSWA are "loose" so all models exist as separate items. The TOXSWA model requires appropriate MACRO or PRZM hourly loadings files, spray drift loadings (from the drift calculator) and pesticide properties for behaviour in a water body (taken from a lab water/sediment study). Computation times for the models vary dramatically with the PRZM model completing a 30 year simulation in under 5 minutes, the MACRO model completing a 7 year simulation in 30 – 60 minutes and TOXSWA completing a 1 year simulation in 15 – 30 minutes depending on the capabilities of the computer. Output from the TOXSWA model will be in the form of peak hourly concentrations in water and sediment plus "time weighted average" concentrations (over a range of intervals) for comparison with acute and chronic eco-toxicity end points respectively.

MANAGING THE SCENARIOS

Because of the complexity of the process of step 3 modelling and the loose coupled nature of the various models, a scenario manager tool (SWASH) was developed to guide the user through scenario selection and which models to be run for which scenarios. To illustrate this further, if tobacco is selected as the target crop then only one scenario needs to be considered (R3) and only one water body (stream), so one PRZM run and one TOXSWA run need to be conducted. However, if winter cereals is chosen as the target crop then 9 scenarios need to be

considered (all except R2) with 15 associated TOXSWA runs. The SWASH tool also contains a database of pesticide properties required as input for the MACRO, PRZM and TOXSWA models with the intention that this database interacts with databases in the model shells, thus ensuring that all databases contain the same information and thereby reducing potential errors from data transcription. SWASH also contains a hard coded version of the spray drift calculator and it is intended that the tool should prepare input parameter files containing drift inputs and pesticide properties for the TOXSWA model. Another function of SWASH is to prepare tables of runs to be conducted with unique run identifiers for the various simulations. These tables can be printed and simulations checked off as they are conducted and provide a written record of work done.

Table 1: Broad characteristics for surface water scenarios

Scenario	Soil	Water body	Slope %	A A Precip ⁿ . mm	Av. spring & autumn temp. °C
D1	Clay	Stream Ditch	Level (0 - 0.5)	600 - 800	<6.6
D2	Clay	Stream Ditch	Gentle (0.5 - 2)	600 - 800	6.6 - 10
D3	Sand	Ditch	Level (0 - 0.5)	600 - 800	6.6 - 10
D4	Loamy	Stream Pond	Gentle (0.5 - 2)	600 - 800	6.6 - 10
D5	Loamy	Stream Pond	Moderate (2 - 4)	600 - 800	10 - 12.5
D6	Heavy loam	Ditch Pond	Level (0 - 0.5)	600 - 800	> 12.5
R1	Silty	Stream Pond	Moderate (2 - 4)	600 - 800	6.6 - 10
R2	Loamy	Stream	Steep (10 - 15)	>1000	10 - 12.5
R3	Heavy loam	Stream	Strong (4 - 10)	800 - 1000	10 - 12.5
R4	Loamy	Stream	Strong (4 - 10)	600 - 800	>12.5

Table 2: Broad characteristics of surface water bodies and their associations with the scenarios.

Water body type	Ditch	Pond	Stream
Width (m)	1	30	2
Depth (m)	0.3	1	0.5
Length (m)	100	30	1000
Distance (m) from:			
top of bank to water	0.5	3	1
crop to top of bank	0.5	0.5	0.5
Average residence time (d)	50	50	0.1
Relevant scenarios	D1, D2, D3, D6	D4, D5, D6, R1	D1, D2, D4, D5, R1, R2, R3, R4

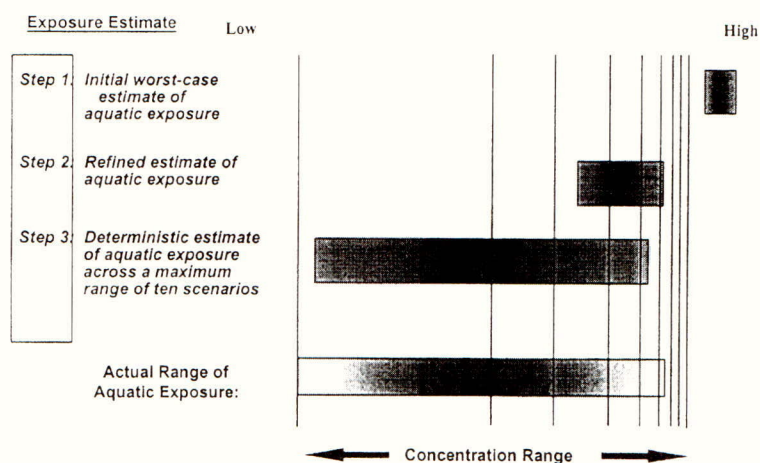


Figure 1. Relationship of predicted exposure concentrations for Steps 1, 2 and 3 calculations.

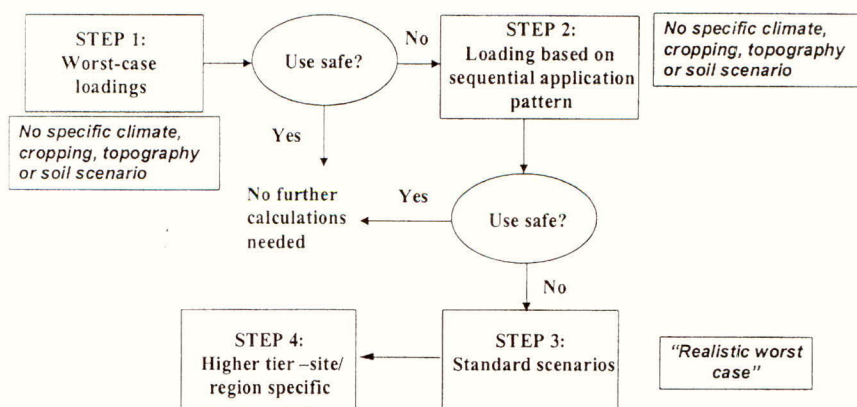


Figure 2. Inter-relationship of the four assessments steps for surface water exposure.

CONCLUSION

The preceding sections have been a quick summary of the current status of the FOCUS Surface water scenarios workgroup activities and condense the activities of four years into a hand full of pages. As of today the final report is in an advanced draft form and beta test versions of the Step 1 and 2 calculator, MACRO, PRZM and SWASH models are available and have been tested for some months. An early release version of the new TOXSWA model is also being tested. A joint FOCUS/ECPA project is underway to evaluate steps 1, 2 and 3 with a range of 9 fictitious compounds with different K_{oc} and DT50 values in order to ensure that the relativity of steps 1, 2 and 3 is correct, with step 1 being most conservative. The results of this may be used to adjust losses for run-off/erosion and drainage at steps 1 and 2. The results of this work have also been presented in a separate presentation at this conference. Seven real example compounds are also being tested and the results from these will be compared with monitoring data to ensure reasonableness of the predicted results. Predicted exposure concentrations will also be compared with eco-toxicity end points and risk assessment conducted. Comparisons have also been made between the old surface water exposure model which was based on drift and the new step 1 and 2 calculator and for a limited set of compounds the results are not very different. This work also continues.

The current timetable for the FOCUS surface water scenarios report calls for completion of the report and all models and submission to the Commission by the end of the year. Adoption and final release is then anticipated mid-2002 after member state review and comment.

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The influence of wind speed and spray nozzle geometry on the drift of chlorpyrifos to surface water

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ABSTRACT

Under the Plant Protection Product (PPP) Authorisations Directive (91/414/EEC) the risk of a PPP to off-crop non-target aquatic organisms is assessed in a tiered approach. From the properties and use pattern of the product, the likely routes of entry into surface water are assessed for PPPs applied as sprays. These assessments are based upon a calculated percentage of the active substance being deposited on a static body of water, 30cm deep, related to the distance from the end of the spray boom to the edge of the water body (Ganzelmeier *et al.* 1995). For some PPPs, such as chlorpyrifos, a buffer (no spray zone) may be applied to "in use" situations to reduce drift off-crop. However, there is little data to demonstrate how well drift events with specific chemicals match Ganzelmeier data or the extent to which application factors such as wind speed and spray nozzle affect the degree and amount of drift. Using a large-scale wind tunnel, a series of controlled, replicated studies were carried out to measure the influence of two wind speeds in combination with a conventional and three star (UK) rated reduced drift nozzle on the spray drift of chlorpyrifos, applied as Dursban 4, and its deposition on to an artificial ditch, simulating a static edge of field water body, 30cm deep. Results showed a clear reduction in amounts of chlorpyrifos as distance from the nozzle increased. The combination of 3mph (low) wind speed and low drift nozzle had a significant influence in reducing drift by ca. ten-fold at 2m from the spray nozzle, and five-fold at the mid-ditch position (4.5 or 5m), as measured by polyethylene strings stretched horizontally across the path of the drift. Water concentrations were reduced by ca. half from an average of $1.11\mu\text{g L}^{-1}$ to $0.45\mu\text{g L}^{-1}$. The presence of a 50cm artificial bank had no significant influence on the concentration of chlorpyrifos in surface water. Results show that both low wind speed and low drift nozzle can contribute to risk reduction of certain PPPs in surface water.

INTRODUCTION

Environmental (ecological) risk assessment of PPPs is usually based on a tiered approach ranging from conservative assumptions at Tier 1 to more realistic scenarios at higher tiers, reflecting normal use patterns of the product. For PPPs applied as sprays, aquatic risk assessments are based upon a calculated percentage of the active substance being deposited on a static body of water, 30cm deep, related to the distance from the end of the spray boom to the edge of the water body (Ganzelmeier *et al.* 1995).

For regulatory purposes, the 95th percentile worst case figures are currently used to calculate a Predicted Environmental Concentration (PEC) which is used in conjunction with single species toxicity data LC50, EC50 or NOEC to derive a Toxicity Exposure Ratio (TER). If acute or chronic TERs are below 100 or 10, respectively, then higher tier approaches based on either less conservative assumptions or using measured data are applied to refine exposure and, consequently, effects on non-target organisms. For some PPPs, such as chlorpyrifos, a buffer (no spray) zone may be applied to "in use" situations as a risk reduction (mitigation) tool to reduce drift to edge of field water bodies. However, there is little data to demonstrate how well drift events with specific chemicals match Ganzelmeier data or the extent to which application factors, such as wind speed and spray nozzle geometry, might affect the level of drift.

Using a large-scale wind tunnel, a series of controlled, replicated studies were carried out to measure the influence of two wind speeds, in combination with a conventional and three star (UK rated) reduced drift nozzle, on the spray drift of chlorpyrifos, applied as Dursban 4, and its deposition on to an artificial ditch, simulating a static edge of field water body.

MATERIALS AND METHODS

The wind tunnel facility used in this study at Silsoe Research Institute, Silsoe, UK, was designed specifically to enable experiments using active pesticide formulations to be conducted under safe and controlled conditions (Miller 1998). The tunnel used a recirculating design such that airborne pesticide spray material was not lost from the system during the experiment.

Following each experimental run, air was drawn into the working section of the tunnel, through the fans and airflow straightening sections, before being blown up a discharge stack to atmosphere. The complete tunnel was sited in a sealed pit in which any liquid discharge, waste or spillage drains to a sump from which could be pumped into a treatment plant. The working section of the tunnel was 3m wide and 2m high and 7m wide. Air movements within the tunnel were generated by two 15kw, 1.25m diameter axial flow fans mounted above the working section. Flow through the fans was ducted through an air straightening section, turned through 180° using vanes, into a contraction section and then into the working section. The system was designed to operate with a plug air flow down the tunnel at speeds ranging from 2 to 19mph. Humidity within the tunnel was controlled using an air-conditioning plant.

An artificial ditch, comprising a stainless steel tank 2m long, 1m wide and 35cm deep, containing 30cm deep (600L volume) tap water, was situated within the working section of the tunnel ca. 4.5m from the spray track with the water level ca. 5cm below the level of the floor of the wind tunnel.

In some experimental 'runs' a stainless steel plate, simulating a sloping (45°), 50cm high ditch bank, was fixed to either side of the ditch and the tank lowered so that the bank top was at floor level. (Figure 1). Experiments were conducted at constant relative humidity and temperature and, after each application of chlorpyrifos, the tunnel was purged for 2 minutes to remove any residual chemical from the atmosphere.

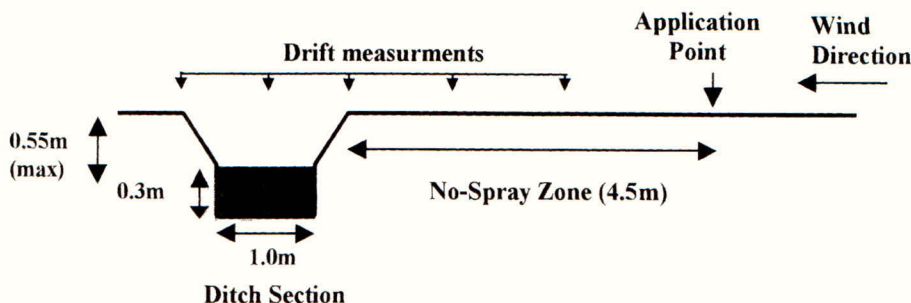


Figure 1. Wind tunnel layout

The formulated product (Dursban 4) was applied from a single spray nozzle at a concentration calculated to represent that arriving at the end of a standard 12m boom under normal use. Spray drift was captured by 1.5m length polyethylene "strings" (diameter 1.98 mm) stretched horizontally across the path of the drift at 2, 3 and 4.5m from the spray nozzle ca. 10cm above the floor surface. Additionally, a string was placed at the centre of the ditch above the water surface at 5.0m distance where no bank was present, or 5.5m with the bank *in situ*.

Following each spray run, chlorpyrifos was removed from each "string" by slowly passing it through a glass U-tube, containing 10ml n-hexane, held in an ultra-sonic bath. Following each spray application the water in the ditch was vigorously stirred for 2 minutes using a stainless steel paddle, in order to mix the chemical, and 3x 250ml samples were collected in acid washed glass bottles. The samples were firstly acidified with pH 4 buffer to prevent hydrolysis of chlorpyrifos and then 50mL n-hexane was added to extract the compound from the water. Non-homogeneity of the formulated product in the water after mixing was evident from the variability in concentrations of chlorpyrifos in some water samples. This was improved by drilling holes in the stainless steel paddle which resulted in better mixing and more even distribution of the chemical. Analysis of chlorpyrifos was carried out by Gas Chromatography – Mass Spectrometry (GC/MS). The organic phase of the extracted sample was separated from the aqueous phase using a sodium sulphate funnel, before reducing under nitrogen and analysis using a Hewlett Packard 6890 Plus GC with Hewlett Packard 5973 mass selective detector and ZB5-MS 30m x 0.25mm x 0.25 μ m column.

Experimental design

The study comprised of replicated randomised treatments based on a statistical design (three factorial randomised block). The first set of experiments reported here evaluated the influence of either 3mph (low) or 6mph (high) wind speed combined with a conventional or a low drift 3 star (UK rated) nozzle, and also compared the influence of a 50cm deep ditch bank on spray drift.

RESULTS

For each treatment combination (Table 1), chlorpyrifos deposition at each of the monitoring points was calculated from the material extracted from the spray drift targets ("strings") as a proportion of the applied mass. Standard statistical methods were used to determine the significance of observed differences between the treatment combinations.

Table 1 Randomisation plan – phase 1 applications (block 1 of 3)

Application	Block	Treatment 1 Wind speed	Treatment 2 Spray nozzle	Treatment 3 Bank height
A1	1	Low	Low drift	5cm
A2	1	High	Low drift	5cm
A3	1	High	Conventional	5cm
A4	1	High	Conventional	55cm
A5	1	High	Low drift	55cm
A6	1	Low	Low drift	55cm
A7	1	Low	Conventional	55cm
A8	1	Low	Conventional	5cm

Results showed a clear reduction in amounts of chlorpyrifos as distance from the nozzle increased (Figure 2).

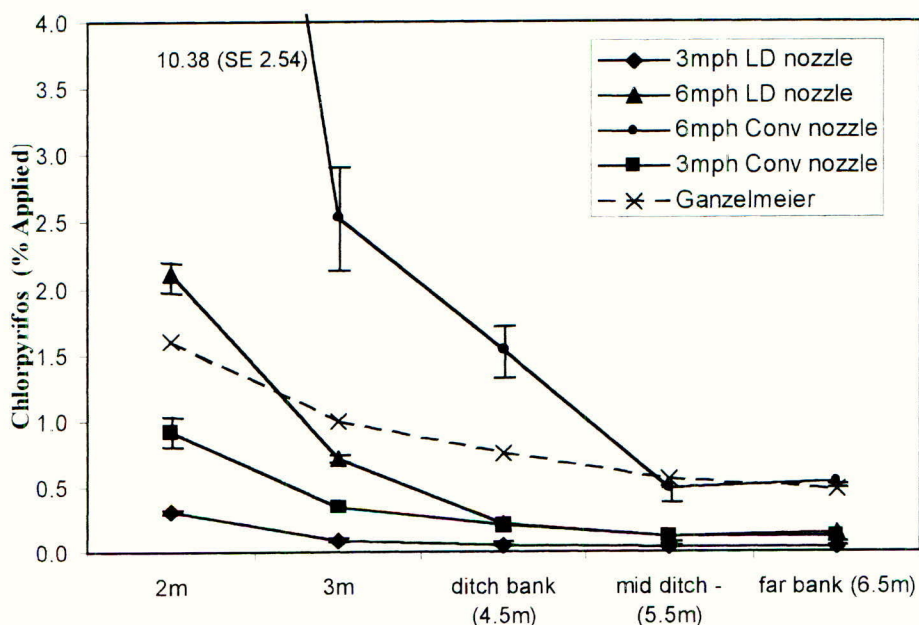


Figure 2. Mean chlorpyrifos deposition at increasing distance from application point (with 50cm deep ditch sides in place)

The high wind speed/conventional nozzle treatment showed the greatest variance with the calculated values given by Ganzelmeier at the 2m position, although the measured and predicted values converged with distance from the application point, and were similar at the mid ditch position (5.5m).

When compared to the high wind speed / conventional nozzle treatment, the combination of 3mph (low) wind speed and low drift nozzle had a significant ($p < 0.001$) influence in reducing drift by ca. ten-fold at 2m from the spray nozzle, seven-fold at 3m and five-fold at the mid-ditch position (Figure 2). The addition of a 50cm artificial bank on either side of the ditch had no significant influence on the deposition of chlorpyrifos at drift capture points across the 4.5m no-spray zone to the ditch section (Figure 3).

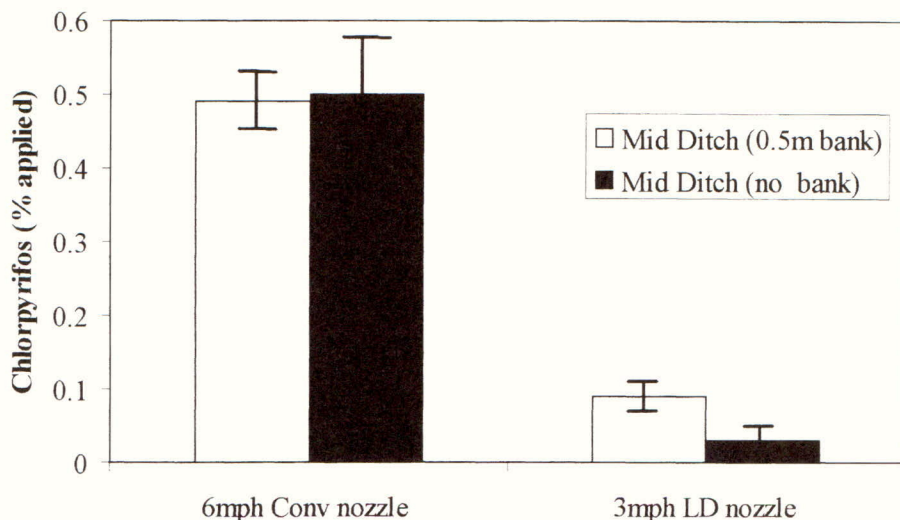


Figure 3. Spray drift deposition (as chlorpyrifos) with and without a 50cm ditch bank

Water concentrations in the initial test runs showed a large amount of variability between replicate samples, which was attributed to insufficient agitation of the ditch water causing non-homogeneous mixing of chlorpyrifos. Re-design of the stainless steel paddle and its use in later tests gave more consistent results. Concentrations were reduced by ca. half from an average of $1.11 \mu\text{g L}^{-1}$ with the high wind speed / conventional nozzle combination, to $0.45 \mu\text{g L}^{-1}$ under the low wind speed and low drift nozzle treatment.

DISCUSSION

The initial phase of the work described here demonstrated the value of using a large-scale wind tunnel to conduct spray drift / exposure potential investigations, as opposed to either field based or small scale laboratory experiments. Controlled conditions within the wind tunnel isolated the test system from external influences, and allowed the implementation of a replicated statistical design to test individual spray application parameters and their

combinations. In addition, field scale application methods and rates could be utilised while retaining laboratory characteristics of measurement and repeatability.

Results from this first phase showed significant differences in the pattern of spray drift deposition for the combinations of spray nozzle and wind speed tested, when compared with Ganzelmeier data. Differences were most marked within 3m of the spray nozzle. In general, the data suggest that the use of both low wind speed and low drift nozzle can contribute to reductions in the amount of certain PPPs deposited on edge of field surface waters. This has significant potential for reducing initial exposure concentrations in the water body and consequent reductions in effects on susceptible non-target aquatic organisms. The issue of uneven distribution (non-homogeneity) of oily formulations in water arose in this study. It was considered that this could be due the tendency of the emulsifiable concentrate micelles to float to the surface of the water. This phenomenon could influence both the rate of loss of chlorpyrifos from surface water and exposure of organisms in the water body. Further work to investigate this issue was identified and will be reported elsewhere.

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Prediction of field efficacy from greenhouse data for four auxenic herbicides

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ABSTRACT

The proposed paper will compare greenhouse and field efficacy data in light of concerns for offsite movement of herbicides. A central issue of environmental concern is how well greenhouse or laboratory data collected on a few species can predict injury to a larger, more diverse set of species in the field. A retrospective analysis of four auxenic herbicides shows that most efficacy data was generated to predict, with a high degree of certainty, the application rates required to cause 90% injury. There was little rate response data generated on the same species in both the greenhouse and field sufficient to estimate the 25% or 50% injury that is the environmental endpoint for most regulatory concerns. For those species where direct comparisons could be made, the greenhouse to field injury varied from approximately equal to as much as 20X with large variations between species. For the species with the lowest EC₂₅ values, the greenhouse data over predicted the field injury. Alternatively, a species sensitivity distribution uses all available data, and is predictive of injury to plant populations. Initial results suggest that the field and greenhouse data can be adequately modeled as log-normal distributions, were non-parallel, and can be used to predict the maximum application rates that are protective of 95% of species.

INTRODUCTION

Risk analysts, when attempting to judge potential impacts to the environment, have traditionally used deterministic calculations with single point estimates of injury to represent what in reality is a range of exposures and effects. Such risk assessments that use single values, i.e., the most sensitive species tested, loose information about both the extreme values and median responses and require some judgement about what information to exclude from the analysis (Cullen & Frey, 1999). In many instances, the person choosing which data to use has little or no knowledge of the underlying assumptions or range of true values. Currently, US EPA guidelines for pesticide registrations require greenhouse data on ten terrestrial species (USEPA, 1989), while German guidelines require data on six species (Füll *et al.*, 1999) for their ecological risk assessments. In both cases, the assessments are based on the single most sensitive species tested with limited or no consideration of other species or the relative sensitivity between greenhouse and field grown plants.

It is generally accepted that a higher application rate is required to cause injury to field grown plants than greenhouse grown plants because of physical and metabolic differences, dissipation/degradation of the product, plant age and structure, cuticle thickness, and other factors. From a review of published data, Fletcher *et al.* (1990) concluded that the ratios of

greenhouse to field EC_{50} values ranged from 0.26 to 3.26. For 30% of the herbicide/species combinations he evaluated, the greenhouse EC_{50} values were lower than the corresponding values in the field. The remaining 70% had field EC_{50} values that were lower than those measured in the greenhouse. In Fletcher's review, it is not clear if the values were calculated from the dose response in individual studies, or from data aggregated across multiple studies. Few dose response studies have made direct comparisons between greenhouse and field grown plants under controlled conditions. In the current investigation using historical data generated during product development, it was found that a limited number of species were tested under both greenhouse and field conditions because of the nature and purpose of discovery screens and field efficacy tests. Direct comparisons of individual species gave variable conclusions. Expressing the data as species sensitivity distributions, however, demonstrated linear relationships between the EC_{25} values and the cumulative percentage of species, and revealed a non-parallel relationship between the greenhouse and field data.

METHODS

Greenhouse and field efficacy data for individual herbicides were retrieved from the archives of Dow AgroSciences LLC and used for comparison between species. Greenhouse data were derived either from studies required to meet product registration requirements or from discovery, efficacy screens. Data on the field response of species were obtained from field development reports or annual data summaries as available. Only those studies with a minimum of three application rates and injury responses that bracketed the appropriate level of injury were included. Estimates of the application rate that caused 25% visual injury (EC_{25}) were made by fitting the data for each study to a four-parameter logistic dose response model. The greenhouse to field ratios were calculated as the average greenhouse EC_{25} divided by the average field EC_{25} across all studies for each species. A species sensitivity distribution for each herbicide was constructed by ranking the EC_{25} values in ascending order and plotted against the cumulative percent of species (Newman *et al.*, 2000; Versteeg *et al.*, 1999). For example, if there were data on 10 species, each species would represent 10% of all species. Initial results showed that the species EC_{25} values adequately fit a log-normal distribution. A linear relationship was obtained by plotting the common log of the EC_{25} values vs. the percent cumulative species for each product. Estimates of the EC_{25} for the lowest 5% of all species were calculated by least squares linear regression and extrapolation as necessary from the regression equation.

RESULTS AND DISCUSSION

There was very little overlap between the species tested in the greenhouse and field. In this analysis, 104 EC_{25} values were obtained from greenhouse tests and 40 from field tests, that together allowed for direct comparisons between 38 data points. The lack of overlap between species probably stemmed from the different purposes for the two test systems. The greenhouse tests were designed to detect herbicidal activity using a representative set of species based on their economic importance and ability to be grown reproducibly in a greenhouse while field tests were designed to determine with high precision the application rate that caused 90% control under varying conditions. Direct comparisons showed that for 13 of the 38 data points, higher EC_{25} values were measured in the greenhouse than in the field. The greatest differences were for ABUTH and DAOTE with all four herbicides, DATST for pyridyloxy A and pyridyloxy C, and NIOTA for pyridyloxy A (Figure 1). The differences for ABUTH, DATST and NIOTA derive

from a single field test and may not be representative. The remaining species had lower EC_{25} values in the greenhouse.

The ability to predict field effects from a limited amount of greenhouse data is an important concern in ecological risk assessment. The small number of species with data from both the field and greenhouse limited the comparisons that could be made. A better approach is to examine the trend using all available data instead of single species. Such an approach has been recommended by several groups including the Aquatics Dialog Group of SETAC (SETAC 1994), ECOFRAM (ECOFRAM 1999) and EPPO (EPPO 2000). Species sensitivity distributions for each of the four herbicides are presented in Figures 2 through 5. In each case, the resulting plots were linear but non-parallel between greenhouse and field data with steeper slopes for the field data. The results suggest that a smaller application rate range was required for species in the field than in the greenhouse. From such a distributional approach, it is not possible to predict the response of any given species, but instead indicates the overall population trend. The non-parallel lines suggest that plants grown in the greenhouse vs. the field behave as two separate populations, though they contain the same species. From the regression equations, application rates that would cause 25% visual injury for the lowest 5% of species, i.e. the rate that would be protective of 95% of species, was calculated. The results are given in Table 1. The differences between the field and greenhouse ranged from 3.4X for pyridyloxy D to approximately 13X for pyridyloxy B with the greenhouse values lower than the field. The use of species sensitivity distributions may provide a useful way to summarize disparate data sets and predict field responses of plant populations as part of ecological risk assessments.

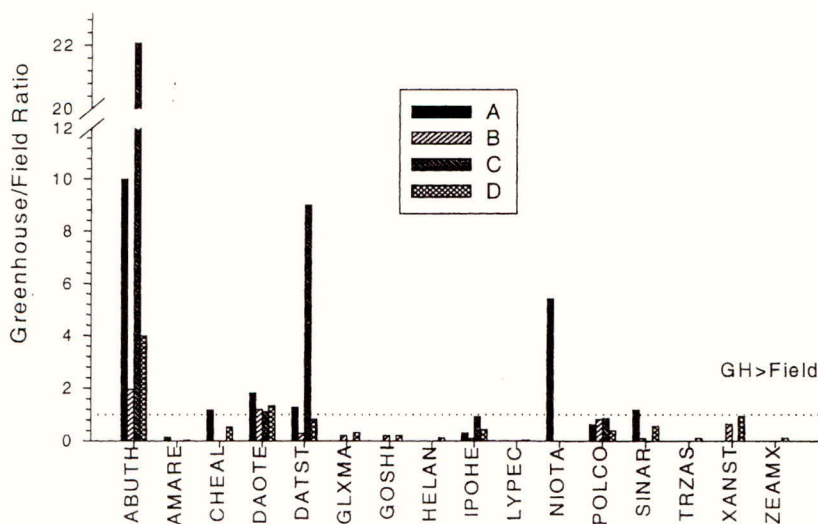


Figure 1. Ratios for the greenhouse EC_{25} to field EC_{25} for four pyridyloxy herbicides (A-D). The dotted line represents a ratio of 1 where the greenhouse equaled the field.

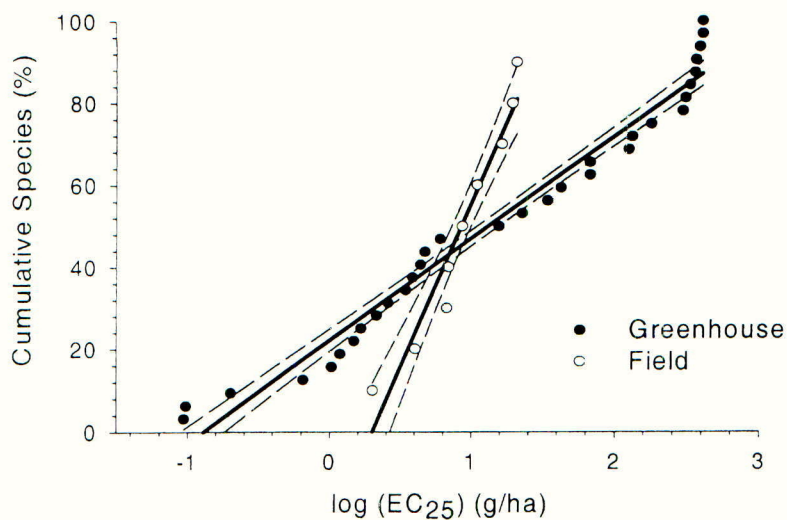


Figure 2. Species sensitivity distributions for pyridyloxy A. The dotted lines are for the 95% confidence interval around the regression lines.

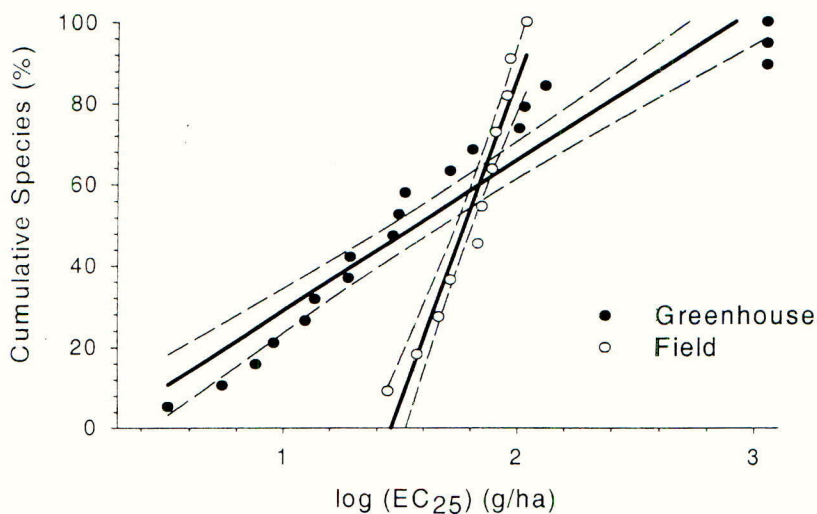


Figure 3. Species sensitivity distributions for pyridyloxy B. The dotted lines are for the 95% confidence interval around the regression lines.

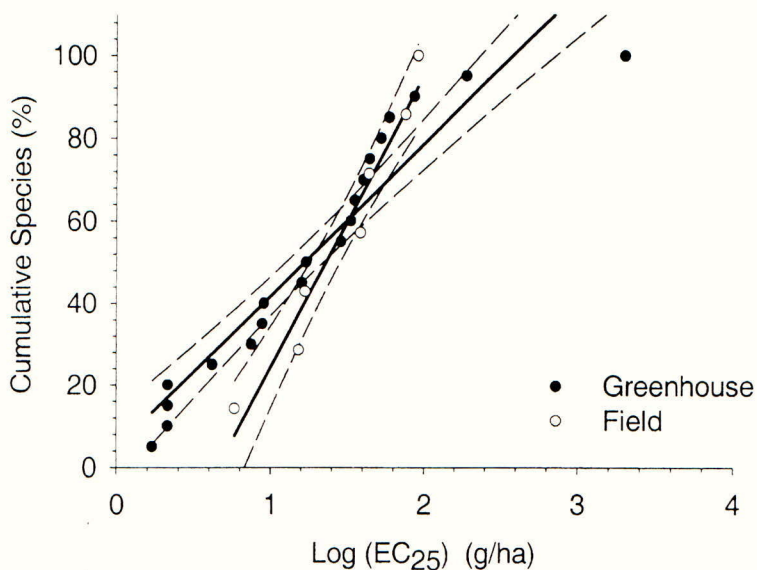


Figure 4. Species sensitivity distributions for pyridyloxy C. The dotted lines are for the 95% confidence interval around the regression lines.

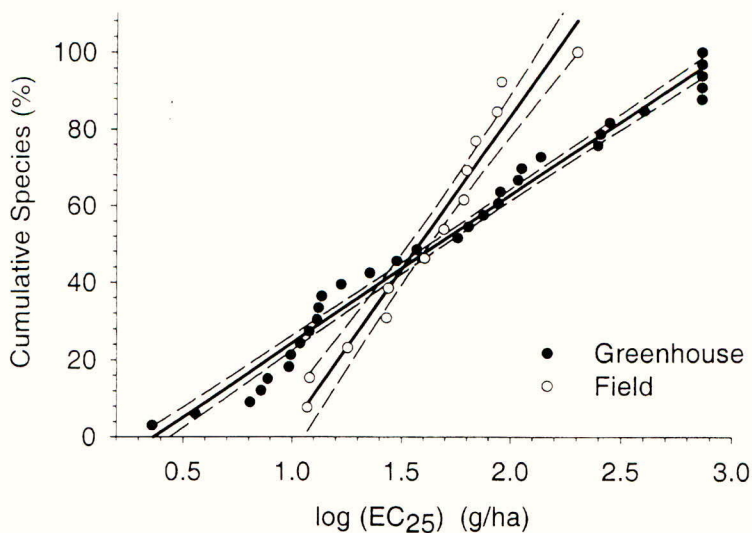


Figure 5. Species sensitivity distributions for pyridyloxy D. The dotted lines are for the 95% confidence interval around the regression lines.

Table 1. Predicted EC₂₅ values for the lowest 5% of species, greenhouse vs. field data

Product	Greenhouse (g/ha)	Field (g/ha)
Pyridyloxy A	0.21	2.3
Pyridyloxy B	2.3	31.0
Pyridyloxy C	1.0	5.3
Pyridyloxy D	3.1	10.6

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