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PESTICIDE RUNOFF: METHODS AND INTERPRETATION OF FIELD STUDIES

(Technical Report)

Prepared for publication by

R. D. WAUCHOPE[1], R. L. GRANEY[2], S. CRYER[3], C. EADSFORTH[4], A. W. KLEIN[5]
and K. D. RACKE[3]

[1]US Dept. of Agriculture, Agricultural Research Service, Tifton, GA, USA
[2]Bayer Agricultural Division, Stillwell, KS, USA
[3]DowElanco Corp., Indianapolis, IN, USA
[4]Shell Research Ltd., Sittingbourne, Kent, UK
[5]Umweltbundesamt, Berlin, Germany

*Membership of the Commission during the preparation of this report (1989–1995) was as follows:

Chairman: 1989–1995 E. Dorn (FRG); *Secretary*: 1989–1995 P. T. Holland (New Zealand); *Titular Members*: A. Ambrus (Hungary; 1983–1991); S. Z. Cohen (USA; 1991–1995); L. A. Golovleva (Russia; 1985–1991); R. M. Hollingworth (USA; 1989–1993); A. W. Klein (FRG; 1993–1995); N. Kurihara (Japan; 1989–1995); G. D. Paulson (USA: 1989–1995); R. D. Wauchope (USA; 1991–1995); *Associate Members*: S. Z. Cohen (USA; 1985–91); B. Donzel (Switzerland; 1987–1993); C. V. Eadsforth (UK; 1989–93); R. Graney (USA; 1989–93); D. Hamilton (Australia; 1991–1993); A. W. Klein (FRG; 1989–1993); J. Kovacikova (Czechoslovakia; 1991–1995); W. J. Murray (Canada; 1991–1995); B. Ohlin (Sweden; 1989–1993); S. Otto (FRG; 1983–1991); M. W. Skidmore (UK; 1991–1995); B. W. Zeeh (FRG; 1991–1995); *National Representatives*: R. Greenhalgh (Canada; 1985–95); Z.-M. Li (China; 1985–1995); J. Kovacikova (Czechoslovakia; 1985–1991); J. Iwan (FRG; 1986–1991); A. Ambrus (Hungary; 1991–1995); A. V. Rama Rao (India; 1989–1993); J. Miyamoto (Japan; 1985–95); H. S. Tan (Malaysia; 1987–93); Ir. D. Medema (Netherlands; 1989–1993); K. P. Park (Rep. Korea; 1989–1993); T. Erk (Turkey; 1989–1993); T. R. Roberts (UK; 1989–1995); P. C. Kearney (USA; 1989–1993); S. Lj. Vitorović (Yugoslavia).

Correspondence on the report should be addressed to the Secretary of the Commission: Dr. P. T. Holland, Horticulture and Food Research Institute of New Zealand Ltd., Ruakura Research Centre, Ruakura Road, Private Bag 3123, Hamilton, New Zealand.

Pesticides report 34. Pesticide runoff: Methods and interpretation of field studies (Technical Report)

Synopsis The objectives, design and interpretation of experimental measurements of pesticide losses in rainfall induced runoff from the surfaces of agricultural fields are reviewed. Microplot- and Mesoplot-scale experiments, which use artificial rainfall, and field- and watershed-scale experiments, which use natural rainfall, provide different but complementary information. The smaller-scale experiments are more controlled, replicable and easier to undertake but cannot represent those processes which vary over larger scales; thus they may not be representative of many real situations. Larger-scale field and watershed monitoring experiments provide realistic runoff concentrations, but they are more difficult and expensive. Because rainfall is uncontrolled, they are likely to provide unrepresentative data which are difficult to interpret and to extrapolate to other field and weather scenarios. A risk-of -runoff assessment of a pesticide may require information from a combination of these tests, together with the use of computer simulation modeling to integrate the results.

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INTRODUCTION

The need for pesticide runoff studies

Pesticides movement from the intended application site to non-target areas can occur during and after application. During application, the mechanisms for off-target movement are primarily direct aerial drift and volatilization. After deposition within the target site, numerous biological, physical and chemical processes determine the fate of the chemical. Certain combinations of soil properties and chemical characteristics (e.g., high infiltration rate and low soil adsorption, respectively) promote vertical movement in the soil profile, increasing the chances of movement to groundwater, but decreasing runoff potential. Similarly, when the physical characteristics of the site promote runoff (e.g., heavy soils with low infiltration), overland surface transport of the chemical becomes more likely (refs. 1-4). During runoff, the chemical may be transported in either the water or soil phase or both . For pesticides with moderate to low soil sorption characteristics (e.g., nonionic pesticides with a water solubility above about 10 mg/l), the majority of the chemical mass is transported in the water phase of runoff. Insoluble, hydrophobic chemicals with a solubility <1 mg/l are tightly bound to soil, and most or all loss occurs in the sediment phase.

Off-target movement of chemicals is both an ecological and human health concern. Sensitive ecosystems are often adjacent to agricultural lands and minimisation of pesticide runoff is consistent with the protection of such resources. Surface waters are often used as drinking water sources and ensuring that the concentrations of pesticides are below toxic levels is an absolute necessity. Understanding the processes which determine pesticide runoff from agricultural fields is critical if the safe and effective use of these products is to continue. Protection of the environment requires that every effort be made to ensure that chemicals remain at the site of application. A knowledge of what controls and influences pesticide runoff will allow growers and regulators to implement effective measures to reduce losses.

Ecological risk assessments require an understanding of both the toxicity of the chemicals to non-target aquatic organisms and the potential exposure levels in the adjacent aquatic habitats. Estimates of exposure can be obtained from either computer simulation modeling or by conducting field studies to actually measure the runoff from the fields or in the receiving system. Numerous simulation models exist and the use of these models in estimating groundwater and surface runoff is increasing (ref. 5). Many of these models are well developed and can, in certain well-defined cases, provide fairly good predictions of runoff potential (from within about a factor of two in the best cases to an order of magnitude in the usual case). However, the validation level for the models varies considerably and many models are not well validated for specific agricultural practices. For example, models are not well developed for estimating the runoff of soil incorporated granular pesticides. In such cases, it may be necessary to perform field studies to actually quantify runoff or exposure in aquatic ecosystems.

Types of runoff studies

The design of a pesticide runoff study will depend upon the specific objectives of the study. Two general categories of studies are (1) Simulated rainfall studies, in which artificial rainfall is used as needed, and (2) "Natural" rainfall studies, which rely on natural rainfall for runoff and are usually of larger scale and duration. Each of these types of study has generally been conducted at two different scales:

- Simulated rainfall studies
  - *microplots* (area <1 - 10 m^2)
  - *mesoplots* (area ca. 0.1 ha)
- Natural rainfall studies
  - *field* runoff measurements (homogeneous field areas 0.5 - 10 ha)
  - *watershed* monitoring studies (heterogeneous areas to many km^2)

Microplot studies are small, artificially constructed boxes of soil, or small diked plots in the field in which the soil characteristics, slope and rainfall are all controlled by the investigator. These test systems, typically no larger than 1-5 square meters, can be easily reproduced and manipulated and are good for comparative evaluations of the effect of specific parameter variation on runoff.

Mesoplot studies are "nearly-field-scale" investigations which are large enough to allow use of agricultural practices and crops which cannot be evaluated in microplot studies. These studies are small enough (typically 0.1 ha), to allow control of rainfall intensity, duration and timing. Extrapolation to larger areas is still required and such extrapolations do introduce uncertainty into the exposure assessment. However, given the combination of realism and experimental control, the studies can be very useful for model calibration. Once calibrated, models can be used for extrapolation to larger areas.

Field studies include the measurement of either actual pesticide runoff from instrumented (gauged) agricultural fields or the monitoring of concentrations in receiving bodies of water. These studies generate natural-rainfall induced runoff similar to that which may occur during the use of a product. Given cooperation of the weather (i.e., runoff-producing rainfall occurs within an acceptable time frame after application), this type of study can provide direct measurement of pesticide runoff in real situations. Problems are encountered with this approach when studying non-persistent chemicals which, by nature, have a potential for runoff for only a short period after application. Considerable effort can be expended establishing the experiment, only to have a rainless period immediately after the application such that useful runoff information is not obtained.

Watershed studies involve monitoring natural runoff from larger, multi-field heterogeneous areas which may include different crops and treatments and nonagricultural areas. Whereas studies discussed up to this point have addressed "edge-of-field" losses, watershed studies are one step removed from the field edge, measuring concentrations within receiving systems such as streams or lakes. The values obtained can be directly related to ecological or human health concerns; however since the monitoring is not associated with specific fields or agricultural conditions, relating the results to specific agricultural practices is difficult.

In general, the smaller the scale, the greater the experimental control. Greater experimental control allows more directed questions to be addressed; however by manipulating the systems to obtain that control, smaller systems are generally farther from reality. For very small test systems, it is often difficult to extrapolate to the "real world", though there are situations where microplot data appears to be realistic (ref. 6-10). As test systems become larger in size, typical agricultural practices can more easily be incorporated and thus the system may become more predictive of the real world; however control of the test system is diminished, and the size, duration and costs of such experiments are increased. The investigator must determine the degree of control versus realism required to meet his or her specific objectives.

Purpose of report

This report will address the following for each of the four study types described above:

Objectives best addressed by each type of study
Experimental design considerations
Site selection criteria
Application and agricultural factors
Sampling procedures and measurements
Advantages and disadvantages of study designs
Recommendations for future research

Results from specific runoff studies will not be reviewed. Review articles are available (refs. 1-4).

For the purposes of this report, we have concentrated on runoff measurements, recognizing, however, that runoff and leaching are intimately related both at the process and the hydrologic scales. In many runoff studies it will be useful for many purposes, including the interpretation of the runoff results, to simultaneously measure leaching. This consideration lies outside the scope of this paper. however, which has been focussed on a practical introduction to experimental methods.

EXPERIMENTAL DESIGN CONSIDERATIONS

Study objectives

The design and implementation of a runoff study will usually be governed by one or more of the following objectives: i) quantification of pesticide runoff patterns for a given region of interest, management practice, pesticide formulation, etc., ii) quantification of soil erosion losses if the pesticides of interest have a high affinity for soil surfaces, and iii) measurement of important parameters and runoff patterns for simulation model validation and use for prediction.

Sites must be selected which are representative of the region, pesticide use, crop and soil management practices and climate to be investigated. Once runoff potentials for a given chemical in a representative area are measured, observed runoff patterns and historical weather patterns will be used to estimate potential risk to non target organisms especially aquatic biota and humans. This requires a coupling between environmental exposure (concentrations and times of exposure) and organism sensitivity to the pesticide (toxicity) to predict potential environmental impact to the organisms in question. Projections of potential impact to non-target organisms are best made through statistical analysis of a large number of field study results (sometimes impractical) or through the use of numerical modeling and/or a combination of both.

To allow extrapolation of results from a study to other sites, complete data must be collected on all the parameters necessary to allow calibration of runoff simulation models. At the current stage of development these data, consisting of site characterization (soil, topography, crop), climatic and management information, and hydrology, erosion and pesticide concentration measurements, are also essential needs for comparison with available computer simulation model results. The direction this science is moving is that field studies are more and more designed to satisfy the data needs of computer models that in turn are used to integrate and extrapolate the data that results. Comparison between field and model predictions can indicate strengths and weaknesses of the current crop of runoff models available to the user (refs. 5, 11,12). A complete data set describing the site characteristics and precipitation patterns can be used to locate areas where model assumptions break down, require further scrutiny and/or modifications, etc. It should be stressed that any information obtained from a discrete field location will be specific to this field/watershed and specific to the natural rainfall patterns and intensities which may occur over the study duration.

It is possible to design a study which gathers all the information necessary to quantitate the runoff behavior from a watershed while simultaneously providing parameter values for computer model simulations. Indeed, this is the most desirable choice if the logistics of the field study can be achieved, so that a runoff data base can be developed. Runoff models could then be utilized to explore different usage and precipitation scenarios in addition to comparing the actual field results with model predictions (i.e. model validation).

Factors to consider

There are many potentially important factors controlling pesticide runoff (ref. 3,13). The large number of independent variables can lead to concentrations varying more than one order of magnitude between and within events (ref. 14). It can be difficult to determine which factors have a major influence without a priori knowledge of the expected results (ref. 15,16). Any previous information regarding agricultural runoff or potential runoff for the pesticide and region of interest should be consulted as this information can be instrumental in determining sensitive parameters. Alternatively, a numerical model sensitivity analysis can be employed to deduce which model input parameters have the greatest effect on model output (i.e. runoff) should an appropriate data base not exist. A sensitivity analysis can indicate which site characterization parameters (i.e. soil type, topography, pesticide degradation rates, etc.) require careful measurement (ref. 17). Microplot experiments can also be a useful tool in determining sensitive input parameters prior to designing a larger scale field study.

Representativeness. The factors to consider and measure in a field study are not uniform from field to field or region to region. A single field study is in essence a single snapshot of an infinite spectrum of possibilities which include climate, soils, crop, and management practices. The variability in the weather from year to year alone would suggest the futility of utilizing only a discrete number of field studies in performing environmental exposure assessments. Study sites should therefore be located in regions where marketing information suggests high potential use or in areas which are perceived as being environmentally vulnerable. The field study should follow the typical agricultural practices in the region of interest. Mechanisms affecting transport of pesticide in runoff should be adequately quantitated (i.e. precipitation, infiltration, surface runoff, and any properties affecting infiltration). Pesticide residues in the water and sediment phase of runoff may need to be analyzed separately to provide data regarding the transport mechanism for the particular pesticide in question.

Weather. Several factors are especially important in controlling the amounts of runoff water, sediment, and pesticides leaving the field. Rainfall amount, intensity and duration as well as the proximity of the rainfall to pesticide application are paramount. Thus climatic patterns drive the transport of runoff soil, water, and pesticides leaving the system being investigated. Precipitation inputs to the system may be lost by infiltration, evapotranspiration, and surface runoff. Each of these mechanisms require investigation if quantification of the relationships between rainfall and runoff yields is desired. On-site weather stations should be provided to measure precipitation, solar radiation, relative humidity, pan evaporation and soil and air temperatures, all of which make a contribution to the overall water balance within the system. Nearby weather stations may be adequate if the area being investigated is not subject to localized thunderstorm activities. Water infiltration into the soil surface can be estimated utilizing the SCS curve number system or more ideally by measurement. For accurate model calibration daily soil moisture of the surface and near surface soil horizon(s) should be measured.

Crop practices and pesticide use pattern. Management practices (ref. 18-23), vegetation cover (ref. 8,24,25) and pesticide application rate and timing play an important role in pesticide transport by altering the soil infiltration of water and by changing the amount of pesticide available within the system when a precipitation event occurs.

Soil factors. Water not infiltrating into the soil profile must either runoff or evaporate. Heavier textured soils (i.e. clays) typically have a higher runoff water yield than coarse or sandy soils because of their low infiltration capabilities. However, sandy soils tend to from a crust which can generate substantial runoff. Pesticides with a high affinity for soil organic matter are much more likely to be transported with eroded sediment than with the water phase of runoff. The kinetic energy of runoff flowing over the field increases as the slope of a field increases. This kinetic energy is responsible for suspending sediment, which can then be deposited further along the flow path if the slope decreases. Thus, deposition and suspension rates for eroded sediment can change throughout the watershed depending upon topography. crop type, surface texture, etc., and these factors should be quantified. An additional parameter of importance is the thickness of the soil layer at the surface which is in direct contact with rain--which is in fact "extracted" by the rain--during a rain event (ref. 26-29).

Pesticide factors. Persistence, solubility, and vapor pressure can all be important factors in determining runoff potential (ref. 3,4,30). Pesticides with long degradation half-lives will typically have greater annual pesticide losses in runoff than pesticides with smaller half-lives due to the longer "key period" window where both significant pesticide mass and precipitation events occur. Pesticide application practices such as pre-plant incorporation and banding of pesticides below the soil surface decrease the pesticide runoff potential. The period of time between the application of a pesticide and the beginning rain event seems to be a decisive factor--and this timing is more critical than soil half-lives suggest. For a number of pesticides "runoff half-lives", the apparent half life of residues available for runoff have been calculated based on concentrations observed in successive runoff events (ref. 31). These times are generally much shorter than the usual soil half-lives, varying between 5 and 20 days for most of the substances. Apparently those residues which are most available for runoff--on the surfaces of foliage and soil--are more rapidly dissipated than pesticides under the soil surface. Finally, formulation effects are beginning to be recognized as quite important especially for events occurring shortly after application (ref. 3,4,8,32).

Tillage practices. Although conservation tillage can decrease soil erosion and accordingly lower runoff of sediment-transported pesticides, there are cases where higher water-phase transport results (ref. 20, 33-40). However, in most cases conservation tillage decreases both water and sediment transport from fields, and in these cases pesticide losses are generally expected to be lowered. For all but the most hydrophobic pesticides, the majority of transport is in the water phase (ref. 4,19,20,23,41).

METHODOLOGY FOR CONDUCTING RUNOFF STUDIES

Microplots

Experimental objectives. Microplots range in size from a packed box of soil with less than 1 m^2 area to in situ plots constructed in a field on the order of 100 m^2. They are usually used with small-scale rainfall simulators--in fact the simulator often dictates the plot size and shape. Pesticide runoff experimenters, especially, have tended to tailor their plots to the rainfall simulators available. Construction of a rainfall simulator that gives realistic drop size distributions and impact energy is a specialized technology (ref. 42-45), and above 10 m^2 pump sizes and the logistic difficulties of obtaining adequate water increase rapidly.

The small size of microplots coupled with rainfall simulation allows for easily replicated "rainfall events" under conditions where the soil is uniform (especially when mixed and packed into a box or "tilted-bed"). Thus microplots allow detailed study of the relative effects of specific parameters such as rainfall intensity and timing, slope, soil compaction, pesticide formulation, and crop residues (ref. 1, 23,25,28,46,47).

Microplot experiments can generate very large fractional losses of pesticides--on the order of 10% of that applied (ref. 7)--because (a) they exhibit almost no sediment deposition, (b) they can have an almost instantaneous runoff response allowing very little pesticide to leach out of the rainfall interaction zone, and (c) they can be exposed to rain immediately after pesticide application. They have also often been used to simulate bare soil and soil surface pesticide applications (e.g., as with pre-plant herbicides), a situation which also tends to produce large losses.

Microplots, especially the smallest microplots, effectively simulate a point in a field and thus should provide excellent calibration data for models which basically simulate vertical point-in-a-field processes also (ref. 12). Indeed, if one is using a packed box of soil one may collect leachate and runoff simultaneously (ref. 46,47). The smallest microplots have such small areas, however, that they are not useful for simulating any conditions where there is variation in soil, crop or pesticide conditions on a scale of a few meters--for example, an incomplete or variable crop canopy, soil variation, banded applications of pesticide, or foliar applications on large crop plants such as maize or cotton. These objections may be answered by using larger plots--and somewhere above 100 m^2 (but closer to 1000 m^2), where such variation can be averaged, one begins to refer to the experiment as a "mesoplot".

Site selection. At the current state of the art, microplots are not considered reliable simulators of any real pesticide application--though the situation with respect to soil surface applications may be changing (ref.7). Thus, microplots are likely to be chosen for experimental ends or for convenience, where site is not the major factor to be explored. The ideal in situ site is one where there is a large enough area of very consistent slope, to allow one to construct the number of replicate microplots desired. Small variations in slope within microplots which are undiscernible to the unaided eye can affect runoff water yields between plots by 20% (ref. 8,32).

Pesticide application. Perfume atomizers, hand pump spray bottles, backpack sprayers, and side-mounted tractor applicators have all been used. With hand applications one simply applies the total dose as uniformly as possible, Given the well-known spatial variation in backpack and tractor sprayers, and the rather general phenomenon of spray volatilization both before and after deposition, it is a good idea to catch spray validation samples by placing e.g., petri dishes or filter paper disks in the spray path or (in the case of very small plots) just in front of and behind the application area. These samples provide an important measurement of the actual amounts of chemical applied. Prior to spraying, berms and runoff collector troughs are covered with plastic or paper. A sample of the spray tank mixture should also be taken for verification of actual active ingredient concentration.

Equipment and sampling procedures. Many designs of microplots have been used, but all have the same purpose--to expose a representative soil surface of homogeneous properties and slope to rainfall, and to collect the runoff from that surface--and only that surface. Tilted beds have been made out of wood, metal and fiberglass. They consist of a rectangular tray and may have a perforated or sealed bottom, depending on whether the experimenter wishes to allow free percolation. Soil is packed into the tray as uniformly as possible and is added until a bulk density near natural values is achieved. A wall may extended above the soil on three sides to retain splashed soil and water, or an area of soil may be constructed adjacent to the plot edge (this must also be treated with chemical) to counteract splash out of the plot. On the lowest side the soil is brought to an edge and a trough is constructed to collect runoff flowing over the edge.

In situ microplots are constructed by hydrologically isolating a rectangular area within a field, either by soil berms or, more often, by inserting metal dikes into the soil. At the lower end a collector trough is constructed below grade, typically out of rain guttering or split PVC pipe. The trough is sloped to one end and a well is built to hold a sample container under the low end of the trough. Construction of in situ plots which do not leak--especially between the lower edge of the soil and the collector trough--requires ingenuity and experience.

Perhaps the most-used rainfall simulator for pesticide microplots is the design of Meyer and Harmon (ref. 43) which uses oscillating fan-spray nozzles and is capable of variable-intensity rainfall with constant drop-size distribution. Very small box experiments have used the multiple capillary tube design (e.g., ref. 28).

One may collect all the runoff from a very small microplot, but with larger plots, consider that 1 cm of runoff generates 10 litres of water per square meter: one must sample the runoff stream at intervals. Samples are best taken simply by hand, holding a sample bottle in the flume or outlet stream. A careful observation should be made of the time when runoff first begins in relation to the beginning of rainfall, and at least ten evenly spaced samples of runoff should be taken throughout the event. Runoff flow rates may be determined by recording bottle fill times and later determining sample volumes.

Ideally one would like to determine a mass balance for the pesticide being studied, but this is seldom accomplished. Since runoff losses are typically only a few percent of the total applied the difference before and after runoff will be small compared to analytical variance in the soil or plant material in the plots. Field soil pesticide analyses are notorious for their variability even immediately after application. Simultaneous data on the leaching losses of pesticides during these experiments is a significant research need. Soil moisture, also, should be measured in as much detail as possible, determining its' distribution with depth before and after the event. This data will be essential for interpretation of the final results, since runoff generation is very sensitive to soil moisture levels at the beginning of rainfall.

Rainfall amount verification. Bottles or cups should be placed in the plots to determine actual rainfall amounts. Periodically this should be done with an array of many containers to determine simulator rainfall homogeneity,

Mesoplots

The term "mesoplot" has come to mean a runoff plot on the order of 0.1 ha in size which is used with a rainfall simulator for pesticide studies. The term was derived in analogy to the "mesocosm" of aquatic toxicologists, which is a constructed pond of a larger size than a "microcosm" which allows aquatic ecosystem simulation on a scale which may simulate natural ecosystems (ref. 48). Mesoplots are a relatively recent development pioneered by the Miles, Inc. (now Bayer Agriculture Division, Stillwell, Kansas, USA), principally through the development of a simple but realistic rainfall simulator capable of generating rainfall on this size plot (ref. 49-51). Thus they combine a plot large enough to represent real fields ,with some control of rainfall timing and intensity and replicability. One may also capture natural events in mesoplot studies.

Experimental objectives. The experimental design and objectives for mesoplot studies are similar to traditional field experiments--the quantitation of edge-of-field pesticide losses under a variety of realistic scenarios. Sampling and field equipment is identical to a larger scale experiment where pesticide mass balance conservation is sought. Mesoplots are constructed in situ in a field. Historical precipitation patterns for the area of interest can be obtained for typical and extreme storms during the time interval when pesticide mass is available for runoff. The rainfall simulator can generate a storm of defined intensity at any time after a pesticide application. Designed storms eliminate the gamble associated with trying to capture a naturally occurring precipitation event at the time that pesticide residues are highest.

Site selection and plot size. The location of the mesoplot should be representative of the watershed and typical of the agricultural region with respect to soil texture and soil organic matter. Soil properties should be characterized (i.e. texture, organic matter, water holding capacity, bulk density, etc.) The soil slope and soil conservation structures should be representative. Water required to support simulated rainfall is taken from a nearby river, lake, irrigation pond, or municipal water source.

Runoff leaving a mesoplot should be quantitated with the use of a gauged flume and flow measuring device (flow meter or pressure transducer/stilling well). For plots of about 0.1 ha, a 60 degree V notch trapezoidal flume (ref. 52) works very well; it measures quite small flows and is almost self-cleaning. Samples for analytical determination of pesticide should be taken using a time-sequenced or flow proportional sampling scheme. Composite or discrete samples may be collected by hand; with discrete samples a "chemograph" can be produced from the experimental data which will indicate the relationship between chemical runoff and storm duration and intensity. Samples should be chilled as quickly as possible to preserve the chemical species present.

Application and agricultural practices. Typical farm practices should be followed when preparing a mesoplot study. The length scales for a mesoplot should be sufficiently large to capture the effects of agricultural machinery (i.e. tyre tracks, grooves, etc.). The fall length of the plot should represent a typical slope length for the region where the mesoplot is located. A berm, typically of dyked soil, may be established around the sides of the mesoplot to isolate the treated drainage area. These berms are typically prepared using a small tractor fitted with a plow or grading blade, but similar earth moving equipment may be used if available. Once treated and bermed, the plot is instrumented with a rainfall simulator and runoff sampling equipment.

Sampling procedures. Soil and plant samples should be taken prior to runoff for pesticide residue analysis to determine the amount of pesticide available on the soil surface and foliage. Foliar pesticide residue persistence data can be useful for model validation and in closing a mass balance on the pesticide being monitored. Runoff volume exiting the test plot during the simulated rainfall event should be measured and runoff samples collected to support chemical analysis and subsequent transport estimations. Special consideration should be given to the procedure for collecting and sampling suspended solids contained in the runoff water, to obtain representative solids levels.

Information gained from mesoplot experiments can provide a data base for estimating parameter ranges required for quantitative mathematical predictions and scaleup to larger fields and watersheds. Mesoplots are less expensive than a large scale field experiment and are much more cost effective if parameter range studies are sought (i.e. surface applied pesticide vs. incorporated, different storm intensities, slopes, etc.). Ideally, mesoplots should be utilized with a large field study and receive the same natural precipitation as the watershed. Runoff from the mesoplots and the watershed should be quantitated. The purpose of using mesoplots in conjunction with a larger watershed is to acquire data for scaling of output data when length scales vary (i.e. mesoplot vs. large watershed). The results will aid in the calibration and verification of simulation models in predicting large watershed behavior from the results for mesoplot experimentation. Simulation models can subsequently be used to evaluate other environmental and climatological conditions to provide a decision support mechanism for environmentally sound pesticide use. Results from a mesoplot experiment are best left to interpretation via simulation models developed to study edge of field pesticide transport (e.g., ref. 2, 53-59).

Natural-rainfall studies: fields

Objectives. The ultimate measurement of the potential for a pesticide to be lost in runoff is a field test under natural conditions. Such a test is not conceptually more difficult than a smaller-scale study; it is, however, much more laborious, time-consuming, and expensive. The final results will also not extrapolate to any other conditions unless a very exhaustive measurement of all affecting variables is made. For example, Hendley (ref. 60) describes an extensive study in which field runoff from a series of field/pond sites was not quantitated at the field edge--the resulting data set was not useable for model calibration and thus it was not possible to extend to the general case. But all smaller-scale and rainfall simulation studies are designed to estimate, using inexpensive and controlled experiments, pesticide losses from real fields. Thus full-scale field experiments are also needed occasionally to verify the smaller scale predictions. They are also the source of most available data on edge-of-field water quality effects generally.

Design considerations. Several general references are available which provide design procedures for these studies (60-65). Two considerations stand out in such a study: first, real fields are too large for rainfall simulation and thus one must depend on the weather to generate data; second, one must thus have a way to sample runoff whenever it occurs. For all in situ experiments the location and construction of hydrologic collectors and flumes, which are used for measuring runoff volumes and as a location to withdraw runoff samples, along with possible land shaping, should be done so as to minimize possible unnatural regions where deposition of sediment in runoff water may occur. Generally, when natural rainfall is used, flumes should be sized to measure a 1 in 10 year precipitation event. The size of the flume can be obtained if historical data for runoff from the watershed/field being investigated is known or through the use of computer modeling (ref. 2,53-59).

Site selection. A hydrologically isolated watershed (i.e. has no water run-on from another watershed) with a single outlet and containing a single crop and soil provide the simplest and most interpretable sites. A flume is installed at the outlet with a stage (water height within the flume) recorder, an automatic sampler which is triggered by a runoff flow, a recording weather station, and the experiment has begun. There are of course many practical considerations typical of any large field experiment such as (i) control of the land use and pesticides applied (often these experiments are done with cooperating landowners)(ii) security and weather protection for the instrumentation (iii) access for sample collection during inclement weather (iv) power and power backup for the equipment (v) ability to chill and rapidly transport samples for analysis. A common problem in areas subject to thunderstorms is lightning strikes causing power outages and damaging equipment, especially electronic instrumentation. Practical experience has shown that the best way to ensure sample collection is to have someone at the site during runoff. Since natural rainfall can occur at night and on weekends. this necessity has been a major motivation for the development of simulated-rainfall techniques.

Application and agricultural procedures. Working in a real field allows all standard cultural and pesticide procedures to be carried out for the crop and pesticide in question. Spray validation catch samples are not always done but spray calibration and totals applied (by measuring volume or weight of spray mixture before and after application) combined with analysis of spray mixtures should be documented.

Sampling procedures and equipment. The peak flows of fields of 10 ha or less are correlated with rainfall intensity. To select a flume size Mutchler (ref. 66) recommends using the runoff rate equivalent to the five-minute-duration intensity of a 100 -year frequency storm; thus, there is a 1% chance of topping the flume during one year. Larger flumes can be used to measure still larger storms; however, as the size of the flume increases the precision of measurement for smaller runoff events diminishes.

Automatic samplers for timed water/sediment sample collection are necessary in sites where natural rainfall cannot be responded to manually. For several reasons, however, automatic samplers are not sufficient. First, power failures and fouled sampling equipment are common. Second, even when everything works it is not easy to obtain a representative sample particularly if representative sediment sampling is needed. A variety of passive (unpowered) composite samplers have been developed (ref. 42) which generate a single sample which is a small but representative subsample of the flow; these can provide useful backup for pump multisample equipment. Nothing, however, will substitute for having a person on-site during the event, if possible, to ensure that authentic samples are taken (ref. 60).

Meteorological and hydrological measurements. Accurate and complete meteorological measurements are critical. The most sophisticated computer simulation models (which will ultimately be necessary to assemble, integrate, and compare these data) require daily data for maximum and minimum temperatures, wind, solar radiation, evaporation, and humidity. Rainfall intensity as a function of time during events is required (or at least a breakpoint approximation of it), and soil moisture as a function of depth.

Natural rainfall studies: watersheds

Experimental design and objectives. The decision to monitor run-off of a crop protection product from an entire natural watershed or basin is usually undertaken for one of several reasons:

> To assess the likely concentration/amounts of a crop protection product in streams or other water bodies caused by run-off under real conditions of application and weather in the use region.
>
> As part of a product stewardship campaign to monitor for any traces of a crop protection agent in aquatic systems which may arise from its normal use under commercial conditions.
>
> To determine the effects of "landscape" features such as losses from different treatments and crops, buffer zones, and sediment and water routing.

Such watershed studies not only measure pesticides in water due to runoff but will also detect results of accidental spills, drift, shallow groundwater flow which re-emerges (interflow), and any other pesticide transport processes. Determining the source of water residues can thus be a problem.

The design of these experiments is crucially dependent on the exact objectives and the information which is desired. The aim of assessing run-off under real conditions is probably best addressed in an experiment designed to allow detailed knowledge of application details and a reasonably intensive sampling programme. An overall risk assessment may best be addressed through a design in which knowledge of the application details may be limited to the amount applied and approximate date/area. A more diffuse sampling programme may be dictated by resource constraints.

Since watershed monitoring studies are too large to allow the use of artificial rainfall, the occurrence of runoff "events" will be dictated by rainfall. As a consequence, if a measurement of runoff contributions to the overall water quality of the watershed is desired, the design of the experiment must allow for sampling to take place during, or at least soon after, heavy rainfall. This may require the installation of automatic samplers (see below) or some system of "alerts" so that personnel may visit the study area to collect samples as near in time as possible to runoff events.

Site selection and size. Probably the most important design consideration is the site of the area to be studied. If the study is to address risk assessment concerns or to monitor use of many pesticides, the study site should be as large as possible. For example Frank et al. (ref. 67) have studied no less than 11 watersheds concurrently, totalling 47,072 ha. The use of a very large area maximizes the chances of detecting traces of a crop protection agent which may occur only in a single water body and will be missed if that particular body of water is not sampled. A range of conditions may also be covered (e.g. sloping or flatter ground, still or running water). The practical limit on size is likely to be the number of samples which can be collected in reasonable time, and travel between sampling points. Twelve locations over an area some 15 kilometers square can comfortably be sampled for water and sediment in a working day (ref. 67).

For a study intended to assess the degree of runoff occurring with a particular pesticide, a smaller study area is likely to be preferred, allowing greater control over the application(s) and more concentrated sampling, with consequent increased confidence in the generated data. Ultimately, the choice of sites may be determined almost entirely by what is available in the areas where the pesticide is used.

Regardless of the study intent, the study area must lie in a region which will receive significant applications of the test material, and must be of a geography such that there is potential for the material to reach water courses by runoff (leaching may also be significant mode of movement for some materials). Site selection must consider whether the objective is to study "worst-cases" or more typical conditions, since this will critically affect the site geography (steepness of slopes, proximity of treated crops to water bodies). Certain products may be applied to a wide range of crops using many different application techniques, so that the study site needs to be in a region where the desired method of application is used.

Application and agricultural procedures. Generally, studies over very large areas for the purposes of regional risk assessment are most practically conducted as "farmer-use" trials, where the applications are made by the individual farmers to their normal practices. Applications cannot be controlled or interfered with, and need not be observed by the experimenters, who merely maintain records of the amounts of material applied to the study area, along with (so far as possible) the exact fields which have been treated and the dates of treatment. Similarly, agricultural practices will be those normal to the area/crop and need only be recorded. Arrangements need to be made to ensure that artificial irrigation, tillage of treated slopes and any other practices which may significantly affect the extent of runoff can be recorded. Thorough surveys (e.g. by questionnaire) of the farms and other land uses in a large area represent a very large input of effort (ref. 68).

Sampling procedures and equipment. Water can be sampled by a wide range of techniques and devices designed to collect water either as a bulk sample (from the "centre" of the water body), from the surface layer (where hydrophobic compounds can concentrate) or including both the surface layer and depths (integrated-depth sample). Automatic samplers (e.g. ref. 69) can sample bulk samples at pre-set intervals or when triggered (e.g. by heavy rain). Other types of sample require manual collection by people close to the site, able to respond quickly to runoff events. In water samples collected by any of these means, suspended solids can be separated from the water itself for separate analysis if desired.

Soil samples may be collected to provide data on the movement of crop protection chemicals to soil down-slope, within or below the field. Normal auger samples can be used, but sediment trapping as above will usually provide a more sensitive measure of soil movement. Sediment samples can be collected from water bodies and can be very informative, since many crop protection products are likely to be associated with the solid material in surface runoff rather than in solution in the water. This solid material may settle out in slower water downstream of the runoff site and can be sampled. Thus, it can be possible to detect material in sediment samples even where it could not be found in water. Various designs of long-handled auger have been used to collect sediment from the beds of water bodies. In shallow water, the upper layer of sediment (ca. 10-20 mm) can be sampled by scraping directly into bottles (e.g., ref. 69). Collecting only surface layers of sediment increases the likelihood of finding measurable pesticide residues, since dilution with deeper, uncontaminated sediment is minimized. In addition, sediment traps can be placed in ditches and streams (though this can be logistically difficult), or in the slopes below treated crops, to intercept solid material as it moves in runoff water. These traps can be simple glass jars and have been effective in trapping soil/sediment (ref. 70). Unfortunately, very large variability is often encountered in sediment sampling and can create heavy sampling burdens and interpretation problems. Compositing can be used but this can increase the "dilution" problem.

For a few chemicals, the bioconcentration factor in fish is high enough to make the analysis of fish a more sensitive indicator of the presence of a pesticide in water than analysis of water itself. In such cases, entry of the chemical into aquatic systems may be monitored by catching and analyzing fish, either indigenous fish or (more easily) fish deliberately held in cages installed in the water bodies. Fish can be placed in cages, then removed and replaced with new fish at intervals, and the removed fish analyzed. Since the fish are resident in the water system over long periods, they can provide information on the flux of chemical over these time scales. In contrast, "grab" sampling of water provides data only on the concentration of chemical present when the sample was collected. Such studies are not trivial, however-survival of caged fish is a problem and experience with the test species is usually required. Both water and fish residue data may be required for either to be interpreted.

Problems have been encountered with fish availability and survival. The easiest fish to obtain (in Europe) are rainbow trout (Oncorhynchus mykiss), owing to the abundance of commercial trout farms. However, O. mykiss are fish of flowing water and do not survive well in all environments. Other species (e.g. carp, Cyprinus carpio) are more hardy under still water conditions but are difficult to obtain reliably.

Artificial samplers. Because of these problems, artificial devices have been studied as replacements for fish in this type of study. The use of membranes filled with lipids or solvents to concentrate organics from water has been reported (e.g., ref. 71,72). Uptake factors similar to those of fish, if not higher, are claimed, and no metabolism occurs. These devices have been compared with fish (O. mykiss) and with porous sheet material containing C18-bonded silica in a mesh of PTFE (3M "EMPORE" discs or sheets). The discs have been used for efficient extraction of residues from water in the laboratory (ref. 73,74) but their use in the field as passive accumulation devices is a recent application (ref. 75).

Meteorological measurements. The primary interest in meteorology in studies of this sort is rainfall, particularly any heavy rainfall events. Other weather data (temperature, sunlight, etc., etc.) are also important and are collected wherever possible. These data are usually obtainable form national meteorological services but such organizations may not have weather stations close to the study area. It is preferable to use one or more portable weather stations which can be erected on or near the study site (hidden or secure from interference) and which will provide detailed information directly relevant to the study. Weather parameters can be measured at intervals (typically daily) and logged to be "down-loaded" into a portable computer at regular visits to the site.

SUPPORTIVE RESEARCH STUDIES

Three supportive experiments may be carried out as part of pesticide runoff studies: soil sorption, half-life, and foliar washoff (in the case of foliar-applied pesticides). These studies provide values for parameters that are in themselves so dependent on soil, crop and climate that an independent value is often needed for accurate interpretation of runoff studies. This is especially true if the data from a runoff study is to be used to calibrate a model for predictive purposes,

Laboratory adsorption/desorption studies

The sorption of a pesticide by soil controls its' leaching through soil by water and thus is an important factor in determining both leaching and runoff (ref. 2,3,30,76,77). The process may be approximately described as a single, reversible, dynamic, equilibrium between soil organic matter and soil moisture, leading to an expression for a "distribution equilibrium constant" K_d and a "soil organic carbon sorption coefficient K_{oc}:

$$K_d = \frac{[P_{soil}]^e}{[P_s]^e} = \frac{x/m}{[P_s]^e} = K_{oc} \times f_{oc} \tag{1}$$

where the quantities $[P_s]^e$ and $[P_{soil}]^e$ are concentrations, at equilibrium, of the pesticide x/m is mass of pesticides sorbed per unit mass of soil and f_{oc} s the mass fraction of organic carbon in the soil. The standard method to determine adsorption/desorption is by batch equilibrium and is well documented in OECD-Test guideline T.G. 106 (ref. 78,79). In theory K_{oc} is supposed to be independent of soils and one need only measure f_{oc} and use a published K_{oc}, but in reality this is not an accurate estimate. The comparison of sorption coefficient for the five different "Euro Soils" (ref. 80) indicates that for atrazine, for example, the normalization of K_d-values to the organic matter of the various soils leads to K_{oc}-values which differ up to a factor of 5. Hamaker et al. (ref. 80) and Kenaga and Goring (ref. 81) found a variation in K_{oc} values for nonpolar compounds within one order of magnitude. A comparison of the K_{oc}-values presented by Kukowski and Brummer (ef. 82) for polar compounds revealed a variance values of a factor of 40.

For hydrophobic compounds with van der Waals interactions and hydrophobic bonding as predominant sorption mechanisms, the variation in K_{OC}- value is within one order of magnitude. For more polar compounds, like amines, amides or carboxylic acids, the variation in sorption coefficients is up to two orders of magnitude. The sorption of amino-groups to clay minerals or pH-dependent sorption of acids play a key role. A normalization to the organic matter of the soil does not significantly reduce the variation in polar substances' sorption coefficients (ref. 83). Standard deviations in K_{OC} values are smaller if only agricultural topsoils are considered (ref. 84). For these soils, the organic matter composition and the humic acid fractions seem to be comparable. Nevertheless using four different agricultural soils a standard deviation of the measured K_{OC} values up to 50% was obtained (ref. 85) In summary, a specific site value for K_d is needed for an accurate analysis and modelling of the data .

Field half-life in soil

The rates of dissipation and degradation of a pesticide in the soil, at the soil surface and on foliage, are usually the most important sinks for a pesticide applied to a field. Such losses, prior to a runoff event, will strongly affect runoff losses. Each of these loss pathways can also involve several mechanisms of loss such as volatilization, photodegradation, and microbial metabolism. Even when the primary application target is foliage much of the pesticide will wash off the foliage on and into the soil where it can undergo all the processes of a soil-applied pesticide.

Data is required on metabolism in soils under laboratory conditions (i.e., at constant temperature and soil moisture), as part of basic data requirements for the active ingredient for pesticide registration In most countries. In theory one can apply such data along with known relationships between degradation rates and soil moisture and temperature (ref. 86-88) to estimate that part of degradation which occurs in the subsurface soil. Comparison of laboratory experiments with undisturbed soil columns under controlled conditions and outdoor plot or lysimeter experiments show that half-life values may differ by a factor of two to three even when temperature and soil moisture are controlled (ref. 89). Undisturbed small and large lysimeter experiments should be preferred if the behavior of pesticides in non-cultivated soils is examined (ref. 89). For testing the degradation and accumulation of relatively persistent pesticides the use of ^{14}C-labelled active ingredients offers the advantage of including the formation of nonextractable residues and the formation and leaching behavior of mobile metabolites. In a runoff study, monitoring residues of pesticides in all three compartments, in the field, is the only way to relate runoff losses to actual residues present.

Foliar wash-off

Foliar wash-off studies, in which the loss of foliar residues from individual crop leaves or plants is measured, may be necessary for full interpretation of runoff studies in which the majority of pesticide is applied to foliage. Foliar wash-off studies have been reviewed by Willis et al. (ref. 90), who have published the majority of the work in this area. There are, however, no examples of experiments where plant wash-off measurements have been combined with edge-of-field runoff measurements.

RUNOFF STUDIES AND COMPUTER MODELING

The use of computer simulation models to integrate and describe runoff data, and to extend that data to other conditions for a general pollution risk assessment. is a very active research area (ref. 11,12,26,27,48,58,91,92-101). Modeling can be utilized to deal with the problems associated with utilizing discrete field study results to predict behavior at other scenarios, scaling experimental data up to the field scale, and the whole question of environmental variability in general. Variability issues have been addressed elsewhere (17,91-93) and will continue to be refined as new and unexplored techniques revolving around surface runoff are implemented. Only through the use of modeling can the combinations of soil properties, climate, use patterns, and mitigation strategies be thoroughly investigated. As a result, field studies should be designed to measure and provide the necessary data sets for current and future runoff models. Data sets for model verifications will ultimately aid and expedite the model refinement process (or eliminate the use of a certain model for runoff predictions if deemed necessary).

The most widely-used computer model for runoff is GLEAMS (ref. 2) a continuous, daily-time-step simulation of edge-of-field losses in runoff water of pesticides, nutrients, and sediment from homogeneous agricultural fields. But there are many other computer programs which have routines which simulate runoff events with similar equations (ref. 5,60,61,95-100). Two significant problems when simulating runoff with most of these models are (a) the minimum time step of 1 day, which works reasonably well in simulating leaching processes but is too long in comparison with the hydraulic processes associated with runoff, and (b) the assumption of instantaneous equilibrium between soil and water for the pesticide. To accurately represent runoff processes it is becoming clear that a shorter time resolution is needed. There is currently a very large amount of research going on in this area, both in evaluating the limitations of current models, and in developing improved models. It is quite likely that model capability will improve greatly in the next few years (12, 98-100).

The interception of sprays by foliage needs to be better understood. Computer simulation models of runoff (specifically, GLEAMS, PRZM2 and USES) (ref. 2, 53, 101) requires a knowledge of the partitioning of a pesticide application between target foliage and the soil surface. GLEAMS provides a default value based on various scenarios (again based on Willis' and McDowell's work, ref. 90). Values currently being evaluated by German and the Dutch regulatory agencies are given in Table 1.

TABLE 1. ESTIMATED FRACTION OF SPRAYS INTERCEPTED BY CROPS (F_{int}) AND THE SOIL (F_{soil}) USED BY GERMAN (UBA) AND DUTCH (WVC) REGULATORS[a]

Crop	Growth stage	Target	F_{int}		F_{soil}	
			UBA	WVC	UBA	WVC
Potatoes, beets	2-4 weeks after emergence	Insects	0.2	0.2	0.7	0.7
Potatoes, beets	Mature	Aphids, diseases	0.8	0.8	0.1	0.1
Apple trees	Spring	1st scab spray	0.4	0.4	0.4	0.5
Apple trees	Full foliage	3rd scab-spray on	0.6	0.7	0.2	0.2
Peas	Shortly after emergence	Insects	0.1	0.1	0.8	0.8
Peas	At bloom	Insects, fungi	0.7	0.7	0.2	0.2
Maize	1 month after emergence	Weeds	0.1	0.1	0.8	0.8
Maize	Mature	Fungi	0.5	0.5	0.4	0.4
Grasses	Mature	Weeds, insects	0.5	0.4	0.4	0.5
Brassica crops	Mature	Insects	0.6	0.7	0.3	0.2
Onions	Mature	Fungi	0.5	0.5	0.5	0.4

[a] UBA: Umweltbundesampt, Berlin (J. Goedicke. private communication, 1994); WVC: Ministry of Welfare, Health and Cultural Affairs, The Hague (ref. 101).

CONCLUSIONS AND RECOMMENDATIONS

Four scales of pesticide runoff experiment have been defined: microplot, mesoplot, field, and watershed. Typical areas for these are 1-10 m^2, 0.1 ha, 1-10 ha and 10 ha to many km^2, respectively. All have in common (a) natural or constructed hydrologic boundaries defining the area generating the runoff (b) measurement or simulation of rainfall (c) measurement of runoff flow from the area, and (d) analysis of the runoff water for pesticide content.

These four scales differ but complement each other in terms of the information they yield and the difficulty of performing them.

The goals and uses of the different experiments described are well understood.

Microplots allow complete control of rainfall and most other variables and allow one to replicate and determine the relative response of pesticide losses to changes in variables, including rainfall characteristics, soil properties, and pesticide properties. However, microplot results are only representative of processes occurring at a point on the soil's surface, however, and thus are realistic only for very homogeneous situations such as soil-applied herbicides on flat soils. Since most current runoff/leaching models are also limited to one dimension, however, microplots are a logical choice for validating such models.

Mesoplots are simulated rainfall experiments which are on a plot big enough to plough and plant and simulate crop canopy processes. Less control of rainfall is possible (large water volumes are required and less control of rainfall intensity is possible), but mesoplots can provide, within a narrow range of storms, replicated representative data for most soil/crop combinations.

Field studies use typical agricultural fields (perhaps with some hydrological modifications for collection and routing of runoff), and undeniably provide data representative of natural conditions. But because such experiments represent the results of a highly complex and uncontrolled system, results are representative only of that system, or at least are difficult to extrapolate to other conditions. Replication is usually not done and often impossible. Published studies of this type has provided rules of thumb for expected losses of pesticides from fields for many situations

Watershed monitoring studies provide information linking edge-of-the-field runoff with water systems and thus the final link between processes and pesticide entrainment up in the field, and the resulting exposures of aquatic organisms.

The methods for these studies are well-developed

At each scale, procedures for measuring or controlling the important parameters needed to completely describe a runoff event, and the associated pesticide losses, are available and well-documented.

Interpretation of these studies, and the strengths and weaknesses of each scale, are understood.

Microplots are research tools especially useful for process investigations. There are a few simple situations where microplots may simulate real agricultural applications.

Mesoplots can simulate most real applications and provide cost-effective ways of determining the "reasonable worst case" runoff concentrations a pesticide may exhibit in runoff--they are recommended for research into larger-scale processes which effect runoff such as washoff, erosion control and tillage practices and also recommended for runoff exposure assessments.

Field-scale runoff experiments provide the ultimate tests for field-scale model validation, particularly when the model has been calibrated using smaller-scale data and when the reasonable worst case results of mesoplot tests need to be extended to full scale. They are too expensive and not informative for risk assessment when used alone.

Watershed and basin-scale monitoring projects are still needed to define the relationships between edge-of-field concentrations and concentrations in receiving bodies of water.

Recommendations for future research

1. There is a need for more experience with mesoplots--in particular their relationship and extrapolation, via models--to determine their limitations as simulators of real fields. Mesoplots are just beginning to be used and they are the least understood of the three scales. For example, there are differences between the rainfall generated for these studies and natural rain (e.g., drop size, angle of impact, tall plant interference), and the consequences of these differences for many aspects of pesticide runoff are not known.

2. *The ability of runoff studies of different scales to be coupled via modeling for accurate estimates of surface water exposure must be demonstrated.* The use of models to integrate information from runoff experiments of different scales is just beginning to be explored and is a major research need. For example, the suggestion that microplots may be used to calibrate physical processes and mesoplots may be used to validate models for worst-case conditions, and field data used to extend simulation results to the general case must be tested and refined with a wide range of models.

3. *Further research is needed to define the potential for small-scale experiments to substitute for larger scale studies for many purposes.* It is not clear at this point what the minimum scale for any pesticide runoff research problem is. Microplots may be used for many of the proposed uses of mesoplots, and mesoplots may fill some of the needs expressed above for fields and even for watersheds--for example, a mesoplot might be linked to a pond mesocosm to allow for controlled experiments on aquatic ecosystem fate and effects.

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