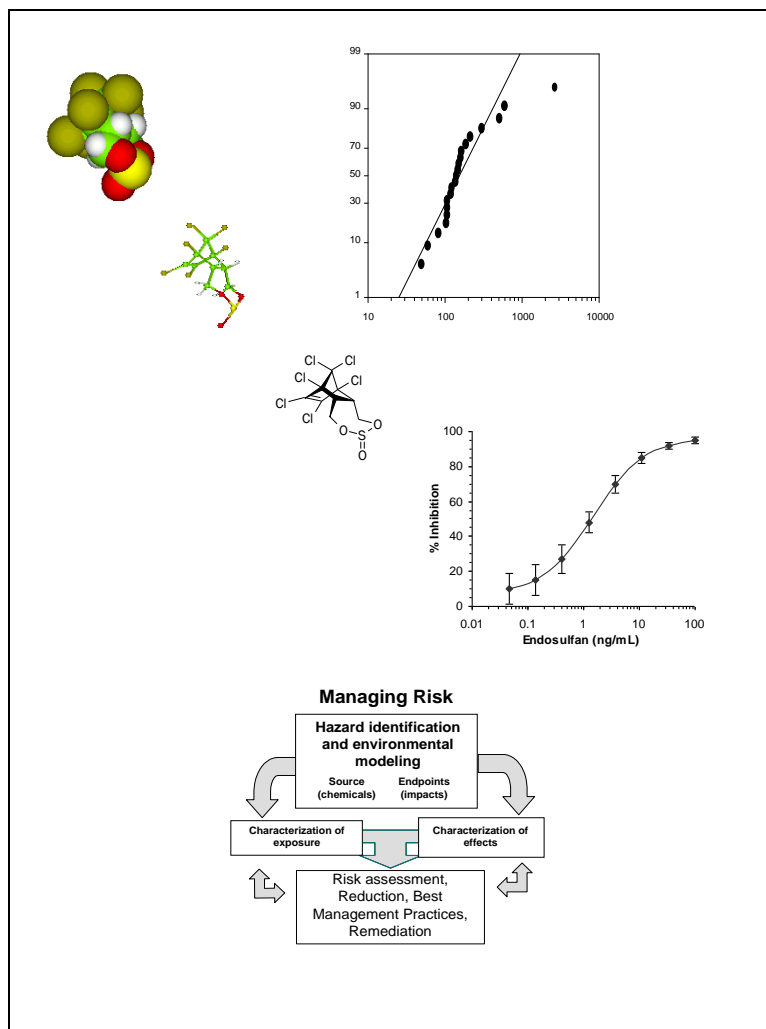


## TRANSPORT AND FATE OF AGROCHEMICALS IN THE ENVIRONMENT

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Refer to:

Ivan Kennedy, Angus Neill Crossan, Mitchell Burns and Yajuan Shi Transport and fate of Agrochemicals in the Environment in *Kirk-Othmer Encyclopedia of Chemical Technology*. Published Online: 15 Apr 2011, DOI: 10.1002/0471238961.trankenn.a01, John Wiley & Sons, Inc.

## **Summary**

Synthetic agrochemicals applied for pest control at high concentration sources in the environment inevitably disperse from these sites – an illustration of the second law of thermodynamics. They must dilute spontaneously, being transported into any available sinks in the environment, determined by all transport mechanisms available. These dispersing chemicals comprise a vast diversity of manufactured products considered essential for modern economic civilisation, largely based on the consumption of fossil fuels. Their life cycles all contribute to the challenges presented by global warming and climate change. Despite the need for environmental protection, it is certain that the agrochemicals known as pesticides will continue to disperse into ecosystems for reasons of global food security that are expected to intensify.

However, we now possess extensive information on the fate and transport of such agrochemicals. In this article, selected case studies using data generated in the past 20 years for a contrasting range of chemicals (DDT, endosulfan, diuron and glyphosate) will be used in illustration, suggesting operating principles for achieving rational environmental management. There is a clear need for all stakeholders including environmentalists, to take responsibility for monitoring agrochemicals, to better assess their risk and manage and minimise their consequences. The benefits from strong and rational stewardship, where manufacturers, regulators users and all those who benefit from their use promote rational management of these products needs clearer recognition by all. Such approaches could largely obviate the less rational precautionary approach.

# TRANSPORT AND FATE OF AGROCHEMICALS IN THE ENVIRONMENT

## 1. Introduction

Worldwide, the products of the chemical industry continue to play a major part in local and international trade. In recent years, the total international trade in manufactured chemicals has exceeded \$1.5 trillion, far greater than the value of international trade in agricultural products because of the large local consumption of food as well as the great diversity of such industrial products. Many of these chemicals are at risk of dispersion in the environment both in urban and in rural settings.

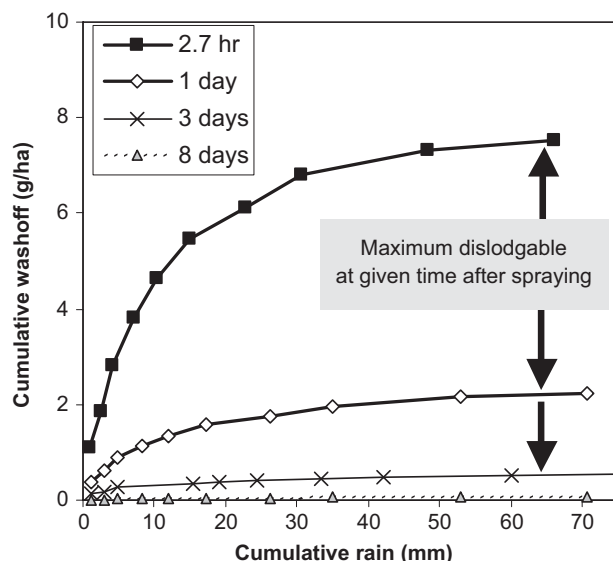
Agrochemicals for pest control continue to be employed in world agriculture because of the favorable cost–benefit ratio to farmers, although this analysis often does not assess environmental costs. Despite advances in integrated pest management (IPM) and the development of genetically modified (GM) crops resistant to insects, agrochemicals are certain to play a continuing role in ensuring world food security for the immediate future. Higher yields are needed to lessen the need for arable land, and agrochemicals are an essential component in reducing the risk of applying IPM. Critical situations such as those presented by swarms of plague locusts attacking crops or the need for long-term storage of grain still require the use of chemicals at least as a weapon of last resort. This article will examine how rational processes of risk management may achieve a satisfactory compromise between the continuing needs for agrochemicals and sufficient environmental protection. An ongoing action process is recommended that teaches how to improve management through experience rather than through the static precautionary approach.

## 2. Factors Affecting Environmental Fate

Once chemicals are applied to the environment, they have the potential to move from the site of application through various processes. Three mechanisms of transport have been identified as the most important, including runoff, drift, and volatile transport. The extent to which a chemical will be removed from the point of application depends on its physicochemical properties including fugacity (1), which affects partitioning into the various environmental compartments where impacts may occur.

**2.1. Surface Runoff.** Chemicals applied to crops and soils are more or less prone to transport in rain events, either dissolved in water or carried on sediments (2,3). Water soluble chemicals such as nutrients or polar organic compounds, including herbicides with low partition coefficient ( $K_d$ ) values for binding to soil or to soil organic matter, will be washed into runoff from plants (Fig. 1) and soils or leached into groundwater. Equally important is the binding of pesticides to soil. Table 1 shows the importance of variation in soil characteristics and the value of site-specific information that may influence the extent to which an agrochemical will partition to the aqueous phase (4). Site-specific information of this kind was incorporated into the environmental decision support

## 2 TRANSPORT AND FATE OF AGROCHEMICALS IN THE ENVIRONMENT



**Fig. 1.** Washoff of  $\Sigma$ endosulfan from cotton plants by rain four times after spraying.  $\alpha$ -,  $\beta$ -endosulfan isomers plus endosulfan sulfate are included (3). Endosulfan is rapidly degraded in plant tissues and foliage, but survives longer in soil.

tool named SafeGauge (5,6). It would be desirable if farmers everywhere—like those in Queensland—could access the georeferenced farm information available regarding soil types using the Internet and with this information select pesticides with less likelihood to run off in surface water.

Lipophilic compounds lacking sufficient polarity to dissolve rapidly will partition into water from soil to a lesser extent but can still become mobile when carried on suspended particulate matter (3) (see Fig. 2). The extent to which this occurs will be a function of the intensity of precipitation and the slope of the terrain, with the carrying capacity of runoff for insoluble chemicals and pesticides being a function of the inertial acceleration affected by the velocity of flow. However, pesticide residues tend to desorb from soil into water less strongly with time so that sediment control traps that slow the flow velocity can become more effective in resisting their transport in surface runoff.

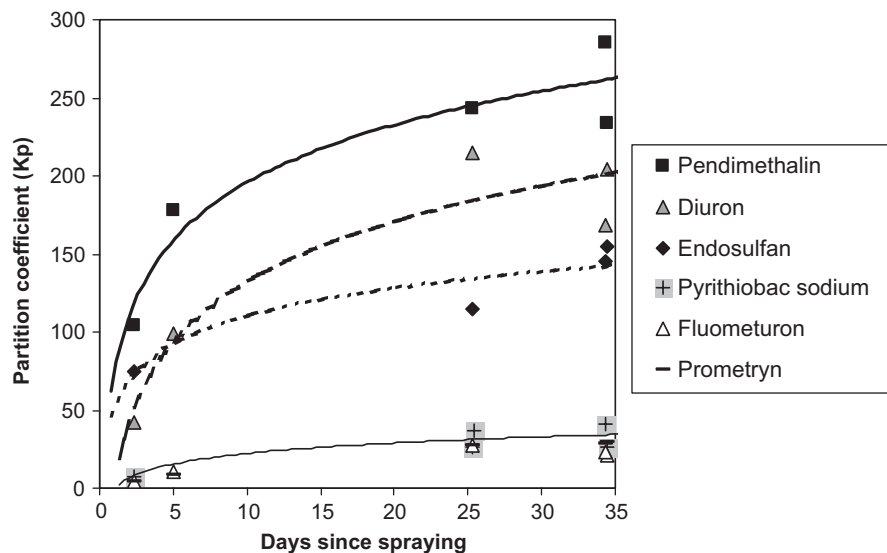
**2.2. Aerial Drift.** The physics of drift during application of chemical products is becoming better understood (7). The idea of providing buffer zones downwind that are adequate enough to ensure that hazardous exposures are minimized has gained acceptance as a best practice worldwide. Complete prohibitions on spraying when wind is either too slight or too great also is widely accepted, as is the greater risk of long-distance drift that occurs during atmospheric inversions, where there is a temperature gradient increasing with altitude. Application of agrochemicals using ground rigs rather than aerial spraying, including special devices such as directed or banded spraying or the use of hoods to prevent vertical dispersion, also has been widely adopted. Computer records of actual aerial conditions with the exact records of pesticides

Table 1. Soil/Water Partition Coefficients on Selected Sugarcane Soils (4)

Pesticide	Site	Yellow chromosol					Grey chromosol					Red chromosol					Redoxic hydrosol				
		Depth	0-2.5	20-30	30-50	0-2.5	20-30	30-50	0-2.5	20-30	30-50	0-2.5	20-30	30-50	0-2.5	20-30	30-50	0-2.5	20-30	30-50	
<i>diuron</i>	Kd <sup>a</sup>	12.1	18.4	18.4	5.2	27.1	21.8	51.8	27.3	15.6	5.4	39.3	17.6	11.6	39.3	17.6	11.6	39.3	17.6	11.6	
	Koc	1,270	2,170	2,170	867	3,390	2,420	7,400	2,220	1,320	635	5,460	2,440	2,320	5,460	2,440	2,320	5,460	2,440	2,320	
	% <sup>b</sup>	32.5	42.4	42.4	17.2	52	46.6	66.9	52.5	37.7	17.4	61.1	41.4	31.6	61.1	41.4	31.6	61.1	41.4	31.6	
<i>ethopropfos</i>	Kd <sup>a</sup>	5.8	4.0	4.0	6.3	12.4	9.9	12.8	10.3	12.4	12.8	10.3	11.4	11.4	10.3	12.4	11.4	10.3	12.4	11.4	
	Koc	611	471	471	1,050	1,550	1,100	1,830	1,430	1,720	1,830	1,430	2,280	2,280	1,430	1,720	2,280	1,430	1,720	2,280	
	% <sup>b</sup>	18.8	13.7	13.7	30.2	33	28.5	22.9	29	33.2	31.3	29	33.2	31.3	29	33.2	31.3	29	33.2	31.3	
<i>trifluralin</i>	Kd <sup>a</sup>	81.2	72.1	72.1	40.9	179	175	81.9	142	55.6	39.6	174	91	39.5	174	91	39.5	174	91	39.5	
	Koc	8,550	8,480	8,480	6,820	22,330	19,480	11,700	11,550	4,710	4,660	24,140	12,640	7,900	24,140	12,640	7,900	24,140	12,640	7,900	
	% <sup>b</sup>	76.5	74.2	74.2	62	87.7	85.7	76.6	85.1	69	64.5	87.4	78.4	61.2	87.4	78.4	61.2	87.4	78.4	61.2	
<i>atrazine</i>	Kd <sup>a</sup>	4.9	3.6	3.6	2.0	16.5	11	18	6.4	13.9	4.7	9.6	7.8	3.3	9.6	7.8	3.3	9.6	7.8	3.3	
	Koc	516	424	424	333	2,060	1,220	2,570	520	1,180	553	2,570	1,080	1,080	1,180	553	2,570	1,080	1,080	1,080	
	% <sup>b</sup>	16.3	12.7	12.7	6.9	39.8	30.7	41.9	20.3	35.2	16	27.7	23.8	11.5	35.2	16	27.7	23.8	11.5	11.5	
<i>desethyl-atrazine</i>	Kd <sup>a</sup>	11.5	12.3	12.3	11	19.9	16.1	22	12.5	5.7	13.2	5.7	24.8	13.5	5.7	24.8	13.5	5.7	24.8	13.5	
	Koc	1,210	1,450	1,450	1,830	2,490	1,790	3,140	1,020	34.6	1,550	792	3,440	2,700	34.6	1,550	792	3,440	2,700	2,700	
	% <sup>b</sup>	31.6	32.9	32.9	29.4	44.3	39.2	46.9	33.5	26.6	5.4	18.6	34.9	33.5	26.6	5.4	18.6	34.9	33.5	33.5	
<i>ametryn</i>	Kd <sup>a</sup>	8.1	8.3	8.3	4.8	22.2	15.2	20.1	8.2	26.6	5.4	12.9	9.1	4.4	12.9	9.1	4.4	12.9	9.1	4.4	
	Koc	853	977	977	800	2,780	1,690	2,870	667	2,250	634	1,730	880	880	2,250	634	1,730	1,260	1,260	880	
	% <sup>b</sup>	24.4	24.9	24.9	16.1	47.1	37.9	44.5	25	50.3	17.7	34	26.7	14.9	50.3	17.7	34	26.7	14.9	14.9	
<i>chlorpyrifos</i>	Kd <sup>a</sup>	114	71.4	71.4	37.1	341	175	149	195	153	54.2	195	54.2	54.2	195	54.2	54.2	195	54.2	54.2	
	Koc	12,020	8,400	8,400	6,180	4,270	19,430	21,240	27,130	21,320	86	88.6	86	68.4	27,130	21,320	10,840	88.6	86	68.4	
	% <sup>b</sup>	82.1	74.1	74.1	59.7	93.2	87.1	85.6	13.8	17.2	6.0	88.6	86	68.4	27,130	21,320	10,840	88.6	86	68.4	
<i>hexazinone</i>	Kd <sup>a</sup>	1.5	2.0	2.0	7.2	1.5	2.0	7.2	13.8	17.2	6.0	13.8	17.2	6.0	13.8	17.2	6.0	13.8	17.2	6.0	
	Koc	188	222	222	1,030	706	1,460	706	1,120	40.7	19.1	1,120	706	19.1	1,120	706	19.1	1,120	706	19.1	
	% <sup>b</sup>	5.7	7.3	7.3	22.3	35.6	40.7	19.1	35.6	40.7	19.1	35.6	40.7	19.1	35.6	40.7	19.1	35.6	40.7	19.1	

<sup>a</sup>Determined using 20g soil/L equilibrated for 30 min (2 days after pesticide application).

<sup>b</sup>Percent of pesticide remaining on sediment.



**Fig. 2.** Partitioning of pesticides between water and sediment in runoff from rainfall simulator plots, increasing at various times after application.  $K_p$  values for desorption measured in runoff are generally greater than  $K_d$  for sorption to soil (3).

applied on the flight path provide quality assurance in regard to compliance with environmental safeguards and their use is to be encouraged. Despite these precautions, drift remains a significant cause of distant transport from the site of application, sometimes with significant impacts on other crops or ecosystems.

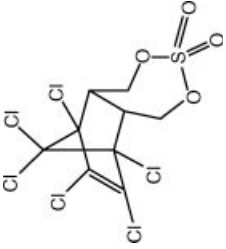
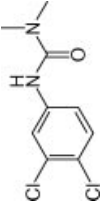
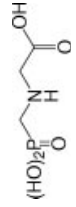
**2.3. Volatile Transport.** For volatile chemicals, there is the added hazard of vaporization and transport of chemicals downwind in the atmosphere. This is considered a feature of the class of persistent organic pollutants (POPs) that include dichlorodiphenyl trichloroethane (DDT), one of Rachel Carson's (8) main subjects in *Silent Spring* published in 1962. Several other compounds have been added to the list of POPs that the Stockholm Convention (9) seeks to ban, with one of the most recent listings being endosulfan (see Table 2, 10–19). The reputed capacity of endosulfan for long-distance transport as vapor, even to the Arctic, is a direct result of its volatility. Its relatively high Henry's coefficient (10) indicates that it potentially can distill from contaminated water traveling aerially on wind some distance from its point of application. Endosulfan may be one of the most studied chemicals in the environment because of its scale of use and high hazard rating resulting from its significant toxicity to aquatic organisms. As a result, it is possible to perform risk assessments more readily than with less studied chemicals, and a focus on this chemical has been included here as a result.

For each of these mechanisms of agrochemical transport from their sites of application, the physical and chemical properties of each chemical are expected to exert a significant role. A complete review of the environmental fates of hundreds of agrochemicals would be impossible in this chapter. Instead, selected

Table 2. Physicochemical and Other Properties of Selected Agrochemicals

Property	Molecular structure	MW	Vapor pressure (Pa)	Henry constant (Pa·m <sup>3</sup> /mol)	Water solubility (mg/L)	logK <sub>ow</sub>	logK <sub>oc</sub>	Typical half-life(days)	Other comments	Reference
DDT (dichlorodiphenyl-trichloroethane)		354.5	$2.5 \times 10^{-5}$		Negligible <0.01, 25°C	6.91		Ca. 3000-5000	insecticide banned for agriculture	(10) (11)
DDE (dichlorodiphenyl-dichloroethylene)										
$\alpha$ -endosulfan(see text); commercial product is 7:3 $\alpha$ - $\beta$ isomer		406.9	$8.3 \times 10^{-4}$ $4.4 \times 10^{-3}$ $1.33 \times 10^{-3}$	1.48 0.70 1.0	0.32	4.74 4.49 3.83	3.6 3.55	2-3 field water 5.4 field soil	insecticide banned in many countries	(10) (12) (13) (14,15) (16)
$\beta$ -endosulfan (conformer in sulfite ring)		406.9	$8.3 \times 10^{-4}$ $4 \times 10^{-3}$ $1.33 \times 10^{-3}$	0.07 0.045 1.93	0.33	4.79 4.78 3.52	4.3	1-2 field water 30.4 field soil	insecticide banned in many counties	(10) (12) (13) (14,15) (16)

Table 2. (Continued)

Property	Molecular structure	MW	Vapor pressure (Pa)	Henry constant (Pa·m <sup>3</sup> /mol)	Water solubility (mg/L)	logK <sub>ow</sub>	logK <sub>oc</sub>	Typical half-life(days)	Other comments	Reference
endosulfan sulfate		422.9		ca. 0.015	0.22	3.64 3.66	3.2	30 field water 97-160 field soil	metabolite Fm + degrdn. Fm + degrdn	(12) (13) (12) (16,17)
diuron(3-(3,4-dichlorophenyl)-1,1-dimethylurea)		233.1	1.1 × 10 <sup>-6</sup> 25°C	7 × 10 <sup>-6</sup>	36.4	2.85		100-134 field soil	herbicide inhibiting photosynthesis	(10) (18)
glyphosate(2-(phosphonomethyl)amino)acetic acid)		169.1	2.59 × 10 <sup>-5</sup> 25°C	1.41 × 10 <sup>-5</sup>	11,600 25°C	-2.6	3.3	3-174 field soil, mean = 32 soil geometric mean = 17 < 14 field water	herbicide inhibiting aromatic synthesis in plants	(10) (19) (19) (19)



case studies involving DDT, endosulfan, glyphosate, and diuron have been chosen to illustrate a range of different behaviors. Table 2 illustrates these contrasting behaviors, which can easily be related to factors such as volatility, water solubility, extent of partitioning into hydrophobic phases, and environmental half-life.

### 3. Factors Affecting Environmental Exposure

The extent to which a chemical will contaminate a nontarget ecosystem through transport processes is a function of the chemical load available for transport, which is affected by the rate of local degradation of a chemical. This factor is often characterized as the time taken in an environmental compartment such as soil or water for the chemical to be reduced to half its current value. Several environmental factors influence the half-life of a chemical at the site of application, which the following section describes.

**3.1. Half-Life.** Most chemicals follow a pattern of dissipation or degradation in which this value falls exponentially, suggestive of zero-order decay patterns like radioactivity. However, the half-life estimated for agrochemicals is far from a constant number from one site to another or even from one time to another, and it can be expected to vary significantly with the environmental conditions. Factors that influence the rate of degradation such as temperature, light intensity varying with latitude, soil properties such as pH values, and organic matter content as well as biological factors such as crop species and the presence of other biota and soil microorganisms collectively control the rate of degradation. Thus, the actual half-life that may be measured also will vary from site to another. Published estimates of half-life inevitably require some consideration of site-specific conditions—edaphic or environmental—to be understood properly.

The apparent half-life in a particular location or environmental compartment will be influenced by factors such as dispersion by transport away in runoff or vapor because its measurement is taken by measuring the rate of decline in local concentration in matrices such as soil and water. Field measurements in soil and water may yield data in poor agreement with values established under controlled conditions in the laboratory. Environmental factors such as high temperature pulses, wind intensity, and heavy rainfall events all contribute to this variability. Thus, the value obtained for the half-life is not restricted to the rate of formation of its specific degradation products, as might be inferred. Factors such as volatilization or stronger binding to the soil matrix with time as noted previously for sediment in runoff (see Fig. 2) all can increase the rate of dissipation without degradation being involved (18). Variations in half-life data can be explained in terms of these varying factors, and they should be analyzed with these factors in mind. However, data that is not consistent with the general principles involved should be regarded as anomalous and given less weight.

**3.2. The Need for Monitoring for Effective Risk Management.** The importance of adequate monitoring for proper risk assessment hardly can be overemphasized. The invention of the electron capture detector (ECD) with its

## 8 TRANSPORT AND FATE OF AGROCHEMICALS IN THE ENVIRONMENT

high sensitivity for organochlorines by the British chemist James Lovelock in the 1960s had major impacts in this area. Until this highly sensitive detector became available to conduct analyses of extracts of soil and water, the fate of chemicals like DDT was purely speculative because the existing methods of analysis were so insensitive, based on thin-layer chromatography and simple chemical tests. For successful monitoring, the ECD was a remarkable boon, enabling vast increases in our knowledge of the fate of organohalogen compounds of all kinds. The success of the Montreal Protocol of United Nations Environment Programme (UNEP) (20) in reducing the impact of the fluorinated organochlorines on the ozone layer can be attributed to Lovelock's invention and to the subsequent ease of analysis of these compounds.

The development of other technologies such as gas and liquid chromatography coupled with multidimensional mass spectrometry in the 1990s has dramatically increased the capacity to identify and analyze organic chemicals in the environment and to know their fate. These developments have allowed for the study of trace quantities of highly toxic compounds such as the dioxins and have enabled multiresidue analysis of entire classes of compounds (eg, organochlorines, organophosphates, pyrethroids, and triazines) to be achieved. This has increased the knowledge of these compounds tremendously, leading to the success of national surveys for the analysis of agricultural produce and other multiresidue programs in regard to food safety to be achieved. However, such analyses remain beyond the reach of many, given the high cost of equipment and of maintaining associated analytical services.

The continuing development of lower level laboratory technologies, such as better methods of sampling extraction (solid phase extractors, passive membrane devices, and microwave techniques) and enzyme-linked immunosorbent assay (ELISA) for compound and class-specific analyses of environmental and food contaminants (21), should not be overlooked. The latter technique requires the synthesis of mimics of contaminants, their attachment to larger proteins, and the raising of specific antibodies in rabbits or other species to prepare a multiwell ELISA plate. ELISA takes many forms, but the competitive assays for pesticides are often just as sensitive as the more sophisticated analytical techniques and their ability to generate data quickly and closer to field sites can be a decided advantage. As a result, they can have even more accuracy (as opposed to precision) than the more expensive methods, as was shown with endosulfan analysis in a field laboratory (22).

However, it might be necessary to continue developing these simpler analytical technologies. Specific biosensor platforms for the rapid analyses of a wide range of analytes have been promised for some time but continue to be elusive, except in a few specific cases (23). Recently, practical rapid immunotests based on liquid flow in plastic cassettes functioning like pregnancy tests are becoming available (24). Unlike ELISA, these rapid tests require no special skills on the part of the user other than the ability to follow simple instructions. The emergence of such rapid tests for water and other media can enable better stewardship of chemicals and reduce the degree of speculation that currently exists about the degree of contamination of produce and the environment. Once these become available for the broader range of possible contaminants, more responsible stewardship should become possible.

#### 4. Improving Methods of Risk Assessment

By acknowledging the potential for chemicals to be transported from their point of application, the need for industries to manage the consequences has become more obvious. A developing approach for managing these concerns is the investigative framework known as ecological risk assessment (ERA). Using a tiered process with increasing levels of rigor, decisions can be made for managing a chemical even under significant uncertainty. Importantly, the ERA approach allows for management strategies to be developed pending the outcome of the assessment. Furthermore, a dynamic feedback system responding to changes in the risk profile over time allows management strategies or concerns to be addressed. An important feature of ERA is that chemical management can be optimized in response to actual risk situations and that strategies to manage risk can be reviewed continually.

Competing with ERA is the precautionary principle that threatens to limit the potential of agrochemicals to enhance productive capacity by taking the viewpoint that any uncertainty is considered risky enough to restrict use severely. In this section, we will critique the precautionary principle, providing a better alternative with several more rational approaches to risk characterization applied at different scales in several case studies. There will also be special reference to developments in genetic modification and the implications that this technology has for reducing risk, despite opposition by many advancing the precautionary principle.

*A Critique of the Precautionary Principle.* Although lauded by some and suggesting a responsible attitude, the use of the precautionary principle (20) actually may lead to unintended consequences causing greater risk. The principle states that the proponents of a particular action or applied technology are required to establish that it will not result in significant harm. Here, the opinion is that we often might do better, even for environmental protection, without it. Civilization usually has advanced by taking calculated risks and measuring the consequences. Although taking sensible precautions to help ensure safety is obviously a sensible course, banning agents or actions simply because there is a lack of evidence that they can be applied safely amounts to a decision for inaction. Inaction carries its own risks and even may allow for harm by encouraging human inertia or preventing access to new, safer alternatives. The widespread acceptance of the precautionary principle extending even to its enshrinement in law (as in the European Union) is surprising, displaying an extreme conservatism. Unfortunately, the principle may encourage decision makers or regulators to act without due effort to establish the factual evidence or to analyze it adequately, justifying regulatory inaction and effectively sanctioning prohibition. In addition, inherent risks in application of the precautionary principle include better measures to manage chemicals that fail to develop or fall into disuse. Worse, harmful effects can result from the action of banning when chemicals with unknown or worse effects take their place. The performance of rational risk assessments would be far better, which include an estimate of the unintended consequences of phasing out the use of a chemical; this would be best achieved as part of an overall action that allows for the substitution of alternative technology only when it can provide the desired result

with less risk overall. However, it is extremely rare for the latter to be included in proposals when the precautionary principle is invoked. Unfortunately, it may encourage an attitude of disengagement.

Nevertheless, significant benefits to the global ecosystem have resulted from banning chemicals prescribed by the *Montreal Protocol on Substances that Deplete the Ozone Layer* (20) in 1987. Here, chlorofluorocarbons used as refrigerants and other halons such as carbon tetrachloride were replaced with effective alternatives already known to be safer in use, shown to be less capable of destroying the ozone layer. As a result of the banning, the ozone layer is now regenerating and is expected eventually to reach its historical levels. Similar benefits also have been achieved with the hazards resulting from the use of motor vehicles, such as the introduction of seat belts, inflatable air bags, and collapsible body sections. These precautions have resulted in marked decreases in the mortality and injury rate suffered by those driving motor vehicles. But in all these cases, a causal relationship has developed between the hazard and the solution directly allowing for reduction of the risk.

## 5. Lessons from Case Studies

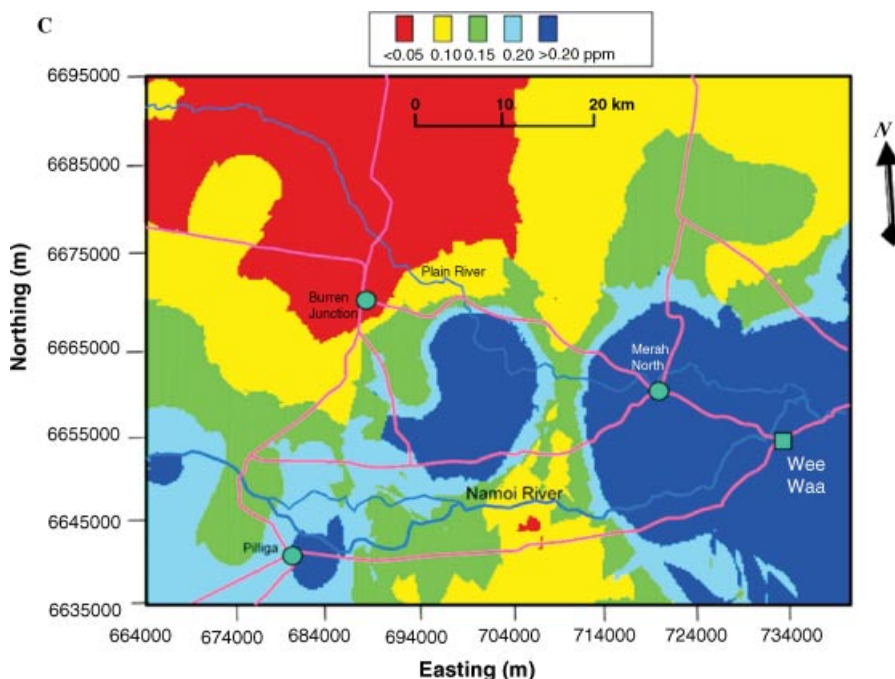
**5.1. Case 1: DDT and Its Environmental Consequences in New South Wales.** Notorious when singled out for special attention in Rachel Carson's *Silent Spring* (8), DDT initially had been hailed as a savior of millions of human lives because of its effectiveness in combating the larvae of the *Anopheles* mosquito acting as a vector for malaria. An early candidate for restricting its use or for banning it, DDT remains in use for medical purposes as required by the World Health Organization (WHO), although it is no longer allowed in agriculture or forestry. This decision was based on its capacity for long-distance transport from the tropical regions where it was mainly applied to higher latitudes of the Arctic and the Antarctic (25). At one stage, significant concentrations of DDT residues as the primary compound, or its breakdown products dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD), were found in the body fat of most humans, given its ubiquitous pattern of use up to the 1970s. After the invention of the ECD detector, the ease with which DDT could be measured at high sensitivity ensured that this occurrence of residues would become well known. Coupled with the demonstration that DDT could directly interfere with the biosynthesis of the egg shells of birds, this demonstration was sufficient to ensure that the use of DDT would soon be restricted (25). Residue levels greater than 10 ppm ( $\text{mg kg}^{-1}$ ) in the fat tissue of pregnant women, largely because of the degree of contamination of food ingested rather than that in water or air (25) were alarming.

Kenaga (26) had drawn attention to the problem of bioconcentration of DDT in biological organisms after exposure or ingestion, resulting in "an increased concentration of the pesticide by the organism or specific tissues." This is possible as a result of differential solubility in different tissues and, in the case of DDT, much greater solubility in lipids. The uniquely large value of the log Kow of DDT shown in Table 2 is indicative of this high solubility in fat and extremely low solubility in water. The use of DDT as an agricultural pesticide was abruptly

discontinued in the United States in 1972, 10 years after the publication of *Silent Spring*, public outcry and a government agency review (25).

Banned in New South Wales 10 years later in 1982, the soils of northern river catchments in this Australian state still contain significant concentrations of DDE, a product of aerobic dehydrochlorination of DDT. By the time of the ban, DDT had proven to be increasingly less effective as an insecticide given the widespread development of genetic resistance by pests. But these residues of DDT and its metabolites can still be found in the range 0–2 mg per kg (ppm) in soil, as shown by geographical information systems (GIS) mapping residue concentrations (see Fig. 3) conducted in 2002 (27). DDE residues, like DDT, are extremely insoluble in water and are strongly bound to the soil organic fraction with a moderate vapor pressure and, as a result, strongly contribute to these residues with a low bioavailability. Similar DDT residues remain all around the globe, largely as DDE strongly bound to soil organic matter, and will do so for many years, given the average half-life of  $\Sigma$ DDT residues of 10–20 years. In urban areas, residues of DDT and its metabolites still can be present at much higher concentrations at manufacturing sites where they occur at greater depths in soil (28,29).

For the most part, DDT residues are so strongly distributed into hydrophobic materials, such as nonpolar organic matter or lipids, that their transport other than suspended in transported soil is minimal. Nevertheless, these



**Fig. 3.** GIS distribution of DDE residues in Namoi Valley topsoil. Riverine vertisols where cotton was first grown at Wee Waa contain up to 2 mg DDE per kg of soil, and it seems that residues are barely moving from the sites of application from more than 20 years ago.



properties did not prevent measurable quantities from migrating to higher latitudes through the food chain and perhaps slowly in the vapor phase at low concentrations (30). So the degree of hazard they currently present to biota and humans in these catchments can be considered low but, unfortunately, has some ongoing risk of exposure to susceptible species with selective nutrition in soil. Analysis of the stomach contents of birds that was undertaken to sample their diet nondestructively (31) showed that soil insects do contribute to an ongoing source of exposure with evidence of some bioconcentration of DDT + DDE, but less so for endosulfan, despite its use current at that time. All these data were obtained using monitoring based on the application of specific ELISA methods. This procedure is relatively inexpensive, allowing for numerous field samples to be analyzed quickly. Few if any other GIS studies have been conducted. In the case of DDT, these residues are long lived in soil with apparent half-lives of 10 years or greater; no special precautions in regard to the cold storage of samples are necessary to conduct analyses given the slow rate of change in ambient conditions. This factor contrasts strongly with other polychlorinated organic compounds such as endosulfan, which degrades fairly rapidly in subtropical regions with an apparent half-life of about 2–3 months. Nor does endosulfan accumulate in body fat.

Many environmentalists had expected to see the discontinuation of DDT much sooner. However, the failure of most other possible methods of mosquito control with chemical agents such as *Bacillus thuringiensis* toxins has meant that the WHO has continued to seek exemptions for targeted applications of DDT in malaria-prone regions. Thus, DDT residues on occasion can still be found at detectable levels in newly grown agricultural produce in Southeast Asia where malaria is sometimes endemic (32). The Stockholm Convention of United Nations Environmental Program (UNEP) now has a revised intention to phase out the use of DDT by 2020, assuming that suitable alternative insecticides will have become available by then, although that seems unlikely without special funding on a large scale. A vaccine solution to malaria is more likely or through some other agent by controlling the life cycle of the malaria parasite causing the condition rather than the *Anopheles* mosquito that merely acts as a carrier from infected humans to those without the disease.

Given the low volatility and other special qualities of DDT of value in combating the mosquito larvae and its use as a surface film that make it ideally suited for this purpose, one might question the intention to ban this chemical completely. It is now employed at a minute fraction of the former annual rate of application to water, and much protection is currently given using the pyrethroid permethrin impregnated into mosquito netting.

Because the total environmental risk is a direct function of global exposure to a chemical, perhaps DDT now can be managed safely enough that an objective risk assessment free of emotion would show that it is the most beneficial means of malaria control available. Resources to protect nontarget species can readily be increased as needed and can strictly restrict any future legacy of environmental harm from DDT. These resources should include facilities for monitoring to verify that protection is being achieved at an acceptable level. Fortunately, in the case of DDT for the future protection of human lives (25), the strict precautionary principle was not applied when DDT was introduced. But it must be

admitted that the emergence of the electron capture detector and the ability to analyze organochlorines like DDT easily has provided important lessons about the fate of chemicals in the environment. Provided the responses are limited to rational, nonhysterical, responses, these lessons have an important role to play that the Stockholm Convention should strive to apply. These social-welfare issues will be discussed in the following case study of endosulfan.

**5.2. Case 2: Endosulfan.** This toxic polychlorinated insecticide affecting the  $\gamma$ -amino butyric acid (GABA) inhibitory function of neurotransmission in insects, a central nervous system function, initially was manufactured in Germany by Hoechst in 1954 registered as Thiodan. It largely replaced the use of DDT worldwide when that organochlorine was banned for application to food and fiber crops from 1972. Recently, endosulfan (6,7,8,9,10-hexachloro-1,5,5a,6,9,9a-hexahydro-6,9-methano-2,4,3-benzo(e)-dioxathiepin-3-oxide) was listed by the Stockholm Convention of UNEP as a persistent organic pollutant, and its worldwide banning is now being promoted by the convention but with resistance in some countries where its effectiveness and low cost is considered worth the risk. Endosulfan has significant volatility and no doubt owes part of its success as an insecticide to its resultant fumigant action, which can exert effective control of grubs and caterpillars consuming vegetation. It is also relatively nontoxic to beneficial arachnid predators and bees and was widely used in the Australian cotton industry to help provide a resistance strategy allowing other insecticides such as pyrethroids to be used selectively for shorter periods during the crop cycle. Its specific toxicity to higher animals including fish is largely based on its inhibition of neurofunction, and it has little or no effect on soil respiration by microorganisms (33). In the early 1990s, annual Australian applications of endosulfan were significantly more than 500 tons, but with the introduction of genetically modified cotton, the need for this chemical has sharply declined in the past 10 years to less than 10% of this quantity, dependent on weather and insect pressure. Given that it controls a broad range of pests (eg, *Helicoverpa*, green mirid, aphids, and green vegetable bug), has only a moderate effect on beneficial insects, and forms a distinct mode of action chemical group, it is an important feature for insecticide resistance management strategies, these rely on the rotation of chemical modes of action, and the cotton industry is reluctant to lose access to endosulfan, which is still regarded as an essential component of IPM.

**Persistence.** Endosulfan also contrasts to DDT in its lack of persistence in the environment, particularly in warmer climates. Table 2 contains a listing of typical half-lives, recorded as a function of ambient temperature or latitude and other conditions. The available data on half-lives have been assessed for quality or any special conditions that make them exceptional. Based on these studies, the most probable values could be calculated for  $DT_{50}$  values at different latitudes. It would be possible to estimate values for the current scale of use in different temperature regimes to produce a value indicative of actual half-life values in the field. Such values focus on reality rather than on the exceptional values or worst-case values for which the risk is small or even nonexistent under defined conditions of use. Table 2 shows that its half-life or that of its minor degradation products can be extended under cold conditions or in dry soil to meet the criterion of a half-life greater than 6 months in soil; its

environmental persistence has been exaggerated without justification so that it can be considered a POP (34).

Endosulfan is relatively stable under acid conditions of low humidity at low temperatures such as in a refrigerator—a conclusion that could be made for many chemicals considered labile in ambient conditions. But under other extreme conditions, endosulfan can be completely detoxified in a few minutes at pH 10 or in several hours at pH 9 by hydrolysis to nontoxic endosulfan diol in dilute  $\text{Na}_2\text{CO}_3$  solution, an unpublished method we favored for easy destruction of endosulfan in the laboratory.

At this pH, endosulfan has a half-life of a few minutes only and even endosulfan sulfate almost completely disappears in 2 weeks in sterile water at this pH value. With microorganisms often present that can use endosulfan or endosulfan sulfate as a biological source of carbon and sulfur (35), the eventual degradation even of the longer lived endosulfan sulfate in soil is assured, reflecting field experience in northern Australia. In studies on estuarine mesocosms (15), half-lives of 25.1, 27.6, and 29.3 h were recorded for  $\beta$ -endosulfan, technical endosulfan, and  $\alpha$ -endosulfan, respectively. In the case of  $\alpha$ -endosulfan, differences in volatility may have contributed to these losses because only 56.5% of this isomer was recovered in a mass balance. By contrast, less than 20% of  $\beta$ -endosulfan was lost by volatilization, with the shorter half-life comprising mainly degradation in the aqueous system to endosulfan diol, whereas  $\alpha$ -endosulfan formed endosulfan sulfate as the main initial product at three times the rate before being converted to endosulfan diol. Endosulfan diol from  $\alpha$ -endosulfan then was rapidly degraded to endosulfan ether, with endosulfan  $\alpha$ -hydroxyether as the main product, confirmed by nuclear magnetic resonance, and endosulfan lactone. However, the latter was a product only under acid conditions below pH 5.7, the  $pK_a$  of endosulfan  $\lambda$ -hydroxycarboxylate. With a  $\log K_{ow}$  of only 2.6 (36), similar to diuron (Table 2), it is unlikely that this relatively polar substance would be noticeably toxic, although this needs confirmation.

In crop or horticultural plants (see Table 2), endosulfan has been regarded as degradable and nonpersistent, even as the product endosulfan sulfate. It has normally been applied to many crops and subject to strict withholding conditions before being consumed by humans or livestock; although, recently, its use has been restricted because of its direct human toxicity although not carcinogenic nor teratogenic. The typical length of half-degradation ( $DT_{50}$ ) of endosulfan isomers plus endosulfan sulfate is 4.6 days for tomatoes, with the beta isomer persisting longer (36)—a finding also observed in cotton leaves (37). Endosulfan and endosulfan sulfate were largely degraded in the foliage of cotton plants within 2 weeks of exposure, where  $DT_{50}$  values of 14.5 and 19.8 d were observed for  $\alpha$ -endosulfan and  $\beta$ -endosulfan, respectively, and 15 days was observed for endosulfan sulfate (37).

Endosulfan and its breakdown products including endosulfan sulfate have been regarded for a long time as only mildly persistent in higher animals, with extensive feeding studies in a large range of species showing that it is almost completely eliminated from all body tissues about a week after exposure ceases in contrast to DDT (38,39). Thus, there is no evidence of significant bioaccumulation in animals or plants unless there is ongoing exposure from substantial sources. For this reason, depuration of contaminated shellfish can be readily



achieved when the source of contaminated water is removed (38). This is expected on physical and thermodynamic grounds, given endosulfan's relative solubility in water compared with DDT and the fact that enzymes for degradation of both endosulfan and the sulfate are widespread (35), with potential use in bioremediation products. Such useful detoxification agents do not exist for DDT.

*Bioconcentration.* Despite claims to the contrary, endosulfan is only subject to bioconcentration on a transient basis while exposure continues. Certainly, endosulfan can concentrate in biota in response to high environmental concentrations in water, as is obtained in the short term in closed systems. But nearly all bioconcentration of endosulfan is transient, and concentrations fall rapidly when the source is removed and metabolic degradation occurs.

It is unlikely that bioconcentration ratios much higher than 1000 would ever be obtained in the field except at the site of application because endosulfan's relatively high solubility in water ensures that it will be eliminated fairly rapidly. Proving this, animals exposed to endosulfan at moderate or low levels accumulate it in their tissues up to a plateau level, but residues decline quickly once the exposure ceases (38,39). Shellfish exposed in aquaria to endosulfan also can be depurated rapidly with fresh water. These rapid declines also reflect the metabolism of endosulfan and its excretion largely as endosulfan diol. This is not the behavior expected of compounds capable of bioaccumulation like DDT.

*Long-Range Transport and Ecological Effects.* Long-range transport of the endosulfan isomers (but not endosulfan sulfate, which is 100 times less volatile (40)) is certainly possible, but its environmental impact is not clear. Low concentrations near the limits of quantitation may be detectable in biota in Arctic regions or in cooler mountainous areas. However, such observations probably result from fairly local use of endosulfan and are captured at the lower temperatures involved. Clear evidence for the substantial long-range transport of endosulfan to the Arctic or Antarctic from endosulfan's main areas of application does not exist as was obtained for DDT. Data from the northern hemisphere (12) of contamination of water and biota was considered to be a result of transport near the point of application. It would be of great interest to test the hypothesis of long-range transport of endosulfan in the Southern Hemisphere where the areas of application in Africa, Australia, and South America are much further from the biota hypothesized to be at risk. Few if any data are available for the Southern Hemisphere showing such long-range aerial transport; this is an unresolved challenge to the Stockholm Convention's listing of endosulfan.

Endosulfan is rapidly degraded to several products formed in soil or water such as equally toxic endosulfan sulfate, lactone, nontoxic endosulfan diol, hydroxyether, and carboxylic acid. Although the toxic endosulfan sulfate formed by microbes is a significant proportion of these products (16), with a longer half-life and similar toxicity (41), the other products, even including the moderately toxic lactone, are extremely small proportions of the initial total mass of the endosulfan applied. They are almost irrelevant in a properly weighted analysis with mass balance. Endosulfan diol is relatively nontoxic from feeding studies, as would be expected from its highly polar structure, and should barely be considered at all.

From analytical experience with applying endosulfan in the field for cotton production (16), it is extremely difficult to recover these minor products other than the sulfate from soil at levels much higher than the limit of quantitation. In any case, the likelihood that they will be transported from the site of application is negligible. All these products are orders of magnitude more polar than the endosulfan isomers and should be firmly bound to soil humic substances by a combination of hydrophobic and polar forces such as H-bonding. This is supported by data examining the extent of preferential flow of pesticides in a Brazilian oxisol (42). They are all relatively nonvolatile by two orders of magnitude, and risk that they will have significant transport causing significant exposure and toxic effects elsewhere is negligible.

Despite endosulfan being applied up to five times each season (3.6 kg ai. per ha per year) for growing cotton in the northern river catchments of New South Wales, totaling more than 50 kg per ha over a period of 20 years, no accumulation of the products of endosulfan greater than about 50  $\mu\text{g}$  per kg of soil, including the more toxic lactone, could be recorded (16). It is anticipated that endosulfan diol would be the main immediate end product, probably conjugated in more water-soluble products or incorporated into humic materials as a result of free radical reactions in soil. Certainly, significant quantities of the hexachlorocyclonorborene rings on which endosulfan is based linked through ester bridges would be expected to persist in some form in these soils. But these derivative polychlorinated products would exist in a highly immobile form firmly incorporated into the soil matrix, presenting little or no environmental risk.

It is surprising that the same endosulfan that was used so extensively in Europe for several decades should now be considered as persistent, bioaccumulative, and too toxic to use. In fact, there are no known cases of accidental effects on human health in Australian experience, where the chemical has been well managed by the Australian Pesticide and Veterinary Medicines Authority (APVMA).

A recent review (12) considering the fate of endosulfan in the Arctic clearly did not establish either endosulfan and its main breakdown product or endosulfan sulfate as POPs. However, it concluded that endosulfan might be considered as marginally fulfilling some criteria under the UNEP Stockholm Convention. They pointed out that recorded aquatic half-lives (41,42) "are much lower than the persistence criteria designated for a POP (i.e.,  $t_{0.5} = > 2$  months)." The authors use of the term "recalcitrant" with reference to the more stable endosulfan sulfate as possibly being ill-advised, as this compound can be biodegraded rapidly within days or weeks in higher biota and under some environmental conditions (eg, in plant tissue or alkaline soils). However, it is more persistent than the parent  $\alpha$ - and  $\beta$ -isomers, but their claim that Kathpal and co-workers (44) found a "long half-life of greater than 200 days in a sub-tropical agricultural soil in northern India" is clearly an error resulting from misreading Kathpal and co-workers' paper. In fact, the observed biphasic half-lives for  $\Sigma$ endosulfan including endosulfan sulfate were much shorter, less than 100 days (in their Table 4), with the dissipation of total residues actually reaching 99% after 238 days.

They also found little if any evidence of trophic magnification of  $\alpha$ -endosulfan in well-defined marine food webs with some evidence of a lower concentration

at higher trophic levels—obviously a result of increased metabolism. Also, neither the isomer nor the sulfate meet the UNEP criterion (9) of  $\log K_{ow}$  less than 5, although they do lie just beyond an order of magnitude below it in the range 3.8–4.9 (see Table 2). Endosulfan also does not clearly meet the criterion regarding half-life in the environment, except perhaps in frigid Arctic regions (12). Table 2 shows some characteristic half-lives observed for endosulfan isomers and endosulfan sulfate in different phases. Such data for each latitude also could be usefully weighted for scale of use to establish an overall half-life value for total global use, which is now biased toward subtropical and tropical values, now that Europe, Canada, and more recently, Australia have deregistered its use. The short half-lives in the field largely reflect the volatility of the two isomers once they have left plants, water, or soil and entered the atmosphere. But here, the suggested half-life of 1.3–3.5 days in the atmosphere, assuming OH-radical concentrations produced by solar radiation in the atmosphere of  $0.5\text{--}1.5 \times 10^6$  molecules per  $\text{cm}^3$  (45), ensures that volatilization from soil or water should hasten their conversion to less toxic products, therefore not extending the recorded half-life. Endosulfan sulfate is more persistent in soil and water, but it does not meet the full set of criteria with less capacity for bioconcentration being almost two orders of magnitude less volatile than  $\alpha$ -endosulfan (Table 2) and therefore cannot be subject to long-range transport. The longer half-life of endosulfan sulfate and other metabolites was used illogically in UNEP's risk profile for endosulfan (34) to support the idea that it is persistent, contrary to the facts and given that the environmental risk from these products is much diminished in soil and water because of their much lower dispersion rate.

Concentrations of endosulfan distant from its site of application are always exceedingly low and require special techniques for concentration from large volumes of material for analysis. For example, endosulfan residues found in the warmer Lake Malawi in southern Africa, in an area where endosulfan was in extensive use, were around 10 pg ( $10^{-11}$  g) per L (46), just above one-millionth of the concentration expected to be lethal to the most sensitive species of fish. Concentrations in open Arctic lake waters were in a similar low range with  $\Sigma$ endosulfan isomers at 45 pg per L of water or less and endosulfan sulfate with a maximum of 32 pg per L (12) (Weber and co-workers referring to Lakes Hazen, Char, and Amituk). These are also exceedingly low concentrations that demonstrate the skill of the analyst more than they do any real threat or risk to biota or of significant long-distance transport of a persistent compound. The concentrations found are so low because neither endosulfan nor endosulfan sulfate is persistent enough to accumulate even in colder climates.

It seems that most current environmental measurements of endosulfan globally reflect an ongoing pattern of use of endosulfan and its undoubted capacity for aerial transport as vapor. For example, Weber and co-workers (12) claimed an ongoing deposition rate for endosulfan in the Arctic, reflecting on recent use with a declining concentration in the Arctic Ocean away from the Canadian Archipelago. This was in contrast to the levels of  $\gamma$ -hexachlorohexane (HCH), which were greater in the colder waters of the Arctic Ocean as expected for an equilibrium situation. The ongoing deposition coupled with degradation

has prevented such a result for occurring in the case of endosulfan. As a result, the current levels in this ocean are a function of ongoing use, with perhaps 10–15 kg of endosulfan per year being deposited from recent use.

The bioaccumulation criterion for a POP requires a value of more than 5000 (9,12). In aquatic species, endosulfan fails in most cases to reach this level by at least a factor of 10–100, and even where exceedances occur, they could be transient spikes as a result of recent exposures to higher concentration, reflecting the time taken for clearance. Biomagnification from fish to marine mammals is slight (about 1–10 (12)).

Transport across a significant distance in air for several days after application was confirmed in an extensive study by Raupach and co-workers (40,47), who showed vapor deposition and release from water trays with predicted redeposition in river water on a scale of more than 10 km in a major study in the mid-1990s in northern New South Wales. Although the probable short half-life in the atmosphere would limit the significant aerial transport of endosulfan to distances downwind much longer than 200 km, most of this volatile endosulfan would be expected to be reabsorbed by vegetation downwind or into organic particulates in the atmosphere and then redeposited by rain into river water or soil. The low concentrations found at high latitudes attest to the minor degree of transport through air. Moreover, Simonich and Hites (30) concluded that endosulfan was unlikely to undergo “global distillation” as observed with DDT—the preferential transfer and enrichment of more volatile compounds to higher latitudes, as drawn attention to by Weber and co-workers (12). Levels of residues in tree bark reflect local or regional use of endosulfan.

Raupach and co-worker’s field studies (40,47) showed that 60% of the endosulfan applied was transported as vapor from the site of application downwind and that concentrations measured in the atmosphere were sufficient to show reabsorption of the two isomers into water trays placed at intervals several kilometers downwind. Such absorbed endosulfan then reemerged as vapor when the concentration in the atmosphere was exhausted as the source concentrations fell after 2–3 days. This result agreed reasonably well with a mathematical model proposing transport as vapor incorporating physical constants such as Henry’s law constant (vapor pressure per unit concentration in water) sufficiently well to confirm the major significance of this mode of transport in air and suggests that endosulfan found in river water also could contain a fraction derived by reabsorption at concentrations sometimes observed.

Therefore, all three mechanisms of transport on runoff as drift from aerial or ground-rig applications can be regarded as contributing to levels found in river water in the same catchment. A hypothesis that the presence of the bioproduct endosulfan sulfate in river water could be used as a diagnosis for runoff of suspended soil had to be rejected when it was found that the endosulfan parent compounds could be rapidly converted to endosulfan sulfate by microbes in river water in several days (48).

There is no doubt that contamination of livestock with endosulfan has done great harm and at times has caused the suspension of the export of beef or other products and has caused severe production losses (39). Important lessons have been learned from these unfortunate experiences with endosulfan, and it is clear that its application needs to be severely restricted. However, in Australia,

the regulatory authority (APVMA) strongly defended the continued use of endosulfan until recently, relenting politically probably because of obligation under the Stockholm Convention because the current recommended management practice on its label has been shown to prevent the contamination of agricultural produce. No cases of untoward effects on human health have been recorded in this country when applied according to the label, even by those directly involved in its application.

Throughout the UNEP process, its reports show that no effort has been made to assess the environmental risk from the responsible agricultural use of endosulfan that and little or no consideration has been given to the consequences of banning its use, contrary to the convention's charter.

## 6. Hazard Versus Risk Assessment

There are several different approaches to characterizing risk. The approaches to risk used most often are the hazard quotient (HQ) and the environmental impact quotient (EIQ). The latter approach is more intellectually rigorous but far less common. This method relates distributions of exposure with toxicology data using joint probability curves (49). The simpler, more commonly used HQ method consists of simply taking the ratio of a measured (and/or predicted) environmental exposure concentration to a predetermined concern concentration (50). A quotient exceeding 1.0 indicates the need for concern. The EIQ applies information on the physical and chemical properties of the chemical together with rates of application to produce a more realistic hazard score. The EIQ approach enables a relative assessment of different application scenarios.

However, neither of these approaches fully characterizes risk, lacking the necessary probabilistic paradigm and rigor (51); such analyses often conclude that it is necessary to gather more information, which is characteristic of a first-tier risk assessment. However, they are used most often (6) because of their smaller data requirements, particularly where little data are available. The probabilistic approach and other higher-tier methods require much larger exposure and toxicity data sets.

The following two case studies from our experience will illustrate these different approaches to characterizing "risk" using different management scenarios, also providing scope for application at different scales. Importantly, a risk assessment for glyphosate is presented to demonstrate its utility in designing a management strategy to minimize environment risk. In this case, the adoption of glyphosate tolerant GM cotton in the Australian cotton industry is analyzed to show the changes in risk and potential benefits with the adoption of this new technology.

**6.1. Case 3: Glyphosate or Roundup.** Glyphosate (2-[(phosphonomethyl)amino]acetic acid, a direct contact herbicide for weeds, is probably the most widely applied agrochemical on earth. Since its introduction in the 1970s as Roundup, a patented product of Monsanto (St. Louis, Mo.), it has been considered a relatively safe herbicide because of its mode of action interfering with the biosynthesis of aromatic structures needed for amino acids phenylalanine and tyrosine and for lignin synthesis. Because no animals carry out these



biosyntheses, this action can only significantly affect species in the plant kingdom. It is also readily inactivated in soil, probably as a result of its strong binding to sesquioxides of iron, aluminum, and organic matter similar to other inorganic phosphate compounds and is degraded rapidly under some conditions. The safety of glyphosate in the environment has been challenged, but most deleterious effects observed have been functions of the adjuvants and other compounds included in commercial formulations rather than glyphosate itself, stressing its relative nontoxicity. A comprehensive ecotoxicological risk assessment and review of the environmental fate for the Roundup herbicide has been made available (19). Here, we intend to use some Australian experiences to illustrate a modern approach to the risk management of herbicides.

This section provides an example of the application of risk-management tools to an agrochemical, using the introduction of Roundup Ready Cotton (Monsanto) as an example. Roundup Ready cotton was introduced in Australia in 2000 and was rapidly adopted by Australian cotton growers. The main argument for the introduction of the technology was that the GM trait expressed with these varieties enabled the use of glyphosate to control weeds in cotton crops, a herbicide that is toxic to conventional cotton varieties. The first part of this study provides an example a desktop hazard assessment followed by a field study to obtain data to enable a risk assessment. A follow-up hazard analysis, using the EIQ conducted after 14 years of using glyphosate is then presented.

There are two main classes of herbicides—residual and nonresidual. Residual herbicides, which include “preemergent” herbicides, are classified by their longevity in soil and subsequent long-term action. Residual herbicides present a higher risk to an ecosystem because they remain active over a longer period of time. They also can reduce subsequent crop yields as a result of their residual effect when their application is poorly managed. Conversely, nonresidual herbicides are short-lived in the environment; they are either degraded rapidly or are soon inactivated by soil contact.

Roundup Ready Cotton, which can tolerate early-season use of the herbicide glyphosate (Roundup), became available to the Australian cotton industry in 2000, and a two-gene variety, Roundup Ready Flex, was introduced more recently. Because of its effectiveness, the acceptance and uptake of Roundup Ready technology was remarkably swift with 50% of the Australian crop using the technology within 2 years and its almost complete adoption 10 years later.

Although glyphosate resistance management for weeds still requires other herbicides, the adoption of Roundup Ready technology allowed cotton growers to decrease the amount of residual herbicides potentially and to increase the amount of the nonresidual herbicide applied (glyphosate). The expected outcome of the introduction of Round-Up Ready cotton was to reduce the environmental risk. Risk assessment techniques can objectively analyze the available data and inform the management process.

Herbicides are relatively water soluble when compared with other chemicals used in cotton production. This property may indicate that a herbicide will be more susceptible to runoff and leaching in subsurface water. There is evidence that some herbicides, including diuron and atrazine, can be detected in ground water as a result of subsurface drainage (52). Similarly, herbicides sometimes are detected in samples taken from riverine ecosystems, either as a result of

overspray or runoff (53). The transport of herbicides from target areas in cultivated paddocks can be minimized with good management (eg, the best management practice initiative of the Australian cotton industry (54)).

*Environmental Properties of Glyphosate.* Glyphosate has a low affinity for hydrophobic organic matter. This is represented scientifically by a low  $K_{OW}$  value, which is a measure of the distribution of a substance between an organic solvent and water. It has high water solubility, roughly three times the water solubility of common table salt (sodium chloride) (see Table 2). At first sight, these data suggest that glyphosate could be prone to leaching. However, numerous studies have reported that glyphosate is likely to be immobile in the environment because it binds tightly to soil in ionic binding (19). Low soil mobility, together with relatively low persistence and human and aquatic toxicity, render glyphosate as potentially one of the least environmentally hazardous herbicides to nontarget organisms. Glyphosate was considered safer for human health and the environment than many herbicides currently used for cotton production (54).

*Hazard Assessment.* The use of glyphosate must be compared with the changes in use of the conventional herbicides it aims to replace. To aid the analysis of all products and associated data, a series of hazard assessments was undertaken to produce a relative assessment that aims to identify priorities for additional data gathering or to indicate that changes in herbicide use are “relatively” improved. A relative assessment usually cannot inform managers about environmental risk per se because the frequency of exposure is not usually included.

The hazard to ecosystems from the herbicides used in the field experiment scenarios was expressed by considering the likely *exposure* of the herbicides and their toxicity (*effect*) to two species found in wetland and riverine ecosystems—trout (*Oncorhynchus mykiss*) and water flea (*Daphnia* sp.). These species were chosen because of the more readily available data for the selection of herbicides included in the assessment. The methods followed the recognized framework for environmental risk assessment (56–58).

Fugacity modeling applied to a model cotton farm (58,59) was used to calculate the expected concentrations and fate of the herbicides glyphosate, 2,4-D, diquat dibromide, diuron, fluometuron, metolachlor, paraquat dichloride, pendimethalin, prometryn, and trifluralin in various environmental compartments, including runoff and groundwater.

Table 3 contains a summary of the results that show glyphosate presents negligible risk to the species assessed, with a risk quotient many orders of magnitude lower than applications using other common herbicides.

Figure 4 presents the relative risk, presented as risk scores rather than risk categories, to compare and contrast ecological risk of a range of potential herbicide applications. The data displayed in this format enable rapid display of the relative assessment, which shows that use of glyphosate, pyriithiobac, and clethodim all resulted in a zero score for this relative hazard assessment and represent negligible environmental risk.

Although scoring the results of hazard assessments is good for making comparisons of chemicals in use scenarios, based on the exposure and effect hazard ratios, any scoring system introduces subjectivity into the assessment.

Table 3. Relative Risk to the Ecosystem of the Herbicides Used in the Field Trial Scenarios

Chemical	Hazard quotients			
	Trout	Category	<i>Daphnia</i>	Category
glyphosate	$7.3 \times 10^{-8}$	negligible	$7.9 \times 10^{-8}$	negligible
diuron	7.5	medium	0.2	low
fluometuron	0.05	low	0.3	low
prometryn	0.08	low	0.01	low
pendimethalin	4.2	medium	ID <sup>b</sup>	—
trifluralin <sup>a</sup>	1.1	medium	0.08	low

<sup>a</sup>Combined conventional and GE.

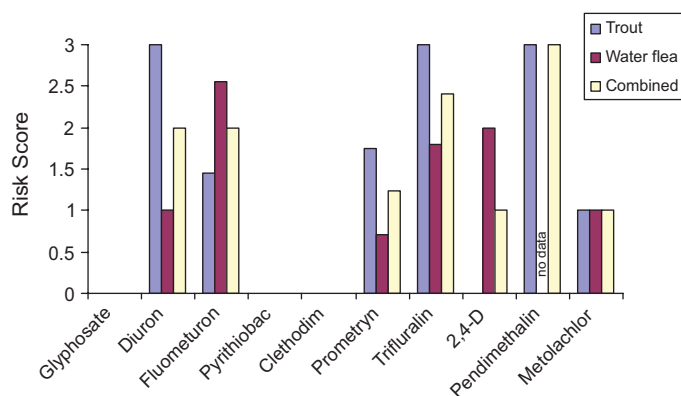
<sup>b</sup>ID = insufficient data.

Experimental data are required to provide the level and frequency of exposure, which will enable risk to be calculated.

**Risk Assessment.** A field experiment was used to gather data to test predictions objectively of reduced environmental risk by introducing Round-Up Ready technology in Australia. The project was managed by the consulting firm Maunsell Australia Ltd. (Melbourne, Australia), with assistance from CSIRO Land and Water (Canberra, Australia) and the University of Sydney (Sydney, Australia). Although desktop approaches are useful to indicate likely risks, real data from the field and risk assessments using real data provide a more reliable basis for management decisions.

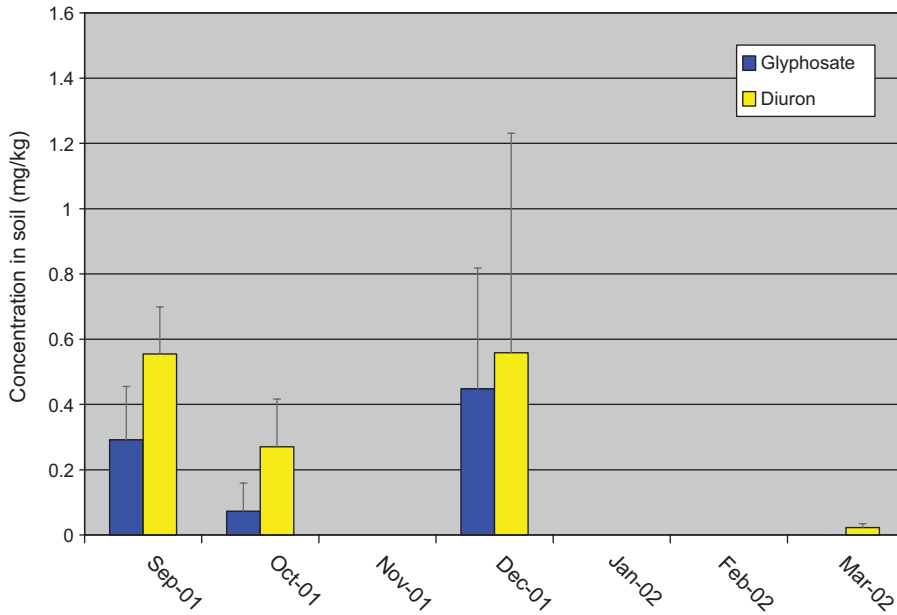
A comprehensive set of soil, sediment, and water samples was taken for chemical analysis, using contemporary and accredited analytical methodology. The data were used for partial validation of the modeled values as well as to formulate a probabilistic risk assessment.

The data for the analyses of glyphosate and diuron in topsoil (0–5 cm) is summarized in Figures 5 and 6. The residues of glyphosate found in the soil were consistent with application rates and the field study conditions, which

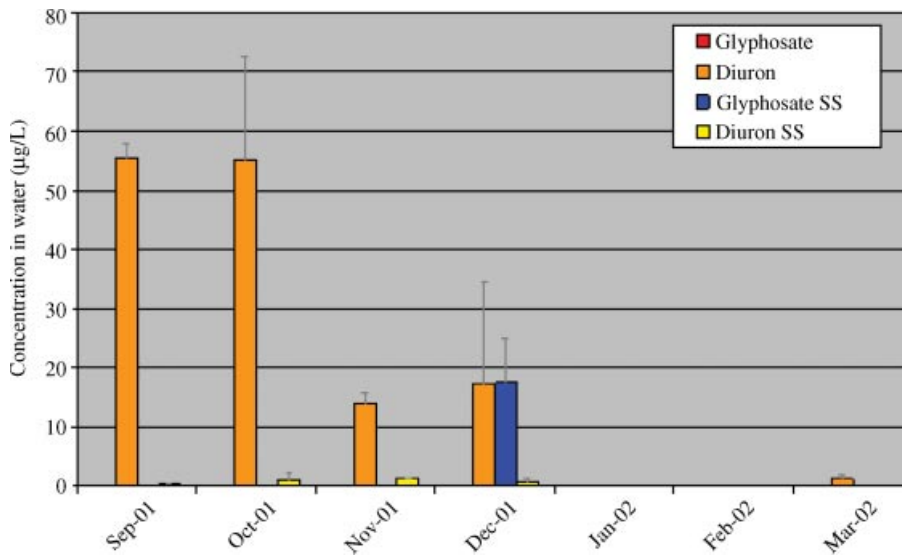


**Fig. 4.** Relative risk scores for each herbicide presented as averages of all scores from all theoretical application scenarios.





**Fig. 5.** Concentrations of glyphosate and diuron in soil throughout the 2001–2002 cotton growing season; averaged results from four experimental fields, standard deviation shown by the error bars.



**Fig. 6.** Concentrations of glyphosate and diuron in runoff water and suspended sediment (SS) presented for each month from four fields; standard deviation shown by error bars.

were typical of Australian cotton-growing practices. Both diuron and glyphosate were detected in topsoil soon after herbicide application in the cotton-growing season (Fig. 5). However, near harvest, toward the end of the season, no glyphosate residues in soil were detected, and there was only a low range detection of diuron (0.022 mg/kg).

No glyphosate was detected dissolved in runoff water at any stage (Fig. 6), with a few detections in suspended sediment soon after application of the herbicide. By contrast, diuron, which has a lower binding affinity for the soil (see Table 2), was detected in runoff water at comparatively high concentrations early in the season soon after application. By the end of the growing season, the diuron concentrations detected were significantly lower in accordance with the decreasing concentrations in soil.

The detected values of diuron were consistently higher than the Australian and New Zealand Environment and Conservation Council (ANZECC) interim guideline for ecosystem protection of  $0.2 \mu\text{g L}^{-1}$  (a low reliability guideline because of a limited data set (60)). Because of its low toxicity, the ANZECC guidelines for glyphosate are  $370 \mu\text{g L}^{-1}$ , and these were not exceeded by a wide margin in any sample, including those with sediments.

*Probabilistic Risk Assessment.* Another approach to risk assessment is to incorporate a probabilistic approach, using frequencies of occurrences of toxic levels of pesticide residues obtained as actual field data. This can result in a better understanding of the actual risk of impacts from herbicide use.

Probabilistic risk assessments are considered the ultimate development and the most recent form of ecological risk assessment (61,62). Most commonly, the exposure data are used to develop frequency distribution and are compared against a similarly distributed range of effect or toxicity data. The two frequency distributions can be combined in a joint probability format to provide an indication of the proportion of species affected across the exposure events.

A similar probabilistic assessment was undertaken using data obtained in the field study by calculating the frequency of exposure. This approach differs from previous studies because, instead of using toxicity data as an exposure endpoint, the example uses regulatory guidelines values or a suitable substitute when such values are not available. The results provide the probabilities that herbicide use will exceed the guideline value.

Table 4 shows the results of the assessment and the probabilities of exceeding the ANZECC water quality guidelines under usual cotton-farming practices. It is clear that the probability of exceeding the water-quality value of glyphosate is extremely low. This analysis suggests the guideline value for diuron would be exceeded eight times out of ten. No guideline values for fluometuron, prometryn, or pendimethalin could be obtained, and therefore, MRL values for cotton seed and oil seed were used to enable a limited comparison.

This study found that herbicides typically used on Roundup Ready cotton crops pose a lower risk to the environment compared with herbicides commonly used on conventional cotton crops. In addition, there is evidence that the weed control programs using Roundup Ready cotton allow for reduced tillage practices and reductions in the precautionary application of residual herbicides, providing additional environmental benefits.

Table 4. Comparison of Probabilities that Use Will Result in Runoff Water Exceeding the Nominated Guideline Value

Chemical	Guideline ( $\mu\text{g L}^{-1}$ )	Probability of exceeding guideline value <sup>c</sup>
diuron (ID <sup>b</sup> )	0.2	0.80
trifluralin	2.6	0.58
fluometuron (MRL <sup>a</sup> )	100	0.08
prometryn (MRL <sup>a</sup> )	100	$1.0 \times 10^{-05}$
pendimethalin (MRL <sup>a</sup> )	50	$3.0 \times 10^{-06}$
glyphosate	370	$1.9 \times 10^{-10}$

<sup>a</sup>Where no ANZECC/ARMCANZ (2000) guideline values were prescribed, MRL values were used.

<sup>b</sup>Refers to the ANZECC/ARMCANZ (2000) "Insufficient Data" condition, and therefore, a value with greater sensitivity is prescribed.

<sup>c</sup>Probabilities were determined from exponential plots of field data for each chemical to determine the likelihood of exceeding the guideline values.

*Assessment of Subsequent Industry Use Data.* To ensure that any risk assessments and subsequent management activities were effective, a follow-up analysis can be useful. A follow-up analysis can be applied at set intervals or when additional data become available. For our example, herbicide application data over a 14-year period have been analyzed to add additional insight. The data set was collected by the Cotton Consultant Association via a survey of its members. These herbicide application data were analyzed using the EIQ (63).

EIQ uses the physical, chemical, and biological properties of the herbicides analyzed together with rates of application to produce a hazard score. The benefit of the EIQ approach or another risk-scoring system is that they enable a relative assessment of different application scenarios or, in this case, a review of the total industry application each year.

EIQ uses a weighted equation to calculate the impact rating and takes into account three principal components of agricultural production systems including farm workers, consumers, and the environment. Figure 7 shows the results of the EIQ analysis for eight herbicides of interest. There are numerous notable results, including those for glyphosate, prometryn, and fluometuron, which all show increases in EIQ scores. Conversely, the EIQ for diuron has reduced. Changes in EIQ indicate changes in the amounts of herbicide applied per hectare.

Additional analysis indicates that the overall industry EIQ score has not been reduced with the introduction of Roundup Ready technology (Fig. 8). Although the use of diuron—a high profile residual herbicide—has been reduced, the data show an increased use of prometryn, fluometuron, and glyphosate. The increased use of glyphosate was expected because of the nature of the Roundup Ready technology, but the increased use as well as EIQ scores for prometryn and fluometuron indicated by the survey was unexpected.

In the EIQ analysis, the increased use of glyphosate has contributed to the overall industry score. Although the risk of glyphosate was considered low in the previous assessment, the EIQ includes a component for risk to plants. Glyphosate as a herbicide is extremely toxic to many plant species when there is direct exposure to sensitive species, but other authors have argued that the score used

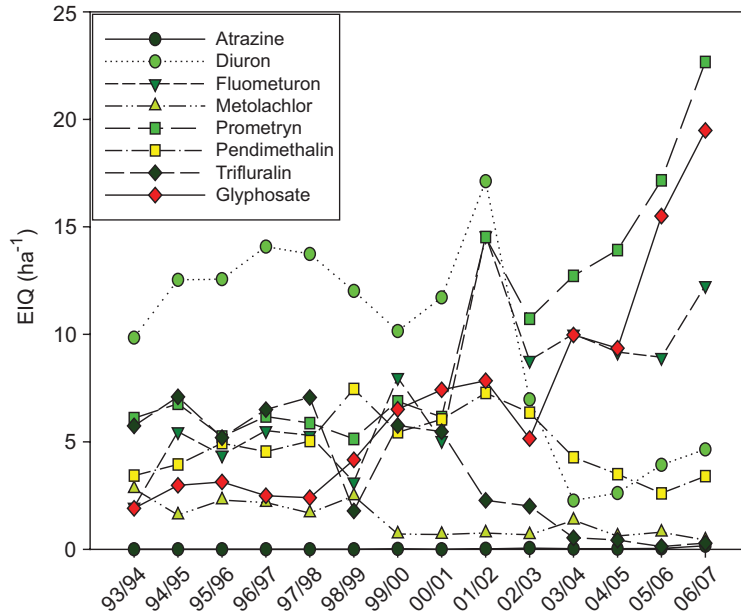


Fig. 7. Fourteen-season comparison of industry herbicide environmental impact quotient.

to calculate foliar residue half-life is not suitable (64). This highlights one main weakness with hazard-assessment scoring approaches, as agronomic practices and actual exposure are not considered. Therefore, the appropriate action in response to this analysis is to recommend a more comprehensive assessment be undertaken.

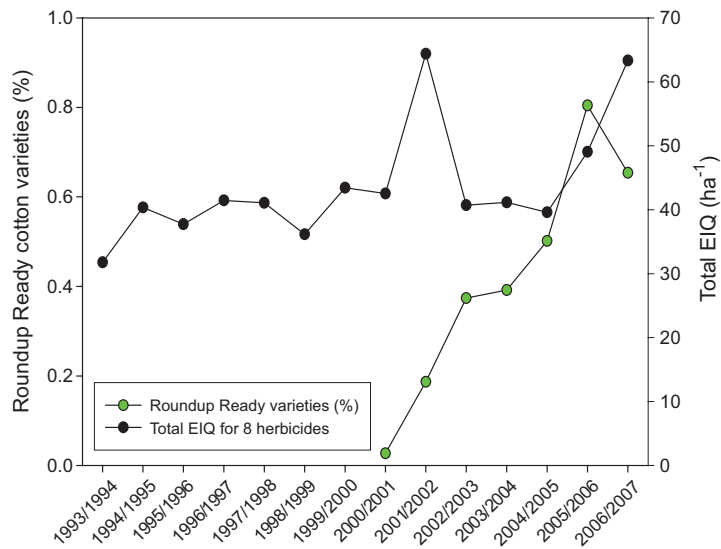


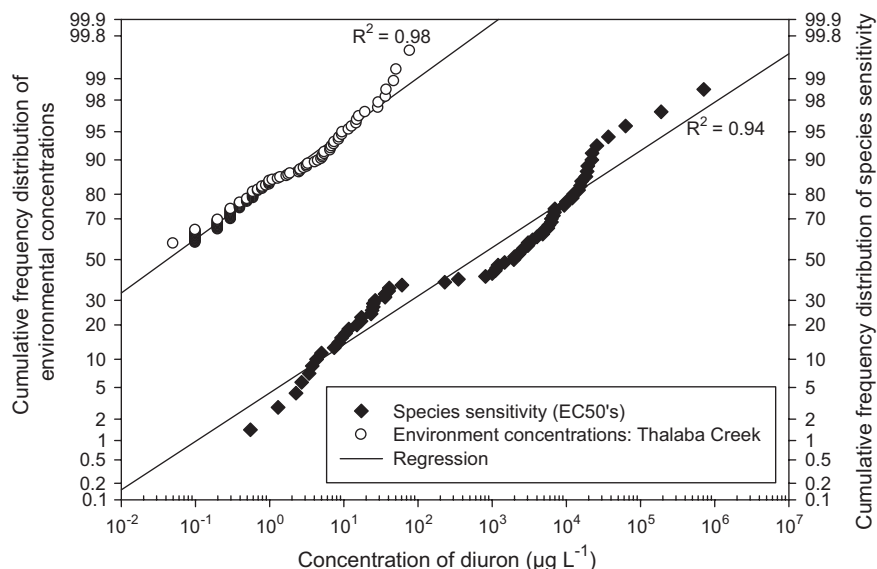
Fig. 8. Combined industry herbicide environmental impact quotient and industry adoption of Roundup Ready technology.

Other scoring systems could be used (eg, the hazard scoring index (65), the priority substances list (66), EcoRR (58), or a custom scoring approach), but the ultimate improved version would involve an assessment for each specific use. Some concern has been raised over the accuracy of the application data used in the EIA assessment (B. Pyke, Cotton Research and Development Corporation, Narrabri, NSW, personal communication.). The use of an average industry figure is also not representative of specific practices. Additional analysis should be used to identify accurate application patterns for site-specific risk scenarios, but it would seem that the introduction of Roundup Ready cotton has not yet reduced the use of all hazardous herbicides and future intervention may be required to manage this situation.

The Roundup Ready, or similar technologies, offer agricultural industries other benefits that are not captured in the analyses presented here. Herbicide-tolerant crops provide environmental benefits by allowing for a shift to conservation tillage practices; farmers can reduce the extent of soil cultivation required to control weeds and prepare the soil for planting. Specifically, herbicide-tolerant crops allow for farmers to eliminate the use of preemergent herbicides that need to be incorporated into soil and to rely on postemergent herbicides directly applied on weeds, such as glyphosate. It has been suggested that the shift to post-emergent control of weeds may promote no-till and conservation tillage practices that can decrease soil erosion and water loss as well as increase soil organic matter and total nitrogen (67,68).

**6.2. Case 4: Diuron and Catchment-Based Probabilistic Risk Characterization in Australia.** Where sufficient application and monitoring data is available, probabilistic assessments may be possible, as in the case of the herbicide diuron (3-(3,4-dichlorophenyl)-1,1-dimethylurea) that has been under review by regulatory authorities in recent years with its total annual application rate reduced as a result. Diuron is a soil-applied, preemergent phenylurea herbicide widely used in Australian agriculture. Its properties contrast strongly with DDT and endosulfan (Table 2). It is mainly used to control weeds and in some cases to defoliate crops prior to harvest (eg, in cotton). Diuron induces a toxic action on photosynthetic organisms by targeting the quinone-binding sites of reaction center II in photosystem II receptors (10,69). It is a relatively water-soluble compound (Table 2) considered mobile in the environment, as has been demonstrated in environmental fate or in water quality-monitoring studies carried out on sugarcane farms of far northern Queensland, Australia (70) and cotton-farming regions of northern New South Wales (71,72) and has been detected in agricultural catchments of Queensland (73–76) and northern New South Wales (77,78). Its largely nonselective mode of action and potential to be transported off farms has made it a target chemical of concern in Australia. The level of concern in regard to contamination events can be estimated using ecological risk assessment, and it is recommended that this is best applied on a catchment-based approach.

Probabilistic risk characterization was applied to diuron exposure data collected from the Gwydir River catchment of northern New South Wales, Australia by the NSW Department of Water and Energy for the period 1991–2007. Sampling was conducted monthly independent of chemical use but with two or



**Fig. 9.** Cumulative frequency (probability-scale) distributions of diuron concentrations ( $\mu\text{g L}^{-1}$ ) (on the  $\log_{10}$ -scale) for environmental observations at Thalaba Creek in the Gwydir River catchment and species sensitivity (data used from USEPA ecotox database 2009).

three samples collected for months that were perceived to be riskier because of higher rainfall and during the cotton-growing season.

Distributions of exposure and species sensitivity are shown (see Fig. 9) using the methods of USEPA, Solomon and co-workers (49), and Maltby and co-workers (51). As one example, distributions of species sensitivity and in stream exposure are presented for the Thalaba Creek site, which had the highest risk. Notably, where the exposure and species sensitivity distributions overlap at the 5% species sensitivity threshold denotes risk (based on Australian regulatory approaches). The probability that the 5% effect threshold (based on standard regulatory approach) can be exceeded at any time then can be determined. More importantly, the joint probability curve, or risk profile, describes the probability that any concentration is exceeded (49). When the calculation of risk was completed, the output was applied to geographical information systems software (ArcGIS), allowing for identification of exposure hotspots in the catchment (Fig. 10). Although the output lacks spatial detail, the results would enable catchment managers to identify whether the upstream management of agrochemicals adequately protects ecosystems and the likelihood that a problem exposure is likely to occur. Spatial modeling of herbicide transport then may define areas in the catchment that may contribute most to exposure and where management resources should be directed if there is a high risk. This illustration of catchment-based risk assessment shows how economic as well as environmental benefits can be achieved, ensuring that scarce resources can be directed to sites where they will yield the strongest effects.

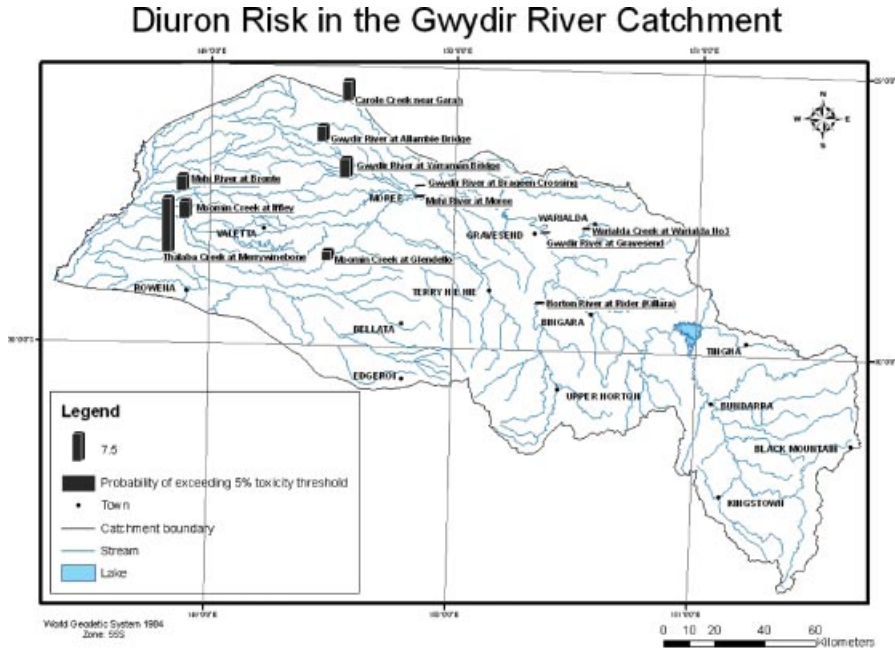


Fig. 10. Map of probability of exceeding threshold for diuron exposure at measurement sites in the Gwydir River catchment.

**6.3. Can Genetic Modification (GM) Provide a Risk-Management Solution?.** There is now global widespread acceptance of the benefits of GM technology for the management of pests and weeds, despite the “precautionary” reluctance of the European community to participate. The Australian cotton industry represents a particularly successful case of introducing GM technology based on the introduction of genes to produce *Bacillus thuringiensis* toxin in the crop varieties. The need for harsh chemicals such as endosulfan and profenofos, as a result, has declined to a small fraction of what it was in the early 1990s with residue levels in the riverine systems showing a similar decline (4). It is remarkable that most Australian cotton crops are now grown almost organically, with respect to insects at least, with aerial spraying now concentrating on the application of herbicides or defoliants. Ironically, organic cotton is known to present much more risk to human health because of the endotoxins produced as a result of insect damage causing “sticky” cotton in which sugars from the phloem stream allow growth of gram-negative bacteria and bacilli. This is a well-documented problem (79) for cotton grown with poor sucking-insect control, resulting in serious lung disease in factory workers in cotton mills.

This is a remarkable reversal of the situation that pertained 25 years ago. Success elsewhere has not been so marked, but even in India and China there has been a reduced need for chemical applications as the GM technology for insect resistance has become widely available. Certain sucking insects such as the white fly cannot be so readily controlled, and climatic or other conditions in particular regions have sometimes allowed these insects to become dominant, as was experienced in China around 2005. However, such negative events are by



no means exceptional in world agriculture, and uncertainty in production levels during the year is normal.

It is unfortunate that the environmental movement has not given a greater measure of support to the development of GM technology. Although a strong degree of caution with a need for excellence in risk assessment to avoid serious mistakes is prudent as with any new technology, the benefits of GM modification of crops have been delayed unnecessarily in many regions because of the doctrinaire application of the precautionary approach. Despite the extreme fears expressed, there are still no significant cases of the predicted hazards being realized and the actual results have tended to be more successful than proponents have hoped. We are now moving into a phase in which benefits are expected to include productivity itself, but it would be helpful if at least part of the green movement was more receptive to GM technology.

## **7. Conclusions: Well-Informed Stewardship**

The Roundup Ready field project (65) has provided valuable information in regard to the fate and transport of glyphosate in Roundup Ready cotton systems. From both field measurements and desktop modeling tested by field measurements, it was shown that the glyphosate herbicide, because of its low toxicity and low mobility, presents an extremely low risk of contamination and rates well against other herbicides. The use of glyphosate in combination with other low risk herbicides for weed control with Roundup Ready cotton provides an opportunity to reduce the risk of off-site herbicide contamination significantly in Australian cotton production. Therefore, by choosing herbicide programs that contain "low risk" herbicide options, it is possible to minimize risk to the environment as well as to provide growers with good crop performance and economic benefits. Following the principles of rational management, it would be prudent to follow up an analysis as more data become available. In our example, we have the benefits of analysis of several years of industry application data.

The follow-up assessment using EIQ indicates that a more detailed analysis with monitoring is required to confirm the expected environmental outcomes. The analysis showed that, although the use of diuron has declined, the use of prometryn and fluometuron has increased. Thus, introduction of the Roundup Ready technology has not resulted in the expected decrease of environmental risk. However, this conclusion is only based on a scoring or relative assessment. Roundup Ready technology can reduce environmental risk, but herbicide application scenarios using chemicals with reduced hazard or risk is required. A structured risk assessment approach and associated techniques, such as those used here, should be used to monitor, manage, and confirm changes and developments in pesticide use, including the effects of the introduction of new technology.

The lessons from all four of these case studies together with the field knowledge and general principles illustrated in their fate and transport can be considered valuable resources for the future. For example, proceeding with the listing and banning of endosulfan in the Stockholm Convention as a POP (a decision not scientifically justified) means the loss of the opportunity to benefit from these



lessons, losing much of the value of the previous research conducted. As an alternative, the use of endosulfan might have continued to be recognized not as a POP but as a hazardous chemical with its use restricted for safety purposes only where there is no suitable alternative and managed strictly according to the methods prescribed by its well-known properties. Its environmental behavior including its variable half-life now has no surprises because this behavior is consistent with its known properties. For example, its rate of volatilization could be controlled if it is formulated in a slow-release form. Although not reducing its equilibrium vapor pressure, much lower exposures of nontarget species could be achieved by this means. Its application also could be restricted to conditions in which it is nonpersistent and breakdown is accelerated as in subtropical climates. Continued benefits from this chemical still could be realized, but using the strictest protocols of stewardship that use new operating parameters. The same approach could be used for the herbicide diuron—a frequent nominee for banning or at least for more restricted use. The current availability of a rapid field test for measuring diuron in the field should facilitate its management.

A similar attitude could even be taken to DDT; although it is hoped that less risky alternatives will be found. Ideal for the control of *Anopheles* larvae, the likelihood that a suitable substitute will become available is small, given the high costs of registering new chemicals and the limited market for such a product. An accurate risk assessment is likely to show that the benefits to human health would outweigh the environmental risks of continuing anything but highly restricted use of DDT. This could be assured through stricter management of its application label coupled with detailed on-site monitoring to ensure better knowledge in regard to the potential for exposure of nontarget species.

Any such decisions to manage exemptions under strict conditions would need to be based on certain information accompanied by the following guarantees:

1. The availability of inexpensive and rapid on-site monitoring methods, allowing users to directly manage their use
2. Environmental risk assessment of the scale and location of use
3. Clear evidence of stewardship with well-defined responsibilities

Similar stewardship could be extended to all agrochemicals subject to environmental dispersion or degradation. If formalized, then manufacturers, regulators, farmers, and the general community could share this task with each stakeholder participating at some points in the supply chain for agrochemicals.

Such a proactive and responsive approach to their management would be far superior to applying the blunt instrument of the precautionary principle that may seriously threaten food security and even environmental safety as farmers continue to combat pests by whatever means available in the 21<sup>st</sup> century.

## 8. Acknowledgments

The authors acknowledge the support of the Cotton Research and Development Corporation and the Cotton Cooperative Research Centres in their research in

this area. Maunsell Australia Ltd. managed the field study on Roundup, funded by Monsanto, with our assistance only in the assessment of their field data and the publication of the final report. We are also grateful to Mark Silburn, Ph.D. (Figs. 1 and 2) and to the American Chemical Society (Table 1, Fig. 3) for permission to reproduce published material.

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