PESTICIDES — HANDLING AND FATE

THOMAS McEWAN
47 Rita Street, Holland Park, Queensland 4121
AUSTRALIA

Pesticides are used in all areas of agricultural and animal production to control the various pests that reduce yields and impair the quality of the product. Application methods range from wide-spread treatment of large areas of plant production or large numbers of animals, through specific treatments of isolated commercial crops or handling facilities, to small scale home garden use or individual dosing of animals. All of these uses contribute to the environmental burden of pesticides.

Following application, residues of the pesticides persist in or on the produce at concentrations and for times that are dependent not only on the amount applied but also on the chemical characteristics of the pesticide and on the conditions that exist in that environment. In addition, residues of pesticides may persist in other parts of the environment such as in soils or on the surfaces of structures.

The impact of such residues will be illustrated by considering the persistence of organochlorine and organophosphorus pesticides in the environment, the ways in which these compounds enter animal products and their rate of disappearance from animal tissues. In addition, some consideration will be given to the many toxic compounds which occur naturally in food.

Control of residues of agricultural chemicals in food is maintained through a system including establishment of legal limits, Maximum Residue Limits, for residues in food and policing observance of these limits by analysing samples of foodstuffs. The setting of limits and the requirements for laboratories involved in analysis are discussed.

INTRODUCTION

Agricultural chemicals are used in many ways to help provide us with ample supplies of good quality food at reasonable prices. They enter many different parts of our environment either by intentional application, by accident, or by misuse. Examination of those parts of our environment associated with food and food production provides insight into some of the ways pesticides enter the food supply. The major part of the discussion will consider pesticides which have had an impact on the animal industry in Australia in recent years. This impact resulted in increased

investigations of residues in meat products. The way in which meat was surveyed for organochlorine pesticide residues will be considered and the extensive escalation of laboratory facilities involved in that task will be illustrated. Some consideration will also be given to the significance of such residues in comparison with poisons which occur naturally in foods.

APPLICATION OF AGRICULTURAL CHEMICALS

Chemicals may be applied directly to animals to control external parasites or they may be incorporated in feed either as intentional additives or as residues remaining in the feed from a use during growth or storage. Plants may be treated at any stage of growth from planting to harvest and again for storage or transport. In addition, soil may be treated pre-planting and during plant growth for control of weeds and various pests which live in soil.

Methods of application are many and varied. Animals may be sprayed, dipped or jetted, chemicals may be applied as spot or line treatments on the skin, deposited subcutaneously in slow release form, injected subcutaneously, intramuscularly or intravenously, infused into the mammary gland or into the eye, administered orally as slow release boluses or continuous release devices, or mixed in feed or water. The rate of absorption into the animal can be influenced by changes in the formulation of the active ingredient and this consequently influences the concentration of residue which results in the edible products, such as meat, milk and eggs, from those animals. For example, antibiotics are used to treat mastitis in dairy cows. Various formulations are used and have differing impacts on residues in milk. When the formulation includes aluminium monostearate, residues of the antibiotic usually persist in milk for extended times, so this product is usually applied to dry cows. When glyceryl monostearate is incorporated, the antibiotic levels decline much more rapidly, and this formulation, with appropriate withholding periods, can be used in milking cows (Schultze, 1975).

Although the range of application methods for plants and soils appears less extensive, there are many ways of delivering agricultural chemicals to the target. Concentration and formulation are varied to suit the mode of application and the target plant surface (Corty, 1983). Application may be as a spot application, general spray, fog or dust, and for large areas spraying or dusting may be performed from aircraft. Some products are applied to soil as pellets which slowly release the active component. Of course, part of the pesticide aimed at plants also arrives on the soil, and residues left on the plant break down with time (Willis and McDowell, 1987).

Addition of pesticides to the local farm environment also occurs when farm buildings are treated for pest control. Termites are a continuous threat to wooden structures and persistent pesticides such as aldrin are used during construction for protection. On occasion, existing fencing has been treated for termite control. Spiders may present a problem in some animal handling facilities. Inappropriate treatment may lead to residual contamination of that environment. In addition, use which was legitimate in years gone by may have left residues of chemicals that are no longer

acceptable. For example, organochlorine pesticide use on sugarcane or cotton was allowed for many years, and pesticide can still be present in the soil. If animals graze on or near such land, they may accumulate residues above the Maximum Residue Limit (MRL).

MAXIMUM RESIDUE LIMITS

The MRLs are legal limits which show the maximum concentration of a chemical residue which may be present in a food at market following correct use of the chemical concerned. In Australia (Anon., 1989a; Hamilton, 1988), they are incorporated in State legislation on recommendations provided by the Pesticides and Agricultural Chemicals Committee of the National Health and Medical Research Council (NHMRC). The MRLs are developed after detailed study of extensive toxicology data provides a No Effect Level (NEL), No Observable Effect Level (NOEL) or No Observable Adverse Effect Level (NOAEL). Although these terms have slightly different meanings, they are usually used interchangeably. The NEL is then reduced by a large factor to give the Acceptable Daily Intake (ADI). This ADI is the intake which, on present knowledge, could be consumed every day for a life time without ill effect. Residue data are examined to determine what is actually present following correct use and the MRL is established at that level, provided the ADI would not be exceeded, considering all foods which may contain the chemical. Note that the MRL is set on residue data generated on products on farm and relates in general to food products before processing. For many products with inedible peel, such as bananas and pineapples, the MRL is still set on the whole product. If the residue is mainly on the skin, the edible portion of treated produce may contain very much smaller concentrations than are specified as an MRL. Occasionally, processing concentrates the chemical in a product and a separate MRL is set. For example, if wheat is treated near harvest or in storage, residues of the chemical may all be on the surface of the wheat grains. When the wheat is milled most of the chemical remains with portions such as bran and the concentration in the bran may be higher than for the whole wheat.

The best way to ensure that MRLs are not exceeded is to analyse samples of all food products at regular intervals. Unfortunately, that is an impracticably expensive operation. Nevertheless, appropriate analytical data must be generated to give a reasonable assessment of the residue status of food. To do this effectively, the system must include laboratories which are adequately staffed and equipped to handle the necessary tasks. This aspect will be discussed later.

BEEF TRADE CRISIS

Over the past few years there have been a few instances of disturbance about pesticide residues in food. Perhaps the most spectacular was the crisis in the USA-Australia beef trade beginning in May, 1987, when the US authorities detected DDT in three samples of Australian beef (Anon., 1989a). Actual levels were 104,

28 and 6.7 mg/kg compared with the US tolerance of 5 mg/kg and the Australian MRL which was then 7 mg/kg and was later reduced to 5 mg/kg. Consequently, additional testing was conducted and several other situations were detected where excessive residues appeared to be present. This precipitated a trade crisis with the USA threatening to close down Australia's export beef trade, valued at about $1 billion. The response by the Australian Commonwealth and State Governments was an Integrated Action Plan which included a range of measures to reduce or remove availability of the chemicals of concern, to detect and correct problems and to educate primary producers about residue problems and their prevention.

Within Australia, residue testing had been in progress in several laboratories since the early 70's. In addition, the Australian Quarantine Inspection Service (AQIS) had testing for organochlorine pesticides in place as part of the National Residue Survey (Anon., 1988) and the export certification process. Thus, an important part of the Integrated Action Plan was to escalate the level of testing of meat at export abattoirs. The initial plan was to increase sampling to one animal in every 100 for beef cattle and this programme was subsequently extended to one animal in every lot presented for slaughter. Samples were also taken of pig and sheep meats, but at lower sampling rates. In due course the sampling programme was extended to include domestic abattoirs.

Another factor which increased the analytical demand was the need to "trace-back" those animals in which excessive residues were detected. Detection alone was not enough to correct the problem. Since the origin of both pigs (through tattoos) and cattle (through tail-tags) could be determined, it was possible to investigate the property of origin of animals with residues. Once the source of the chemical involved was found, measures to clean up the problem could be commenced. Finding the source often involved analysis of many diverse samples—soil, dust from feed bins, scrapings from rails and posts, feed materials, as well as other environmental samples.

ANALYTICAL ESCALATION

The initial escalation of testing requested by AQIS was handled by the relatively few laboratories actively involved in pesticide residue analysis in meat products. Additional laboratories became involved over the following months either by diverting effort from other areas or by developing new laboratories for the purpose. One laboratory which was involved from the early stages was the Biochemistry Branch of the Queensland Department of Primary Industries, located at the Animal Research Institute at Yeerongpilly. The Pesticide section of the Branch had, over the preceding 20 years, analysed approximately 45,000 samples of beef, pig and poultry fat, as part of research, method development and Departmental surveys, so staff were well experienced in this area of analysis. Analyses were continuing during 1986/87 at 80 samples/week. When AQIS requested analytical support in late May, numbers were immediately increased. By 9 June, 1987, capacity was 100-120 abattoir fat samples/day and a turn-around time of 48 hours was promised. Industry quickly intimated that was not adequate, because it was essential that results were available

for each day's slaughter by 6 a.m. on the next working day, to allow boning out to commence. The turn-around time was therefore reduced and results of samples received by 4.00 p.m. were forwarded by facsimile from 6.00 a.m. the following day.

Further escalation was in place by 6 July, 1987—to 300 samples/day; and by 1 September, 1987—to 500 samples/day plus 100 samples/day from traceback investigations. On 1 October samples from domestic abattoirs were included and this sampling plan was extended from 1 February, 1988.

In the period from 9 June, 1987 to 11 March, 1988, this group analysed:

Slaughter fat samples, export	52,500
Slaughter fat samples, domestic	6,000
Traceback—Biopsy fat samples	3,900
Environment samples	2,900
Cartoned meat samples	1,000
TOTAL	66,300

To appreciate the extent of this work we must consider briefly what is involved in analysis of each sample of fat. Note also that environmental samples generally require a higher work input per sample than the fat samples because each sample must be assessed to decide the appropriate extraction method and samples frequently require individual attention. Each fat sample is received individually wrapped and labelled. It is then unwrapped and detail recorded. The analytical procedure is:

(i) Chop and melt fat;

(ii) Inject fat into clean-up column;

(iii) Elute pesticide from trap;

(iv) Inject into Gas Chromatograph;

(v) Confirm positives; and

(vi) Over MRL—confirm by GC-MS.

To ensure reliability of results it was essential to include standard spiked fat samples in every run—each run was 8 samples plus 2 standards. Results from each standard had to show adequate recovery, correct retention times and absence of contamination.

MECHANISM OF ESCALATION

This vast increase in throughput was achieved mainly by reorganising the logistics of the analytical process. No significant changes were made to the analytical

methodology. Obviously there was a considerable increase in the numbers of units of equipment available, and additional staff, initially untrained, were employed.

Before June, 1987, individual analysts received samples and then handled the whole analytical procedure and reported the results. To handle large numbers it was necessary to set up the procedure on an assembly line basis. Groups, each under the supervision of an experienced person, were set up to handle each step of the procedure. Duties were:

(i) Receive and identify samples with a code which was carried through the whole process;

(ii) Macerate the fatty tissue, melt, recover fat;

(iii) Inject the fat into codistillation units and elute traps to recover pesticides;

(iv) Analyse by gas chromatography (GC);

(v) Check identification and quantitate in a second GC when pesticides are detected. Confirm, when appropriate, by GC-MS;

(vi) Report results by facsimile. Enter results into data base; and

(vii) Administrative group—ordering of equipment and reagents; Preparation of invoices.

The overall supervisor maintained an overview of the whole operation and ensured maintenance and repair of equipment and organised staff training. Particular care was taken to ensure that the identity of each sample was maintained throughout the process, because any error in identification could create major problems in the abattoirs and in field investigations.

Working hours were reorganised, with the first staff arriving at 5.30 a.m. and increasing numbers starting as the samples began to arrive at the laboratory. Work continued until all samples were processed and placed in the sample trays of the automatic GCs, usually from 8.30 p.m. to 11 p.m., but sometimes later. During the peak demand months, considerable overtime was worked.

The extra labour needed was obtained initially by stopping all other work relating to pesticides and allocating the staff to this programme and coopting, from the rest of the Branch, all staff with any relevant experience. Then additional staff were employed, first as casuals and subsequently as temporary staff. Many of these had little or no previous laboratory experience but were enthusiastic and diligent in their duties and were rapidly trained to do specific tasks.

EQUIPMENT NEEDS

Laboratory space was obtained by reallocating laboratories used for other purposes. Additional GCs were purchased, and codistillation and fat-melting units were constructed in the workshop. Necessary glassware construction was provided

by the Agricultural Chemistry Laboratory's workshop. Thus, achievement of this enormous analytical task was the result of tremendous cooperation among very diverse groups, but it must be recognized that it could not have been accomplished without the expertise and dedication of the laboratory staff involved and the cooperation of the Departmental Administration and the Minister in providing finance and the mechanisms to obtain quickly the needed staff and equipment.

When such a laboratory is needed for pesticide residue analysis, the whole situation must be considered: the location of sample collection; collection of samples without contamination; integrity of labelling; transport to the laboratory; analysis methodology and procedures; reporting of results; turn-around time from sampling to reporting; and follow up action when residues of concern (not just over MRL but also near MRL) are detected. The following comments relate only to the section from receipt of samples at the laboratory to reporting of results.

We will look very briefly at each step from arrival of the samples at the laboratory to reporting, examining three of these steps in more detail. Remember, of course, that the logistics of collecting samples, accurately labelling them and getting them to the laboratory are an extremely important part of short turn-around times.

Samples arrive chilled in insulated containers and are unpacked and details recorded. This step needs adequate space so that unpacked samples can be spread out for sorting. Then the fatty tissue is chopped up and heated. Rendered fat is collected and rewarmed in preparation for clean-up by sweep codistillation.

As an example, consider the equipment needed for the next steps to analyse 96 samples per day, simplifying the real world (described previously) by assuming that we are allowed a standard eight-hour day, all the samples arrive promptly at starting time and results can be reported at the start of the next working day.

CLEAN-UP

In the clean-up step, each unit has 10 tubes. This means we must handle 12 batches, each of 8 samples and two standards, and make some allowance for faulty runs requiring repeat analysis. So in these steps of Clean-up, Gas Chromatography and Confirmation of identity and quantitation, we will calculate the number of units of equipment needed at each point and make some estimates of allowances needed for maintenance and repair.

The clean-up process requires first an injection into each tube mounted in a heated block. The fat spreads over the interior packing and the pesticides are carried in the gas stream to the trap where they are absorbed on florosil. Traps are eluted with hexane-ether. Each batch takes about one hour, and if everything goes perfectly, each unit could process eight batches in the 8-hour day, but seven is a more realistic assessment. Hence we need two units which could be operated by one skilled operator, with support staff to clean columns, pack the traps, prepare elution solvents and carry samples to the next step. These two units would have some spare capacity—one batch each per day—to cope with any repeat analysis requirements. There is no allowance

for breakdown and essentially no time for maintenance. I would want a spare unit. Also needed would be two spare sets of traps for each unit.

GAS CHROMATOGRAPHY

First samples for GC analysis arrive about 1.5-2 hours into the day. Some calibration with standard solutions has already been done. Each scan takes about 15 minutes. Hence four injections can be completed per column hour. Twelve batches require 120 injections but there will be some repeats and additional calibrations—possibly a total of 140 injections. These require 35 column hours. Assume GC units are automatic, dual-column and so can run overnight to provide results by starting time next morning. There are 22 hours available, so one dual-column unit can handle this task, but there has been no checking of identity of any detected peaks and no check of quantitation. We need at least one extra unit for checking purposes and another as reserve for breakdowns and to allow for maintenance. Note that under these conditions the report after 24 hours is only "Sample clear" or "Sample suspect". One skilled operator could handle the first GC screen and do the checking of quantitation.

CONFIRMATION

Samples with residues above MRL must have the identity of residue confirmed, if possible by GC/MS. An alternative is accurate checking of retention times on at least three different columns. Calculations of needs in this area depend on the incidence of residues above MRL. At the Australian incidence of 0.2 - 0.4% for organochlorines we might have one or two samples per week. Of course sampling is not likely to be random and will be targeted at sources where residues are more likely to be detected. This will provide additional samples for confirmation, but will not be sufficient to keep a GC/MS fully occupied. The versatility of the equipment is sufficient that this should not be a problem in any working laboratory.

Recording and reporting of results are essential tasks. The reports must be checked by an experienced officer before being sent out. When time is important, results are sent by facsimile. Recording on micro-computer offers many advantages.

This sketch of an approach to planning laboratory development is a brief introduction aimed at stimulating thought on the subject. Many operational problems have not been addressed—for example, 500 samples of about 200 g each of fatty tissue received each day—how long do you keep the remaining sample to allow later checking of the result? How do you dispose of the remains (100 kg/day)?

LABORATORY ACCREDITATION

In all laboratory work it is important that analytical results be reliable. Thus, it was necessary to have external as well as internal checks on the quality of the work done. The laboratory performed extremely well in tests organised through AQIS.

There were about 50 different laboratories providing results for the monitoring programme. AQIS required new laboratories entering the programme to be accredited by the National Association of Testing Authorities (NATA) and all laboratories to participate in a Check Sample Analytical Programme. Fat samples with added pesticide were prepared by Australian Government Analytical Laboratories and distributed to participating laboratories. Analyses had to be completed and results returned within a fairly short time slot. Results were assessed to determine which laboratories needed to improve performance. All results were distributed to all laboratories, but each participant was identified only by a code letter. These requirements were good first steps towards attaining consistent performance across laboratories. To ensure continuing high quality results from all laboratories, it would be necessary to introduce regular audits of performance by an independent authority and insertion of secret check samples into each laboratories work load. Such checks would be extremely expensive, and difficult to organise.

ORGANOCHLORINE RESIDUES—ACCUMULATION

The major pesticides of concern during 1987-88 were the group including BHC, chlordane, DDT, dieldrin and heptachlor and commonly known as organochlorines. Problems were also experienced with some organophosphates but these were more easily corrected because organophosphate persistence in animals and in the environment was much less than for the organochlorines.

The nature of the organochlorine pesticides is that they accumulate in animals exposed to them. Being fat-soluble, within the animal they distribute throughout the fat deposits. Metabolism and excretion is generally very slow, but absorption is fairly efficient. In the short term, it is a reasonable approximation to assume that all organochlorine compounds ingested by a ruminant are absorbed and excretion is negligible. So an estimate of the impact of environmental contamination on a food producing animal can be assessed by making a few calculations. Consider a 300 kg bullock. This animal has about 20% of its body weight as fat, about 60 kg. Now suppose some posts in that animal's environment have been treated with aldrin to prevent termite attack, and soil around the base of the posts has been soaked during application. The bullock occasionally licks the posts and ingests some soil. Over the course of a week or so, it ingests 12 mg of aldrin. This is absorbed, converted to dieldrin and approximately 12 mg of dieldrin is distributed in the animal's fat—12 mg/60 kg or 0.2 mg/kg, equal to the Australian MRL for dieldrin. If the soil had 120 mg/kg of aldrin, ingestion of 100 g (about 4 ounces) of soil would provide the 12 mg.

Similar calculations are made for other species. A review of the literature (Noble, 1989) provides data summarised in Table 1, indicating that the factors of accumulation from the levels in feed are high, but vary considerably depending on species and the compound involved. Detailed analysis of fatty tissues of five steers which had been accidentally exposed to dieldrin (H. Mawhinney, Biochemistry Branch, Queensland Department of Primary Industries, Personal Communication) showed

levels were consistent in all clean dry fat from the various tissues of each animal. Actual fat concentrations ranged from 0.15 to 2.0 mg/kg in the five animals.

These ratios come from a wide range of experimental situations and the table conveys a sense of precision which is not really valid, because conditions influence the numbers considerably. Even when conditions are seemingly uniform, individual variations occur between animals. Groups of cattle have been examined for pesticides (H. Mawhinney, Biochemistry Branch, Queensland Department of Primary Industries, Personal Communication). Levels found are illustrated in Table 2. The figures in Groups 2 and 3 are representative of those groups and include the highest and lowest results obtained. It was believed that each group these animals had received consistent

TABLE 1: Accumulation Ratios

Pesticide	Milk fat	Body fat				Eggs
		Dairy	Beef	Layer	Broiler	
Aldrin	3.3	3.0	—	14	13	1.3
Dieldrin	5.9	1.3	—	14	13	1.3
α-BHC	2.0	—	11.4	1.8	3	1.3
β-BHC	7.5	2.9	9.8	19	14	1.9
γ-BHC	0.9	—	—	2	2.3	0.2
DDT	1.8	—	—	12	11	1.1
Heptachlor	5.7	—	4.0	11.5	18	1.0

TABLE 2: Residue Variations in Groups

Group 1 9 Cattle Dieldrin	Group 2 40 Cattle Dieldrin	BE	Group 3 120 Cattle DBBE	Ethion
0.09	0.32	0.51	0.39	0.78
0.09	0.37	<0.1	<0.1	0.34
0.11	0.21	0.39	0.39	0.48
0.12	0.28	0.74	0.52	1.10
0.12	0.38	1.63	2.99	0.39
0.16	0.44	0.85	1.18	0.78
0.07	0.35	0.62	0.58	0.60
0.13	0.32	1.38	2.04	0.85
0.27	0.37	0.85	1.18	0.78

BE = Bromophos-ethyl
DBBE = Desbromo-bromophos-ethyl

treatment in the same environment. Bromophos-ethyl and ethion are organophosphorus pesticides used in dipping vats in Queensland to treat cattle for control of cattle tick. Desbromo-bromophos-ethyl is formed in some cattle dips by replacement of a bromine atom by hydrogen. It was apparent that some animals in Group 3 had escaped being dipped in bromophos-ethyl, but this would not be unusual on a large property. The figures in Table 2 indicate that residues might be expected to vary by a factor of two across a group of apparently uniform animals. I suspect this could be an underestimate.

ORGANOCHLORINE RESIDUES—PERSISTENCE

The organochlorine pesticides also persist for long times in the environment and in animals. A wide range of factors influence what happens, so it is not possible to be precise about half-lives. In fact, it seems likely that different mechanisms control what is going on at different concentrations in animal tissues, so depletion does not necessarily follow expected trends. In soils it is likely that the breakdown depends on the specific microorganisms present and on the conditions which influence the activity of those microorganisms, although movement of pesticides in soil appears to be governed by physico-chemical properties (Jury *et al.*, 1987; Suntio *et al.*, 1988). The figures in Table 3 are assembled from a wide range of references (e.g. Anon., 1980; Bull, 1972; Connell, 1988; Edwards, 1966; Knipling and Westlake, 1966; Stickley, 1972) and experience of Biochemistry Branch, Qld. Department of Primary Industries staff participating in more than two hundred investigations of contaminated properties. These figures give a rough idea of how long the chemicals may stay in the environment, but we can hope that workers attempting to develop methods to accelerate the breakdown process will soon be successful.

A recent paper (Petterson *et al.*, 1988) describes the long slow process of elimination of heptachlor epoxide (HCE) and oxychlordane (OCD) from cattle which initially had 1.2-67 mg HCE/kg and 0.3-18 mg OCD/kg in their fat following accidental exposure to commercial heptachlor. Commercial heptachlor can contain

TABLE 3: Persistence of Pesticides

	Half-life in fat (Live animals)	Half-life in soil
DDT	4-12 weeks	3-10 years
Dieldrin	6-12 weeks	1-7 years
BHC	3-6 weeks	2-3 years
Heptachlor	6-12 weeks	7-12 years
Ethion	*c.* 5 days	—
Bromophos-ethyl	*c.* 4 days	—
Chlorpyriphos	*c.* 2 days	—

up to 30% chlordane and within the animal these compounds are converted to heptachlor epoxide and oxychlordane. After 488 days residues were 0.01-0.26 mg HCE/kg and 0.01-0.43 mg OCD/kg, so even after this interval some of the animals still had residues above the MRLs (heptachlor 0.2 mg/kg; chlordane now 0.2 mg/kg then 0.05 mg/kg).

OTHER RESIDUES IN FOOD

Another residue situation which has had some publicity in recent months is the use of daminozide (Alar) on apples. The compound is a plant growth regulator which makes fresh fruit firmer, controls induction of flowering, prevents premature fruit drop and enhances storability and colour. It is used on apples, pears and peaches in Australia while in the USA there is also use on cherries. During processing, daminozide degrades to UDMH (Unsymmetrical dimethyl hydrazine) which is a potential carcinogen. The Australian MRLs for daminozide are 30 mg/kg for peaches and pome fruit. It is interesting to compare these figures with the results of a recent small US survey (Saxton *et al.*, 1989). The levels found are listed in Table 4.

TABLE 4: Daminoxide Residues

Daminozide	(Canned)	Apples	0.6 mg/kg
		Cherries	5.9 mg/kg
		Apple Juice	1.1 mg/l
UDMH	(Canned)	Cherries	0.6 mg/kg
		Apple Sauce	0.06 mg/kg

Although the product has been on the market since 1963, it is only in recent years that concern has been expressed about possible hazards from residues, particularly in processed apple products. The very extensive debate about this use illustrates how difficult assessment of the situation is. Two recent letters present different attitudes. One (Groth, 1989) from the Consumers Union of the US argues about interpretations of what is safe but the most important comment relates to the public perception of risk: "However big a risk may be, whether it is acceptable or not is a value judgement and is heavily influenced by the MORAL dimensions of the risk". The letter goes on to state that risk management must balance values and ethical choices and is inevitably a political process, and that public reaction to risk is related to perception of the ethical aspect of the risk and bears little relation to the magnitude of the risk. The next letter (Ames and Gold, 1989) emphasises the need to compare the risks from pesticide residues with those from natural components of foods. The authors provide some risk calculations to show that common foods such as one daily mushroom, or 100 g daily servings of celery, cabbage or Brussels sprouts provide much higher risks than are likely from residues of UDMH in a daily glass of apple juice. Information is also given about natural carcinogens in food and the significance of risk assessment.

DOSE-RESPONSE

Public concern over pesticide residues in foods is stirred up from time to time and is often fuelled by rather exaggerated statements about the adverse effects such pesticides might have. The dose-response relationship is ignored and effects at high dose are emphasised with the tacit assumption that the same response occurs following consumption of the trace amounts present in food. There is also an assumption that pesticides are somehow worse than the naturally occurring, but often extremely toxic chemicals in foods.

Dose response is readily apparent to us in many aspects of daily life although we often overlook it. Medications such as antibiotics are prescribed at specific doses to obtain the effect of destroying a microorganism with minimal effects on the person. Doses for children are smaller than for adults because of lower body weight and sometimes greater susceptibility. Ethyl alcohol is a chemical with well-known dose related effects. Many people in our society consume ethyl alcohol in a wide range of alcoholic drinks and experience a dose related response. Most are aware of the immediate dose response and adjust intake accordingly. Legally the dose response is taken into account by relating blood alcohol levels to capability to drive motor vehicles. When the dose is sufficiently high, acute toxic effects are observed—staggering, slowing down of reaction time and other symptoms of alcoholic intoxication. Repeated high dosage over an extended period of time produces other dose responses such as cirrhosis of the liver.

Generally the dose-response relationship is that the higher the dose the greater is the biological effect. This concept of "*The Dose Makes The Poison*" cannot be too strongly emphasised.

TOXIC COMPOUNDS IN FOODS

Natural foods contain a whole pharmacopoeia of hazardous chemicals (Fenwick, 1986; Hoskins, 1978; Kaplan, 1983; Liener, 1980; Wogan, 1969). For example: *cyanide* occurs widely in foods such as sweet potato, maize, peas, beans (especially haricot, navy and lima), in the kernel of almonds, cherries, apricots, prunes, plums, and in seeds of apples and pears; *saponins* occur in spinach, beetroot, asparagus, soybeans and tea; *estrogens* occur in wheat, oats, rice, barley, potatoes, apples, cherries, plums, rice, carrots and in some vegetable oils; *enzyme inhibitors*, such as anti-trypsins, occur in soybeans, potato, sweet potato, in most varieties of beans, in peas, peanuts, all grains and more than 50 common plant foods; *goitre-inducing thioglycosides* occur commonly in all *Brassica* such as cabbage, cauliflower and kale, and in mustard, horse radish, turnips and onions; *oxalate* is present in high concentrations in rhubarb; and in addition there are numerous allergens, anti-vitamins, organic acids, tannins and alkaloids intrinsic in common foods. In the course of cooking we pyrolize complex carbohydrates and proteins to yield, among other toxic chemicals, 3,4-benzpyrene—a potent cancer-producing agent.

Other foods such as milk and honey can accumulate highly toxic natural chemicals and many other foods such as bananas, chick peas and condiments contain active compounds which would be harmful in larger doses. Consequently, it is not appropriate to exaggerate possible hazards of traces of pesticide residues in foods.

INTAKE OF PESTICIDES

Following treatment, residues may be on a food product or in the product. MRLs normally apply to the whole product, so additional safety margins are in place when portions of the product containing residue are discarded.

When most of the residue is on the surface of a vegetable or fruit product, amounts in the food consumed are reduced, sometimes eliminated, by washing or peeling. However, when the chemical has been absorbed systemically and is present in the product, its distribution and the way residues are bound in the product structure are controlled by the chemistry of that compound.

Although data are not very extensive as yet, more investigations are being directed at determining the effect processing has on the amount of residues actually consumed. In addition to concentration changes reflecting changes in moisture content during cooking, residues may be removed by boiling, baking or roasting. For example, studies of dieldrin in pig meat have shown approximately 50% reductions in concentration following cooking in several ways — pan-frying, baking, microwave and braising, although there is a trend through this sequence of reduced losses (Maul *et al.*, 1971).

In some circumstances the apparent possible intake of a chemical present in a food is much greater than the actual intake. If, for example, we have a 500 g steak, nominally containing 1 ppm (1 mg/kg) DDT, we naturally expect 0.5 mg DDT to be present. However, since DDT is a fat soluble pesticide, the analytical result is expressed as a concentration in fat, so the 1 mg/kg is actually 1 mg in every kg of fat in the meat. Now if the 500 g steak is moderately fatty it will have about 20% fat—100 g, so at 1 ppm the raw steak actually contains 0.1 mg DDT. When the steak is grilled about 50% of the fat is lost and the DDT it contains goes with it. So actual intake of DDT by consuming that steak is 0.05 mg not 0.5 mg.

Considerable international attention has been directed at estimating dietary intake of pesticide residues. "Guidelines for Predicting Dietary Intake of Pesticide Residues" (Anon., 1989b) has been developed over many years through cooperation between World Health Organisation, the United Nations Environment Programme, the Food and Agriculture Organisation and the Codex Committee on Pesticide Residues. It is recognized that sufficient food intake data to make accurate calculations is rarely available and is expensive to generate. Consequently, effort is directed at assessing whether or not possible residues could be a cause for concern, so that resources can be used to generate data in appropriate areas.

Since food consumption patterns differ markedly from country to country, and even within a country, it is not possible to generate a single standard diet from which to assess pesticide intake. Thus, it is appropriate for each country to do its own calculations.

When assessing intake, the simplest and crudest calculation is the TMDI—Theoretical Maximum Daily Intake—which uses the MRL and the average daily per capita consumption of each food for which an MRL has been established:

Quantity of food (kg) × MRL (mg/kg), the sum all foods.

This gives mg/person/day. Assume body weight is 60 kg and so convert the amount to mg/kg/day and compare with the ADI. The TMDI is a gross overestimate of intake but if the result is less than the ADI, no further examination is necessary. If the TMDI is larger than the ADI, then calculations must be refined to provide a more realistic intake figure.

The next step is to calculate the EMDI (Estimated Maximum Daily Intake). The EMDI uses data on residue concentration in the edible portion of the foods involved, rather than the MRL, and applies correction factors for changes in residues during processing and cooking. These factors do not necessarily reduce the estimate. This still provides a considerable overestimate of intake but is closer to reality than the TMDI. Again, if the EMDI is less than the ADI, no further examination is necessary, but if it is greater than the ADI, the next step in assessment is to calculate the EDI (Estimated Daily Intake). In addition to food intake the following data is needed:

(i) Known uses of the pesticide;

(ii) Known residue levels;

(iii) Proportion of the crop treated;

(iv) Ratio of home-grown to imported in the market place; and

(v) Changes during storage, processing and cooking.

If the EDI is greater than the ADI, use of the compound may need to be restricted. It is important to understand that the TMDI and EMDI are exaggerated figures —gross overestimates of actual intake. They are steps in a process designed to identify those situations where more careful examination of possible intake is warranted. They do not, of themselves, indicate cause for concern.

SOURCES OF PESTICIDES

As mentioned earlier, pesticides are absorbed into animals from their environment. During investigations of excessive residues detected in 1987-88, it was found that in Queensland, the organochlorine pesticides most frequently detected were dieldrin (*c.* 70%), heptachlor and BHC (*c.* 10% each), and DDT (*c.* 7%).

The most important sources of organochlorines in the environment of food animals were:

(i) From termite and spider control, in animal handling yards; on posts where animals have access; in buildings where animals are housed or their feed materials are stored; and in silos particularly where feed grains are stored;

(ii) Land used for sugarcane or cotton growing when the organochlorine compounds were permitted. In addition, adjacent areas may also be a source of residue because of soil movement as washings or dust, or possibly from spray drift during application; and

(iii) From use for animal feed of small crops, especially root crops, grown in land previously treated with organochlorine compounds.

Another possible source is vegetable waste from canneries. Although this does not appear to be a significant source, the waste is used as animal feed and care must be exercised to prevent accumulation in animals. Any residues present in produce are likely to be predominantly in the discarded portions which go for animal feed. Accumulation as described above could lead to unacceptable residues in the animals or their produce.

The sources of dieldrin detected following 131 successful field investigations by officers of the Queensland Department of Primary Industries have been summarised (McEwan and Stocks, 1988). Animal handling yards and poles treated for termite control accounted for 42 sources while yards around dipping facilities provided another eight. Treated sheds and silos caused contamination of hay in 20 cases and of grain in another 13 cases, while contaminated grain transported to feed lots caused five cases. Pasture grown on land previously used for small crops (14 cases) and cane growing (17 cases) was an important source. The remaining 12 were miscellaneous sources.

CONCLUSION

It is important therefore to realise that all different parts of the environment interact. This discussion illustrates some aspects of the way residues appear in food and how animal industries can be affected by chemical use in other areas. We must therefore be aware that in all areas, unexpected interactions are possible, even likely, and be alert to detect these and prevent adverse side effects.

REFERENCES

Ames, B. and Gold, L. (1989). "Pesticides, risk and applesauce". *Science*, **244**, 755-757.

Anon. (1980). Namoi Environmental Study. New South Wales State Pollution Control Commission. ISBN 0-7240-4227-X.

Anon. (1988). Report on National Residue Survey 1986 Results''. Australian Government Publishing Service, Canberra. ISBN 0-644-07961-4.

Anon. (1989a). Health, Politics, Trade: Controlling Chemical Residues in Agricultural Products. A Report to the Prime Minister by the Australian Science and Technology Council (ASTEC). Australian Government Publishing Service, Canberra. ISBN 0-644-08948-2.

Anon. (1989b). Guidelines for Predicting Dietary Intake of Pesticide Residues. World Health Organisation, Geneva. ISBN 92-4-154250.

Bull, D.L. (1972). Metabolism of Organophosphorus Insecticides in Animals and Plants. F.A. Gunther and J.D. Gunther (Eds). Springer-Verlag, Berlin. *Residue Reviews*, **43**, 1-22.

Connell, D.W. (1988). Bioaccumulation Behaviour of Persistent Organic Chemicals with Aquatic Organisms. G.W. Ware (Ed.). Springer-Verlag, New York. *Rev. Environ. Contam. and Tox.*, **2**, 17-154.

Corty, C. (1983). Developments in formulation and application technology for safe use of agrichemicals. in Pesticide Chemistry: Human Welfare and the Environment. J. Miyamoto and P.C. Kearney (Eds). Vol 4. Pesticide Residues and Formulation Chemistry, R. Greenhalgh and N. Drescher (Eds). Pergamon Press, Oxford. pp 281-288.

Edwards, C.A. (1966). Insecticide Residues in Soil. F.A. Gunther (Ed.). Springer-Verlag, Berlin. *Residue Reviews*, **13**, 83-132.

Fenwick, G.R. (1986). The Natural Toxicants of common foods for animals and man. *Proc. Nut. Soc. Aust.*, 11-23.

Groth, E. (1989). Alar in Apples. *Science*, **244**, 755.

Hamilton, D. (1988). Setting MRL values for pesticides in foods. *Qd Agric J.*, July/August, 225-228.

Hoskins, F.H. (1978). Naturally occurring toxicants in food in Chemical Toxicology of Food, C.L. Galli, R. Paoletti and G. Vettorazzi (Eds). Elsevier/North-Holland Biomedical Press, Amsterdam. pp 233-246.

Jury, W.A., Winer, A.M, Spencer, W.F. and Focht, D.D. (1987). Transport and Transformations of Organic Chemicals in the Soil-air-water Ecosystem. G.W. Ware (Ed.). Springer-Verlag, New York. *Rev. Environ. Contam. and Tox.*, **99**, 19-164.

Kaplan, H. (1983). Toxicities of natural foods in man: A survey. *Trans. Illinois State Acad. Sci.*, **76**, (1/2), 181-194.

Knipling, E.F. and Westlake, W.E. (1966). Insecticide Use in Livestock Production. F.A. Gunther (Ed.). Springer-Verlag, Berlin. *Residue Reviews*, **13**, 1-32.

Liener, I.E. (1980). Toxic Constituents of Plant Foodstuffs. Second Edition. Academic Press, New York.

Maul, R.E., Funk, K., Zabik, M.E. and Zabik, M.J. (1971). Dieldrin residues and cooking losses in pork loins. *J. Amer. Dietetic Assoc.*, **59**, 1-484.

McEwan, T. and Stocks, D.C. (1988). Pesticide residues in meat. *Aust. Sci. Mag.*, **28** (3), 4-11.

Noble, A. (1989). The relation between organochlorine residues in animal feeds and residues in tissues, milk and eggs: a review. *Aust. J. Exp. Agric.* in press.

Petterson, D.S., Casey, R.H., Ebell, G.F. and McIntyre, B.L. (1988). Residues in beef cattle accidently exposed to commercial heptachlor. *Aust. Vet. J.*, **65**(2), 50-53.

Saxton, W.L., Steinbrecher, K. and Gundersón, E. (1989). Results of a survey for the presence of daminozide and unsymmetrical dimethylhydrazine in food. *J. Agric. Food Chem.*, **37**, 570-573.

Schultze, W.D. (1975). Dry Cow Therapy—A Review. Proc. Ann. Meeting, National Mastitis Council Inc., Feb 10-12.

Stickley, B.D.A. (1972). Studies on the persistence of aldrin, dieldrin, heptachlor, lindane and crude BHC in four Queensland soils. *Bur. Sugar Expt. Stns.*, No.1, 1-38.

Suntio, L.R., Shiu, W.Y., Mackay, D., Sieber, J.N. and Glotfelty, D. (1988). Critical Review of Henry's Law Constants for Pesticides. G.W. Ware (Ed.). Springer-Verlag, New York. *Rev. Environ. Contam. and Tox.*, **103,** 1-59.

Willis, G.H. and McDowell, L.L. (1987). Pesticide Persistence on Foliage. G.W. Ware (Ed.). Springer-Verlag, New York. *Rev. Environ. Contam. and Tox.*, **100,** 3-73.

Wogan, G.N. (1969). Naturally occurring carcinogens in foods. *Progr. Expl. Tumor Res.*, **11,** 134-162.