HERBICIDE RESIDUES IN PLANTS

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It is distressing to hear of accidental deaths resulting from herbicides. In this era of pollution-consciousness it is fashionable to condemn all pesticides. The following presentation aims at being factual, with an Australian slant.

The subject is limited to herbicide residues on and in plants. These residues could be important when eaten by humans or domestic animals. In addition hazards could arise from the eating of products such as eggs and milk from animals fed on treated plants. Apart from dangers to wildlife, there can be the death of useful insects such as bees (affected mainly by dinitrophenols, paraquat, and 2,4-D).

Side effects of 2,4-D and related herbicides can make poisonous plants more attractive to stock, raise nitrate content of sugar beets to a toxic level, and increase cyanide and alkaloid contents. Another side effect is carry-over of the herbicide into seeds, thereby lessening germination.

The term deposit refers to the chemical as laid down, whereas residue refers to the chemical regardless of locale, with implications of alteration. The total residue comprises external residue (affected by weathering, hydrolysis, photodecomposition and elution), and internal residue (translocated internally and altered by metabolic processes). The limit of detectability is the concentration level of the herbicide above which a given sample of the material can be said to contain the chemical analyzed with a high degree of assurance. Few, if any herbicides are subject to the process of biological magnification as occurs for some chlorinated-hydrocarbon insecticides, though some soil-applied herbicides continue to be absorbed over a period of months.

The disappearance of most pesticide residues follows a first-order reaction, theoretically never complete. Specifications of 'no residue' and 'zero tolerance' are scientifically untenable, and administratively refer to a level below the limit of detectability. Crops with both an aqueous and oily phase can demonstrate first-order decay curves with two different slopes.

All forms of microanalysis are used for residues, though gas chromatography is often preferred on account of great sensitivity. Often, a herbicide at an early state of development is prepared in radioactive form to facilitate the development of methods of analysis and to elucidate metabolic processes.

The pathways by which a herbicide can be metabolized are oxidation, reduction, hydrolysis and conjugation. Higher plants

are less able than microorganisms to cause ring opening, though they may use similar methods for the early breakdown of compounds. Plants can cause oxidation and hydroxylation of 2,4-D, also can complex or conjugate it (at least three different complexes occur). Maize converts symmetrical triazines into the hydroxy-analogue by replacement of the chlorine atom. MH is fairly resistant inside a plant, and has unchanged residues lasting up to 8 months in potato tubers; it can also be complexed. ATA undergoes considerable alteration.

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Testing starts during commercial development. Criteria have been prepared in detail by the World Health Organization, the U.S. Food and Drug Administration, and the Australian National Health and Medical Research Council. Requirements include studies of acute toxicity, sub-acute toxicity, chronic toxicity, and metabolism in at least two species of animals, also effect on reproduction in at least one species over three successive generations. Now, in addition, the technical formulation and its impurities are studied in detail; moreover it is necessary to identify all biologically active metabolites and to study each as the parent compound. Field samples of residues, from a wide variety of climates, are also analyzed for breakdown products. Cancer tests are also started if considered necessary.

A herbicide is approved for sale only if evidence from appropriate tests shows that the crop treated as recommended (and in accordance with good agricultural practice) will not contain a residue harmful to consumers. One of the most important considerations is the required interval between the last application and harvesting. For a herbicide to be marketed in Australia it must be registered beforehand with a Department of Agriculture or Department of Health (depending on the State); registration must be renewed periodically. The permitted residue is extrapolated from a no-effect level on experimental animals, with a safety factor of 100 to 1. There are at least three schools of thought as to how permissable residues are best calculated from such data. Nevertheless, the case of the simultaneous presence in food of several herbicide residues having similar pharmacological action is provided for by assuming that the herbicides together have an additive action.

In spite of the valuable work done by FAO/WHO committees, much remains to be done as regards international pesticide tolerances. At the request of the Australian Agricultural Council the Commonwealth has undertaken to evaluate pesticides and the implications of their uses, and through the appropriate technical committees, to issue clearances for registration by

State authorities. Legal tolerances are specified by the National Health and Medical Research Council. These are somewhat smaller than those ruling in America, on account of the more uniform climates here. These tolerances are written into State legislation as conditions permit. The N.H.M.R.C. also specifies any required withholding period after harvesting or processing.

A recent overseas list of some 80 herbicides includes 7 with LD_{50} values to rats lying between 30 and 100 mg/kg, viz. acrolein, DNBP, DNOC, endothal, ioxynil, paraquat and PCP. Any of these licensed for use on crops in Australia are required to leave no residues of the unchanged compounds in or upon foods as consumed. 2,4-D, with an LD_{50} value of 375 mg/kg can occur to the extent of 5 p.p.m. in fruits, grains and vegetables. Amitrole, with LD_{50} value exceeding 1,110 mg/kg, is classified amongst those required to leave no residue, on account of a goitrogenic action.

Residues in 'total diet' have been monitored in England, Canada, and the United States. The last country applies over 50% of all pesticides used annually throughout the world. Yet in all three countries the detectable quantities are generally less than one-hundredth of the amount considered to be safe. From data available, Australian values are expected to be lower. In this country the Department of Primary Industry regularly surveys levels of residues in foodstuffs being exported.

Claims that the above tolerances do not adequately protect consumers against carcinogenic herbicides are not supported by the evidence available. Workers concerned with the manufacture and application of herbicides are exposed to much larger quantities, yet are no more susceptible to cancer than the rest of the population.

As regards general safety it may be pointed out that in England and Wales about 1500 people a year die from accidental poisoning, and that there are more deaths in one year from accidental poisoning by aspirin than have occurred from all agricultural chemicals over the last 30 years. The main dangers which arise from herbicides (or any chemicals) are attributable to careless or improper use.