

RESIDUE REVIEWS

VOLUME 62

RESIDUE REVIEWS

Residues of Pesticides and Other
Contaminants in the Total Environment

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Foreword

Worldwide concern in scientific, industrial, and governmental communities over traces of toxic chemicals in foodstuffs and in both abiotic and biotic environments has justified the present triumvirate of specialized publications in this field: comprehensive reviews, rapidly published progress reports, and archival documentations. These three publications are integrated and scheduled to provide in international communication the coherency essential for nonduplicative and current progress in a field as dynamic and complex as environmental contamination and toxicology. Until now there has been no journal or other publication series reserved exclusively for the diversified literature on "toxic" chemicals in our foods, our feeds, our geographical surroundings, our domestic animals, our wildlife, and ourselves. Around the world immense efforts and many talents have been mobilized to technical and other evaluations of natures, locales, magnitudes, fates, and toxicology of the persisting residues of these chemicals loosed upon the world. Among the sequelae of this broad new emphasis has been an inescapable need for an articulated set of authoritative publications where one could expect to find the latest important world literature produced by this emerging area of science together with documentation of pertinent ancillary legislation.

The research director and the legislative or administrative advisor do not have the time even to scan the large number of technical publications that might contain articles important to current responsibility; these individuals need the background provided by detailed reviews plus an assured awareness of newly developing information, all with minimum time for literature searching. Similarly, the scientist assigned or attracted to a new problem has the requirements of gleaning all literature pertinent to his task, publishing quickly new developments or important new experimental details to inform others of findings that might alter their own efforts, and eventually publishing all his supporting data and conclusions for archival purposes.

The end result of this concern over these chores and responsibilities and with uniform, encompassing, and timely publication outlets in the field of environmental contamination and toxicology is the Springer-Verlag (Heidelberg and New York) triumvirate:

Residue Reviews (vol. 1 in 1962) for basically detailed review articles concerned with any aspects of residues of pesticides and other chemical contaminants in the total environment, including toxicological considerations and consequences.

Preface

That residues of pesticide and other contaminants in the total environment are of concern to everyone everywhere is attested by the reception accorded previous volumes of "Residue Reviews" and by the gratifying enthusiasm, sincerity, and efforts shown by all the individuals from whom manuscripts have been solicited. Despite much propaganda to the contrary, there can never be any serious question that pest-control chemicals and food-additive chemicals are essential to adequate food production, manufacture, marketing, and storage, yet without continuing surveillance and intelligent control some of those that persist in our foodstuffs could at times conceivably endanger the public health. Ensuring safety-in-use of these many chemicals is a dynamic challenge, for established ones are continually being displaced by newly developed ones more acceptable to food technologists, pharmacologists, toxicologists, and changing pest-control requirements in progressive food-producing economies.

These matters are of genuine concern to increasing numbers of governmental agencies and legislative bodies around the world, for some of these chemicals have resulted in a few mishaps from improper use. Adequate safety-in-use evaluations of any of these chemicals persisting into our foodstuffs are not simple matters, and they incorporate the considered judgments of many individuals highly trained in a variety of complex biological, chemical, food technological, medical, pharmacological, and toxicological disciplines.

It is hoped that "Residue Reviews" will continue to serve as an integrating factor both in focusing attention upon those many residue matters requiring further attention and in collating for variously trained readers present knowledge in specific important areas of residue and related endeavors involved with other chemical contaminants in the total environment. The contents of this and previous volumes of "Residue Reviews" illustrate these objectives. Since manuscripts are published in the order in which they are received in final form, it may seem that some important aspects of residue analytical chemistry, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology are being neglected; to the contrary, these apparent omissions are recognized, and some pertinent manuscripts are in preparation. However, the field is so large and the interests in it are so varied that the editors and the Advisory Board earnestly solicit suggestions of topics and authors to help make this international book-series even more useful and informative.

"Residue Reviews" attempts to provide concise, critical reviews of timely advances, philosophy, and significant areas of accomplished or needed endeavor in the total field of residues of these and other foreign chemicals in any segment of the environment. These reviews are either general or specific, but properly they may lie in the domains of analytical chemistry and its methodology, biochemistry, human and animal medicine, legislation, pharmacology, physiology, regulation, and toxicology; certain affairs in the realm of food technology concerned specifically with pesticide and other food-additive problems are also appropriate subject matter. The justification for the preparation of any review for this book-series is that it deals with some aspect of the many real problems arising from the presence of any "foreign" chemicals in our surroundings. Thus, manuscripts may encompass those matters, in any country, which are involved in allowing pesticide and other plant-protecting chemicals to be used safely in producing, storing, and shipping crops. Added plant or animal pest-control chemicals or their metabolites that may persist into meat and other edible animal products (milk and milk products, eggs, etc.) are also residues and are within this scope. The so-called food additives (substances deliberately added to foods for flavor, odor, appearance, etc., as well as those inadvertently added during manufacture, packaging, distribution, storage, etc.) are also considered suitable review material. In addition, contaminant chemicals added in any manner to air, water, soil or plant or animal life are within this purview and these objectives.

Manuscripts are normally contributed by invitation but suggested topics are welcome. Preliminary communication with the editors is necessary before volunteered reviews are submitted in manuscript form.

Department of Entomology
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March 1, 1976

F.A.G.
J.D.G.

Bulletin of Environmental Contamination and Toxicology (vol. 1 in 1966) for rapid publication of short reports of significant advances and discoveries in the fields of air, soil, water, and food contamination and pollution as well as methodology and other disciplines concerned with the introduction, presence, and effects of toxicants in the total environment.

Archives of Environmental Contamination and Toxicology (vol. 1 in 1973) for important complete articles emphasizing and describing original experimental or theoretical research work pertaining to the scientific aspects of chemical contaminants in the environment.

Manuscripts for *Residue Reviews* and the *Archives* are in identical formats and are subject to review, by workers in the field, for adequacy and value; manuscripts for the *Bulletin* are not reviewed and are published by photo-offset to provide the latest results without delay. The individual editors of these three publications comprise the Joint Coordinating Board of Editors with referral within the Board of manuscripts submitted to one publication but deemed by major emphasis or length more suitable for one of the others.

March 1, 1976

Coordinating Board of Editors

Table of Contents

| | |
|---|-----|
| Worker reentry safety. I. An overview of the reentry problem on citrus in California | |
| By G. E. CARMAN | 1 |
| Worker reentry safety. II. The viewpoint and program of the National Institute for Occupational Safety and Health | |
| By JON RICHARD MAY | 7 |
| Worker reentry safety. III. Viewpoint and program of the Environmental Protection Agency | |
| By ORVILLE E. PAYNTER | 13 |
| Worker reentry safety. IV. The position of the California Department of Food and Agriculture on pesticide reentry safety intervals | |
| By KEITH T. MADDY | 21 |
| Worker reentry safety. V. Reentry intervals as health standards | |
| By EPHRAIM KAHN | 35 |
| Worker reentry safety. VI. Occupational health aspects of exposure to pesticide residues | |
| By B. DWIGHT CULVER | 41 |
| Worker reentry safety. VII. A medical overview of reentry periods and the use of urinary alkylophosphates in human pesticide monitoring | |
| By J. E. DAVIES, M. T. SHAFIK, A. BARQUET, C. MORCADE, and J. X. DANAUSKAS | 45 |
| Worker reentry safety. VIII. The determination of urinary metabolites—An index of human and animal exposure to nonpersistent pesticides | |
| By M. TALAAT SHAFIK and DIANE E. BRADWAY | 59 |
| Worker reentry safety. IX. Techniques of determining safe reentry intervals for organophosphate-treated cotton fields | |
| By GEORGE W. WARE and DONALD P. MORGAN | 79 |
| Selenium in the environment | |
| By C. M. JOHNSON | 101 |
| Diquat and endothall: Their fates in the environment | |
| By G. V. SIMSIMAN, T. C. DANIEL, and G. CHESTERS | 131 |
| Index | 177 |

Worker reentry safety. I. An overview of the reentry problem on citrus in California.*

By

G. E. CARMAN**

When I was first contacted with regard to participation in this colloquium on worker reentry safety, an interest was indicated in having me present "The viewpoint of the Industry Committee on Citrus Additives and Pesticides." I intend to fulfill that topic assignment even though I exercised some prerogative in effecting a title change, since it would be ultimately difficult to reflect inclusively the Committee's views.

The Industry Committee on Citrus Additives and Pesticides, more commonly identified as the ICCAP, is a nonprofit industry-wide organization supported by all citrus growers through production-based assessments collected and dispersed through a State Marketing Order. A Citrus Advisory Board comprised of grower members elected from specified districts has the responsibility of allocating funds made available through the Marketing Order and, in addition to other disbursements, provides the operating funds for the ICCAP.

Under this arrangement the ICCAP is the functional organization of the California citrus growers delegated with the responsibility of coping with all marketing problems, domestic and foreign, related to pesticide and food additive residues. It consults with and is guided by a committee of representatives from the cooperative and independent citrus marketing organizations, allied industries, governmental agencies and educational institutions. Its ultimate objective is to provide information and procedural guidance to California citrus growers which will enable them to avoid violations of domestic and foreign food laws relating to pesticide residues and to undertake all appropriate efforts to assist foreign countries in avoiding the enactment of food laws which would become unwarranted trade barriers to the California citrus industry.

The ICCAP is governed by a Board of six members and, as the desig-

* This and the following eight reports were presented as part of a symposium, 167th National Meeting, American Chemical Society, Los Angeles, CA, April 3, 1974.

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nated Board member from the University of California, I will endeavor to reflect for you the basic understanding that the citrus industry has of the reentry problem and its viewpoints concerning the means by which the problem can be circumvented.

Sulfur, with its elemental capacity to cause eye irritations, may well be claimed to have caused the first reentry problem in the reviewable history of agricultural enterprises, but the more serious aspect of the problem as currently evaluated surfaced shortly after extensive commercial use of the first organophosphorus compound, parathion, began in the early 1950s. Even prior to the grower use of parathion an incident occurred which demonstrated its potential for difficulties related to post application exposures to parathion. A grower-cooperator on whose property a test plot involving parathion applications was established, implicitly followed all of our instructions about what to do and not to do but since the trees were relatively young we failed to anticipate that he might attempt to prune the trees, let alone from a prone position on the ground, looking up and inevitably with his mouth open. While not seriously affected, our grower friend did exhibit undeniable symptoms of parathion poisoning. For us, this was the birth of the dislodgeable residue concept. The first commercial and significant focus of concern was on parathion-treated vineyards in the Delano area of California. Workmen lifting vine leaders up over the wire supports developed illnesses not previously experienced. Dr. Hamblin of the American Cyanamid Company sent a professional medical worker from his New York headquarters to Delano to study the situation and it was established that significant cholinesterase depressions in blood tissue did occur in workers following such exposures.

The first major episodes on citrus which appeared to relate to post-application exposures to parathion occurred when pickers were put into orchards shortly after the applications had been made. The newly enacted Miller Bill was not fully understood at that time and the observance of waiting intervals to meet tolerance requirements for fruit residues had not as yet become a recognized ingredient of the decision process by growers and packinghouse field men insofar as picking schedules were concerned. Unlike the apple people and others, the citrus growers had had virtually no experience with residue problems since HCN fumigation, petroleum oils, tartar emetic, nicotine, and a very limited selection of miticides constituted their main use of pesticides. These limited episodes served to emphasize the existence of the new legal requirements for fruit residues, but did not impress growers or others with the possibility of overriding concerns about the exposure of pickers since it was assumed that no difficulty would have been experienced if the full 30-day period for the dissipation of the parathion residues on the fruit to legally acceptable levels had been observed.

However, in the late fifties some members of a picking crew working in the Riverside area reported illnesses while working and were promptly

given medical attention. It was generally concluded that the illnesses were associated with organophosphorus compound exposures, but orchard records indicated that the last application prior to the picking operation, one of parathion at the relatively high dosage used for scale control, had been completed over 55 days earlier.

This circumstance was disturbing to many, and the group at the University of California Citrus Research Center, in consultation with State and Federal health officers, formulated a plan whereby a research group of the U.S. Public Health Service would be notified immediately at the time of any subsequent episodes for the purpose of getting to the location promptly and conducting an in-depth study of what actually happened and of the relatable factors. As you have probably immediately suspected, no episodes occurred during the next several years. The U.S. Public Health team of experts completed their original and primary mission or missions and were dispersed to new assignments.

When the problem resurfaced on citrus early in 1970, there were several incidents. They all occurred in Central California and appeared to implicate several other organophosphorus materials besides parathion. These included ethion, Guthion® (azinphosmethyl), and Delnav® (dioxathion), and possibly malathion by virtue of its inclusion in one of the spray applications.

The waiting periods required for the dissipation of the residues on the fruit had in all cases been observed and, as a result, concerns about this aspect of organophosphorus compound usage began to receive increased attention at the regulatory levels. What has transpired subsequently will be detailed in great part in the discussions being presented here today and so, with this very brief and generalized background of the problem, I would like at this time to limit further remarks to what in my opinion is the overview of the California citrus industry as regards this problem, along with thoughts and suggestions as to the best means of dealing with the problem.

At this time the citrus industry of California recognizes fully that even though the occurrence of episodes has been extremely limited in relation to the total background of past worker exposures and has failed to suggest totally consistent relationships to identifiable causant factors or circumstances, it is disturbingly factual that certain orchard operations undertaken following the application of some pesticide materials, notably the organophosphorus-type compounds, may predispose field workers to the uptake of toxic moities during prolonged periods of actual and substantial contact with the treated plant surfaces to the extent that initial symptoms of poisoning will be experienced.

The prospect of any illnesses stemming from work assignments is truly disturbing even though the available evidence indicates that the uptake of any toxic material via such exposures would be at a gradual rate which, in the case of the organophosphorus compounds, would elicit symptoms of poisoning sufficiently soon to avoid extended illnesses,

let alone the prospect of fatal exposures. Historically, the citrus industry of California has evidenced unusual concern for the welfare of its workers at all levels and any failure to deal with this problem objectively would be inconsistent with operational attitudes and policies.

The Industry is convinced that the dimension of the problem relates largely, if not solely, to the part of the pesticide residues on the plant surfaces associated with particulate matter which can be dislodged physically. Residues that have penetrated into the leaf peel, or wood surfaces do not constitute a significant part of the workers' exposure. Further, knowledge of the physical attributes of the various pesticides being used and the results of limited studies with several of the materials of immediate concern indicate an inappreciable potential for bodily uptake in the vapor phase. The key to the problem is the so-called "dislodgeable residue" and the Industry believes that a knowledge of such residues and their attenuation is fundamental to the resolution of the problem.

Its concern is to see that any exposure to such residues is so limited that no worker will experience any manifestation of an adverse physiological response. Industry members generally have a clear understanding of the "dosage concept"—an appreciation of biological tolerances and adaptability. Surviving exposures to California's infamous smog helps to make the point.

These understandings negate the view that such exposures must be totally eliminated and support the view that restrictions are needed to minimize exposures to a safe level. There is also the realization that because of the slow low-level accumulation of any toxin through such exposures, the primary concern is to avoid any significant occurrence of sickness or discomfort. And, since the relative amounts of intake of toxic residues, whether dermally, orally, or by inhalation, have not been quantified adequately in relation to plant surface burdens of dislodgeable residues and work activities, the Industry further believes that any near-term means of avoiding poisoning episodes must relate to the total level of the dislodgeable residues.

With recognition that a real and continuing problem existed and with an unqualified interest in having the problem resolved in the most practical manner, the Industry was greatly impressed with the very comprehensive and understandable analysis the Pest Control Advisory Committee of the then California State Department of Agriculture made of an array of solution options. The Department's ultimate decision to specify safe reentry intervals was outwardly based on the assumption that dislodgeable residues dissipated with extensions of time following treatment much in the manner of total residues and offered the promise of an effective and practical means of protecting the field workers. The safe reentry approach was, admittedly, somewhat easier for the citrus industry to accept as a restriction on harvesting operations than was possible for certain other commodity groups because of the possibilities

of tree storage of citrus fruits, but certainly other approaches such as the wearing of protective clothing or devices by the workers were far less practical for all commodity groups. The possibility of washing plant surfaces with water or water and detergent and/or degradative agents was another valid alternative but at least on citrus crops the efficacy of such washing operations was not established adequately and the cost of such operations was prohibitive. On the other hand, there is ongoing interest in determining the most efficient procedures for tree washing with the end in view of providing the grower with a means of scheduling an earlier harvest of fruit if marketing or other considerations such as pest control needs would justify the expense. Washing studies are being conducted at the Riverside Citrus Research Center with citrus industry support and if it is found that mechanical spray equipment of the type available in the field can be used in such a manner as to remove reliably a significant proportion of the dislodgeable residue from citrus trees, the industry would then be interested in having regulations amended to permit harvesting immediately after an approved washing if the grower elected to make the expenditure. The industry is firmly opposed to any mandatory washing requirement.

In accepting the safe reentry approach as the most compatible and practical method of dealing with this worker problem, the Citrus Industry of California, along with all others including regulatory agencies, acknowledged that the information needed to determine what safe reentry intervals might be for various materials on any crop were not initially available. There was also the realization that it was not certain what kinds of information were actually needed and what data collecting procedures needed to be invoked. The industry representatives were and are forced to believe that poisoning episodes occur only when several factors are confluent. Otherwise they find it difficult to explain why such a limited number of episodes have occurred over a span of some twenty years of organophosphorus compound usage. The industry response has been to provide genuinely significant levels of support during the past three years through the Marketing Order, to a research endeavor at the Citrus Research Center. This support has been primarily for the identification and interrelating of factors which contribute to poisoning episodes and for the determination of dislodgeable and soil residues for established materials which are not the preemptive interest of a single manufacturer. It will be the intention of the industry to continue such support.

And finally, the Citrus Industry of California acknowledges that for reasons not fully understood, citrus growers in this State are confronted with a problem that is not shared across the board in the agricultural enterprises of this country, let alone the world. A similar problem has surfaced on certain other crops and, again, in the basically arid producing areas. And in all cases there is shared commitment to deal with the problem and to institute procedures which will obviate future involvements of field workers. But the Citrus Industry of California is concerned

not to have such procedures invoked on an across-the-board basis, whether on citrus and the other involved crops or on any other crops when and where there have been no authenticated instances of field worker poisoning during the post application period. Overburdening agricultural production and marketing with restraints that are not clearly justified is counterproductive from the standpoint of both the producer and the consumer.

In summary, the Citrus Industry of California is facing up responsibly to the fact that it has a field worker safety problem; in the interim it accepts reentry requirements as the best means of circumventing further episodes, it is providing ongoing support for research studies which will contribute to the establishment of viable reentry standards and, hopefully, suggest other means of preventing field worker poisoning, and it believes that current evidence suggests its involvement is part of a unique and restricted involvement and that any blanket imposition of restraints on segments of agricultural production in this country which have not experienced this type of difficulty should be avoided.

Manuscript received April 8, 1974; accepted May 20, 1975.

Worker reentry safety. II. The viewpoint and program of the National Institute for Occupational Safety and Health.

By

JON RICHARD MAY*

The National Institute for Occupational Safety and Health (NIOSH) was established by the Occupational Safety and Health Act of 1970 which became effective on April 28, 1971. Relatively shortly thereafter, during the latter part of 1971 to be exact, NIOSH became interested in the various means of achieving protection of agricultural workers from the potentially harmful effects of pesticides. As you recall, DDT and other environmentally persistent organochlorine insecticides had been under attack for some time and it was a rather widely held opinion among scientists and other interested parties that DDT would be banned for crop protection, either partially or completely, in the near future. NIOSH along with other federal government departments and agencies realized that DDT, if banned for crop protection, would be replaced by the less environmentally persistent but generally more acutely toxic organophosphorus (OP) and carbamate (C) insecticides. The suspicion that a sudden increase in the use of more acutely toxic compounds might result in an increase, even possibly epidemics, of pesticide poisonings caused us to focus attention on agricultural worker protection.

Since up to that time NIOSH and its predecessor organization, the Bureau of Occupational Safety and Health, had been involved almost exclusively in nonagricultural efforts, insufficient expertise relating to the health hazards of pesticides existed in house. Therefore, it was decided to seek information and scientific opinion on this subject by using an "expert committee" approach. As you are aware a Task Group on Occupational Exposure to Pesticides, chaired by Dr. Thomas Milby and operating under the aegis of the Federal Working Group on Pest Management, was established in the first quarter of calendar 1972. NIOSH was instrumental in the establishment of the Task Group and provided travel funds for the group. Much valuable information became

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available to NIOSH through our participation on the Task Group. The final report with recommendations of the group is not yet available, although it is in the final stage of preparation. The most important fact to emerge from the lengthy deliberations of the Task Group is the inadequacy of the scientific data base on which to establish unilevel federal field reentry safety intervals.

Our evaluation of the available evidence gathered by the Task Group as well as from other sources indicates the following:

The majority of reported episodes of poisoning resulting from field worker contact with pesticide-treated foliage have been regional in nature, the majority occurring in the State of California.

On a national basis there is no adequate pesticide morbidity-mortality reporting system in effect. Thus, it is presently impossible to accurately assess the magnitude of pesticide reentry poisonings on a national scale. However, based on the size, composition, and complexity of the agricultural field labor force and the incidence of illness associated with field reentry in California it is highly probable that more cases occur on a nationwide basis than are reported.

However, despite the lack of concrete evidence to indicate a national problem it is the belief of NIOSH that the potential for harm to field workers inherent in the use of many pesticides dictates the adoption of federal standards in this area. During the OSHA regional hearing held in Washington, D.C. in August of 1973 I, as a spokesman for NIOSH, testified that we believed in the protection of field workers' health by requiring the use of adequate protective measures. In the case of harvesters the Institute subscribes to the concept of a safe working environment without the use of personal protective clothing or equipment. This concept is embodied in field reentry safety intervals. NIOSH reaffirms its support for the adoption of such standards. However, it is imperative that flexibility be built into any federal standards promulgated. Flexibility in this case takes the form of regionalization. Where normal climatic conditions and cultural practices favor the persistence of pesticide residues or contribute to the formation of more toxic species, relatively long reentry intervals may be required to provide the needed protection. The arid conditions prevailing in many major agricultural areas of California and the fact that many epidemics of so-called "picker poisoning" have occurred in these areas attest to this fact. On the other hand, certain areas of the country have cooler climates or receive significant amounts of rainfall during the growing season making it highly unlikely that reentry intervals, on a same-crop, same-pesticide basis, equal in length to those deemed necessary for arid regions are required. Another complicating factor is the rate of application of pesticides. It is common knowledge that rates of application on a same-crop, same-pesticide basis vary widely from one state to another, even from one region to another within the same state. Equal protection for all exposed

workers is called for—not equal intervals. California's field reentry intervals may be ideal for California considering the prevailing climatic conditions, the rates of application commonly used, and the reported magnitude of the problem there; however, the same intervals are probably not needed in many other areas of the United States. Reentry standards based on different climates and cultural practices including varying rates of application may present considerable obstacles in establishment, especially in light of the available scientific data; nevertheless, these factors are important and should be considered in order to set standards that will protect the health of workers while at the same time not being overly restrictive.

In light of the foregoing, it seems more reasonable to NIOSH to establish federal reentry standards at this time based on conditions other than those existing in the State of California, which, in the absence of sufficient residue degradation data and mass episodes of pesticide reentry poisoning from other states, would have to be considered severe. Then, under a regional approach to the problem, states like California with a past history of mass poisonings from early reentry into primarily organophosphorus insecticide treated orchards could promulgate longer reentry intervals as dictated by their particular set of circumstances. In this case all exposed workers would be protected, assuming the intervals established were valid, with no unnecessary hardship placed on the grower. It is also important to realize that NIOSH occupational safety and health recommendations are based on safety and health factors alone and do not consider economic or technical feasibility; these factors are incorporated later by the Department of Labor during development of a standard. NIOSH believes that adequate worker protection can be achieved through the establishment of flexible field reentry standards. The concept embodied in field reentry safety intervals has been accepted by industrial hygienists for many years—make the workplace safe for the workers. NIOSH wholeheartedly supports the establishment of such standards for the protection of agricultural field workers.

Our viewpoint on the subject would be incomplete without a brief statement concerning the Proposed Occupational Safety and Health Standards for Farm Workers Dealing with Pesticides published by the Environmental Protection Agency on March 11, 1974 (*Federal Register*, Vol. 39, No. 48, pp. 9457-62). As stated by EPA in their proposed standard the harvest entry intervals are synonymous with established pre-harvest intervals (PHI's); the rationale, or basis for direct comparison, is that what is presumably safe for the consumer to eat is likewise safe for the worker to come in dermal contact with or breathe. This may well be the case, but it has yet to be shown to be true. In order to accept the harvest entry intervals for the 13 insecticides listed in section 170.100 *et seq.* as providing adequate protection for harvesters, it would be essential to know the comparative degradation rates of the insecticides on both the edible or marketable part of the crop and the foliage