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RECOMMENDED APPROACHES TO THE PRODUCTION AND EVALUATION OF DATA ON PESTICIDE RESIDUES IN FOOD

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CONTENTS

1. INTRODUCTION

The use of a pesticide on crops or commodities for human or animal consumption can lead to and occasionally aims at a residue remaining at harvest or other appropriate stage. Additionally a pesticide may move from the site of application and remain for a time elsewhere in the environment.

The ability of a pesticide to persist for a certain length of time can be desirable and has been recognized as important in some situations for successful control of pests and diseases. Thus a knowledge of residues of a pesticide, or arising from the use of pesticide, is useful in establishing its efficacy. However, the assessment of the human hazards arising from very small quantities of a pesticide in food and the environment has become an important part of the overall risk/benefit evaluation and is essential before a pesticide can be introduced.

One of the basic prerequisites of such assessments is the availability of reliable data on pesticide residues in food, feed and the environment so that a realistic estimate can be made of the human exposure. The increasing demands of national registration and health authorities include residue data on treated crops and commodities and additionally in water, soil, air, wildlife. These authorities will only reach conclusions and make decisions if they are satisfied that the data are reliable.

However, variations in methods and techniques used in obtaining these data, including the selection, preparation and analysis of samples, have made it difficult to compare results and decide if the results are valid. Secondly the validity of a set of results depends primarily on an adequate design of the trial. These variations have made it difficult to compare information from different sources and have contributed to differences in the regulations adopted in different countries.

These difficulties are most apparent when considering the conclusions reached by national authorities during the registration of pesticides and the use of residues data to set and enforce legal maximum residue limits for pesticides in food and feed. These limits have become important in the movement of food and feed commodities in international trade and the harmonization of the methods used in the production of residue data. A more uniform approach to evaluating the data is also urgently needed.

Guidance on the many aspects of producing and evaluating residue data is desirable. It will be of particular value to those countries still in the process of initiating procedures for the official control of pesticides. The need for guidance has been recognized by a number of national and international organizations and committees and several are already making contributions. Therefore, the IUPAC Commission on Pesticide Chemistry considered the need for a compilation on the various aspects involved justified the production of the present publication. It brings together a manual of procedures for designing residue trials; sampling food and feed; determining pesticide residues using good analytical practice and interpreting the data obtained in relation to estimating maximum residue levels and proposing and enforcing legal maximum residue limits.

Some general editing of available guidelines has been carried out in assembling the publication but most of these remain unchanged. Since some of the guidelines are subject to review, attention is drawn to the relevant sources for updates of the guidelines.

The guidelines have been developed because of an urgent need to improve and harmonize the procedures for obtaining residues data for proposing and enforcing maximum residues limits of pesticides in food. Much of the advice, however, is relevant to, and may be adapted for, other types of residue data including environmental samples. Care must be taken to ensure that adaptation is done carefully and selectively since objectives will be different in certain situations. In monitoring environmental samples, for example, the scope and aims of the monitoring, the levels investigated and need for confirmation of "detected" pesticides can introduce other, overriding considerations.

Residue data in crop and food commodities can be classified according to the objectives in obtaining the data. In Fig. 1 the information developed in the lower classes can be used

progressively in subsequent (higher) classes although the information from individual classes is of limited value. Radio-labelled pesticide studies designed mainly to identify the components of a residue and to contribute to analytical procedures cannot be used by themselves to indicate residue levels that occur following practical field use. Data from supervised trials alone cannot give reliable estimates of levels that will occur in food commodities on sale, nor can data from monitoring food commodities be used alone to predict the daily intake of pesticides by a population. In Fig. 1 higher classes incorporate information from lower classes but embody more uncertainties, especially in sample history.

On the other hand data from lower classes are either essential or at least very useful in conducting investigations in a higher class. A detailed definition of the residue is essential before supervised trials can be carried out and data from such trials must be taken into account by any authority carrying out surveillance or monitoring. In successful planning of total of diet or market basket studies it is essential to know what residues to look for.

Data on pesticide residues in food are thus obtained from a variety of sources from the precise experimentation of radio-labelled studies, through supervised trials with a spread of climatic and agricultural conditions, to commodity monitoring where the treatment on source of the sample is unknown. In the case of dietary studies even individual food commodities may not be identified. It is important to recognize the limitations of the conclusions which can be legitimately drawn from the data of each class.

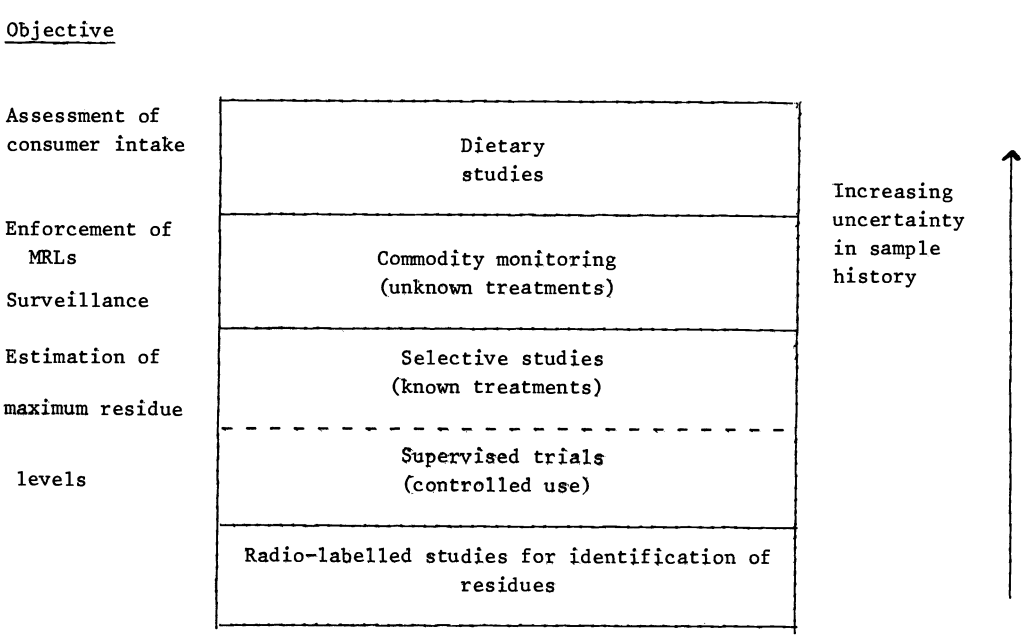

Fig. 1 Classes and objectives of residue data

2. DEFINITIONS

The main purpose of these definitions is to secure a proper description and evaluation of pesticide residues within the framework and programmes of the Commission on Pesticide Chemistry of IUPAC (Ref. 1).

2.1 A pesticide residue

A pesticide residue is any substance or mixture of substances in or on any substrate resulting from the use of a pesticide and includes any derivatives, such as degradation and conversion products, metabolites, reactions products and impurities.

This definition of a residue, whilst precise, gives no indication of the significance of that residue.

The following substrates and media have to be considered when evaluating the residue situation of a pesticide with regard to potential exposure of human beings and animals:

- agricultural commodities, including processed (or prepared) products derived from them that are used for human consumption,
- agricultural commodities and products derived from them that are used as feed in animal production,
- food products derived or prepared from pesticide-treated animals or from animals kept in pesticide-treated livestock premises,
- stored products that have been treated with or exposed to a pesticide and are then used as food for humans or as feed for animals.

Depending on the amount of a pesticide applied, the size of the areas treated and the particular properties of its residue(s), the following additional substrates have to be considered:

- rotational crops that are cultivated in an area previously treated with a pesticide,
- drinking water and air,
- inadvertently exposed non-target organisms that are used for human consumption or in animal production (fish, shellfish, birds, deer, etc.).

Although not immediately connected with the presence in human food or animal feed, official legislation may ask for the evaluation of residues in the following risk areas:

- potentially adverse biological effects on non-target organisms,
- potentially adverse effects on humans applying pesticides or entering pesticide-treated areas (re-entry).

2.2 A significant pesticide residue

Whether a pesticide residue is significant or not is a matter of judgement that depends on:

- the toxicological properties of the substance or substances in the residue and
- the degree of exposure to the residue.

In addition, it is essential before a residue can be called significant that it has occurred under realistic conditions of use of that pesticide and not just under artificial or model conditions.

The determination of the significance of a residue involves consideration of the toxicological properties of the compound. This aspect is outside the terms of reference and competence of the IUPAC Commission on Pesticide Chemistry and as such no attempt is made here to define or describe toxicological significance.

The following criteria are listed to assist in the evaluation of a pesticide residue beyond that of merely mentioning its concentration, its structure or its physical/chemical properties. The applicability of the criteria has to be considered for each particular residue situation.

The significance of a residue is enhanced when,

- its biological (toxicological) effects have been recognized to be harmful to human health or to specified non-target organisms in

concentrations corresponding to those of the residue as observed under conditions of practical application,

- it is persistent, i.e.half the applied dose persists more than six months in a relevant substrate (soil, natural water, etc.). Whenever possible persistent compounds ought to be qualified with regard to their potential biological (toxicological) effects on non-target organisms,
- its physical/chemical properties (stability, polarity, partitioning behaviour, etc.) indicate the possibility of accumulation by non-target organisms or magnification in food chains,
- it has been transformed to a more toxic form.

The significance of a residue is reduced when,

- it has been demonstrated to be innocuous to human health or to specified non-target organisms,
- it has been recognized to be unstable or non-persistent under environmental conditions (this includes transitory or intermediate metabolites and reaction products),
- its physical/chemical properties are such that bioaccumulation or biomagnification may be excluded,
- it has been transformed to a less toxic form.

2.3 Description of a residue (see also 3.1 and Appendix I)

Residues should be described in both quantitative and qualitative terms.

The amounts should be expressed in millograms (mg) of the residue(s) per kilogram (kg) of the substrate analysed $mg.kg^{-1}$*. When the molecular structure of a particular residue cannot be clearly established the amount may be expressed in equivalent terms relative to the molecular weight of the parent molecule.

In qualitative terms, characterization and chemical identification (including synthesis of the proposed structure) should be conducted on all residue components in edible crops comprising more than 10% of the total residue at sampling. However, one need not normally determine residues when the proportion is as low as this if the total residue is below 1 $mg.kg^{-1}$. On the other hand, provided specific toxicological reasons exist, components that are present in even smaller concentrations than those indicated above should also be characterized and identified.

3. DATA REQUIREMENTS FOR RISK EVALUATION

There are three basic prerequisites in assessing the significance of residues of a pesticide in a crop or food:

1. primary physical/chemical/biological properties of the pesticide;
2. reliable residues data from supervised trials or selective studies;
3. reliable toxicological data to estimate the potential toxicity of the pesticide residues (an assessment of the acceptable daily intake for man is desirable).

The consideration of the toxicological properties of a pesticide is outside the scope of this report but the other two inputs are considered both in relation to registration requirements and prediction of consumer risks and in estimating the actual intake of pesticide residues with food.

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* Note: IUPAC nomenclature $mg.kg^{-1}$ is equivalent to mg/kg.

In principle it is possible to distinguish between pre- and postregistration activities although some registrations are stepwise and can be obtained and developed over a period of several years.

Prior to registration data have to be developed to allow a reasonable judgement to be made of the residues left in a crop or commodity when the product has been applied according to the recommendation for use. Such data are essentially predictive and enable a registration authority to estimate the maximum residue level which might be expected. This estimate is normally based on data from supervised trials and may be used as a guideline level to what may be expected when the pesticide is used by the farmer. Subsequently, after considering the potential toxicity of such a residue to man and using appropriate safety factors, legal maximum residue limits (MRLs) may be established.

After a pesticide has been registered and used in practice it is desirable for a competent authority to be able to confirm that the estimate of expected residues made at the time of registration is a valid one. If doubts arise about the validity of the estimate, surveillance and monitoring studies may have to be carried out to ascertain if any revision of the estimated maximum residue level is required. Enforcement programmes of MRLs also produce information relevant to the need to reconsider maximum residue levels (or limits).

Fig. 2 shows the inputs and conclusions involved in a prediction of risk from pesticide residues and also indicates further inputs necessary before the actual risk to the consumer can be evaluated (see Section 6).

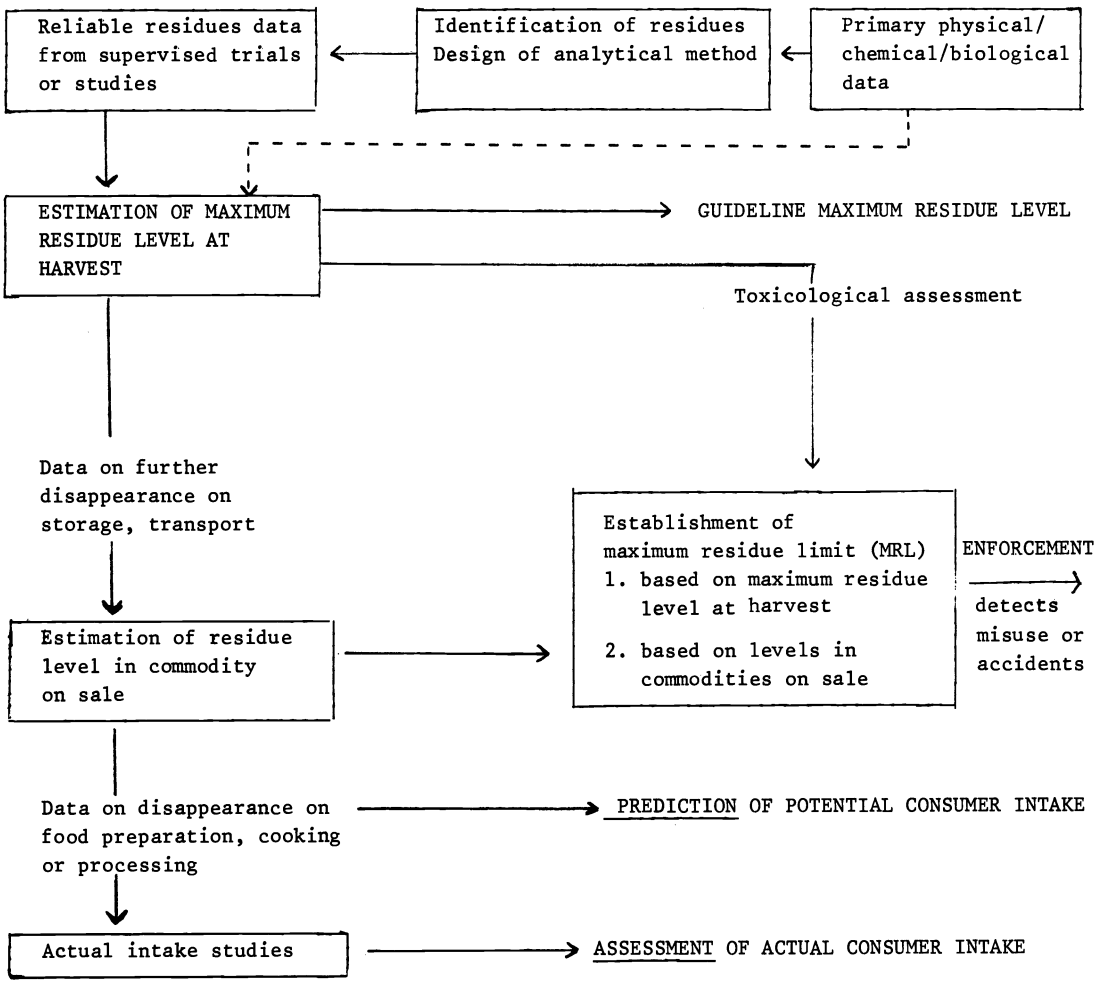


Fig. 2 Inputs and conclusions on pesticide residues in food

3.1 Primary data requirements

In order to characterize a pesticide it is necessary to have precise details of its physical and chemical properties. Information is required on the properties and purity of the technical grade product used in formulations and the nature and amounts of isomers, impurities and other by-products together with an indication on the possible variations in production.

Metabolism of the pesticide in the plant or soil has a major influence on the identity of the residues which need to be measured. Metabolism studies are important pre-requisites of supervised field trials. The term "metabolite" is not a suitable description for all the compounds or degradation products resulting from the parent pesticide but is often used. Consideration must be given to which of these need to be determined by the analytical procedure and which then should be included in the "total residue". A special problem in metabolic studies and in the measurement of pesticide residues is created by "bound" and "conjugated" residues. Any statement to the effect that residues are "bound" (in a substrate or matrix) must necessarily be a function of the effort taken to "free" them, that is the efficacy of the extraction procedure in an analytical context. Thus the term "non-extractable residue" is preferred to "bound residue". A more detailed discussion of these matters is given in Annex 1.

3.2 Reliable residue data from supervised trials

The initial reason for carrying out supervised residue studies is to assist the evaluation, during registration, of the safety and efficacy of the product. In some countries another important reason for carrying out these studies is to obtain the data for establishing maximum limits for residues of the pesticide in food or agricultural commodities. Usually the same data serve for registration purposes and for the estimation of maximum residue levels on which the legal limits are based.

Good agricultural practice

Residue data from supervised trials carried out in conformity with registered or approved use patterns, defined as "good agricultural practice" (Annex 2), are the main source of data.

The uses of any compound for pest control on a particular crop vary considerably from region to region, owing to differences in ecology, climate and cultural practices; consequently residues levels at harvest will vary. As far as possible, agricultural practices in all regions from which data are received and the pesticide residues likely to result from these practices are considered when estimating maximum reside levels. These estimates are based on normal agricultural practices in the regions where there is a need to use the pesticide. If the requirements of certain regions justify multiple applications or applications shortly before harvest, consideration should be given to these needs and recommended levels should not necessarily interfere with pest control practices.

Planning of residue trials

In designing residue trials, early consideration must be given to the intended use of the residue data and to the sampling programme required. If the data are to support registrations or establishment of a maximum residue limit through registration procedures, results from a number of replicated experiments in several soil and climatic conditions are normally required. Major trials should only be done with commercial formulations and equipment in a manner similar to that used by farmers. Treatments should be made at the rate recommended or likely to be recommended for the commercial product. A treatment at twice or three times the recommended rate should be included. Data from such a treatment would indicate what might happen if users deliberately or accidentally apply quantities greater than those recommended. Since supervised residue trials provide the basis for legal maximum residue limits in some countries, the design of the experiment should include the determination and evaluation of the conditions and factors which lead to the highest residue levels following recommended use patterns.

As a result of a recommendation from the ad hoc Government Consultation on the

Standardization of Registration Requirements held in Rome, October 1977, ad hoc Working Group on Sampling of the Codex Committee on Pesticide Residues has developed guidelines which cover residue trials with growing crops and stored commodities (Annex 3). Revisions of and additions to these guidelines will be published in the reports of meetings of the Codex Committee on Pesticide Residues (CCPR).

Sampling

The importance of careful sampling in the field by trained personnel cannot be over-emphasized. The best approach for any given situation can be best determined by someone who is capable of recognizing and interpreting the importance and usefulness of the results.

It is necessary to take samples which, when reduced and analysed, will give residue results which will both represent the average residue levels of the entire crop in the plot and indicate the range of residues found. The field sample must be representative of the plot and the individual units comprising it must be typical of those taken in a commercial harvest. It is very important that residue data obtained from field samples should be comparable with data obtained following sampling procedures used in enforcing maximum residue limits.

Adequate sampling of the untreated (control) plot is also important especially if the residue level of the treated crop is expected to be low. Arrangements need to be made in advance if the samples have to be stored for any length of time, or as frequently happens a sample is transported elsewhere for analysis.

The Guidelines on Residue Trials developed by the CCPR ad hoc Working Group on Sampling contain advice on sampling residue trials and on sample packing and storage (Annex 4 - Sampling for Pesticide Residue Analysis).

Portion of the commodity which is analysed (and to which Codex maximum residue limits apply)

It has been the exception rather than the rule to describe clearly the portion of a crop or commodity (and its treatment) which has been analysed for pesticide residues. Thus it is often not clear how the analytical result relates to the crop as grown or the food as consumed and until recently the Codex Alimentarius Commission did not define that part of a commodity to which a Codex maximum residue limit applied. The CCPR ad hoc Working Group on Sampling has now prepared guidelines on the portion of the commodity to which Codex maximum residue limits apply and which is to be prepared as the analytical sample for the determining of pesticide residues (Annex 5).

Method of analysis and good analytical practice in the determination of pesticide residues

Adequate analytical procedures are required for a precise knowledge of the nature and the amount of the residues that are likely to be present in food. Although fundamental research requires the availability of the most sensitive and specific procedures, which often involve elaborate and expensive equipment and intrumentation, the examination of residue levels in food commodity samples consists mainly of the identification and measurements of residues at the levels of the maximum residue limits. Analyses have to be performed on samples of unknown as well as known history and by many laboratories that might share the responsibility for enforcing residue limits. There is a need, therefore, for procedures of identification and measurement that are reliable in the hands of a trained technician who is required to deal with market samples and must be able to identify and measure any pesticide residue in a possible mixture of several residues. Methods that are adequate for the determination of residues from supervised trials of known pesticides are not necessarily satisfactory for regulatory purposes when samples with an unknown history of pesticide treatment are being examined.

In view of variability in analytical results due to experimental conditions, the presence of other pesticides or their metabolites, or the presence of other contaminating compounds of either natural or synthetic origin, it is impossible to specify any procedure that will always

satisfactorily determine a residue of a particular pesticide in any substrate (Ref. 2). It is usually necessary to use a procedure validated for that situation or to adapt a generally acceptable procedure to the particular circumstances involved, i.e. the reason for the analysis, the nature of the sample, the nature of the residue and the interferences likely to be met. In addition, some form of positive identification of the residue is highly desirable, particularly if the maximum residue limit appears to be exceeded.

Because methods of pesticide residue analysis are undergoing continual modification to take advantage of the latest developments in analytical techniques, established "referee methods" quickly become outdated. Interference from natural materials or from traces of other chemicals makes it difficult to describe a "referee" method with the required degree of specificity. Thus it is impracticable to attempt to specify any analytical procedure for the determination of pesticide residues as a "referee method of analysis".

Particular attention is currently paid to multi-detection systems of analysis which are now widely used for regulatory purposes. Such systems can be adapted to suit individual regulatory problems but some pesticides are difficult or impossible to fit into broad general schemes. Many collaborative studies of individual multi-detection systems have now been made and these systems have the great advantage that, if correctly used, they provide evidence of identity and afford means of measuring one or more of a wide range of residues. The IUPAC Commission on Pesticide Chemistry prepares reports on the status of clean-up and determination procedures and confirmatory techniques. These describe current and projected applications of analytical principles and equipment to pesticide residue analysis (Ref. 3).

The ad hoc Working Group on Methods of Analysis of CCPR recommends analytical methods that, from the practical experience of its members, can be applied to the determination of pesticide residues for regulatory purposes. The 1981 recommendations of the Group are given in Annex 6.

Although most multi-detection systems are based on gas-liquid chromatography (GLC) the need for sophisticated maintenance and expensive supplies makes GLC less attractive in some countries. Alternative techniques, mainly thin-layer chromatography (TLC) are being used with comparable success in monitoring residues at the level of MRLs and at an appreciably lower cost. The IUPAC Commission on Pesticide Chemistry has made recommendations on this simplified approach to residues analysis (Ref. 4) (Annex 6).

The Codex document Alinorm 76/24 Appendix IV (Report of the ad hoc Working Group on Methods of Analysis) contains the following statement:

> "It was considered that the ultimate goal in fair practice in international trade depended, among other things, on the reliability of analytical results. This in turn, particularly in pesticide residue analysis, depended not only on the availability of reliable analytical methods, but also on the experience of the analyst and on the maintenance of 'good practice in the analysis of pesticides".

The influence of the analyst on the final result has been underestimated in the past since his/her contribution to variability is neither constant nor easily controlled. To produce reliable results it is essential that the residues analyst is experienced in the work and maintains good standards of analytical practice in using the analytical methods. Ultimately the only satisfactory way to control analyst performance variability is through the conscientious application of a quality control programme such as those described by Cochrane and Whitney (Ref. 5) and Carl (Ref. 6). Annex 7 defines "good analytical practice" (Ref. 7) and then examines the contribution of the errors of individual procedures to variability in results.

4. THE USE OF RESIDUE DATA IN ESTIMATING MAXIMUM RESIDUE LEVELS

The estimation of a maximum residue level is based mainly on a knowledge of the residues which occur following the use of a pesticide in accordance with good agricultural practice normally obtained by the analysis of samples from supervised trials. This may be supplemented by selective surveys of crops/commodities where there is detailed information available on

the use of a pesticide.

Data obtained from trials and studies is limited by practical considerations and the estimation of a maximum residue level must be part assessment and part prediction. It is obviously impossible to carry out sufficient trials to cover all the various conditions of climate, soil, farming practices etc. under which a pesticide may be used on a crop. Therefore although well-planned trials demonstrate a range of residues, emphasis should be directed towards the identification of conditions and factors which lead to the highest residue levels following recommended use patterns.

The magnitude and distribution of pesticide residues on a treated field are influenced by many factors. A few which are considered particularly important can be grouped as follows:

1. Application factors. Type of application, number of treatments, formulation of pesticide, applied dose (l/ha), type of applicator, size and spatial position of nozzles. Diameter and number of drops on a unit area are partly interdependent and can be selected to achieve the best biological effect according to the purpose of the application.
2. Crop and environment factors. Mode of cultivation, type and variety of plants, distance of rows, population density, height and shape of plants and character of soil. Weather conditions during and after application may vary from field to field and frequently within a field.
3. Disappearance factors. Chemical, physical and biological factors result in a gradual degradation and a consequently more uniform distribution of the pesticides after the application.

Well-planned trials take all factors into account so that the residue data represent the widest range of growing/treatment conditions possible. Although the number of variables can be reduced in a supervised trial it is rarely possible to isolate the influence of an individual parameter and subsequently use the information accurately in predictions.

For a given chemical and crop a set of residue values is obtained which possesses a certain range and distribution. A typical example of such a set of data has been published by Ambrus, Fig. 3 (Ref. 8). A large number of primary samples, composited in different ways were taken from a treated orchard to study the effect of the number of primary samples and the replicates of final samples on the result of the residue analysis.

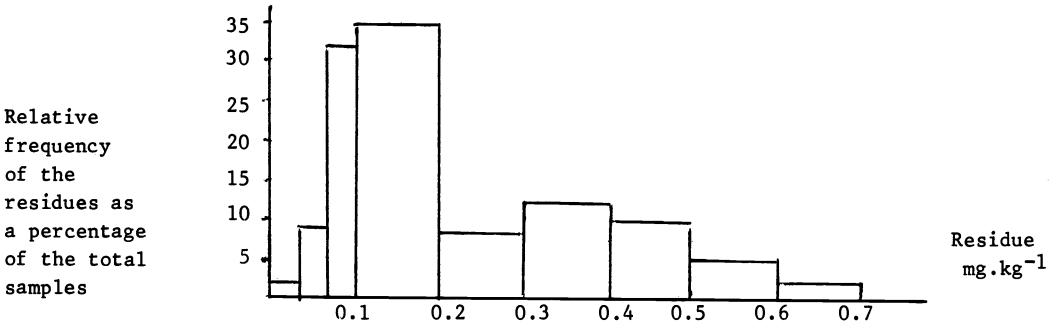


Fig. 3 The relative frequency of phosphamidon residues in apples

The mean residue value was 0.16 $mg.kg^{-1}$ with a standard deviation of 0.14. It is interesting that the standard deviation in this study is approximately the same magnitude as the mean value with a coefficient of variation (CV = $s/\bar{x}$ = 0.14/0.16 = 0.88) of almost 1.

These data were obtained from an application of phosphamidon to a 20 ha area at one site, in one year, and thus the influence of climatic and geographical differences from year to year was excluded.

Variations in climatic conditions increase the range of residue data considerably and it has been shown that environmental factors contribute more to the variance of the residue values than any other factor.

The contribution of the variance of the different operations involved in obtaining residue data to the total variance is discussed by Ambrus and Horwitz (Refs. 2&8). The estimation of the coefficient of variation (CV) of the sampling operation can be derived from the literature already cited, and it has to be accepted that it is not lower than 0.5. The long-term weather changes (from year to year) may contribute a coefficient of variation of approximately 2 and the total CV (including analysis, sampling and weather changes) may be estimated to lie around 2.

The distribution of pesticide residues on a crop also changes with time and Fig. 4 shows a series of typical distribution curves over a period 14 days after treatment.

The range and distribution of residues for each selected interval after treatment gives a full picture of the disappearance of the residues and such curves provide an ideal data base for estimating the maximum residue level.

However, the production of such a data base for each pesticide/crop is obviously impracticable and a means must be sought to increase the prediction component of the estimate.

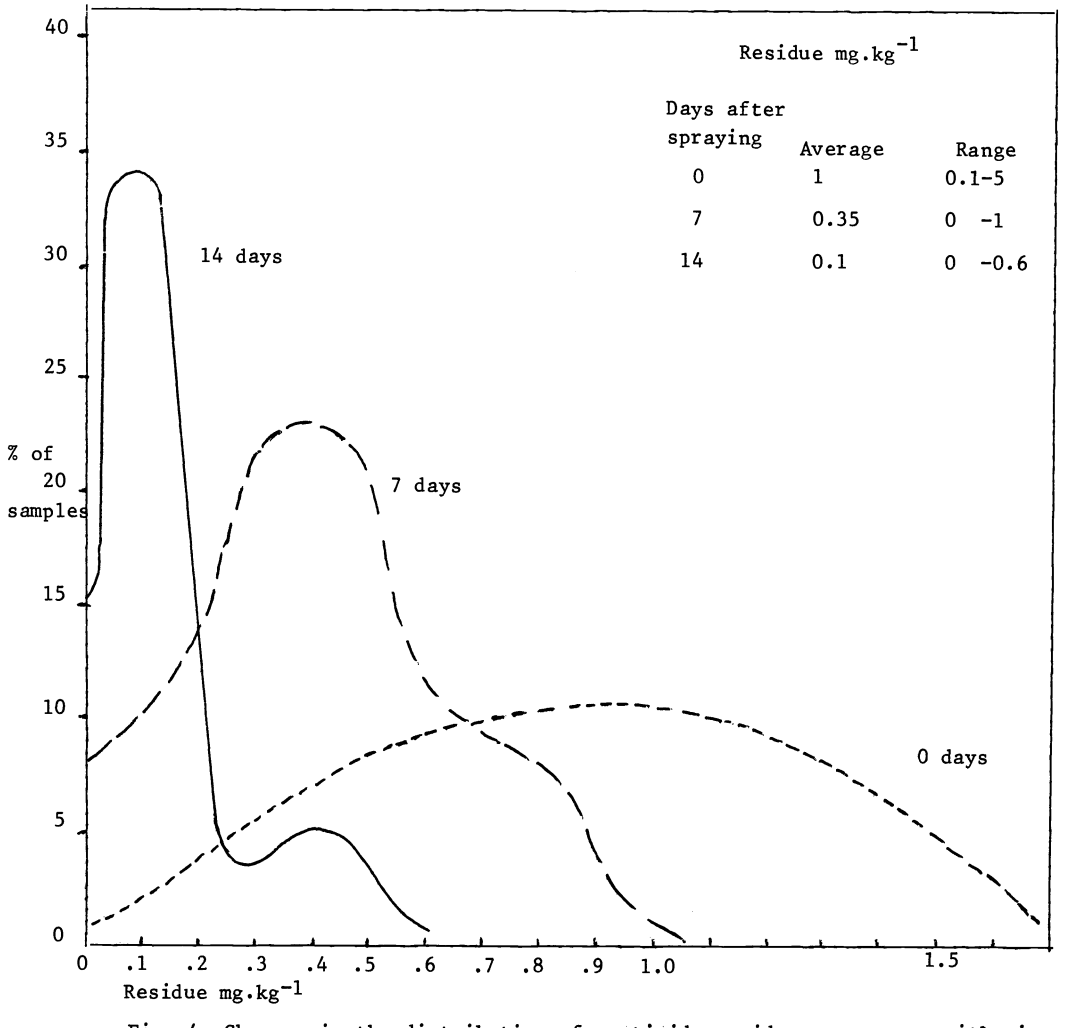


Fig. 4 Changes in the distribution of pesticide residues on a crop with time

Legal maximum residue limits are mostly based on a study of pesticide disappearance curves by considering the average residue level at an interval after harvest which represents good agricultural practice. This, however, can be very misleading since each point on such a disappearance curve is usually the average of a range of residues which are likely to be found if enough units are analysed separately. Clearly in Fig. 5 (based on experimental data) ranges overlap and the maximum residue level at 14 days may be higher than the average at 7 days. Thus were a legal maximum residue limit based on the average residue at 7 days it could be exceeded by the residue in a sample taken at 14 days.

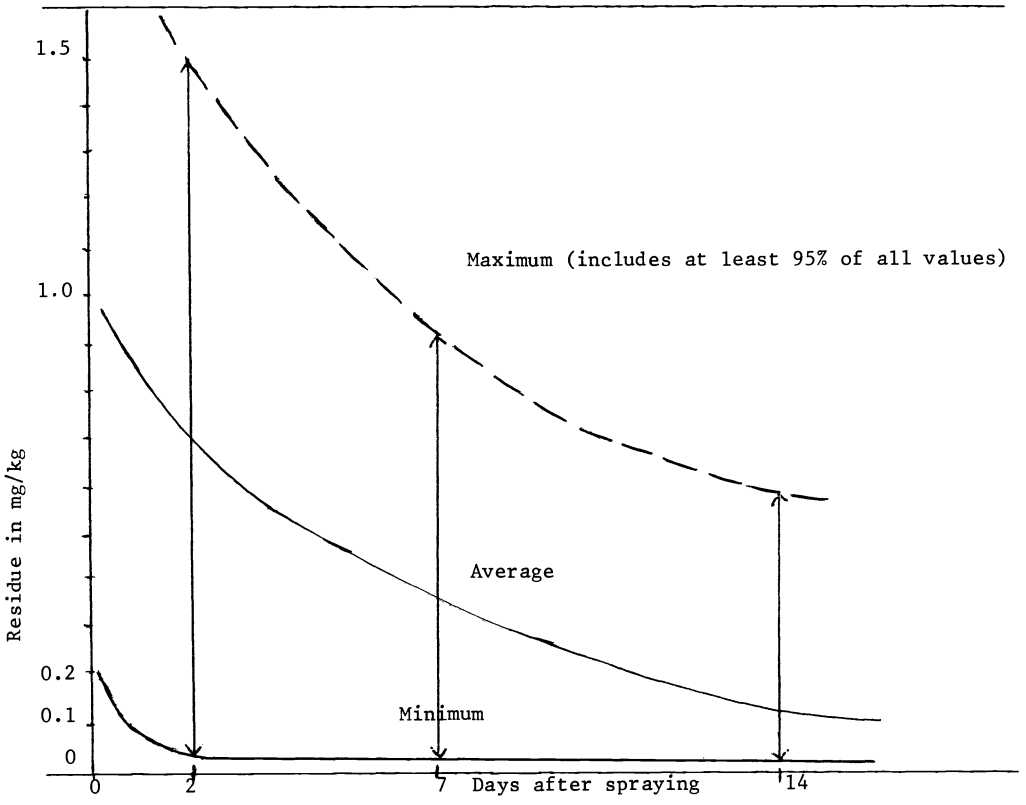


Fig. 5 Pesticide disappearance curves showing averages and ranges of values

For the example in Fig. 5 where the interval between last application and harvest in good agricultural practice may vary, say, between 7 and 14 days it is valuable to have enough information to estimate the upper level curve during this period to predict a maximum residue level at harvest - in this example the estimate would be 1 mg/kg.

The maximum residue levels estimated in this way implicitly include and allow for random errors inherent in the sampling and analytical procedures and may thus be regarded as a true "maximum residue level". If this is acceptable on toxicological grounds it may then be proposed as a maximum residue limit (MRL) with all the legal implications that the definition involves.

Since the production of residue data is time consuming and expensive it is important to get the required information from a minimum of experimental work. Useful additional information can be obtained if the primary samples are taken from fixed locations where exposure to the spray deposit is likely to be the highest. Residue data from trials under adverse or extreme weather conditions are of importance in trying to cover the variability in data due to year-to-year climate differences. By assembling the individual values from a number of disappearance experiments for a given chemical/crop a scatter of values along the average disappearance curve is obtained from which an estimate of the upper curve level can be made. This upper level curve should include at least 95% of all values.

Sampling a crop to estimate maximum residue levels near harvest, when many of the sample units may contain less pesticide than the limit of determination of the analytical method, should be biased toward units which may have been highly exposed to the treatment or for other reasons might be expected to contain the higher values in the range. Work may be needed to identify the conditions and factors which lead to these higher residue levels.

Generally the bulk of the information available for assessment comes from pesticide manufacturers and has been submitted to national pesticide registration authorities. This usually consists of residues data from supervised trials and these data continue to serve as the primary source of information for estimating maximum residue levels. A second source, of growing importance, is an increasing number of comprehensive selected surveys that include many essential features of supervised trials. These are usually conducted by government agencies and necessarily include detailed treatment records. Broadly based monitoring studies on samples of unknown history are of no value in estimating maximum residues levels since the required data base must be related to known good agricultural practice.

Good agricultural practice and intervals between application and harvest

In considering residue data from supervised trials or selected surveys attention should be paid to the effects on the residue levels of the number of applications, application rates and the interval between last application and harvest. These treatments should be in accordance with registered or approved use patterns (good agricultural practice).

Information on agricultural practices is valuable and recommendations are usually based on normal conditions in the regions where there is a need to use the pesticide. If, however, the requirements of certain regions justify unusually frequent or late applications then consideration may be given to these special needs. In some circumstances it may not be possible to estimate significantly lower levels without seriously prejudicing necessary pest control practices. Residue data resulting from an exceptional need to use high application rates immediately before harvest are not generally used as a basis for estimating maximum residue levels. The minimum interval permitted between the last application of a pesticide and harvesting a crop may vary considerably from country to country. This does not necessarily mean that the residue level at harvest varies to the same degree.

Results reflecting the most generally approved interval are usually selected unless there are special circumstances that indicate that some other interval should be considered.

Mathematical expression of residue levels

In view of variability found in residue levels there is little significance in estimating maximum residue levels in a way that would suggest a greater accuracy than is practicable (Refs. 2, 9, 10). Thus it is current practice to estimate levels that are based on intervals such as 0.1, 0.2, 0.5, 1, 2, 5, 10 $mg.kg^{-1}$. The percentage error involved in residue analysis is not constant but decreases as the concentration of residue increases. The proposed figures are most useful over the range of about 0.10 to 10 $mg.kg^{-1}$. Concentrations between 0.01 and 0.05 $mg.kg^{-1}$ approach the current limits of determination of most pesticides in foods. Above 10 $mg.kg^{-1}$ the accuracy improves and figures such as 10, 15, 20, 25 $mg.kg^{-1}$ have greater statistical significance. Fortunately such a combined set of figures encompasses almost all the situations that require consideration.

Because of the lack of precision of the various procedures used in the determination of pesticide residues, it is unrealistic to express maximum residue levels below 10 $mg.kg^{-1}$ to more than one significant figure.

Residues levels "at or about the limit of determination"

Many approved uses for pesticides do not result in detectable residues in food commodities at harvest or at any stage thereafter. Such situations represent the ideal of "good agricultural practice" and it has been usual to assume that no estimate for a maximum residue level was required and generally none has been made. The absence of an estimate, however, indicates either that no residue occurs or that an estimate has not been made.

Any analytical reference to "nil" or "zero" (in respect of pesticides) is scientifically unjustified and residue levels should be estimated "at or about the limit of determination" in those cases where data indicate that there is little likelihood that significant residues result from approved uses of the specific pesticide concerned.

The magnitude of such limits depends upon the pesticide, the food, and the method of determination. At these low levels, experience with the analytical method and considerable care are required to eliminate interference from a variety of artifacts and contaminants. The identity of such traces is essential but often difficult to establish.

5. MAXIMUM RESIDUE LIMITS

Governments, representing the interests of the public as consumers, have attempted to minimize any hazard from pesticide residues in one of two basic ways.

- By controlling the use of pesticides, legally or by advice so that good agricultural practice is carefully followed. Such control, with cooperation of users, should ensure that residues in food do not exceed the acceptable maximum residue levels estimated from data from supervised trials.
- In addition, by the establishment and enforcement of legal maximum residue limits.

Residue levels at harvest do not, except in the case of immediate consumption, indicate in any way the amount of pesticide which may be consumed. Residues of most pesticides continue to degrade after harvest and information on the further disappearance on storage and transport enables an estimate to be made of the residue level in the crop or commodity when it is normally offered for sale. These levels are usually appreciably lower than the maximum residue level at harvest and if sufficient data are available for a sound estimate to be made, legal MRLs may be based on these levels as an alternative to the harvest levels. Such a decision requires that any enforcement sampling is at a stage compatible with the stage to which the data refers. In any case sampling is rarely practicable at the "farm gate" even for the enforcement of MRLs based on maximum residue levels at harvest.

Residues are often reduced even further during food preparation, cooking or processing and a realistic prediction of consumer hazard is possible only when all these factors are taken into account. The only realistic way to assess consumer hazard is by carrying out actual intake studies (see Fig. 2).

When the legal limit is based on the maximum residue level at harvest and has been arrived at from the consideration of reliable data then a determined residue during enforcement in excess of the maximum level/limit can be regarded as a clear indication that (1) good agricultural practice has not been followed (2) there has been a deliberate misuse or (3) there has been some accidental contamination of the food.

A residue in excess of the maximum level/limit does not in itself imply a health risk although an enforcing authority could take appropriate action on the basis of a "substandard" food produced as a result of one of the three indications above. A legal limit does not have any real effect unless it is enforceable and a clearly "substandard" food ought to be rejected for trade or consumption.

The chances of a food produced by good agricultural practice being rejected in this way is very small indeed since the recommended Codex sampling method (Annex 4) is aimed at determining the average pesticide residue content of a lot of goods. This average would then be compared with the maximum residue limit and there should be an ample safety margin for the producer against a false rejection.

The real risk to a commodity lot lies in the situation where a country has based its legal maximum residue limits on either limited data or on average data from supervised trials or both. This will result in a falsely low legal MRL which can be exceeded by many samples especially if the samples are drawn from crops grown under conditions not covered by the supervised trials. This may be the case when a country sets limits on a home-produced

commodity and then finds difficulty in accepting the same commodity produced in a country where pesticides are used in a way different from the one stipulated by the importing country.

This situation can best be avoided by either the harmonization of the MRLs of various countries or by the initial study of residues data from a wide enough variety of growing conditions so that an MRL is applicable to both home-grown and imported commodities.

A valid criticism of MRLs soundly based on the maximum residue levels at harvest is that, although time of harvest is a well recognized stage and an easy reference point for control purpose, the majority of sampling for enforcement is at a later stage. By this time the residue has often declined further and there is ample evidence to show that the consumer is normally exposed to levels much lower than the MRL. There are two general aspects.

1. Because time of harvest is an easy definable reference point maximum residue levels are determined at this stage (or its equivalent). These levels are then often used directly to establish legal limits. Because they may represent a wide variety of "good agricultural practice" the MRL may well be higher than is considered necessary in countries where the local good agricultural practice results in much lower residue levels at harvest.

2. MRLs based on data at harvest do not take into account further disappearance of residues between harvest and consumption. If a country considers that it needs MRLs to protect health then it might wish to set lower limits and enforce them at a later stage in the commodity distribution chain. This logically requires data on the further disappearance of residues during storage and transport which are not often available.

Codex maximum residue limits

For the purposes of the FAO/WHO Codex Alimentarius a "Codex maximum residue limit" is the maximum concentration of a pesticide residue that is recommended by the Codex Alimentarius to be legally permitted in or on a food commoity. Codex definitions and procedures for the elaboration of Codex MRLs are given in the "Guide to Codex Maximum Limits for Pesticide Residues" (11). A summary of procedures and problems in setting maximum residues limits has been published by Bates (Ref. 12).

The Codex "Guide" lists recommended limits for over 120 pesticides in a wide range of food commodities. These limits were proposed by the FAO/WHO Joint Meeting on Pesticide Residues in a series of reports (Ref. 13) and are based on an estimate of the maximum residue level expected in "good agricultural practice" and a consideration of the acceptable daily intake (ADI) for the pesticide in question.

The acceptable daily intake (ADI) of a chemical is defined as "the daily intake which after a lifetime of exposure at that level is almost certain not to result in injury of any kind". It is usually based on a daily level of intake having no observable effect on a sensitive species of animals, applying a margin of safety to allow for differences in sensitivity between the animal species and human beings, the wide variations in sensitivity among humans and the small numbers of experimental animals in comparison with the human population which might be exposed (Ref. 14). Thus although ADIs carry no guarantee of "absolute" safety they do represent levels at which all pesticides are "equally safe" (based on the assessment of all available data). Daily intakes of carbophenothion 0.0002 $mg.kg^{-1}$ body weight, DDT 0.005, malathion 0.02 and dichlofluanid 0.3 are all equally safe (or equally hazardous).

The margin of safety involved in these estimations can be realized by an examination and analysis of the many hundreds of separate decisions reached by the Joint FAO/WHO Meeting on Pesticide Residues and the Codex Committee on Pesticide Residues. A maximum residue level of 2 $mg.kg^{-1}$ on a wide range of food commodities has been recommended for pesticides, with ADIs ranging from 0.002 $mg.kg^{-1}$ body weight to 0.3 $mg.kg^{-1}$ body weight. If 2 $mg.kg^{-1}$ of a pesticide with an ADI of 0.002 $mg.kg^{-1}$ body weight is acceptable on a commodity and includes an adequate margin of safety for health then safety to health cannot be a criterion in setting a maximum residue limit of 2 $mg.kg^{-1}$ for pesticides with higher acceptable daily intakes.

Thus, residues resulting from good agricultural practice are clearly shown to be the dominating influence on MRL setting.

The Codex recommendations can be summarized by plotting the ADIs (x 1000) against MRLs for all commodities. Over 99% of the recommendations fall below the diagonal line which could therefore be regarded as a boundary of recommendations and a guideline for future recommendations (Fig. 6). If it is assumed that a standard person weighs 60 kg and eats 1.5 kg food/day then:

1. The acceptable daily intake estimated from no-effect levels in animal experiments after applying safety factors would be (60 x ADI) mg.
2. The possible actual daily intake if all the food contained the maximum residue level would be (1.5 x MRL) mg.

If the possible actual intake is considered as a fraction (percentage) of the acceptable intake the MRL for all food intake providing x% of the ADI is $MRL = \frac{2x}{5}.ADI.$

An approximation of a series of percentage curves in Fig. 6 to the Codex "boundary line" shows that this line represents recommendations covering factors from 1 to 100.

Thus if all a person's food over a lifetime contained 10 $mg.kg^{-1}$ of a pesticide with an ADI of 0.01 $mg.kg^{-1}$ then the daily intake would be 25 x the ADI (which has large margins of safety). Clearly this can never occur but this calculation based on Codex MRLs does indicate the "absolute ceiling" of risk from residues in food at MRL limits. It also helps to focus on the "risk ratio" which is greater at low ADIs than high ADIs. Another possible conclusion is that the establishment of MRLs below 10 $mg.kg^{-1}$ for pesticides with ADIs greater than 0.1 $mg.kg^{-1}$ body weight, and subsequent monitoring is not justifiable on the grounds of consumer protection.

6. ASSESSMENT OF EXPOSURE - DIETARY INTAKE OF PESTICIDES

Monitoring

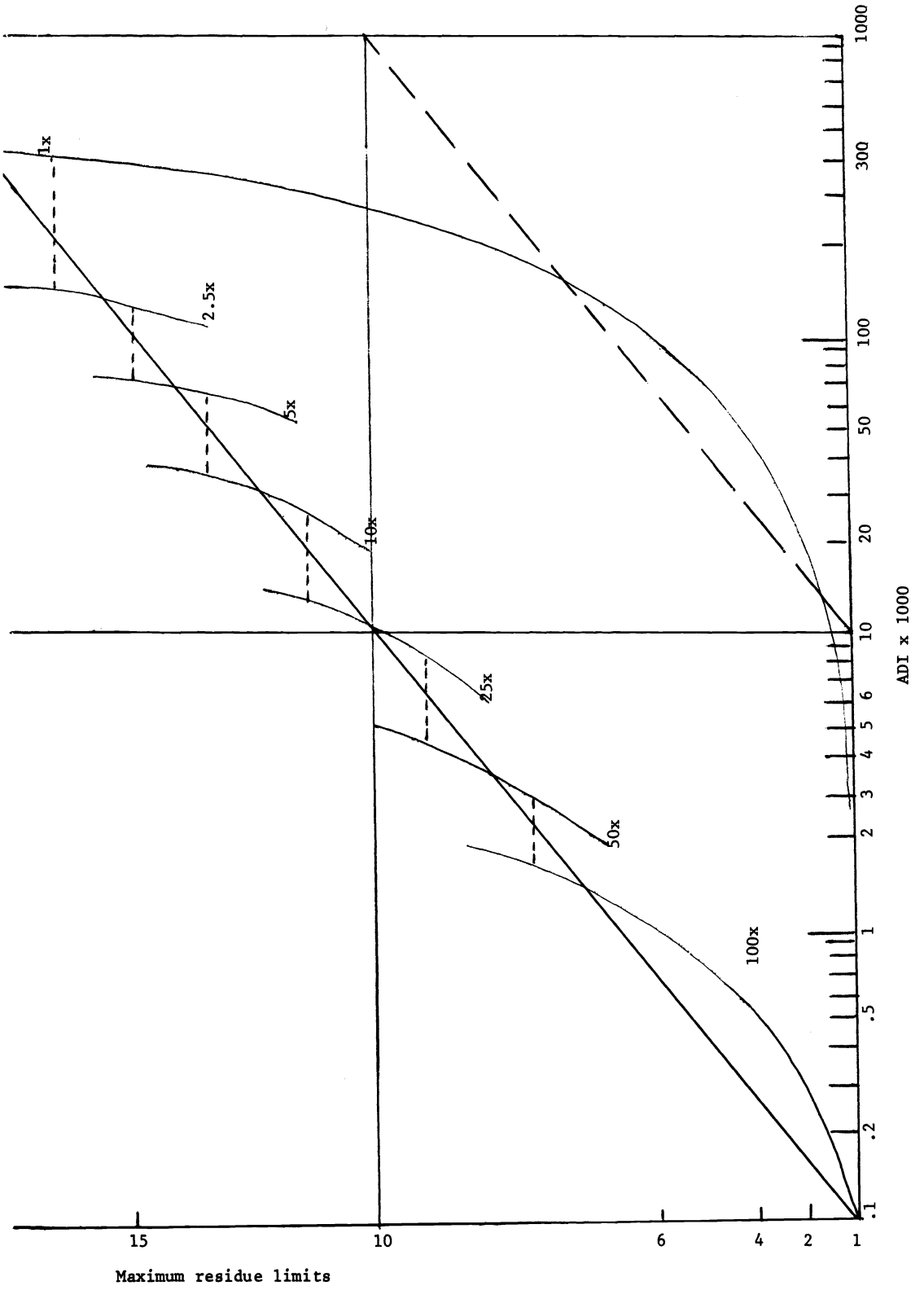
Some food control activities are necessary, both for the direct protection of the consumer and in relation to the acceptability of commodities in trade. However, both commodity monitoring and dietary studies should be undertaken only after a careful study of the real need for such activities. These of course may be justifiable on the basis of administrative "reassurance" of the consumer but it is difficult to justify massive monitoring programmes for pesticides in food on the basis of current scientific evidence.

Furthermore it is rarely possible to remove a "contaminated" foodstuff from the market place before it is sold because of the time required to analyse samples for a range of pesticide residues. For perishable foodstuffs it is unlikely that even re-sampling is possible if the initial sample is taken when the produce enters the distribution network. At best the results of monitoring may be used to introduce corrective measures to prevent something happening again.

From the results of many years of monitoring in several countries the scientific conclusions of this impressive investment of time and money can be summarized quite simply: "high residues (i.e. greater than expected) of pesticides in food are rare". A recent (June 1979) report of a study group on FDA residue programs in the United States of America states "A close examination of FDA's surveillance and total diet study programs for the past decade reveals that chemical residues found in the American food supply seldom exceed established tolerances (maximum residue limits) and are consistently well below acceptable daily intakes established by the World Health Organization and the Food and Agriculture Organization of the United Nations" (15).

The scientific arguments for initiating or continuing monitoring programmes are weak but there is a political and administrative need to continually reassure consumers that their

FIGURE 6


1x
2.5x
5x
10x
25x
50x
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1
.5
.2
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ADI x 1000
15
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1
Maximum residue limits

food is not contaminated. The decision on how much reassurance can be afforded will vary from country to country but where analytical resources are at a premium a very close examination should be made of the real benefits of monitoring. The position of minimal scientific return from routine monitoring has probably been reached.

An alternative approach to the protection of the consumer is to concentrate on fairly narrow carefully selected objectives, currently called "selective studies". These are of two kinds:

1. Studies of selected crops or foodstuffs with known treatments where the undesirable element of uncertain sample history is eliminated and the analytical results can be related to the crop treatments. Such studies, apart from providing data which ultimately give the same information as the monitoring of commodities with unknown treatment, will provide valuable input to the exercise of estimating maximum residue levels and will be more likely to identify emerging problems than will routine monitoring.

2. Studies of a range of crops or foodstuffs for a selected pesticide. The value of these selective studies was recognized by the 1979 FAO/WHO Joint Meeting on Pesticide Residues which suggested criteria for the initiation of such work, namely,

   - pesticides with a known high volume of use on specific important commodities or on a wide range of commodities;
   - newly introduced pesticides, known to leave residues, that are undergoing intensive development in agricultural use;
   - pesticides for which the calculated theoretical daily intake based on appropriate maximum residue limits (when such a calculation is carried out at national level) exceeds the ADI.

Maximum theoretical daily intake

A dietary study is the only accurate way to assess actual consumer intake but even this gives information on average diets only unless very extensive studies are made to include dietary differences attributable to age, sex and geographical distribution. In the absence of dietary studies, predictions can be made on the basis of information available from other sources of residue data and a knowledge of certain relevant physical and chemical properties of the chemicals forming the residues.

Assuming that MRLs are based on maximum residue levels estimated from data from supervised trials and/or selective studies (which they normally are) then it is possible to calculate the maximum theoretical daily intake by simply multiplying the MRL on each commodity by the daily per capita consumption of the food commodity in a country (which is often based on the 9th decile figures developed by the World Health Organization). The calculation assumes that for a given pesticide:

1. the residue on the food at the point of consumption will be at the level of the MRL and
2. a residue will be present on all commodities for which an MRL has been established.

These assumptions are known to be false and hence such calculated figures are likely to be greatly in excess of the actual intake. They are thus unrealistic for several reasons since

- only a portion of any commodity is ever likely to be treated by a particular pesticide:
- MRLs are based on maximum residue levels which usually reflect maximum application rates and minimum intervals between treatment and harvest, circumstances unlikely to occur with regularity in practice;

the effects of storage, transport, food preparation and cooking or processing on the residue are ignored.

In spite of its considerable limitations this calculation has a value as an indicator or screening mechanism for the advisability of selecting a pesticide for further residue studies. Thus if the maximum theoretical daily intake does not exceed the toxicologically estimated acceptable daily intake (ADI) for humans, there is not even a theoretical risk of exposing the consumer to harmful residues (the ADI already has an inbuilt safety factor of about 100 or more). In these circumstances it would be wasteful of resources to analyse food for residues of such a pesticide.

Although MRLs are normally based on the estimated maximum residue level at harvest (or equivalent) if information is available on the fate or disappearance of the residue during storage or transport then an estimate can be made of the residue level in a commodity "offered for sale" (see Fig. 2). An MRL based on such an estimate would be appreciably lower than an MRL based on harvest levels and is of course a step nearer the consumer and a therefore more realistic figure to use in the calculation of a maximum theoretical daily intake. However, it is difficult to standardize transport and storage conditions and data on the effects of these factors on known residues are only available in a few situations.

Realistic prediction of consumer intake

More important to the successful prediction of consumer intake is information on the disappearance of the residue during the preparation and cooking or processing of the commodity. Although it is also difficult to standardize the preparation of food and cooking procedures the disparity between the maximum theoretical potential daily intake calculated from MRLs and the actual daily intake as obtained from dietary studies is so great - as illustrated by Table 1 - that a technique for the realistic prediction of consumer intake is urgently required. Such an approach has been described by Frawley and Duggan (16) in an attempt to arrive at a better prediction of daily intake than the maximum theoretical daily intake based solely on MRLs. When dietary studies for a pesticide are not available because the pesticide is new and not in commercial use or if the analytical methods used in a dietary study is not able to determine a specific pesticide, then such predictions are a reasonable alternative to dietary studies. Thus the application of a number of items of information about the residue, its occurrence, its distribution within a commodity and its fate during the preparation and cooking of the food can provide a more reliable predicition of consumer intake.

Table 1 - Comparisons of actual intake of some pesticides and theoretical daily intakes in the U.S.A. with acceptable daily intakes (ADIs) 1974-76

	Theoretical potential daily intake $mg.kg^{-1}$	Actual daily intake $mg.kg^{-1}$	Acceptable daily intake for 60 kg person $mg.kg^{-1}$
captan	18.0	0.0012	6.0
methoxychlor	10.2	0.0004	6.0
dieldrin	0.06	0.0024	0.006
parathion	0.78	0.00006	0.3
carbaryl	5.58	0.0012	0.6

1. Although it is difficult to generalize for all crops/commodities it is unlikely that more than 50% of any crop is treated with a particular pesticide. The actual figure is probably between 10 - 20% for most major crop/pesticide combinations.

2. MRLs are based on estimated maximum residue levels but the average level at harvest is usually between 20 and 40% of the maximum (see distribution curves in Fig. 4).

3. The pesticide residue may occur in or be partitioned into a specific part or parts of a crop/commodity. MRLs apply to the whole commodity as it occurs in commerce yet residues are not always uniformly distributed e.g.

   - in citrus, some pesticide residues are concentrated in the oily peel and are not transferred to the pulp or juice. (However, in some situations the peel may be used separately for food or feed).
   - in peas and some beans the normal edible part is protected by the pod which is discarded.
   - for fruiting vegetables and assorted fruits with inedible peel such as melons, pumpkin, banana, kiwifruit, the peel which often contains most of the residue is discarded.

4. Some crops are rarely if ever eaten raw, e.g. potatoes, Brussels sprouts and cereals, and information on the fate of any residue during preparation and cooking is important in developing a reasonable estimate of the consumer intake of a pesticide in such crops. Analytical data are needed on the effects of various cooking techniques e.g. boiling, baking or frying since each may have a different effect on the results.

5. Certain crops such as cereals, sugar beet and oilseeds are normally processed to produce "derived" food commodities such as flour, bran, sugar and cotton-seed oil. These processes normally lead to a reduction or even disappearance of pesticide residues.

In developing a more realistic prediction from 1 and 2 above a maximum theoretical daily intake can be reduced by a factor of 20 even before considering other factors. If, in the absence of data, no losses are expected during transport and storage (there are usually some) and the average losses of residues on preparation/cooking/processing are assumed to be about 80% then the realistic prediction of consumer intake is about 100 times less than the maximum theoretical daily intake (see Fig. 7).

Where possible specific factors from measurements should be used for individual pesticides. However, the factor of 100 is supportable as a general indication by data for a considerable number of pesticides in common use. Table 1 shows that, with the exception of dieldrin which requires special consideration, there are additional safety factors since the actual measured intake is even lower still. Such a prediction of consumer intake for a pesticide can be used for safety evaluation with confidence, when actual daily intake values are not available.

Need for maximum residue limits - Relevance of MRLs to exposure

Many countries have established legal maximum residue limits as a measure to protect consumers. At best these limits can only offer a division between food legally (not necessarily scientifically) considered fit, or unfit for consumption. As the numbers of pesticides and countries with MRLs increase so do the administrative problems associated with the application or enforcement of maximum residue limits. The demands on the analyst for multi-residue procedures to cover over a hundred pesticides on a range of crops/commodities are unrealistic. In addition, there is a demand for confirmatory methods of analysis. Many pesticides are related compounds and are occasionally difficult to distinguish one from another and sometimes produce similar or identical metabolites or breakdown products. Thus there is a growing need to examine the relevance of setting legal maximum residue limits and to determine whether the consumer can be protected equally well by less, rather than more, legislation. It should be remembered that some countries already achieve satisfactory consumer protection without legal MRLs. During the registration process enough information

FIGURE 7. Realistic prediction of consumer intake

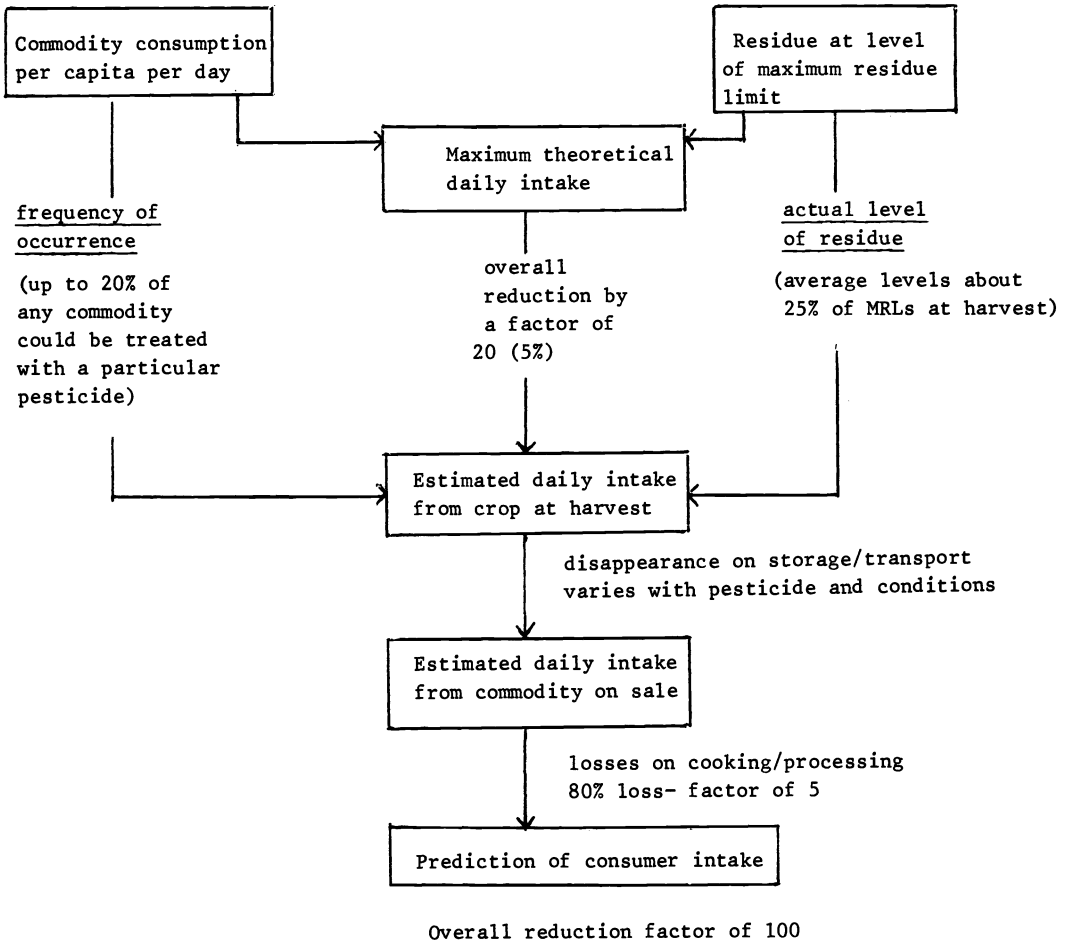
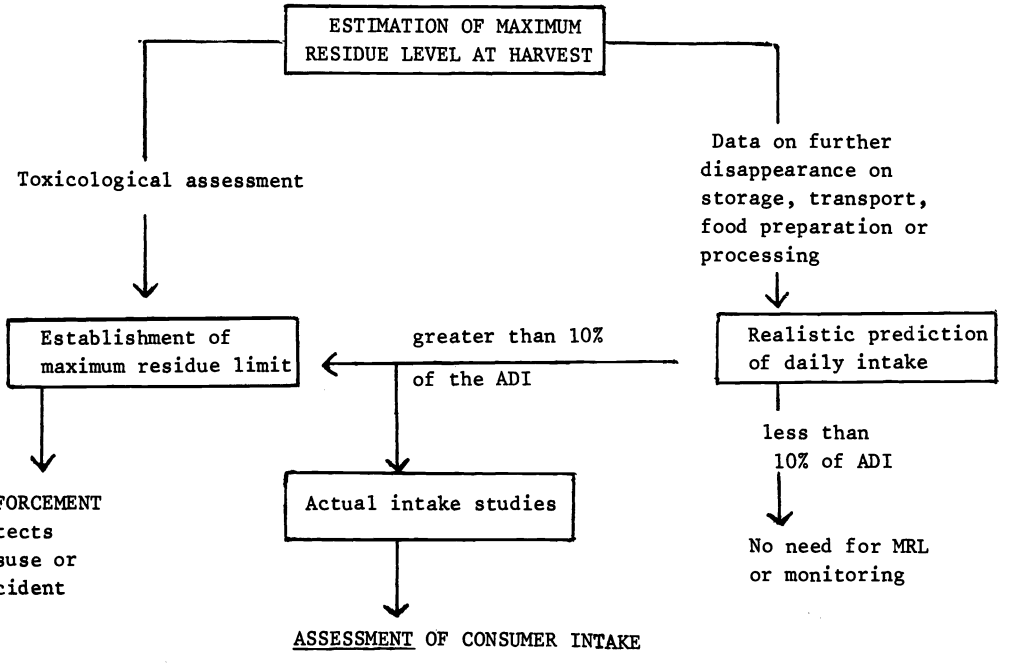


FIGURE 8. Proposals for the selection of pesticides for establishing MRLs.



should be available on the size and fate of a residue to enable a realistic prediction of consumer intake to be made and two possible approaches may be summarized as follows:

1. An MRL can be established and enforced by existing procedures. In this option the data requirements concentrate on the estimation of maximum residue levels at harvest and the enforcement by regular sampling and analysis by a food monitoring programme.

2. The second option also requires adequate data to estimate a maximum residue level at harvest but then places emphasis on data on residue disappearance during transport/storage/food preparation/cooking and processing to ensure a realistic prediction of consumer intake. If the predicted intake for a given pesticide shows that there is not even a theoretical possibility of approaching the ADI (say by a factor of 10) then MRLs and their subsequent enforcement are unnecessary for consumer protection and should be deleted or omitted. Such a step could relieve analysts and administrators of a large amount of unnecessary and unrewarding work (Fig.3).

Further simplification without risk can be achieved by an increased use of "group MRLs", using terms such as "pome fruit" or "root vegetables" where residues from the use of a pesticide have been shown to be similar. For example permethrin is a non-systemic synthetic pyrethroid insecticide which leaves a residue only on parts of the crop which are exposed. Maximum residue levels in $mg.kg^{-1}$ have been estimated (by the 1979 JMPR) for carrots (0.01), potatoes (0.05), radish (0.1) and sugar beets (0.05). The possibility of any root crop containing residues of permethrin above 0.1 mg/kg is very remote indeed, yet four separate MRLs will be established for the four crops mentioned and all other root crops may be excluded until confirmatory data are provided, when further crops will be added to the list. This is difficult to justify, scientifically or administratively. Although it is necessary at present to establish MRLs for some situations where the presence of a residue could be of concern to the consumer, the Commission considers that experts and advisers should be much more selective in making recommendations on this subject.

REFERENCES

1. IUPAC Commission on Terminal Pesticide Residues Pure and Appl. Chem., 51, 677 (1979).

2. Horowitz, W. in Pesticide Residues: Special Symposia at IV International Congress of Pesticide Chemistry Zurich (1968) Ed Frehse H. GeissbuhlerH. Pergamon Press (1979).

3. IUPAC Commission on Pesticide Residue Analysis Pure and Appl. Chem., 51, 1603 (1979).

4. IUPAC Commission on Pesticide Chemistry Pure and Appl. Chem., 53, 1039 (1981).

5. Cochrane, W.P. and Whitney, W. in Pesticide Residues Special Symposia at IV International Congress of Pesticide Chemistry Zurich (1968) Ed Frehse H. GeissbuhlerH. Pergamon Press (1979).

6. Carl, M. in Pesticide Residues: Special Symposia at IV International Congress of Pesticide Chemistry Zurich (1968) Ed Frehse H. GeissbuhlerH. Pergamon Press (1979).

7. Telling, G.M., Proc. Analyt. Div. Chem. Soc., January 1979, p. 37.

8. Ambrus, A. in Pesticide Residues Special Symposia at IV International Congress of Pesticide Chemistry Zurich (1968) Ed Frehse H. GeissbuhlerH. Pergamon Press (1979).

9. Gunther, F.A. Res. Rev., 76, 155 (1980).

10. Frehse, H. and Timme, G. Res. Rev., 73, 27, (1979).

11. FAO/WHO Guide to Codex Maximum Limits for Pesticide Residues. Codex Alimentarius Commission CAC/PR 1-1978 Rome (1978)

12. Bates, J.A.R. J. Sci. Food Agric., 30 401 (1979).

13. FAO/WHO Pesticide Residues in Food 1980. FAO Plant Production and Protection Series No. 26 (Contains references to all documentation of the FAO/WHO Joint Meetings on Pesticide Residues).

14. WHO Procedures for Investigating Intentional and Unintentional Food Additives Technical Report Series No. 348 (1967).

15. US Department of Health, Education and Welfare. FAO Monitoring Programs for Pesticide and Industrial Chemical Residues in Food HEW Publication No (FDA) 79-2116 (1979).

16. Frawley, J.P., Duggan, R.E. in Pesticide Residues Special Symposia at IV International Congress of Pesticide Chemistry Zurich (1978) Ed Frehse H., Geissbuhler H. Pergamon Press (1979).

GENERAL REFERENCES

'Pesticides' 5th Edition Council of Europe, Strasbourg 1981.

Report of Ad Hoc Government Consultation on International Standardization of Pesticide Requirements FAO 1977 AGP:M/9.

Reports of Codex Committee on Pesticide Residues FAO/WHO Alinorm 78/24 (1977 Meeting): Alinorm 79/24 (1978 Meeting): Alinorm 79/24a (1979 Meeting): Alinorm 81/24 (1980 Meeting): Alinorm 83/24 (1981 Meeting).

Annex I

PRIMARY DATA REQUIREMENTS

The results from supervised trials are only relevant if an analytical method is available which will determine the components of the residue as defined in Chapter 2. Until the composition of the residue is known its toxicological relevance cannot be estimated.

Before an appropriate analytical method can be designed, the components of the residue must be identified. Furthermore it is some help to elucidate their behaviour with respect to translocation, volatilisation and binding to or conjugation with plant constituents. The latter is particularly related to the bioavailability of the residue and the ease with which it can be extracted for determination.

The study of possible translocation is important to determine whether or not residues can occur in the crop at harvest. For example, a post-emergence herbicide in cereals may not be translocated in the crop either as active ingredient or a metabolite. Therefore a residue cannot be expected at harvest and unnecessary analytical effort can be avoided. A clarification of such properties is valuable before residue field trials are planned. The necessary experiments may be carried out in the laboratory, outdoors or in simulated outdoor conditions using the active ingredient with or without radio-labelling.

In practice it is more convenient to use radio-labelled material to obtain the following information:

1) the behaviour of the residue from the time of application until harvest - distribution in the plant, kinetics of disappearance, binding to plant constituents etc.;

2) the possible formation and identity of metabolites;

3) the changes in composition of the residue including metabolites with time; and

4) an overall material balance for the applied active ingredient.

It is recommended that the pesticide, formulated in an intended commercial formulation should be applied at twice the proposed rate to one or two of the relevant major crops. The treatments should be at the time(s) required by good agricultural practice and relevant climatic conditions should be simulated as far as possible. The conditions for the experiments should be chosen so that the behaviour of the active ingredient can be investigated in both the target crop and in soil which may receive part of the applied dose. After harvest the test system should be kept for a possible study of the uptake of residues from soil by subsequent rotational crops.

Most pesticides, however, leave very low residues at harvest and the identification of metabolites at this stage is often difficult. To identify metabolites it is advisable to carry out a duplicate experiment but sample the crop at a time when the total residue and metabolites are present in relatively high amounts. It is necessary to produce enough metabolites for isolation and comparison of chemical and physicochemical properties (e.g. mass spectra, infrared and ultraviolet spectra, chromatographic characteristics etc.) with compounds synthesized with a theoretical knowledge of possible structures formed by metabolism.

Toxicological considerations may also require the synthesis of metabolites in sufficient quantity to carry out toxicological tests.

Metabolites as components of the total residue

There are two general considerations which are basic to the decision as to whether or not specific metabolites/degradation products should be included in the definition and expression of a residue:

1) their basic toxicology; and

2) their presence in significant amounts.

A number of principles and subsequent specific options may be used in deciding which metabolites/degradation products to include in definition of residue and the expression of the residue, namely:

A. Residues may be expressed as parent compound if:

1) there are no metabolites;

2) metabolites are known to be insignificant and can be ignored;

3) metabolites are known to be of toxicological concern but are not present in significant amounts;

4) metabolites of toxicological concern are known to be present in significant amounts and the analytical method measures the total residue as a single compound which may be numerically expressed as parent compound. In this case the metabolites included in the residue are listed; and

5) metabolites of toxicological concern are known to be present in significant amounts and the analytical method measures parent compound and metabolites separately. In such cases the compounds of the total residue may be expressed additively as parent compound, with recalculation for differences in molecular weight, only when the differences are substantial (e.g. greater than 20%).

B. Residues may be expressed as a single metabolite or alteration product if:

1) parent is quantitatively converted to another chemical entity e.g. aluminium phosphide to phosphine;

2) metabolites of toxicological concern are known to be present in significant amounts and the analytical method measures the total residue as a single metabolite. The results may be expressed as that metabolite but the compounds included in the residue should be listed; and

3) metabolites of toxicological concern are known to be present in significant amounts and the analytical method measures residue components, including parent compound if present, separately. The result may be expressed additively in terms of metabolite with recalculation for differences in molecular weight only when differences are substantial (e.g. greater than 20%).

C. Residues may be expressed as parent and metabolites separately if:

1) metabolites are known to be present in significant amounts and the analytical method measures each component of the total residue separately.

All metabolites/degradation products included in the definition of residue should be listed regardless of the method of determination. Highly toxic impurities in pesticides must be treated separately.

Non-extracted or "Bound" residues

A special problem in both metabolic studies and description of residues is created by conjugates and bound residues. Any statement to the effect that residues are "bound" (to a substrate, or matrix) must necessarily be a function of the effort undertaken to "free" them, e.g. of the extraction procedure used, and remains meaningless unless the conditions under which such bound residues were found to be unextractable are specified. It is preferable, therefore, not to use the term "bound residue" in an analytical context but to substitute it by "not extracted residue", each individual case being supported by a statement of the method of investigation.

Only in such instances where residues are found to be unextractable under usual chemical laboratory conditions, e.g. without running the risk of changing them by applying very

rigorous extraction methods, should they be termed "bound" or "chemically unavailable". The question then remains whether such residues will be available to biological systems, e.g. to micro-organisms, invertebrates, or following crops (when persisting in the soil), or to the digestive tract of ruminants or other warm-blooded animals, including man (when persisting in certain constituents of feed or food). If chemical and biological unavailability or residues can be demonstrated, such residues should be considered negligible.

"Conjugated" residues or metabolites may be subject to hydrolysis in biological systems different from those in which they were shown to have formed. If such a process can be demonstrated or regarded as very likely to occur, the respective conjugate should be evaluated in the same way as unextractable residues. For example, a conjugate found in an edible plant should be considered as a residue only if it can be demonstrated, or it is considered highly likely, that the nonphysiological portion of the conjugated molecule may become physiologically available to an animal via its digestive tract.

These considerations, for both unextractable and conjugated residues, will apply only in such instances where the compound in question (e.g. the "bioavailable" substance, or the aglycone) satisfies the agreed definition of a "residue". When it does so, the respective substance should be included in the residue analytical procedure.

Analytical methods

Only when a decision has been made on whether or not specific metabolites/degradation products should be included in the definition and expression of the residue from a particular pesticide can the residue analytical procedure(s) be established. The design of suitable analytical procedures and criteria for their applicability and performance are outside the scope of this Appendix but it is advantageous if the parent compound, metabolites and conjugates can be artificially degraded to a single common moeity. Such a "total residue" approach reduces the number of chemical entities to be determined and improves the efficiency and sensitivity of the analysis.*

Other characteristics of the active ingredient such as

- solubility in water
- vapour pressure
- partition coefficient in water/n-octanol
- hydrolysis rate at pH 5, 7 and 9
- rate of photolysis

may also be of help in designing the analytical method as well as predicting the behaviour of the compound in the crop or in the environment

Appendix 7 - Good Analytical Practice in the Determination of Pesticide Residues - gives guidance on various aspects of residues analysis.

* This is of particular importance for an analytical method required for enforcement purposes but not so for methods used in the development of a pesticide when measurements of specific metabolites may be required.

Annex 2

GUIDELINES FOR GOOD AGRICULTURAL PRACTICE IN THE USE OF PESTICIDES
(prepared by the Codex Committee on Pesticide Residues)

These guidelines indicate principles for the use of pesticides in agriculture, and in the harvesting, marketing, transport and storage of foodstuffs. Taking into account the attainment of the desired degree of control of pests at an economic cost and with minimum of danger to operators, agricultural workers, consumers, beneficial animals and the environment, the following represents a list of goals which should be aimed at in good practice in the use of pesticides for the above mentioned purposes. It should be understood that the information presented in the guidelines is not intended as a substitute for actual supervised trials under the growing conditions of the area involved.

General

1. If pesticides reach man or animals through different routes and thus give rise to additional body loads, the use patterns may have to be adjusted and if necessary, priority should be given to those uses which are indispensable and for which no adequate alternatives are available.

2. Maximum residue limits established for products for human consumption are not necessarily acceptable for the same product when this is destined for animal consumption, and in such cases this should be indicated.

3. In view of the necessity of preserving a balance between cost, productivity, quality and freedom from residues, the concept of good agricultural practice in the realm of pesticide residues embrances all interrelated and essential factors and functions which ensure that the pests will be controlled effectively, leaving residues that are the smallest amounts practicable and that are toxicologically acceptable.

4. Therefore, pest control treatments should only be made when necessary. The requirements for pest control should first be established, followed by the application of the preferred method of control.

Choice of pesticide

5. All pesticides which are used should be authorized (registered) by appropriate authorities in the country of use. They should only be marketed with labels indicating recommended or approved uses, times, methods and rates of application, and safety precautions for the users. Such recommended methods of application should be based on supervised trials and other experimental work, and should take into account such variations in climate, in crop husbandry, and in incidence of pests as may occur under practical conditions from time to time in the various places in which the pesticide may be used (see WHO Technical Report Series No. 592, page 40, Explanatory note on good agricultural practice).

6. Bearing in mind the actual conditions under which the pesticide will be used, the pesticide should be adequately safe to man and the environment and at the same time provide adequate pest control.

7. Where a choice of pesticides is possible, the cost and effectiveness of available pesticides should be weighed against the risks involved, and those which show a more favourable benefit-risk ratio for the particular purpose in question should be preferred.

8. When pest control is required in the early growing stage of the crop, a pesticide may be needed which has an adequate and acceptable degree of persistence, in order to avoid repeated applications of non-persistent pesticides.

9. When plant quarantine and/or phytosanitary requirements make it necessary to apply pesticides close to harvest, those which have a short persistence should be preferred (see also 23 and 24).

10. The agricultural use of persistent and/or cumulative pesticides on crops for human consumption should be restricted as much as possible, and be limited to the control of pests, weeds and diseases for which at present no suitable alternative chemicals are available.

11. As a general rule, persistent and/or cumulative pesticides should not be used on fodder crops and not be applied directly to animals for veterinary purposes.

12. Where post-harvest treatments are required, pesticides which leave residues that are the smallest amounts practicable and that are toxicologically acceptable, do not interact with the food commodity, and/or are readily removed during storage, preparation or cooking, should be preferred.

13. With respect to post-harvest treatment of stored products (e.g. cereal grains) it is recommended not to use persistent and cumulative pesticides as direct admixture.

14. The application of adequately durable pesticides to the exterior of packing material for stored products is acceptable, but the use of highly persistent and cumulative pesticides should be avoided as much as possible.

Choice of formulation

15. Formulations which combine maximum efficiency of the pesticide with minimum risk should be preferred.

16. Supplementary adjuvants should be used only if their effect is known and where their use produces a significant improvement in performance.

17. In general, the use of combined pesticide/fertilizer formulations should be avoided. However, such practices are recommended by local authorities when they are considered beneficial.

Dosage

18. The quantity of pesticide applied should not be greater than the minimum required to achieve the desired degree of control.

19. The number of treatments should be determined by the desired degree of control and by the severity of pest conditions.

Application

20. The method of application should be selected to ensure optimum pest control with the minimum contamination of the crop and the environment.

21. Indirect treatment (such as soil application, seed dressing, treatment of alternate hosts) can in some cases be used to supplement or replace direct application to food crops.

22. Application equipment should at all times be maintained and used according to the makers' instructions.

Timing of treatment

23. Treatment should preferably be carried out when the pests are at the most vulnerable stage of development, and when climatic conditions and cultural practices will ensure that the optimum effect can be attained from the treatment. In some instances, however, action may be necessary immediately following detection of the pest species.

24. The interval between last application and harvest (slaughter in the case of veterinary use) should be as long as possible in order to permit the greatest reduction in pesticide residues, bearing in mind the pest incidence, the degree of control required for a maximum utilization of the commodity, and the vulnerability of the treated crop immediately pre-harvest. To this end official pre-harvest intervals should be established and adhered to.

Post-treatment practice

25. Crop rotation should be adjusted in such a manner that unintentional residues in the edible parts of the crop, as a result of previous treatments, will be minimal, particularly if the crop may be used as animal feed, and accumulation in the animal body may lead to undue residues in food products of animal origin.

26. Seed-grain, treated with pesticides at dosages to provide long-term protection in the soil, must, under no circumstances, be mixed with commodities destined for human or animal consumption. Sufficient safeguards ought to be provided which would minimize the accident risk of such practices.

27. Where grain intended for consumption must be protected in storage, only compounds with low toxicity and/or short persistence should be used.

28. In storage practice the selection of the pesticide for treatment of empty warehouses or ship holds, and the subsequent storage arrangements should be such that there is a minimum risk of contaminating feed or food products.

Annex 3

GUIDELINES ON PESTICIDE RESIDUE TRIALS*

Introduction

Residues remaining on or in the crop commodity depend on many interacting influences of varying importance including growth dilution, ratio of crop surface to mass, volatility of deposit and degree of adsorption on to and absorption into surface layers. The residue resulting from a given method, timing and dosage of pesticide application will also vary with site and climate and the limits of such variation are important to the assessment of safety and particularly to the establishment of maximum residue limits. In order to obtain the necessary data to estimate a maximum level, crop commodities should be analysed from crops with known pesticide treatment, reflecting good agricultural practice and grown under a representative range of agricultural and climatic conditions. Factors which may influence the disappearance of residues should be recorded. Thus, the procedures outlined in these guidelines refer to "supervised trials" which have served for many years as the primary source of residues information for the registration of pesticides and for setting maximum residue limits.

Because of legal and commercial implications such trials must be carefully planned, conscientiously executed, carefully evaluated and intelligently interpreted to ensure that the decisions taken are meaningful and that they reflect the practical situation resulting from approved uses of the chemical.

Cooperation between scientists of several disciplines is usually necessary to achieve the desired result and careful consideration must be given to all the factors and their variability. For example, if the crop sample is not truly representative of the material from which it is obtained, all the careful and costly work put into the subsequent analysis will be wasted. An erroneous result is worse than none at all. The analyst's residue data may be precisely determined but the results can be inaccurate because of inadequate field sampling.

Variations in residues trials techniques have contributed to the difficulties in evaluating data relating to the occurrence, disappearance and fate of residues in or on crops and often make it difficult or impossible to compare information from different sources.

Thus, there is an urgent need for internationally accepted guidelines on the experimental design, procedures and reporting of supervised trials and the purpose of these Guidelines is:

- to indicate the techniques which should be followed in order to secure valid experimental data appropriate to the above objectives; and

- to promote the establishment of harmonized procedures to facilitate international acceptance of the data obtained.

They refer to the use of pesticides on crops and stored products intended for food for humans or animals. It is intended to extend the guidelines later to cover trials when treated crops are fed to animals or when the pesticide is applied directly to the animal.

1. DESIGN OF RESIDUE TRIALS

In designing a residue trial, early consideration must be given to the intended use of the residue data to be obtained and to the sampling programme and analytical work that this entails. If data are sought to support petitions for establishing a maximum residue limit, results from a number of experiments in several geographical areas or during typical periods of the year and farming practices are often required. When a product is applied to a crop near maturity studies on residue disappearance with time are usually needed to determine acceptable pre-harvest intervals. Such considerations markedly influence the location of the test plots. The size and number of samples that must be taken from each plot determines

* Recommendations on sampling pesticide residue trials are in Appendix 4.

the size of the experimental plots.

Major trials should only be done with proposed commercial formulations. It is meaningless to carry out this work with laboratory preparations since the fate of the residue may be influenced by the nature of the formulation. It is preferable to make the application with commercial equipment in a manner analogous to that used by farmers, but the greatest care should be exercised to see that the application is uniform and thorough.

Trials should be designed to cover a range of representative field conditions, typical periods of the year, cropping and farming practices which are commonly encountered. Since climatic conditions have an important influence on the persistence and performance of a chemical, trials should be carried out in those areas where the product is to be finally used.

Whenever possible, and certainly whenever it is considered likely to influence residue levels, trials should be repeated on different varieties, different stages of growth at typical periods of the year and under different agricultural regimes to determine residue levels under various conditions.

Since one of the objectives of residue studies is to provide the basis for the estimation of maximum residue levels, the design of the experiments should be directed to the determination and evaluation of the conditions and factors which lead to the highest residue levels following recommended use patterns. If it is anticipated that the interactions of various factors could produce widely varying residue levels, experiments should be designed to demonstrate the effect of such interactions on residue levels.

Residue trials have to be especially designed in most cases and the presence of a target organism is not necessary. Trials intended for biological evaluation may be suitable for obtaining residue samples if the full range of the recommendations is reflected and if the plot size is large enough to obtain adequately representative samples.

Where the product is applied to the growing plant the prime objective should be to obtain data on the residue remaining in or on the crop at the time of harvest. If significant residues are expected at the time of harvest it will be necessary to obtain information on the effects of storage and processing on the residue subsequent to harvesting, as this will provide a basis for assessing the likely intake by consumers. After post-harvest treatments, commodities should also be sampled when they leave the store.

When the product is applied to the harvested crop, information should be obtained on the alteration of the amounts and nature of the residues during the normal course of storage and handling of the crop after treatment. It is desirable to know, in the case of a fumigant, for example, how much is taken up by a foodstuff during treatment, and whether and to what extent the pesticide disappears or reacts with particular food constituents.

Residue data will normally not be required for a crop which is not used for human or animal consumption. Examples are: flower bulbs, ornamental shrubs, etc.

However, the possible persistence of pesticides in the soil and their subsequent uptake by edible crops should not be overlooked. Where the use of a pesticide is likely to result in soil residues after harvest of the treated crop or residues in water used for irrigation purposes, residues data in edible parts of subsequent crops should be obtained.

Because of the large variety of crops and commodities on which a pesticide may be used it may not always be necessary to carry out trials on all crops/species/commodities. The Codex Committee on Pesticide Residues has recently adopted a Classification of Food and Food-Groups in which assignment of a commodity to a group involved considerations such as botanical family, use of different parts of the commodity, potential for residues and agricultural practices.

Although residues data will normally be required for most major commodities in a group a study of this classification will suggest circumstances when the results of trials on one or more major commodities may be regarded as applicable to others in the group provided the rates and methods of application of the pesticide and cultural conditions are similar. However, care must be exercised in the extrapolation of the results from one commodity to

another.

1.1 Trials lay-out

1.1.1 Selection of sites

Trials should be carried out in major areas of cultivation or production and should be sited to cover the range of relevant representative conditions (climatic, seasonal, soil, cropping system, farming, etc.) likely to be met for the intended use of the pesticide. Areas or sites where atypical conditions occur and which are not representative should be avoided unless it is expected that use under these conditions can result in higher residues.

1.1.2 Number of sites

The number of sites needed depends upon the range of conditions to be covered, the uniformity of crops and agricultural practice, and the data already available. Whilst it may not be necessary to require that trials be repeated for all regions with different ecological and climatical condition in which the use of the product is intended or all seasons with widely varying climatical conditions, sufficient data must be available to confirm that patterns determined hold for all regions and the total range of conditions including those which are likely to give rise to the highest residues. Trials in at least two growing seasons are normally needed.

1.1.3 Replication

Since the variations in residue levels between replicates at individual sites are small compared with those found in data from different sites, it is usually not necessary to replicate treatments at individual sites. However, it is useful to have three or four replicates at one site to study experimental uniformity and determine the within-site variations. In glasshouses or stores, the use of products with a high vapour pressure, fumigants, aerosols, smokes or fogs will generally not allow for true replicates at one site. If an efficacy trial with replicated plots has to be sampled, then samples taken from plots receiving "identical" treatments should be analysed separately to provide an indication of the within-site variations.

1.1.4 Plots

Residue data should not be generated from plots which are too small to be representative. The size of the individual plots will vary from crop to crop but should be large enough:

1) to apply the pesticide in an accurate and realistic manner, preferably under the same conditions as in normal local commercial practice; and

2) to provide representative crop samples (see Annex 4. Guide to Sampling).

A control plot for the supply of untreated samples is necessary for the reasons indicated in 1.2.3. The control plot should be large enough to satisfy these requirements and should be located close enough to secure identical growing and climatic conditions. However, it has to be sufficiently separated to exclude any contamination from the treated plots (drift, volatilisation, leaching, etc.). For products with a high vapour pressure, fumigants, aerosols, smokes or fogs used in glasshouses or in stores, provisions should be made for control samples from untreated crops or stored products e.g. in separate glasshouses/stores or separate compartments, grown/kept under almost the same conditions.

A sufficient buffer zone (lanes, guard rows, etc.) should be left between plots to prevent cross-contamination. In general, close proximity of a high dose level treatment and control plot should be avoided and untreated plots should be placed upwind from the treated plots.

1.1.5 Type/variety of crop/commodity/cropping system

The type or variety of a crop and the way in which it is grown may influence the residue pattern. In these circumstances, data should be available on the most commonly used type or

variety or cropping system and on the factor or combination of factors most likely to result in the highest residue levels.

1.2 Application of the pesticide

1.2.1 Formulation

The formulation to be marketed (or one of similar type and composition) should be used in the residue trials. Prior to the introduction of other formulations a limited amount of information from comparative trials should be obtained to check that the residue levels will not be significantly affected by changes in formulation.

1.2.2 Method of application

The method of application should reflect the intended recommendation. As far as possible, applications should be made with equipment similar to that used in local commercial practice. Experimental plot applicators are convenient and readily calibrated and can be used in residue trials as an alternative method of application provided they are compatible with normal practice. Care should be taken to ensure uniformity of application and to avoid contamination of neighbouring plots, either during or after application. In glasshouses, using products with a high vapour pressure, fumigants, aerosols, smokes or fogs, the whole glasshouse/store or compartment has to be treated. It will not be possible, in general, to have replicated plots, other dosage rates and untreated control in the same glasshouse/store or compartment. With fumigants, aerosols, smokes and fogs, special attention should be paid to equal and uniform distribution and a preliminary check on this particular aspect may be required. Furthermore, recommended procedures in the glasshouse/store during and after the application (e.g. doors/windows - shut/open) should be carefully followed.

1.2.3 Dosage rates

At least two dosage rates should be included in a residue trial: the maximum rate which is likely to be recommended and another rate, preferably double the recommended rate, if considerations of phytotoxicity allow. This will give guidance on likely residue levels should dosage rates exceed recommendations and allow some assessment of the relationship between dosage and residue levels.

When sprays are used the volume per unit area should reflect practical conditions and be the same for all sites in the region and the volume applied recorded if relevant. The concentration of pesticides should be expressed as units active ingredient per unit area recorded in international units (SI). In glasshouses/stores, for products with a high vapour pressure, fumigants, aerosols, smokes or fogs dosage rates should be expressed both per unit area and per unit volume.

In addition to the two treatment rates mentioned, a control plot should always be included in any residue experiments carried out to provide the analyst with a sample known to be free from residues of the pesticide under investigation.

Control samples are needed:

(a) to ascertain that no artefact in the crop derived from local conditions could give rise to interference in the analysis;

(b) to establish the recovery level of the pesticide from the crop or soil by the analytical method;

(c) in the case of a new crop, to investigate the storage stability of any residue.

When two or more dosage rates are included particular care should be taken to avoid cross-contamination. In glasshouses or stores, the use of products with a high vapour pressure, fumigants, aerosols, smokes or fogs will not allow in general for more than one dosage rate per glasshouse/store or compartment nor for untreated control. Provision has to be made in order to obtain samples from untreated crops/commodities and from treatments at another dosage

rate e.g. from separate glasshouse/stores or separate compartments, grown/kept under as near the same conditions as possible.

1.2.4 Number and timing of applications

Unless unavoidable, no pesticide in addition to that to be analysed should be applied to control or test plots before or during the same period. However, since it is or primary importance that both the untreated and treated plants be healthy, the use of other pesticides may be necessary. In this case only those pesticides that will not interfere with the analysis of the residues of the test compound may be used. The pesticides used should be noted; where possible the advice of the analyst should be obtained. It is important that control and test plot receive the same treatment.

1.3 Degradation studies

Residue trials are sometimes used to obtain information which, although supplementary to the main purpose of the trial, is extremely valuable in studying the properties of the compound under test and in enabling a fuller safety assessment to be made. The trial may be used, for example, for studies on the metabolism and degradation of a pesticide under field conditions. Such requirements should be given early consideration in the planning of the trial.

1.4 Residue Disappearance Studies and Safety Intervals

The disappearance of a pesticide deposit may be due to one or more of several factors, principally:

1. Physical removal, e.g. by washing or volatilisation
2. Chemical degradation or metabolism in/on the plant
3. Apparent disappearance due to crop growth dilution.

Disappearance studies are of particular value in understanding the significance of these factors, especially when at the moment of application a considerable amount of the future consumable part is already developed or when soil-applied volatile or systemic pesticides are used.

Samples should be taken as soon as the spray has dried; (care should be taken if a risk to people handling treated plants is anticipated) one to three days later and at intervals thereafter; the intervals will vary from one trial to another and will depend on the persistance of the chemical and on the anticipated waiting period between treatment and harvest. If multiple applications are anticipated a sample taken just prior to the final application may be of value. Sampling on at least four occasions, up to and including harvest, is recommended and it is important that the plot size is large enough to allow for valid sampling after each interval. More than one replicate should be sampled and analysed separately.

The range of residue levels at sampling times is much more important than the average levels particularly just before and at harvest. Residue disappearance curves may be plotted using maximum values as well as average levels.

The weather conditions and age and growth of the crop during this type of experiment are particularly important and should be carefully recorded.

2. REPORTING ON RESIDUE TRIALS

All the data relating to the treatment and history of the residues trials should be recorded. It is usually convenient to record these data in standard form and essential items for specific trials may be drawn from the following list. These refer to the supervised trial, field sampling and shipment of sample to the laboratory. Further data on the chemical analyses will be provided by the analyst. Model report forms are included. (See also Annex 7)

2.1 General information on the supervised trial

Pesticide (active ingredient and trade name)
Formulation
Trial number and type (field/glasshouse/other)
Commodity
Variety
Test locations (country and site)
Soil characteristics pH, physical and chemical properties
Name (and signature) of the person(s) responsible for the trial and for collecting the sample.

2.2 Application data for field trials

Crop planting or sowing date
Description of plot plan/crop layout/cropping system
Plot size or number of plants per plot/unit area
Number of plots per treatment
Target pest or disease (if any)
Method of application and equipment
Number of applications and application date(s)
Application details (overall, banded, etc.)
Dose rate - active ingredient/ha
- weight/volume of formulation/ha
- applied dilution
Climatic conditions during and after applications preferably for the whole period of the trial
Other pesticides applied to trials plot with relevant details as above
Cultural treatments before, during and after application - include irrigation and fertilizer information
Growth stage at (last) treatment.

In glasshouse/stores for the application of fumigants, aerosols, smokes or fogs, the procedure of the application and the disposition of fixed equipment/generators should be described. Any anomaly occuring during the application or during the post-application period (e.g. doors or windows opened) should be reported. Dosage rates should be expressed both per unit and per unit volume.

2.3 Application data for stored products/post-harvest trials

- district, number, volume and area of the trials site;
- description of the store including total capacity at time of trials, type of ventilation and state of hygiene;
- details, if available, of other recent pesticide treatments in store;
- description and quantities of products and details of packaging conditions (whether in sacks, boxes, bales, tins or in bulk);
- formulation(s) used;
- rates, methods and dates of application;
- temperature and humidity in the storage area during and shortly after applications of pesticide and the mean temperature and moisture content within the stored product between time of treatment and sampling.

2.4 Sampling data

Growth stage at sampling - normal harvest date.
Method of sampling.
Sampled part(s).
Number of samples taken per test/treatment replication.
Number of units in sample, if relevant, (e.g. lettuce, pomefruit).
Sample weight and preparation (trimming/washing/other if common practice in preparing the commodity).

Control treated.
Date of sampling with time interval between last application and sampling.
Storage conditions before shipment.
Date shipped.
Method of packaging.

REPORT ON PESTICIDE RESIDUE TRIAL. PART A. FIELD REPORT

Please type or use block capitals

1. RESPONSIBILITY

1 YEAR		3 Company or Organisation Name and Address	
2 Trial identity or number			
4 Person(s) responsible for (include signature)		a. Trial design ..... b. Application ..... c. Sampling ..... d. Analysis	

2. IDENTITY OF TRIAL

5 Active ingredient(s) (common name)	6 Class of pesticide or agricultural use	7 Trade name(s) or Code number(s)	8 Formulation		
			Type	Conc'n in SI units	Comm/ Exper'l
....					

crop/commodity

9 Type	
10 Variety/ cultivar	
11 Codex commodity classification	

location

12 Country/ Region	
13 Site or Map ref. (include address)	

14 Pests/ diseases	

REPORT ON PESTICIDE RESIDUE TRIAL. PART A. FIELD REPORT.

3 GENERAL INFORMATION ON THE TRIAL	Trial identity or number	
15 Crop production sytem or lay-out. e.g. commercial orchard/ glasshouse; crop planting date; age of crop; guard rows; soil type		

plot data

16 Plot dimensions in International units		19 Crop spacing	
17 Number of plots per treatment (replicates)		20 Number of plants per plot (if relevant)	
18 Number of control plots		21 Number of rows per plot (if relevant)	

22 Previous year's pesticide treatment	
23 Other pesticides applied to the plot (rates and times) during trial	
24 Cultural treatments e.g. irrigation, fertilizers	
25 Summary of climatic conditions. e.g. temperature (°C) rainfall wind sunlight (attach details if available)	1. before application (96 hours) 2. during application 3. after application (up to sampling)

REPORT ON PESTICIDE RESIDUE TRIAL. PART A. FIELD REPORT.

4. APPLICATION DATA	Trial identity or number	
26 Method/Equipment Type of application e.g. spray to run-off, band, overall volume applied		
27 Dose rate a.i. g/ha		
28 Dilution or spray conc'n in SI Units		
29 Numbers of applications		
30 Dates of applications		
31 Growth stage at last treatment*		

* Internationally recognised scales if available

5. SAMPLING

32		Control / Treated (delete as applicable)
33 Sampled part of crop		34 Growth stage at sampling
35 Method of sampling		
36 No of samples per plot	38 Sample weight and treatment	
37 No of units in primary sample		

39 dates

sampling				
freezing				
receipt in laboratory				

40 intervals (days)

last treatment/ sampling				
sampling/freezing				
sampling/receipt in laboratory				

Annex 4

SAMPLING FOR PESTICIDE RESIDUE ANALYSIS

A. General Principles of Sampling

The practice of sampling stems from the theoretical possibility of dividing a lot or consignment into a number of smaller portions which may be separately analysed. In general, precisely identical results would not be expected on each of the portions; the results would be scattered about the average lot quality of the whole. The range of such a collection of results on every portion from the lot may be expected to embrace the mean value of pesticide residues in the lot, and also permits an estimate to be made of the variation of the measured residues throughout the lot. The observable pattern of variability is dependent on the size of the portion examined. (Any measures of variability should therefore include a statement of the size of the portions chosen).

If, instead of examining every portion, a selection of portions is examined, then the choosing and removal of the portions is a sampling operation. Further, if the selection is truly random then it can be shown that the average value of the residues measured in the selected portions is a sound and unbiased estimate of the average lot quality of the whole. If the portions selected are sufficient in number, the variability of the whole can also be estimated and the accuracy of both these estimates may be stated in quantitative terms. In general, measurement of variability requires the separate analysis of a number of parts of the lot but where the degree of variability is known or assumed from past experience, measurement of the mean value of the residues may require only the analysis of a single sample drawn from a mixture of a number of parts of the lot.

The fact that the results obtained on a sample may be compared with a standard value namely maximum residues limits implies that sampling has been carried out previously on similar material. In practice it is generally a continuing process, carried out on successive lots or consignments, so that prior information on the mean and standard deviation, or on the average per cent defective, is available. Such information is required in drawing up sampling plans. At the same time further information is continually accumulating and may well be used in setting up maximum residues limits for future use. Sampling and limits cannot be considered independently, each having its influence on the other and they therefore should be considered together.

Errors

The estimate of the residues in the material differs from the average lot quality by the error of the estimate. This deviation may arise from many causes but in general the contribution to the total error from these causes may be classified as either random errors or systematic errors.

A random error is one which arises solely by chance. Its specific characteristic is that the mean value of random errors tends to zero as the number of estimates made is increased by replication. All other errors are systematic. A systematic error or bias in mean value does not tend to zero on replication. Bias is likely to arise when a sampling choice is made under conditions which fail to ensure that it is a random choice. Systematic error can arise in both sampling and analysis because the method is not valid or the equipment is faculty or the operator does not carry out the method as specified. With data that are subject to random error the magnitude of the error can often be estimated from the data but bias can never be estimated from dat that is subject to systematic error. In practice both kinds of error are likely to be present in the estimates obtained for the residues determined. It is never safe to assume absence of bias when a truly random choice of sample has not been made.

It is never possible to prove the absence of bias because even random samples are subject to random errors. It is, however, possible to estimate the probability of the bias present exceeding any chosen value by continued replication of sampling and analysis in order to diminish the random error until it is significantly smaller than the level of bias that is to be detected. When random sampling is impractical and a restriction on freedom of choice

has to be accepted, experience of sampling the material under examination or similar materials may be used as a guide to the type of restricted list likely to minimize bias, but such experience should be renewed from time to time by deliberate attempts to detect bias by taking samples under a different set of restraints.

Both random error and bias may be introduced in sample preparation process. Unless a collection of primary samples is well mixed and the final selection for the laborary sample is a random choice, unnecessarily large random errors can arise. Mixing and random selection are made easier if the material being handled is first reduced in particle size by appropriate techniques. Bias is certain to be present unless the whole of each of the primary samples goes through the size reduction process and is totally recovered for mixing into the final sample. The above errors are those arising from the sampling operation itself which is only a part of the whole process of measuring residues. All analyses are additional sources of both kinds of error in the final estimate of pesticide residues.

In general there is little point in performing an elaborate and costly sampling exercise to achieve small sampling errors if the analytical methods introduce greater error. Conversely, crude techniques of sampling completely destroy the value of very precise analysis.

Types of Variability

If the mean values of the pesticide residues of each of the portions into which a lot may be divided are not significantly different (this is also the mean value for the whole) then in terms of this size of portion the material is said to be homogeneous. It is obvious for homogeneous material that a sample fully representative of the whole is obtained by withdrawing any single portion and that this need not be a random choice.

Material which is not homogeneous is defined as being heterogeneous and is characterized by portions of the whole having significantly different mean values of pesticide residues. If in a heterogeneous material it is found that the level of residues in a given portion is independent of the levels of neighbouring portions or of its position in the whole, then the whole mass exhibits random heterogeneity. In a quantity of material exhibiting random heterogeneity, collections of non-random choices of portions cannot be distinguished from collections which are chosen at random. Random heterogeneity is not a property which is independent of the size of the sub-unit. In random heterogeneity there is no discernible pattern and, in particular, it is impossible to predict the value of any one portion from knowledge of the values of the others.

Food commodities normally exhibit either homogeneity or random heterogeneity as regards the levels of pesticide residues.

Effects of Variability on Sampling

It is generally assumed that levels of pesticide residue blend linearly by mass, i.e. if portions of equal mass are mixed then the residues in the mixture is an arithmetic average of those of the component portions. In most cases this is sufficiently near the truth for practical purposes.

Consider the result of withdrawing portions at random from quantities exhibiting the above types of variability and analysing these portions separately. For homogeneous material the results on all portions are identical (assuming negligable analytical errors) and in fact once the results on two portions are available all subsequent information merely confirms the mean value and absence of variability. If it is known in advance that the material is homogeneous, analysis of a single portion would give the mean value of the whole. It is emphasised that the choice of sample need not be random in a homogeneous system.

If a similar operation is performed on heterogeneous material however the results obtained on individual portions are not in general indentical. If the portions are similar in size and the choice of portions is random, then as the results on portions are accumulated, an increasingly clearer picture of the type and extent of variability becomes apparent.

Further, a mean value estimate may be obtained not only by averaging the results on the

individual portions, but also by preparing a composite sample from the portions and determining the residues in this sample. The result of this second estimate contains a larger error, however, because of the smaller number of examinations carried out. It also involves losing part of the information available from the separate portions, namely, the measure of variability; this precludes an estimation of the error attached to the mean value. However, a replication of the sampling exercise can produce an estimate of this mean value error.

Because it is usually the average residue of the whole quantity which is to be measured, most sampling plans are directed to securing a sample representative of the whole with the minimum of effort in such a way as to minimize the bias and reduce the likely random errors to an acceptably low level.

The error of the estimate of average lot residue based on separate analyses of a number of individual portions depends on two factors. The first is the variability between these portions, which is an inherent property of the goods being examined and is consequently not controllable by the sampler. The second is the number of portions examined, the error being inversely proportional to the square root of the number of portions examined. This remains true when the portions are not separately examined but are mixed together to produce a representative sample. In practice complete random mixing is neither easy to achieve nor easy to measure and some additional random error is incurred if mixing is imperfect.

It follows that the general approach of obtaining a representative sample from the heterogeneous material comprising a lot is to select at random a number of portions of equal quantity from the whole and to combine these to form the bulk sample. This may be inconveniently large and therefore may be reduced to give a final sample.

Sampling Techniques

All sampling plans are affected by economic considerations and it is usually neither economical nor practical to make a random selection of portions. From the definitions of homogeneity and random heterogeneity it is apparent that if either of these terms can be applied to a consignment of fruit for example then a random selection is not necessary; any convenient portions may be taken to form a sample. It follows that an immediate practical solution to this sampling problem may lie in mixing the contents of the consignment to ensure not necessarily homogeneity but random heterogeneity; having achieved this, a simple withdrawal of any portions, and in particular, portions withdrawn simultaneously, would be as good a sample as the random selection previously described. This alternative to the general approach depends on adequate mixing at some stage. The processes of harvesting a crop with subsequent packaging in boxes and loading of boxes in a consignment may be assumed to produce random heterogeneity of the items. The validity of the assumption of adequate mixing should be periodically verified by taking two such samples, analysing them separately and comparing the results obtained.

Optimum Sample Quantity

The criterion of homogeneity given is not absolute but depends on the size of the portions analysed. In general it can be assumed that homogeneity does not persist if smaller and smaller portions are examined. It therefore follows that is a sample purporting to represent a quantity of material is considered as a collection of very small portions, then as the number of these small portions is diminished, the composition of the sample increasingly reflects the consequences of the chance selection of small components the composition of which is different. In other words for any specified set of conditions there is likely to be a minimum sample quantity that is just large enough to ensure that its mean residues level does not differ significantly from the mean residues level of the material it represents. This minimum is referred to as the 'optimum sample quantity' since it is the smallest sample capable of giving the necessary information and any unnecessary increase in quantity is likely to lead to increased costs of sampling, losses of material, etc.

In the case of continuous solids (bulk grain), and liquids which do not contain particulate matter, quantity of sample taken does not affect its mean composition and all spot samples are truly representative of the material at the point of sampling. The sample preparation step should ensure that the analyst can take a representative portion from the final sample.

In the case of solids this usually leads to a degree of comminution and in all cases the laboratory sample should be so mixed that it is homogeneous on taking the laboratory sample. The optimum sample quantity should not be less than the quantity necessary for testing, nor should it be less than the quantity necessary for efficient blending and mixing in the equipment used. Usually, it should be large enough to permit triplicate analyses on the prepared sample.

For single and multiple items, although a quantitative description of the optimum sample is always possible, the precise definition of quantity may present difficulties. The sampling of materials presented in multiple items involves two distinct sampling operations. First a number of the items is chosen and then each is sampled. The decision as to how many items should be chosen in the first step is a special case of deciding optimum sample quantity. In order to obtain a sufficiently large selection for an initial survey of the lot and in absence of a specially designed sampling plan, several arbitrary tables have been designed; one of these for example recommends that the number of items to be sampled is the next highest integer to three times the cube root of the number of items in the lot except when the number of items is small.

Statistical Information

Examination of a Single Representative Sample

Goods are frequently examined on the basis of the analysis of a single representative sample. Though replication of the analysis can reduce the analytical error no statistical information on the lot quality can be obtained from this type of sample. No statement of the reliability of an estimate of the quality of the lot under examination can be given unless at least two representative sampling operations are performed. Such samples, being representative of the whole, cannot give any information concerning the variability within the lot. More common than the isolated sampling situation is that in which similar goods in similar quantities are regularly examined. In these circumstances, provided that the assumptions of similarity are justified, knowledge of the random errors of sampling is accumulated. In effect, it is assumed that although the mean value of each lot may be different, the errors arising from sampling are due to exactly the same small causes.

Sampling and Testing Errors

Values for the sampling and analytical errors can be obtained by replicate sampling and analysis. Knowledge of these and of the relative costs of sampling and testing make it possible to calculate the optimum rate of sampling and analysis for a minimum cost. Casual and ill-considered sampling may be cheap when costed on the basis of the sampling operation but expensive when costed on the basis of the precision purchased.

Measurement of Variability within a Lot

So far, the sampling situations covered have been those in which the total quantity under examination is considered as a whole. That is to say that the objective of the sampling operation and subsequent analysis is to assess the average quality of lots,consignments, etc. It is, however, occasionally necessary to consider the variations of quality within the whole. In residues analysis an important consideration is the estimation of the number of individual items having residues values greater than the maximum residues limit.

There is one important difference between this requirement and the general problem of assessing the average quality of the whole. This is that in effect there are two distinct sampling operations. This is because variability is essentially a property associated with the individual items in the lot. Assuming that the number of items present is large, the first sampling operation is to choose an appropriate number of items which will serve to represent all the items; the second sampling operation, or rather set of operations, is the separate sampling of each number of the chosen collection of items. This introduces a new source of error in addition to the two sources of error already mentioned, namely, (a) errors in analysis; and (b) errors in representative sampling of the product. To these is now added (c) errors arising from small collection of items failing to represent the full collection of items in the lot.

The only way to diminish the uncertainty associated with sampling a collection of individual items is to increase the number of items included in the sample; in the extreme case, when all the items form the sample, errors from this source disappear. An assumption in using statistics here is that a small number of defects is admissible. If not then all the lot must be analysed and the question of sampling does not arise.

It can be shown that samples comprising a small number of items, representing a batch or consignment of many such items, give very imprecise information about the risks of defective items being present. Increasing the sample size improves the precision of this information but increases the costs of sampling and analysis. Consideration of the costs of hazards incurred by failing to detect a defective item should play an important part in choosing sample size. In all cases, a statement of acceptable error is necessary in order to design a sampling plan. All sampling plans contain an implied acceptance of error in the final estimate.

B. Guide to Sampling Pesticide Residue Trials

In most cases, it is not practical or feasible to collect all of the crop from a trials plot and it is generally necessary to devise a means of taking a sample referred to as the field sample, which, when reduced and analysed, will demonstrate a residue that, for all practical purposes, will represent the maximum residue level of the crop in the plot.

It has always been recognized that it is extremely difficult to obtain uniform application of a pesticide in the field and deposit data following careful application have demonstrated up to 10-fold differences in deposits, thus in taking a sample for residue analysis, it is necessary to approach the task in an intelligent, realistic manner if the results of analysis are to be valid or useful for estimating maximum residue levels.

Generally, the selection of the portions that make up the field sample is done randomly, systematically, or selectively from predetermined "stations", depending upon the circumstances. The best approach for any given plot can only be determined by a fully qualified person who is capable of recognizing and interpreting the importance and usefulness of the residue data sought. In setting up sampling stations and/or the sampling method, it is necessary to give consideration to all factors that control the residue distribution over the entire experimental plot. In certain cases where there is likely to be considerable within plot variation, such as orchard and glasshouse trials there should be at least three sample replicates per plot at or near harvest and the sample integrity should be maintained through to separate analyses to determine the within plot variation and collect information on the performance of the analytical method. The field sample must, as far as possible, be representative of the treated plot and the individual units comprising it must be typical of those taken in a commercial harvest. The units of the field sample should be identical with the normal harvested product as regards any trimming or cleaning. Separate guidance is available on the recommended portion of the field sample to be prepared for the determination of pesticide residues.

Adequate sampling of the untreated crop is an important consideration especially if the residue level in the treated crop is expected to be low. While it is not so important to select control crop samples with the care needed for treated samples, it is important to have an abundant amount of such samples.

1. Representative field samples

Representative samples of the crop in each plot must be taken by a recognized procedure. Although each plant or fruit should normally have an equal chance of being chosen emphasis should be directed towards identifying the highest residue lvels.

Consider the following points:

(a) when taking a sample at harvest avoid taking diseases or undersized crop parts or commodities at a stage when they would not normally be harvested;

(b) sample the parts of the crop that normally constitute the commercial commodity;

(c) take samples in such a way as to be reasonably representative of typical harvesting practice;

(d) take care not to remove surface residues during handling, packing or preparation; and

(e) take and bag the required weight of samples in the field and do not sub-sample.

The weight of the sample suggested in the paragraph 4, is the minimum that experience has shown is needed to give a valid sample. Detailed procedures, in specific cases, are given for guidance; in other cases special protocols may be required. The guidance is specifically on taking a field sample; advice on sample packing and sample storage is given in Section D.

2. Contamination

It is vital to avoid contamination of the field sample with the pesticide under study during sampling, transporation or subsequent operations. Pay special attention to the following:

(a) be certain tools are clean;

(b) use new storage bags of suitable type and adequate strength;

(c) avoid contamination of the sample by hands and clothes which may have been in contact with pesticides;

(d) do not transport field crop samples for analysis in vehicles carrying pesticide formulations; and

(e) avoid any damage or deterioration of the sample which might affect residue levels.

3. Control samples

Always take control samples. These are as important as samples from test plots. Control samples should be of similar quality to that of the test samples and may be from plots treated with another pesticide providing these are specified in the trial details. Control samples should be taken before the treated samples, so as to avoid the possibility of contamination from handling. For control samples, using products with a high vapour pressure, fumigants, aerosols, smoke or fogs in glasshouses or stores, see under 2.2.2 in Appendix 3.

4. Sampling Procedures for Field Crops

The amounts of different commodities required to constitute a satisfactory sample obviously vary according to the commodity. The amount indicated below have been found to be satisfactory and are given as minima. The recommended size of the field samples may differ from those recommended for the enforcement of maximum residue limits because field samples are often required to satisfy other needs such as research programmes.

Crops quoted are meant as examples and are grouped as far as possible according to the classification under consideration at the Codex Committee on Pesticide Residues (CAC/PR 1-1978). The lists are not exhaustive.

VEGETABLES (A01)

Root, tuber and bulb vegetables (A01, 0100 and A01.0200)

Take samples from all over the plot. Remove as much adhering soil as possible from crops but do not wash. (Note: In some cases, where leaf parts are used as feed, they may need to be sampled separately).

Quantity

(a) Root crops (large) - 5 kg samples (not less than 5 items)
Beet (red, sugar, fodder), onions parsnips, potatoes, sweet potatoes, turnips.

(b) Root crops (small) - 2 kg samples
Carrots, radish, spring onions.

Leafy, stem, fruiting and legume vegetables (A01.0300 to A01.0800)

Take the sample from all parts of the plot. Sample items of crops such as fruiting vegetables, peas or beans from those protected from the spray by foliage as well as from those exposed to the spray. Remove as much soil as possible from crops such as celery.

Quantity

(a) Leafy or stem vegetables (large) - 5 kg samples (not less than 5 items)
Brassicae (cabbage, cauliflower, broccoli, kohlrabi, curly kale).

(b) Leafy or stem vegetables (small) - 2 kg samples
Asparagus, brussels sprouts, celery, chicory, lettuce, spinach, turnip tops.

(c) Fruiting vegetables (large) - 5 kg samples (not less than 5 items)
Cucumber, melon, squashes, eggplant (aubergines).

(d) Fruiting vegetables (small) - 2 kg samples.
Peppers, tomatoes, gherkins.

(e) Legume vegetables - 2 kg samples
Beans, peas etc., (with pods)

FRUITS (A02)

All tree and bush fruit, including vines, small and other fruits

Select fruit from all parts of the tree/bush, high and low, and from both sides of the row, and select fruits according to abundance wether in each segment or the whole tree/bush. More fruit will therefore be selected from the more densely laden parts of the crop. Sample fruits exposed to the spray and also those apparently protected by foliage. Take large and small fruits, perfect or slightly blemished, but not so small or blemished that they would not normally be saleable.

Quantity

(a) Tree fruit (large) - 5 kg samples
Applies, citrus, palm fruits (coconut and oil palm), peaches, pears.

(b) Tree fruit (small) - 2 kg samples
Cherries, dates, nuts, olives, plums.

(c) Small fruits, berries, and vines - 2 kg samples
Bush fruit (all types), grapes, strawberries.

(d) Miscellaneous (large items) - 5 kg samples (not less than 5 items)
Bananas (take four fruits from each bunch), pawpaws, pineapples.

GRASSES (A03)

Cereal grains (A03.1500)

Cut not less than ten small areas (approximately 0.1 m^2) chosen randomly from all over the plot. Cut stalks about 10 cm above the ground. Remove the grain from the straw. If an experimental mechanical harvester is available the whole plot may be harvested but residue samples should not include material from the first few metres of a plot in order to avoid contamination from the previously harvested plot. Take not less than ten grab samples of grain and/or straw from the harvester uniformly spacing them over the entire plot. (Note: Care should be taken to avoid contamination when mechanical methods are used to separate the parts of the crop).

Quantity

(a) Maize (grain and cobs) - 2 kg samples

(b) Small grains - 1 kg samples

Fodder and straws (A03.1600)

Harvest the crop in a way to simulate cutting practice. Record height of cutting and avoid soil contamination. Samples should be taken from not less than ten points (approximately 0.1 m^2) in each plot.

Quantity

(a) Grass and forage (smaller leaves) - 1 kg samples
Clover, grass

(b) Forage (larger leaves) - 2 kg samples
Alfalfa, beet tops, etc.

(c) Straw (all cereals except maize) - 1 kg samples
Maize silage (green plant at various stages of growth) and stover (dry remains of plants after grain harvesting): five plants (excluding roots).

(d) Other animal feed items. Samples of 1-2 kg are normally sufficient depending on nature of the material.

NUTS AND SEEDS (A05)

Oil seeds

(a) Cotton

Pick the cotton at the normal stage of harvesting and remove as much fibre from the seeds as convenient.

Quantity

1 kg of delinted seed (or 2 kg with fibre)

(b) Sesame, rape, soyabeans: Collect the heads when they have reached the stage of maturity at which they are normally harvested and if convenient thresh to remove the seeds.

Quantity

1 kg of seeds

(c) Sunflower: Select ripe heads randomly over the plot and remove the seeds by shaking.

Quantity

1 kg of seeds

(d) Groundnuts: 1 kg (or 2 kg in fibre)

Coffee, Cocoa

Samples representative of each treated plot should be taken in the field in a manner reflecting common practice and should then be processed through to the dried state using the locally typical process. Normally, the freshly harvested product is not required.

Quantity

Cocoa, coffee - 2 kg

HERBS, SPICES AND TEA LEAVES (A06)

Samples representative of each treated plot should be taken in the field in a manner reflecting common practice and should then be processed if appropriate through to the dried state using the locally typical process. Normally the freshly harvested product is not required for tea although herbs such as parsley and chives should be samples fresh.

Quantity

tea - 1 kg

OTHER PRODUCTS NOT CLASSIFIED

Sugar-cane

Take short sections (about 20 cm) from various portions of the length of the canes, and from all parts of the plot.

Quantity

5 kg samples

Juice: Care is necessary due to the rapid changes which normally occur in cane juices. If required, samples (1 litre) should be taken and frozen immediately and sent in cans.

5. Samples of Processed Commodities

Where a commodity is normally processed between harvest and marketing, such as by milling, pressing, fermentation, drying or extraction, data may be required on the processed crop or its products. Details of the processing method should be supplied with the samples along with storage and handling histories. In such cases, the trials should be planned to provide samples with appropriate residue levels so that the fate of residues can be studied during the processing. Sample separately any cleanings, husks or by-products which could be used for animal feed.

6. Sampling Procedures for Stored Commodities

Supervised trials with stored products/post-harvest treatments should be carried out over a wide range of storage facilities and the sampling technique must be carefully chosen if a valid sample is to be obtained. Sampling procedures for taking a valid sample from most commodities in storage units are well established. Such procedures are acceptable in sampling for pesticide residues analysis and may be used if adequate references are given.

The sampling procedures are usually designed for three kinds of storage conditions.

6.1 Sampling from bulk

Obtaining a representative sample from a (large) bulk container (e.g. cereal grains) is difficult and if possible, the sample should be taken at frequent regular intervals from the stream during a transfer into another container. A probe sample is not representative but may be acceptable if:

- it is possible to reach every part of the storage container.
- a large number of individual samples are taken before mixing and reducing to get a final sample.

Pesticide residues are normally higher in the dust fraction and this should be recognized in the sampling procedure.

2. Definitions

2.1 Lot

An identifiable quantity of goods delivered at one time, having or presumed by the sampling officer to have common properties or uniform characteristics such as the same origin, the same variety, the same consignor, the same packer, the same type of packing or the same mark. Several lots may make up a consignment.

2.2 Consignment

A quantity of material covered by a particular consignment note or shipping document. Lots in the same consignment may be delivered at different times and may have different amounts of pesticide residues.

2.3 Primary Sample

A quantity of material taken from a single place in the lot.

2.4 Bulk Sample

Combined total of all the Primary Samples taken from the same lot.

2.5 Final Sample

Bulk sample or representative part of the Bulk Sample to be used for control purposes.

2.6 Laboratory Sample

Sample intended for the laboratory. The Final Sample may be used as a whole or subdivided into representative portions (Laboratory Sample) if required by national legislation.

3. Employment of Authorised Sampling Officers

The samples must be taken by officers authorised for the purpose by the appropriate authorities.

4. Sampling Procedures

4.1 Material to be sampled

Each lot which is to be examined must be sampled separately.

4.2 Precautions to be taken

In the course of taking the Primary Samples and in all subsequent procedures precautions must be taken to avoid contamination of the samples or any other changes which would adversely affect the amount of residues or the analytical determinations or make the Laboratory Sample not representative of Bulk Sample.

4.3 Primary Samples

As far as possible these should be taken throughout the lot. Departures from this requirement must be recorded (see para 7). As far as possible the Primary Samples should be of similar size and the combined total of all the Primary Samples (Bulk Sample) must not be less than that required for the Final Sample bearing in mind the possible requirement of further subdivision and the provision of adequate Laboratory Samples. The minimum number of Primary Samples to be taken is given in the following table.

Weight of lot in kilograms	Minimum number of Primary Samples to be taken
50	3
51 - 500	5
501 -2000	10
2000 (1)	15

(1) For whole cereals and other materials shipped in bulk well established alternative sampling procedures are available and may be used providing these are recorded (see para 7) and the minimum requirements in 4.6.4. are met.

For processed products in cans, bottles, packages or other small containers, especially when the sampling officer does not know the weight of the lot, the following sampling plan may be followed.

Number of cans packages or containers in the lot	Minimum number of Primary Samples to be taken
1 - 25	1
26 - 100	5
101 - 250	10
250	15

For homogeneous lots a sample fully representative of the whole is obtained by withdrawing any single sample.

4.4 Preparation of Bulk Sample

The Bulk Sample is made by uniting and mixing the Primary Samples.

4.5 Preparation of Final Sample

4.5.1 The Bulk Sample should, if possible, constitute the Final Sample.

4.5.2 If the Bulk Sample is too large the Final Sample may be prepared from it by a suitable method of reduction. In this process however individual fruits and vegetables must not be cut or divided.

4.6 Preparation of the Laboratory Sample

4.6.1 The Final Sample should if possible be submitted to the laboratory for analysis.

4.6.2 If the Final Sample is too large to be submitted to the laboratory a representative subsample must be prepared.

4.6.3 National legislative needs may require that the Final Sample be subdivided into two or more portions for separate analyses. Each portion must be representative of the Final Sample. The precautions in para 4.2 should be observed.

4.6.4 The minimum amount of material to be submitted to the labortory, is the size of the laboratory sample in the following:

6.2 Sampling bagged commodities

Sampling of the commodity within a bag must be random and a representative sample from a large stack of bags can be obtained only if every bag is accessible. This is not always possible in practice and the alternative is to obtain a sample from a number of randomly chosen bags by probing. Since pesticide treatments are often directed to the surface of the bag then selective sampling to show the effect of the position of the bag in the stack and the penetration of the pesticide into the bag may be necessary.

6.3 Sampling fruit and vegetables in packing houses

Where post-harvest treatments are applied to fruit and vegetables in packing houses an adequate number of samples must be taken to determine the range of residue levels resulting from variations in the treatment process. The effects of concentration, temperature, duration of treatment, drying (of dip treatments) and subsequent handling on residue levels may need to be considered.

7. Soil sampling

During the course of obtaining information on residues in a crop useful information may be obtained, if needed, on the degradation of the pesticide in soil under local conditions. It will then be necessary to take samples at intervals, possibly over a period of at least one season. The first sample should be taken immediately after the last application to be made to the crop or soil and subsequently at intervals, the duration of which will depend on the compound. Samples taken at the time of harvest and at the beginning of the following season are particularly important if there is a possibility of carry-over into a subsequent crop.

8. Sample size reduction

Ideally, the field sample should be submitted intact for analysis although the requirements of the analyst should not influence the sampler to take a smaller sample than is necessary for a valid field sample. In practice, a valid field sample is often much larger than the sample needed by the analyst and cannot be handled economically especially if freezing and long transport is involved. In such cases, a reduction in the size of the field sample is desirable.

For samples consisting of small units such as cereal grains or even small fruit there is little difficulty in valid sample reduction and the normal procedure of mixing, quartering and rejection of opposite quarters until the desired reduction is achieved is satisfactory. With samples of medium sized products such as apples, potatoes, beans and peas in the pod and citrus there is an increased risk of losing sample validity by sample reduction. However, the random selection of the required number of units to make up the laboratory sample from a well-mixed field sample is probably the most satisfactory procedure.

Since it is unacceptable to cut or divide sample units, the problem is greatest with large fruit and vegetables such as cabbage or melons. In these situations, there is little alternative to shipment of the whole field sample to the laboratory particularly since the number of items required for an acceptable laboratory sample is often the same as that required for the field sample.

C. Enforcement of Maximum Residue Limits

CODEX RECOMMENDED METHOD OF SAMPLING FOR THE DETERMINATION OF PESTICIDE RESIDUES

1. Objective

For the examination of a lot to discover whether it complies with Codex Maximum Limits for Pesticide Residues it is necessary to provide a representative sample for analysis. The objective of the sampling procedure is to obtain a Final Sample representative of the lot in order to determine its average pesticide residue content. The Final Sample is considered representative of the lot when the procedure outlined below has been followed. The Codex limit applies to the final sample.

Commodity	Examples	Minimum requirements
small or light products unit weight up to about 25 g	berries peas olives parsley	1 kg
medium sized products unit weight usually between 25 and 250 g	apples oranges carrots potatoes	1 kg (at least 10 units)
large sized products unit weight over 250 g	cabbage melons cucumbers	2 kg (at least 5 units)
dairy products	whole milk cheese butter cream	0.5 kg
eggs		0.5 kg (10 units if whole)
meat, poultry, fat, fish and other fish and animal products		1 kg
oils and fats	cotton seed oil margarine	0.5 kg
cereals and cereal products		1 kg

5. Packaging and Transmission of Laboratory Samples

The Laboratory Sample must be placed in a clean inert container offering adequate protection from external contamination and protection against damage to the sample in transit. The container must then be sealed in such a manner that unauthorized opening is detectable, and sent to the laboratory as soon as possible taking any necessary precautions against leakage or spoilage e.g. frozen foods should be kept frozen, perishable samples should be kept cooled or frozen.

6. Records

Each Laboratory Sample must be correctly identified and should be accompanied by a note giving the nature and origin of the sample and the date and place of sampling, together with any additional information likely to be of assistance to the analyst.

7. Departures from Recommended Sampling Procedure

If, for any reason, there has had to be a departure from the recommended procedures, especially paragraph 4, full details of the procedure actually followed must be recorded in the accompanying note (see para 6).

D. SAMPLE PACKING AND STORAGE

Once packed and labelled, samples may be stored or immediately sent to the Residue Laboratory according to the nature of the sample, the stability of the residue and the kind of study

undertaken.

It is important that the packing and shipment be done so that the samples arrive as soon as possible (normally within 24-36 hours) after being taken and without change of any kind, e.g. deterioration, physical damage, contamination, loss of residue, or change in moisture content.

1 Packing

1.1 Containers

Individual samples should be placed in suitable containers, e.g. heavy polyethylene bags and then put inside additional heavy paper bags and where necessary frozen or refrigerated as soon as possible after sampling, according to the nature of the chemical involved. Polyethylene bags alone may become brittle in contact with dry ice and therefore risk breakage and subsequent loss of sample.

Avoid other plastic containers, or plastic-lined caps, unless made of Teflon or other inert plastic which does not interfere in the analytical method; laboratories frequently have experienced such interferences and PVC bags should be avoided. If cans are used, they should first be checked to demonstrate the absence of materials such as oil films, lacquers, resin from soldered joints, etc., that could interfer with analyses.

Glass containers should be used for water or liquid samples and should be thoroughly cleaned and rinsed with one or more suitable pesticide free solvents such as acetone, isopropanol, or hexane, and dried before use. Pesticides can migrate to the walls of a container and be absorbed; hence even a glass container, after the water sample is poured out, should be rinsed with solvent if the extraction is not made in the container itself.

In summary, any type of container or wrapping material should be checked before use for possible interferences in the analytical method and at the limit of detection employed in the analysis. Fasten boxes securely with strong twine, rope or tape.

1.2 Shipment of samples

Non-perishable commodities containing residues that are known to be stable over the period required to reach the laboratory can be shipped in a non-frozen state but samples should be protected against any effects which might cause degradation or contamination.

Where samples need to be frozen use shipping containers of polystyrene foam, if available, as they are excellent for this purpose. If not available, used two cardboard boxes of slightly different size with insulation in between. Proper insulation is essential to ensure samples arriving at the residue laboratory still frozen. Sufficient dry ice must be used so that some will still remain when received at the residue laboratory. This usually requires a minimum of one kg of dry ice per kg of sample. For journeys lasting more than two days, two kg of dry ice or more per kg of sample may be required. Poorly insulated containers require more dry ice. Use caution in handling dry ice (gloves and ventilated work area). Packages must of course comply with current transport regulations.

Frozen samples must never be allowed to thaw, either before or during shipment. They must be shipped under conditions that permit their arrival at the residue laboratory still solidly frozen.

Advise consignee by telegram or telex full details of shipment of samples, including shipping document numbers, flight numbers etc., so that delay in delivery to the laboratory is avoided.

When samples have to be shipped across national boundaries, quarantine regulations must be observed and appropriate permits obtained well in advance of despatching samples.

2. Labels and Records

Label each sample with the appropriate sample identification. The label and ink should be such that the writing cannot become illegible if it becomes wet. Attach the label securely

so that it cannot become loose during shipment and place the label so that it will not become wet from condensation.

Complete the residue data sheets clearly and accurately with the requested trial details. Failure to do this may mean that that data will not be acceptable. The completed sheets should be protected by enclosing them in protective polythene bags and they should be sent with the sample. Duplicate sheets should be kept by the sender.

Use a label on the outside of the shipping container showing the following; "Perishable Goods": "Deliver immediately upon arrival" and "This material is not fit for human consumption".

3. Sample Reception and Handling

Immediately upon arrival of the samples, the Residue Laboratory personnel should:

3.1 Verify that the copy of the residue form is included with the samples.
Check and report on the condition of the samples.
Check to see that the samples match the details of the residue form.
Check the residue form for accuracy (especially the rate and interval data) and to verify that the information is complete.
Check the residue form to determine if any special treatment or testing is indicated.

3.2 If there are any deviations of any consequence or the residue form is not received, or is incomplete (in such a way that a proper comparison is not possible), then the samples should be preserved in the simplest form that will preserve the residue and the crop. The trial organizer should then be immediately contacted to determine how to proceed.

3.3 Note: It is dangerous to put packages containing dry ice into deep freeze.

4. Storage of Samples

Samples should be analysed as quickly as possible after collection before physical and chemical changes occur. If prolonged storage is required, it is usually preferable to extract the sample, remove most or all of the solvent and store the extracts at a low temperature preferably at or below -20°C. This removes the residue from contact with enzymes which might degrade the pesticide and also prevents further possibility of "bound" residues in the tissue. Do not store homogenized samples for analysis unless an adequate check has been made on the stability of the residue.

Studies of the stability of residues in samples or extracts, with time at temperature of storage, should be carried out with representative pesticides and substrates. When there is doubt about the stability of residues in storage, spiked control samples should be held under the same conditions as the samples or extracts.

Light degrades many pesticides, therefore it is advisable to protect the samples and any solutions or extracts from needless exposure. Samples other than water should ordinarily be stored in a freezer, preferably at -20°C or below. Even then, physical and chemical changes may occur in either the sample or in the residues sought. Extended storage in freezers can cause moisture to migrate to the surface of the sample and then to the freezer coils, slowly desiccating the sample. This effect may be of importance if water content affects the subsequent analysis and can affect the calculated residue concentration. Water samples should be stored slightly above freezing to avoid rupture of the container as a result of freezing.

Annex 5

PORTION OF COMMODITY TO WHICH CODEX MAXIMUM RESIDUE LIMITS APPLY AND WHICH SHOULD BE ANALYSED

Introduction

Codex maximum residue limits are in most cases stated in terms of a specific whole raw agricultural commodity as it moves in trade. In some instances, a qualification is included that describes the part of the raw agricultural commodity to which the maximum residue limits applies, for example, almonds on a shell-free basis and beans without pods. In other instances, such qualifications are not provided. Therefore, unless otherwise specified the portion of the raw agricultural commodity to which the MRL applies and which is to be prepared as the analytical sample for the determination of pesticide residues is as described in the following table.

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION BY CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
GROUP 1. ROOT AND TUBER VEGETABLES	
Root and tuber vegetables are starchy foods derived from the enlarged solid roots, tubers, corns or rhizomes, mostly subterranean, of various species of plants. The entire vegetable may be consumed.	
Code No. Commodity	
A01.0100 root and tuber vegetables .0106 beets (beta vulgaris var. conditiva) .0109 carrots (daucus carota) .0112 celeriac (apium graveolens var. rapaceum) .0115 chicory (cichorum intybus) .0144 horseradish (armoracia cochlearia) .0127 parsnips (pastinaca sativa) .0128 potatoes (solanum tuberosum) .0129 radishes (raphanus sativa) .0131 rutabagas (brassica napus var. napobrassica) .0136 sugar beets (beta vulgaris var. altissima) .0137 sweet potatoes (ipomoea batatas) .0139 turnips (brassica rap var. radifera)	Whole commodity after removing tops. Remove adhering soil (e.g. by rinsing in running water or by gentle brushing of the dry commodity).
GROUP 2. BULB VEGETABLES	
Bulb vegetables are pungent flavourful food derived from the fleshy scale bulbs, or growth buds of alliums of the lily family (liliaceae). The entire bulb may be consumed following removal of the parchment like skin.	
Code No. Commodity	
A01.0200 bulb vegetables .0201 garlic (allium ampeloprasum, a. sativum) .0202 leeks (allium ampeloprasum, a. porrum, a. tricoccum) .0203 onions (allium cepa, a. fistulosum)	Bulb/dry onions and garlic. Whole commodity after removal of roots and adhering soil and whatever parchment skin is easily detached. Leeks and spring onions: whole vegetable after removal of roots and adhering soil.

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION BY CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
GROUP 3. LEAFY VEGETABLES (EXCEPT BRASSICA VEGETABLES)	
Leafy vegetables (except Group 4 vegetables) are food dervied from the leaves of a wide variety of edible plants including leafy parts of Group 1 vegetables. The entire leaf may be consumed. Leafy vegetables of the brassica family are grouped separately.	
Code No. Commodity	
A01.0300 leafy vegetables .0305 beet leaves (beta vulgaris) .0313 chicory leaves (cichorum intybus) .0314 corn salad (valerianela olitoria) .0320 endive (cichorum endivia) .0327 lettuce (lactuca sativa) .0334 parsley (petroselinum crispum) .0339 radish leaves (raphanus sativas) .0346 spinach (spinacia oleracus) .0347 sugar beet leaves (beta vulgaris) .0348 swiss chard (beta vulgaris, var. cicla)	Whole commodity after removal of obviously decomposed or withered leaves.
GROUP 4. BRASSICA (COLE) LEAFY VEGETABLES	
Brassica (cole) leafy vegetables are food derived from the leafy parts, stems and immature inflorescences of plants commonly known and botanically classified as brassicas and also known as cole vegetables. The entire vegetable may be consumed.	
Code No. Commodity	
A01.0400 brassica leafy vegetables .0401 broccoli (brassica oleracea var. italica) .0403 Brussels sprouts (brassica oleracea var. gemmifera) .0404 cabbage (brassica oleracea var. capitata) .0405 cabbage, Chinese (brassica pekinensis, b. chinensis) .0406 cabbage, savoy (brassica oleracea var. sabuda) .0407 cauliflower (brassica oleracea var. botrytis) .0408 collards (brassica oleracea var. acephala) .0409 kales (brassica oleracea var. acephala) .0410 kohlradi (brassica oleracea var. gongylodes) .0411 mustard greens (brassica juncea)	Whole commodity after removal of obviously decomposed of withered leaves. For cauliflower and headed broccoli analyse flower head only; for Brussels sprouts analyse "buttons" only.
GROUP 5. STEM VEGETABLES	
Stem vegetables are food derived from the edible stems or shoots from a variety of plants.	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION IN CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMOITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
Code No. Commodity	
A01.0500 Stem vegetables	Whole commodity after removal of obviously decomposed or withered leaves. Rhubarb stems only. Celery and asparagus: remove adhering soil.
.0501 artichoke (cynara scolymus)	
.0502 asparagus (asparagus officinalis)	
.0505 celery (apium graveolens)	
.0508 rhubarb (rheum rhaponticum)	
.0509 witloof chicory (cichorium intybus)	
GROUP 6. LEGUME VEGETABLES	
Legume vegetables are derived from the dried or succulent seeds and immature pods or leguminous plants commonly known as beans and peas. Succulent forms may be consumed as whole pods or as the shelled product. Legume fodder is in Group 18.	
Code No. Commodity	
A01.0600 legume vegetables	Whole commodity.
.0604 braod bean (vicia faba)	
.0608 kidney beans (phaseolus vulgaris)	
dwarf beans - see kidney beans	
French beans " " "	
green beans " " "	
navy beans " " "	
.0609 Lima beans (phaseolus lunatus)	
.0613 runner beans (phaseolus coccinius)	
.0614 soybeans (glycine soja, g. max)	
.0620 peas (pisum spp., vigna spp.)	
.0623 cow peas (vigna sinensis spp. sinensis)	
.0626 lentile (lens esculenta)	
.0628 sugar peas (pisum sativum var. saccharatum)	
GROUP 7. FRUITING VEGETABLES - EDIBLE PEEL	
Fruiting vegetables - edible peel are derived from the immature or mature fruits of various plants, usually annual vines or bushes. The entire fruiting vegetables may be consumed.	
Code No. Commodity	
A01.0700 fruiting vegetables - edible peel	Whole commodity after removal of stems.
.0705 cucumbers (cucumis sativa)	
.0706 egg plants (solanum melongena)	
.0707 gherkin (cucumis anguria)	
.0708 okra (hibiscus esculentus)	
.0710 peppers (capsicum annum)	
.0712 summer squash (cucurbita pepo var. patissonina)	
.0713 tomato (lycopersicum esculentum)	
GROUP 8. FRUTING VEGETABLES - INEDIBLE PEEL	
Fruiting vegetables - inedible peel are derived from the immature or mature fruits of various plants, usually annual vines or bushes. Edible	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION IN CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
portion is protected by skin, peel or husk which is removed or discarded before consumption.	
Code No. Commodity	
A01.0800 fruiting vegetables - inedible peel	Whole commodity after removal
cantaloupe - see melons (cucumis melo var. reticulatus)	of stems.
.0804 melons (cucumis melo spp.)	
.0805 pumpkin (cucurbita spp., c. pepo)	
.0806 squash (including winter squash) (cucurbita moschata)	
.0807 watermelon (citrullus vulgaris)	
.0810 sweet corn (zea mays)	
GROUP 9. CITRUS FRUITS	
Citrus fruits are produced by trees of the rue family and characterized by aromatic oily peels, globular form, and interior segments of juice filled vesicles. The fruit is fully exposed to pesticides during the growing season. The fruit pulp may be consumed in succulent form and as a beverage. The entire fruit may be used for preserving.	
Code No. Commodity	
A02.0900 citrus fruits (citrus spp.)	Whole commodity.
.0907 lemons (citrus limon, c. jambhiri)	
.0909 mandarin (tangerine) (citrus reticulata)	
.0910 orange, sweet (citrus sinensis)	
GROUP 10.POME FRUITS	
Pome fruits are produced by trees related to the genus pyrus of the rose family (rosaceae). They are characterized by fleshy tissue surrounding a core consisting of parchment like carpels enclosing the seed. The entire fruit, expecting the core, may be consumed in the succulent form or after processing.	
Code No. Commodity	
A02.1000 pome fruits	Whole commodity after removal
.1001 apples (malus pumila, pyrus malus)	
.1004 pears (pyrus communis)	
.1006 quince (cydonia oblongo)	
GROUP 11.STONE FRUITS	
Stone fruits are produced by trees related to the genus prunus of the rose family (rosaceae) characterized by fleshy tissue surrounding a single hard shelled seed. The entire fruit, except seed, may be consumed in a succulent processed form.	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION BY CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
Code No. Commodity	
A02.1100 stone fruits (prunus spp.) .1101 apricots (prunus armeniaca) .1102 cherries (prunus spp.) .1103 sour cherries (prunus cerasus) .1104 sweet cherries (prunus avium) .1105 nectarines (prunus persica) .1106 peaches (prunus persica) .1107 plums (prunus domestica spp.)	Whole commodity after removal of stems and stones but the residue calculated and expressed on the whole commodity without stem.
GROUP 12.SMALL FRUITS AND BERRIES	
Small fruits and berries are derived from a variety of plants having fruit characterized by a high surface-weight ration. The entire fruit, often including seed, may be consumed in a succulent or processed form.	
Code No. Commodity	
A02.1200 small fruits and berries .1203 blueberries (vaccinum spp.) boysenberries - see dewberries .1206 cranberries (vaccinum macrocarpum) .1207 currants, black, red, white (ribes spp.) .1208 dewberries (rubus sp.) .1210 gooseberries (ribes grossularia) .1211 grapes (bitis spp.) .1215 raspberries, black, red (rubus occidentalis, r. strigosus) .1217 strawberries (fragaria spp.)	Whole commodity after removal of caps and stems. Currants: fruit with stems.
GROUP 13.ASSORTED FRUITS - EDIBLE PEEL	
Assorted fruits - edible peel are derived from the immature or mature fruits of a variety of plants, usually shrubs or trees from tropical or subtropical regions. The whole fruit may be consumed in a succulent or processed form.	
Code No. Commodity	
A02.1300 assorted fruits - edible peel .1306 dates (phoenix dactylifera) .1309 figs (ficus carica) .1316 olives (olea europea)	Dates and olives: whole commodity after removal of stems and stones but residue calculated and expressed on the whole fruit. Figs: whole commodity.
GROUP 14.ASSORTED FRUITS - INEDIBLE PEEL	
Assorted fruits - inedible peel are derived from the immature or mature fruits of different kinds of plants, usually shrubs or trees from tropical or subtropical regions. Edible portion is protected by skin, peel or husk. Fruit may be consumed in a fresh or processed form.	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION BY CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
Code No. Commodity	
A02.1400 assorted fruits - inedible peel	Whole commodity unless qualified e.g. bananas (pulp). Pineapples: after removal of crown. Avocado and mangos: whole commodity after removal of stone but calculated on whole fruit.
.1402 avocados (persea americana)	
.1403 bananas (musa paradisiaca sapientum)	
.1415 guavas (psidium guajava)	
.1419 kiwi fruit (actinidia chinensis)	
.1423 mangos (mangifera indica)	
.1428 papayas (carica papaya)	
.1430 passion fruits (passiflora edulis)	
.1431 persimmons (diospyros virginiana)	
.1432 pineapples (ananas comosus)	
.1434 pomegranates (punica granatum)	
GROUP 15.CEREAL GRAINS	
Cereal grains are derived from the clusters of starchy seed produced by a variety of plants, primarily of the grass family (gramineae). Husks are removed before consumption.	
Code No. Commodity	
A03.1500 cereals grains (gramineae)	Whole commodity. Fresh corn and sweet corn; kernels plus cob without husk.
.1501 barley (hordeum spp.)	
.1508 maize (zea mays)	
.1509 millet (panicum miliacum)	
.1510 oats (avena spp.)	
.1513 popcorn (zea mays var. microsperma)	
.1515 rice (ory sativa)	
.1516 rye (secale cereal)	
.1517 sorghum (sorghum spp.)	
.1521 wheat (triticum spp.)	
GROUP 16.FODDERS AND STRAWS	
Fodders and straws are various kinds of plants, mostly of the grass family (gramineae) cultivated extensively as animal feed and for the production of sugar. Stems and stalks used for animal feeds are consumed as succulent forage, silage, or as dried fodder or hay. Sugar crops are processed.	
Code No. Commodity	
A03.1600 fodders and straws	Whole commodity
.1610 barley fodder and straw (hordeum spp.)	
.1603 grasses, fodder (gramineae family)	
.1604 maize fodder and straw (zea mays)	
.1606 mint fodder (mentha spp.)	
.1607 oat fodder and straw (avena spp.)	
.1608 rice fodder and straw (oryza sativa)	
.1609 rye fodder and straw (secale cereale)	
.1610 sorghum fodder (sorghum spp.)	
.1612 wheat fodder and straw (triticum spp.)	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION BY CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
GROUP 17.LEGUME OILSEED	
Legume oilseed are mature seed from legumes cultivated for processing into edible vegetable oil or for direct use as human food.	
Code No. Commodity	
A04.1700 legume oilseed	Whole commodity after removal of shell.
.1701 peanuts (arachis hypogaea)	
GROUP 18.LEGUME ANIMAL FEEDS	
Legume animal feeds are various species of legumes used for animal forage, grazing, fodder, hay or silage with or without seed. Legume animal feeds are consumed as succulent forage or as dried fodder or hay.	
Code No. Commodity	
A04.1800 legume animal feeds (leguminosae)	Whole commodity.
.1801 alfalfa fodder (medicago spp.)	
.1802 bean fodder (vigna spp.)	
.1803 clover fodder (trifolium spp., melilotus spp.)	
.1808 peanut fodder (arachis hypogaea)	
.1809 pea fodder (lathyrus spp., pisum spp.)	
.1811 soybean fodder (glycine soja, g. max)	
GROUP 19.TREE NUTS	
Tree nuts are the seed of a variety of trees and shrubs which are characterized by a hard inedible shell enclosing an oil seed. The edible portion of the nut is consumed in succulent, dried and processed forms.	
Code No. Commodity	
A05.1900 tree nuts	Whole commodity after removal of shell. Chestnuts: whole in skin.
.1901 almonds (prunus amylgdalus)	
.1906 chestnuts (castanea spp.)	
.1910 filberts (corylus spp.)	
.1913 macadamia nuts (macadamia ternifolia)	
.1917 pecans (carya illinoinensis)	
.1922 walnuts, black, Persian, English (juglans spp.)	
GROUP 20.OILSEED	
Oilseed consists of the seed from a variety of plants used in the production of edible vegetable oils. Some important vegetable oilseeds are byproducts of fibre or fruit crops.	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION IN CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
Code No. Commodity	
A05.2000 oilseed	Whole commodity.
.2004 cottonseed (gossypium spp.)	
.2008 linseed (linum usitatissimum)	
.2010 poppyseed (papaver somniferum)	
.2011 rapeseed (brassica spp.)	
.2012 safflower seed (carthamus tinctosius)	
.2015 sunflower seed (helianthus annus)	
GROUP 21.TROPICAL SEED	
Tropical seeds consist of the seed from several tropical and semitropical trees and shrubs mostly used in the production of beverages and confections. Tropical seeds are consumed after processing.	
Code No. Commodity	
A05.2100 tropical seed	Whole commodity.
.2101 cacao beans (theobroms cacao)	
.2102 coffee beans (coffee spp.)	
GROUP 22.HERBS	
Herbs consist of leaves, stems and roots from a variety of herbaceous plants used in relatively small amounts to flavour other foods. They are consumed in succulent and dried forms as components of other foods.	
Code No. Commodity	
A06.2200 herbs	Whole commodity.
GROUP 23.SPICES	
Spices consist of aromatic seed, roots, fruits and berries from a variety of plants used in relatively small amounts to flavour other foods. They are consumed primarily in the dried form as components of other foods.	
Code No. Commodity	
A06.2300 spices	Whole commodity.
.2317 ginger - root (zingiber officinale)	
.2323 mustard - seed	
GROUP 24. TEAS	
Teas are derived from the leaves of several plants, but principally camellia sinensis. They are used in the preparation of infusions for consumption as stimulating beverages. They are consumed as extracts of the dried or processed product.	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION IN CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
Code No. Commodity	
A06.2400 teas	
.2402 tea, dried, black, green (camellia sinensis)	Whole commodity.
GROUP 25.MEATS	
Meats are the muscular tissue, including adhering fatty tissue from animal carcasses as prepared for wholesale distribution. The entire product may be consumed.	
Code No. Commodity	
B07.2500 carcase meat	Whole commodity. (For fat soluble pesticides a portion of carcase fat is analysed and MRLs apply to carcase fat.)
.2503 carcase meat of cattle (bos spp.)	
.2504 carcase meat of goats (capra spp.)	
.2506 carcase meat of horses (equss spp.)	
.2507 carcase meat of pigs (suidae spp.)	
.2509 carcase meat of sheep (ovis spp.)	
GROUP 26.ANIMAL FATS	
Animal fats are the rendered or extracted fat from the fatty tissue of animals. The entire product may be consumed.	
Code No. Commodity	
B07.2600 animal fats	Whole commodity.
.2603 cattle fat (bos spp.)	
.2607 pig fat (suidae spp.)	
.2609 sheep fat (ovis spp.)	
GROUP 27. MEAT BY-PRODUCTS	
Meat by-products are edible tissues and organs, other than meat and animal fat, from slaughtered animals as prepared for wholesale distribution. Examples: liver, kidney, tongue, heart. The entire product may be consumed.	
Code No. Commodity	
B07.2700 meat by-products	Whole commodity.
.2703 cattle meat by-products (bos spp.)	
.2704 goat meat by-products (capra spp.)	
.2706 pig meat by-products (suidae spp.)	
.2707 sheep meat by-products (ovis spp.)	
GROUP 28. MILKS	
Milks are the mammary secretion of various species of lactating herbivorous ruminent animals, usually domesticated. The entire product may be consumed.	

CLASSIFICATION AND EXAMPLES OF COMMODITIES UNDER CONSIDERATION IN CODEX ALIMENTARIUS COMMISSION	PORTION OF COMMODITY TO WHICH THE MRL APPLIES (AND WHICH IS ANALYSED)
Code No. Commodity	
B07.2800 milks	Whole commodity.
GROUP 29. MILK FATS	
Milk fats are the rendered or extracted fats from milk.	
Code No. Commodity	
B07.2900 milk fats	Whole commodity.
GROUP 30. POULTRY MEATS	
Poultry meats are the muscular tissues including adhering fat and skin from poultry carcasses as prepared for wholesale distribution. The entire product may be consumed.	
Code No. Commodity	
B08.3000 poultry meats (carcase fat)	Whole commodity. (For fat soluble pesticides a portion of carcase fat is analysed and MRLs apply to carcase fat).
GROUP 31. POULTRY FATS	
Poultry fats are the rendered or extracted fats from fatty tissues of poultry. The entire product may be consumed.	
Code No. Commodity	
B08.3100 poultry fats	Whole commodity.
GROUP 32. POULTRY BY-PRODUCTS	
Poultry by-products are edible tissue and organs, other than poultry meat and poultry fat from salughtered poultry.	
Code No. Commodity	
B08.3200 poultry by-products	Whole commodity.
GROUP 33. EGGS	
Eggs are the fresh edible portion of the reproductive body of several avian species. The edible portion includes egg white and egg yolk after removal of the shell.	
Code No. Commodity	
B08.3300 eggs	Whole egg whites and yolks combined after removal of shell.

Annex 6

METHODS OF ANALYSIS FOR PESTICIDE RESIDUES

A. Recommendations of the Codex ad Hoc Working Group on Methods of Analysis (1980)

1. INTRODUCTION

1.1 Scope

In this report recommendations are given for those analytical methods which can, from practical experience of the Working Group on Methods of Analysis to the CCPR, be applied to the determination of pesticide residues for regulatory purposes. The list, given in 2, covers the pesticides for which Codex MRL's (T, TT, PRL or TPRL) are under discussion.

The list is not exhaustive and methods not mentioned in the last can also be applied under certain conditions.

1.2 Criteria for the Selection of Analytical Methods

Whenever possible, the Working Group used the following criteria when selecting analytical methods:

A. Published in the open literature.

B. Collaboratively studied or known to have been validated in a number of laboratories with validation data being reported in the publication.

C. Capable of determining more than one residue, i.e. multiresidue methods.

D. Suitable for as many pesticide-commodity combinations as possible at or below the specified MRL's.

E. Applicable in a regulatory laboratory equipped with routine analytical instrumentation.

In addition, preference was given to gas liquid chromatography as the determinative step for the recommended methods.

Spectrometry, thin layer chromatography, and high performance liquid chromatography were normally included under "other analytical methods". Mass spectrometry has been indicated for confirmatory purposes only.

1.3 Confirmatory Tests

In the last column confirmatory tests are listed. Confirmation of a supposed residue by an independent test to be considered as an essential part of Good Analytical Practice (cf 1.4), especially when the initial result suggests that a Codex MRL is exceeded. The ultimate choice of a confirmatory test depends upon the technique used in the initial determination and upon the available instrumentation and necessary expertise.

1.4 Application of Methods

Although the methods listed have been carefully selected it will always be necessary for the analyst to validate the method before it is first applied in a practical situation. There is a further need for regular assessment of the methods in use both at the MRL and at the lower limit of determination. The methods are only recommended for the pesticide-commodity combinations reported in the quoted references. For all new pesticide-commodity combinations the method must be validated following Good Analytical Practice (for Annex II to Appendix II of ALINOR 81/24).

2. LIST OF METHODS OF ANALYSIS

compound (CCPR - number in parentheses)	collaboratively checked or otherwise assessed methods	other analytical methods	confirmatory tests
acephate (95)	2c, 2d	Leary Richmond	2e
aldrin/dieldrin (1)	1a, 2a, 2d, 3a, 4 (S1-5, S8-10, S12) Greve (2) Holmes Mestres (1,4) Panel (4) Telling	5 Porter Sissons Specht	2f, 3b, 4a Abbott (2) Mestres (5)
amitrole (79)	none	2e, 4(4) Lokke	none
azinphos-methyl (2)	2c, 2d, 3a, 4 (S5, S8) Abbott (1) Panel (3) Mestres (1)	2e, 4(63) Bowman (1) Eichner Krause	2f Cochrane (3) Ernst (1) Mendoza (1) Mestres (5)
binapacryl (3)	2a, 3a	4 (8, 43) Baker (3) Specht	Baker (3)
bromophos (4)	2a, 2d, 4 (S5, S8-10, S13, S17) Abbott (1) Mestres (1) Working Group	4 (210) Krause Specht	Ernst (1) Mestres (5)
bromophos-ethyl (5)	2a, 2d, 3a, 4 (S13, S17) Abbott (1) Mestres (1)	4 (263) Specht	Ernst (1) Mestres (5)
bromopropylate (70)	2a	Stijve (1)	Stijve (1)
sec-butylamine (89)	none	2e Baker Day	non
captafol (6)	2d Mestres (1)	Baker (2) Eichner	Pomerantz (1) Kilgore (2) Pomerantz (2) Specht Zweig (4)
captan (7)	1g, 2a, 2d, 3a, 4 (S8, S12) Mestres (1)	4(12), 5 Baker (2) Kilgore (1) Pomerantz (2) Specht	3b Pomerantz (1)

carbaryl (8)	1e, 1h, 2d, 3a Mestres (6)	4 (100) Cohen Lawrence (2)	2f Cochrane (3) Ernst (1) Mendoza (1, 2)
carbofuran (96)	1e, 3a	2e Lawrence (2) Moellhoff (2)	2e, 2f Cochrane (3) Mendoza (2)
carbophenothion (11)	1c, 2c, 2d, 3d, 3a, 4 (S8, S10, S13, S16)	2e Bowman (1) Specht	2f Ernst (1) Mestres (5)
cartap (97)	none	Official Gazette Zweig (1)	none
chinomethionate (80)	2d	4 (189) Tjan (1)	2e Francoeur Mestres (1)
chlordane (12)	2a, 2d, 3a, 4 (S9, S10, S12) Mestres (1)	5 Cochrane (2) Specht	2f, 3b Chau (1) Mestres (5)
chlordimeform (13)	none	2e Zweig (1)	Zweig (1)
chlorfenviphos (14)	2d, 3a, 4 (S13, S17) Abbott (1) Mestres (1)	2e, 4 (239) Krause Specht	2f Ernst (1) Mestres (5)
chlormequat (15)	none	Mooney Nierle Sachse Stijve (2) Zweig (1)	Tafuri (1, 2)
chlorobenzilate (16)	2a, 3a Mestres (1)	Fromica	Mestres (5)
chlorothalonil (81)	2a, 2d, 3a	Zweig (2)	none
chlorpyrifos (17)	2a, 2c, 2d, 3a, 4 (S9, S13) Mestres (1, 6)	5 Bowman (1) Braun Specht	2f Ernst (1) Mestres (5)
chlorpyrifos-methyl (90)	2c, 2d Mestres (6)	Desmarchelier	none
crufomate (19)	none	2e Bowman (1)	2f Greenhalgh (1,2)
cyanofenphos (91)	none	Takimoto (2)	none
cyhexatin (67)	none	2e Gauer Love	2e Moellhoff (3) Zweig (1)

2,4-D (20)	2b, 3a	4 (27), 5 Allebone Bjerke Clark Dupuy Meagher	2f Cochrane (3) Mestres (5) Suffet
DDT (21)	1a, 2a, 2d, 3a, 4 (S1-5, S8-10, S12) Greve (2) Holmes Mestres (1, 4) Panel(4) Telling	4 (30), 5 Porter Sissons Specht	2f, 3b Abbott (2) Chau (1) Mestres (5)
demeton (92)	2c, 2d, 4 (S5,S16) Abbott (1)	none	2f Ernst (1)
demeton-S-methyl (73)	2c, 2d, 4 (S5, S13, S16) Abbott (1)	Krause Thornton (2) Vandermerwe Wagner (2)	2f Ernst (1)
dialifos (98)	2a, 2d	4 (281) Westlake	Ernst (1)
diazinon (22)	1a, 2a, 2c, 2d, 3a, 4 (S5, S8, S10, S13, S17) Abbott (1) Mestres (1) Working Group	4 (35) Bowman (1) Krause Machin Specht	2f Ernst (1) Mendoza (1, 2) Mestres (5) Singh
dichlofluanid (82)	4 (S8, S12)	4 (203) Specht	Mestres (5)
dicloran (83)	2a, 2d, 3a	DeVos	none
dichlorvos (25)	2c, 2d, 3a, 4 (S5, S13, S17) Abbott (1) Panel (1, 3) Mestres (1, 6)	4 (200) Dale Draeger (1) Elgar Krause	2f Cochrane (3) Ernst (1) Mendoza (2) Mestres (5)
dicofol (26)	2a, 2d, 3a, 4 (S9, S12) Mestres (1) Telling	4 (69) Morgan Specht	2f
dimethoate (27)	2c, 2d, 3a, 4 (S5, S8, S13, S17) Abbott (1) Mestres (1) Panel (3) Working Group	4 (42, 236), 5 Krause Specht Steller Wagner (1)	2f Greenhalgh (2) Mestres (5)
dioxathion (28)	2c, 2d, 4 (S8, S13) Abbott (1)	none	Ernst (1)

diphenyl (29)	1f, 2d Mestres (3)	4 (256) Farrow Pyysalo	Beernaert
diphenylamine (30)	none	2e Allen Gutenmann Luke	none
diquat (31)	none	2e, 4 (37) Calderbank(2) Zweig (4)	King
disulfoton (74)	2a, 2c, 2d, 3a, 4 (S5, S8, S13, S16, S17) Abbott (1) Working Group	2e Bowman (2) Specht Thornton (1)	2e, ef Mendoza (1) Mestres (5)
dithiocarbamates (105)	3a, 4 (S15) Keppel Mestres (7)	2e Mc Leod Ripley (1) Rosenberg	none
dodine (84)	1i, 2e	Newsome	none
edifenphos (99)	none	Vogeler	none
endosulfan (32)	1b, 2a, 2d, 3a, 4 (S5, S8, S12) Mestres (1) Teeling	4 (50), 5 Porter Sissons Specht	2f, 3b Abbott (2) Chau (2) Cochrane (3) Greve (1) Mestres (5) Musial Putnam
endrin (33)	1a, 2a, 2d, 3a, 4 (S5, S9-10, S12) Holmes Mestres (1, 4) Panel (4) Telling	5 Sissons Specht	2f, 3b Abbott (2) Chau (3, 4) Mestres (5) Musial
ethiofencarb (107)	none	4 (393) Draeger (2)	none
ethion (34)	1a, 2a, 2c, 2d, 3a, 4 Abbott (1) Mestres (1)	Bowman (1) Ivey Specht	2f Ernst (1) Mendoza (1, 2) Mestres (5)
ethoxyquin (35)	none	2e, 4 (500) Ernst (2) Winell	Weilenmann
fenamiphos (85)	2d, 4 (S15)	Thornton (3)	none
fenbutatin oxide (109)	none	Zweig (4)	none

fenchlorphos	1a, 2a, 2c, 2d, 3a, 4 (S8-10, S13, S17) Abbott (1) Mestres (1)	Specht	2f Ernst (1) Mestres (5) Singh
fenitrothion	2a, 2c, 2d, 3a, 4 (S5, S8, S13, S17) Abbott (1) Mestres (1) Working Group	4 (58) Desmarchelier Krause Specht Takimoto (1)	2f Ernst (1) Mestres (5) Singh
fensulfothion (38)	2c, 2d, 3a, 4 (S13, S16, S17)	Bowman (3) Williams Zweig (1)	none
fenthion (39)	2a, 2c, 2d, 3a, 4 (S5, S8, S13, S16, S17) Abbott (1) Mestres (1)	2e Bowman (2) Krause Wright	2f Ernst (1)
fentin (4)	none	2e, 4 (55)	2e
ferbam (105)	see dithiocarbamates		
folpet (41)	2a, 2d, 3a, 4 (S8, S12) Mestres (1)	4 (91) Baker (2) Pomerantz (2)	Pomerantz (1)
formothion (42)	2c, 2d, 4 S5, S8) Abbott (1) Mestres (1)	4 (236) Specht Zweig (2)	Ernst (1) Mestres (5)
guazatine (114)	none	Kobayashi	none
heptachlor (43)	1a, 2a, 2b, 2d, 3a, 4 (S1-4, S8-10, S12) Greve (2) Holmes Mestres (1, 4) Telling	5 Eichner Porter Sissons Specht	2f, 3b Abbott (2) Chau (1, 4) Cochrane (3) Mestres (5) Musial Ward
hydrogen cyanide (45)	none	2e, 4 (11) Heuser (1) Jaulmes	none
hydrogen phosphide (46)	none	2e, 4 (13) Bruce Greve (4)	Robison
imazalil (110)	none	Greenberg Norman Specht Wijnants	none
inorganic bromide (47)	Greve (3) Panel (12)	2e Heuser (2)	none

iprodione (111)	Mestres (1)	4 (419) Zweig (5)	none
lindane (48)	1a, 2a, 2d, 3a, 4 (S1-5, S8-10, S12) Greve (2) Holmes Mestres (1, 4, 6) Panel (5) Telling	4 (70), 5 DeVos Porter Sissons Specht	Abbott (2) Cochrane (1) Mestres (5)
malathion (49)	1a, 2a, 2c, 2d, 3a, 4 (S5, S8, S10, S13, S17) Abbott (1) Mestres (1, 6) Panel (1, 3) Working Group	4 (72) Bowman (1) Desmarchelier Krause Specht	2f Cochrane (1) Ernst (1) Mendoza (1, 2) Mestres (5) Singh
mancozeb (5)	see dithiocarbamates		
maneb (105)	see dithiocarbamates		
methamidophos (100)	2c, 2d, 3a	4 (365), 5 Leary Lubkowitz Moellhoff (1) Specht	none
methidathion (51)	2a, 2c, 2d, 3a, 4 (S5, S13)	2e, 4 (232) Krause Leary Specht Zweig (2)	Ernst (1) Mestres (5)
mevinphos (53)	2c, 2d, 3a, 4 (S5, S8, S13, S17) Abbott (1) Mestres (1)	4 (93) Krause Specht	2f Cochrane (3) Ernst (1) Mendoza (1) Mestres (5)
monocrotophos (54)	2c, 2d	2e Lawrence (1)	2f Ernst (1) Lawrence (1) Mestres (5)
omethoate (55)	2c, 2d, 4 (S13, S17) Abbott (1) Panel (3)	4 (236), 5 Specht Steller Wagner (1)	Ernst (1) Mestres (1)
ortho-phenyl-phenol (56)	2d Mestres (3)	4 (256) Farrow Pyysalo	Beernaert Cochrane (3) Nose
paraquat (57)	none	2e, 4 (134) Calderbank (1) Khan Lott Zweig (4)	Cochrane (3)

parathion (58)	1a, 1c, 2a, 2c, 2d, 3a, 4 (S5, S8, S10, S13, S17) Abbott (1) Mestres (1) Panel (3)	4 (87) Bowman (1) Krause Specht	2f Cochrane (3) Ernst (1) Mendoza (1, 2) Mestres (5) Singh
parathion-methyl (59)	1a, 2a, 2c, 2d, 3a, 4 (S5, S8, S13, S17) Abbott (1) Mestres (1)	4 (88) Bowman (1) Krause Specht	2f Cochrane (3) Mendoza (1, 2) Mestres (5) Singh
phosalone (60)	2a, 2c, 2d, 3a Abbott (1) Mestres (1)	5 Eichner Specht Zweig (1)	Ernst (1) Mestres (5)
phosmet (103)	2c, 2d Mestres (1)	Bowman (1, 4)	none
phosphamidon	2c, 2d, 3a, 4 (S5, S13) Abbott (1) Mestres (1)	Voss	Mestres (5)
piperonyl butoxide(62)	none	11, 2e, 4 (163) Isshiki Munday Specht	none
pirimicarb (101)	none	5 Zweig (1)	Mestres (8)
pirimiphos-methyl (86)	Mestres (1,6) Working Group	Brealey Desmarchelier Zweig (2)	Mestres (6)
propargite (113)	2d, 3a	2e Devinel (1,2) Zweig (1)	none
propineb (105)	see dithiocarbamates		
propoxur (75)	1e	4 (216) Cohen Lawrence (2) Specht Stanley Zweig (1)	Cochrane (3) Ernst (1) Mendoza (2)
pyrethrins (63)	Mestres (6)	2e Specht	none
quintozene (64)	2a, 2d, 3a, 4 (S8, S9, S12) Mestres (1)	4 (99) Baker (1) DeVos Goursaud Specht	2f Baker (1) Mestres (5)
tecnazene (115)	2a, 4 (S8, S12)	4 (108) DeVos Specht	none

thiabendazole (65)	2d Mestres (2b)	4 (256) Aharonson Farrow Gorbach Maeda Rajzman Tjan (2)	Tanaka Wegman
thiometon (76)	2c, 2d, 4 (S13) Abbott (1)	Zweig (2)	Ernst (1)
thiophanate-methyl (77)	Mestres (2a)	2e, 5 Engst Gnaegi Gorbach Shiga	Wegman
thirman (105)	see dithiocarbamates		
trichlorfon (66)	2d, 3a, 4 (S5, S13) Abbott (1) Mestres (1)	2e, 4 (112), 5	2f Cochrane (3) Ernst (1) Mestres (5)
triforine (116)	none	4 (338) Zweig (4)	none
zineb (105)	see dithiocarbamates		
ziram (105)	see dithiocarbamates		

3. REFERENCES

3.1 Manuals

(1) Official Methods of Analysis of the Association of Official Analytical Chemists, 13th edition (1980); cf also McMahon, B. and Burke, J.A., JAOAC, 61, 640-652 (1978).

(a) 29.001-20.018 - Multiresidue methods for chlorinated and certain organophosphorus pesticides.

(b) 29.029-29.034 - Alternate elution system for endosulfan

(c) 29.029-29.043 - Organophosphorus pesticides, "Storherr" multiresidue method

(d) 29.056-29.057 - Fumigants, multiresidue method

(e) 29.058-29.063 - Carbamates, "Holden" multiresidue method

(f) 29.067-29.074

(g) 29.076-29.080

(h) 29.082-29.090

(i) 29.108-29.111

(j) 29.112-29.118

(k) 29.123-29.126

(l) 29.161-29.164

(2) Pesticide Analytical Manual, as revised June 1979, Food and Drug Administration, Washington, D.C.

(a) Volume I, Tables 201-A, 201-G, and sections 211, 212, 231, 232.1 and 252 Multiresidue methods for chlorinated and organophosphorus pesticides in fatty

and non-fatty foods.

(b) Volume I, Table 201-D and sections 221 and 222 - Chlorophenoxy acids in fatty and non-fatty foods.

(c) Volume I, Table 201-H and section 232.3 - Storherr organophosphate/carbon clean-up for non-fatty foods

(d) Volume I, Table 201-I and section 232.4 - Luke et al., for various pesticides in non-fatty foods.

(e) Volume II, Method under compound name (when in this reference several methods have been given, they are generally listed in order of preference).

(f) Volume I, Table 651-A and section 650 and 651 - Confirmatory tests.

(3) Canadian Manual on Analytical Methods for Pesticide Residues in Foods, Information Canada, Ottawa, Canada, Cat. No. H 44-2869-REV (1973).

(a) analytical methods (section 5-8)

(b) confirmatory methods (section 11)

(4) Methodensammlung zur Rueckstandsanalytik von Pflanzenschutzmitteln, 5. Lieferung (1979), Verlag Chemie GmbH, Weinheim/Bergstrasse, Federal Republic of Germany (the numbers in parentheses refer to the numbers of the methods in this manual).

(5) Laboratory Manual for Pesticide Residue Analysis in Agricultural Products, compiled by the R.B. Maybury, Pesticide Laboratory, Food Production and Inspection Branch, Agriculture Canada, Ottawa, Ontario K1A 0C5, Canada (1980).

3.2 Literature

Abbott (1), D.C. et al., Pestic. Sci., 1, 10-13 (1970).

Abbott (2), D.C. et al., J. Chromatog., 16, 481-487 (1964).

Aharonson, N. and Ben-Aziz, A., JAOAC, 56, 1330-1334 (1973).

Allebone, J.E. and Hamilton, R.J., J. Chromatog., 108, 188-193 (1975.

Baker, H.J., JAOAC, 61, 1001-1003 (1978).

Baker (1), P.B. and Flaherty, B., Analyst, 97, 378-382 (1972).

Baker (2), P.B. and Flaherty, B., Analyst, 97, 713-718 (1972).

Baker (3), P.B. and Hoodless, R.A., Analyst, 98, 172-175 (1973).

Beernaert, H., J. Chromatog., 77, 331-338 (1973).

Bjerke, E.L. et al., J. Agr. Fd. Chem., 20, 963-967 (1972).

Bong, R.L., JAOAC, 58, 557-561 (1975).

Bowman (1), M.C. and Beroza, M., JAOAC, 50, 1228-1236 (1967).

Bowman (2), M.C. and Beroza, M., JAOAC, 52, 1231-1237 (1969).

Bowman (3), M.C. and Hill, K.R., J. Agr. Fd. Chem., 19, 342-345 (1971).

Bowman (4), M.C. and Beroza, M., JAOAC, 49, 1154-11 (1966).

Braun, H.E., JAOAC, 57, 182-188 (1974).

Brealey, C.J. et al., J. Chromatog., 168, 461-469 (1979).

Bruce, R.B. et al., J. Agr. Rd. Chem., 10, 18-25 (1962).

Calderbank (1), A. and Yuen, S.H., Analyst, 90, 99-106 (1965).

Calderbank (2), A. and Yuen, S.H., Analyst, 91, 625-629 (1966).

Chau (1), A.S.Y. and Lanouette, M., JAOAC, 55, 1058-1066 (1972).

Chau (2), A.S.Y., JAOAC, 55, 1232-1238 (1972).

Chau (3), A.S.Y., Bull. Envir. Cont. Tox., 8, 169-176 (1972).

Chau (4), A.S.Y., JAOAC, 57, 585-591 (1974).

Clark, D.E. et al., J. Agr. Fd. Chem., 23, 573-578 (1975).

Cochrane (1), W.P. and Maybury, R.B., JAOAC, 56, 1324-1329 (1973).

Cochrane (2), W.P. et al., JAOAC, 58, 1051-1061 (1975).

Cochrane (3), W.P., J. Chromat. Sci., 17, 124-137 (1979).

Cohen, I.C. et al., J. Chromatog., 49, 215-221 (1970).

Dale, W.E. et al., J. Agr. Fd. Chem., 21, 858-860 (1973).

Day, E. W. et al., JAOAC, 51, 39-44 (1968).

Desmarchelier, J. et al., Pestic. Sci., 8, 473-483 (1977).

Devine (1), J.M. and Sisken, H.R., J. Agr. Fd. Chem., 20, 59-61 (1972).

Devine (2), J.M., J. Agr. Fd. Chem., 23, 598-599 (1975).

DeVos, R.H. et al., J. Chromatog., 93, 91-98 (1974).

Draeger (1), G. Pflanzensch. Machr. Bayer, 21, 377-384 (1968).

Draeger (2), G., Pflanzensch. Machr. Bayer, 27, 144-155 (1974).

Dupuy, A.E. et al., J. Agr. Fd. Chem., 23, 827-828 (1975).

Eichner, M., Z. Lebensm. Unters. Forsch., 167, 245-249 (1978).

Elgar, K.E. et al., Analyst, 95, 875-878 (1970).

Ernst (1), G.F. et al., J. Chromatog., 133, 245-251 (1977).

Ernst (2), G.F. and Verveld-Roeder, S.Y., J. Chromatog., 269-271 (1979).

Farrow, J.E. et al., Analyst, 102, 752-758 (1977).

Formica, G., Meded. Fac. Landb. Gent., 40, 1135-1148 (1975).

Francoeur, Y. and Mallet, V., JAOAC, 59, 172-173 (1976).

Gauer, W.O. et al., J. Agr. Fd. Chem., 22, 252-254 (1974).

Gnaegi, F. et al., Trav. Soc. Pharm. Montpellier, 34, 91-100 (1974).

Gorbach, S., Pure Appl. Chem., 52, 2569-2590 (1980).

Goursaud, J. et al., Ann. Fals. Expert. Chem., 69, 327-336 (1976).

Greenberg, R. and Resnick, C., Pest. Sci., 8, 59-64 (1977).

Greenhalgh (1), R. et al., Bull. Envir. Cont. Tox., 7, 237-242 (1972).

Greenhalgh (2), R. and Kovacicova, J., J. Agr. Fd. Chem., 23, 325-329 (1975).

Greve (1), P.A. and Wit, S.L., J. Agr. Fd. Chem., 19 372-374 (1971).

Greve (2), P.A. and Grevenstuk, W.B.F., Meded, Fac. Landb. Gent. 40, 1115-1123 (1975).

Greve (3), P.A. and Grevenstuk, W.B.F., Meded, Fac. Landb. Gent. 41, 1371-1381 (1976) and JAOAC, 62, 1155-1159 (1979).

Greve (4), P.A. and Hogendoorn, E.A., Meded. Fac. Landb. Gent. 44, 877-884 (1979).

Gutenmann, W.H. and Lisk, D.J., J.Agr. Fd. Chem., 11, 468-470 (1963).

Heuser (1), S.G. and Scudamore, K.A., J. Scr. Fd. Agric., 20, 566-572 (1969).

Heuser (2), S.G. and Scudamore, K.A., Pestic. Sci., 1, 244-249 (1970).

Holmes, D.C. and Wood, N.F., J. Chromatog., 67, 173-174 (1972).

Isshiki, K. et al., Bull. Envir. Cont. Tox., 19, 518-523 (1978).

Ivey, M.C. and Mann, H.O., J. Agr. Fd. Chem., 23, 319-321 (1975).

Jaulmes, P. and Mestres, R., Ann. Tecnol. Agric., 11, 249-269 (1962).

Keppel, G.E., JAOAC, 54, 528-532 (1971).

Khan, S.U., Bull. Envir. Cont. Tox., 14, 745-749 (1975).

Kilgore (1), W.W. et al., J. Agr. Fd. Chem., 15, 1035-1037 (1967).

Kilgore (2), W.W. and White, E.R., J. Agr. Rd. Chem., 15, 118-1120 (1967).

King, R.R., J. Agr. Fd. Chem., 26, 1460-1463 (1978).

Kobayashi, H. et al., J. Pest. Sci., 2, 427-430 (1977).

Krause, C. and Kirchhof, S., Deutsche Lebensm. Rundsch., 66, 194-199 (1970).

Lawrence (1), J.F. and McLeod, H.A., JAOAC, 59, 637-640 (1976).

Lawrence (2), J.F., J. Agr. Fd. Chem., 25, 211-212 (1977).

Leary, J., JAOAC, 57, 189-191 (1974).

Lokke, H., J. Chromatog., 200, 234-237 (1980).

Lott, P.E. and Lott, J.W., J. Chromat. Sci., 16, 390-395 (1978).

Love, J.L. and Patterson, J.E., JAOAC, 61, 627-628 (1978).

Lubkowitz, J.A. et al., J. Agr. Fd. Chem., 21, 143-144 (1973).

Luke, B.G. and Cossens, S.A., Bull. Envir. Cont. Tox., 24, 746-751 (1980).

Machin, A.F. and Quick, M.P., Analyst, 94, 221-225 (1969).

Maeda, M. and Tsuji, A., J. Chromatog., 120, 449-455 (1976).

Malone, B., JAOAC, 52, 800-805 (1969).

McLeod, H.A. and McCully, K.A., JAOAC, 52, 1226-1230 (1969).

Meagher, W.R., J. Agr. Fd. Chem., 14, 374-377 (1966).

Mendoza (1), C.E. et al., Analyst, 93, 34-38 (1968).

Mendoza (2), C.E. and Shields, J.B., JAOAC, 54, 507-512 (1971).

Mestres (1), R. et al., Proc. Int. Soc. Citriculture, 2 426-429 (1977) and Trav. Soc. Pharm. Montpellier, 39, 323-329 (1979).

Mestres (2a), R. et al., Proc. Int. Soc. Citriculture, 3, 1103-1106 (1977) and Trav. Soc. Pharm. Montpellier, 38, 81-86 (1978).

Mestres (2b),R. et al., Ann. Fals. Exp. Chim., 67, 585-598 (1974) and 69, 369.370 (1976).

Mestres (3),R. et al., Trav. Soc. Pharm. Montpellier, 35, 87-100 (1975).

Mestres (4),R. et al., Trav. Soc. Pharm. Montpellier, 36, 43-58 (1976).

Mestres (5), R. et al., Ann. Fals. Exp. Chim., 70, 177-188 (1977).

Mestres (6), R. et al., Ann. Fals. Exp. Chim., 72, 577-589 (1979).

Mestres (7), R. et al., Trav. Soc. Pharm. Montpellier, 33, 191-194 (1973).

Mestres (8), R. et al., Trav. Soc. Pharm. Montpellier, 31, 97-108 (1971).

Moellhoff (1) ,E. Pflanzensch. Nachr. Bayer, 24, 252-262 (1971).

Moellhoff (2), E. Pflanzensch, Nachr. Bayer, 28, 370-381 (1975).

Moellhoff (3), E. Pflanzensch. Nachr. Bayer, 30, 249-263 (1977).

Mooney, R.P. and Pasarela, N.R., J. Agr. Fd. Chem., 15, 989-995 (1967).

Morgan, N.L., Bull. Envir. Cont. Tox., 3, 254-258 (1968).

Munday, W.H., JAOAC, 46, 244-245 (1963).

Musial, C.J. et al., Bull. Envir. Cont. Tox., 16, 98-100 (1976).

Newsome, W.H., J. Agr. Fd. Chem., 24, 997-999 (1976).

Nierle, W., Getreide, Mehl u Brot, 27, 48-51 (1973).

Norman, S.L. and Fouse, D.C., JAOAC, 61, 1469-1474 (1978).

Nose, N. et al., J. Chromatog., 125, 439-443 (1976).

Official Gazette, No. 4, Notification issued on March 20, 1979 by the Japan Environment Agency.

Panel (1) on Dichlorvos and Malathion in Grain, Analyst, 98, 19-24 (1973).

Panel (2) on Fumigant Residues of Inorganic Bromide in Grain, Analyst, 101, 386-390 (1976).

Panel (3) on Organophosphorus Residues in Fruits and Vegetables, Analyst, 102, 858-868 (1977).

Panel (4) on Determination of Organochlorine Pesticides in Foodstuffs on Animal Origin, Analyst, 104, 425-433 (1979).

Pomerantz (1), I.H. and Ross, R., JAOAC, 51, 1058-1062 (1968).

Pomerantz (2), I.H. et al., JAOAC, 53, 154-157 (1970).

Porter, M.L. and Burke, J.A., JAOAC, 56, 733-738 (1973).

Putnam, T.B. et al., Bull. Envir. Cont. Tox., 13, 662-665 (1975).

Pyysalo, H., J. Chromatog., 168, 512-516 (1978).

Rajzman, A., Analyst, 99, 120-127 (1974).

Robinson, W.H. and Hilton, W.H., J. Agr. Fd. Chem., 19, 875-878 (1971).

Rosenberg, C. and Siltanen, H., Bull. Envir. Cont. Tox., 22, 475-478 (1979).

Sachse, J., Z. Lebensm. Unters. Forsch., 163, 274-277 (1977).

Shiga, N. et al., J. Pest. Sci., 2, 27-32 (1977).

Singh, J. and Lapointe, M.R., JAOAC, 57, 1285-1287 (1974).

Sissons, D.J. et al., J. Chromatog., 33, 435-449 (1968).

Specht, W. and Tillkes, M., Fresenius Z. Anal. Chem., 301, 300-307 (1980).

Stanley, C.W. et al., J. Agr. Fd. Chem., 20, 1265-1269 and 1269-1273 (1972).

Stein, V.B. and Pittman, K.A., JAOAC, 59, 1994-10.. (1976).

Steller, W.A. and Pasarela, N.R., JAOAC, 55, 1280-1287 (1972).

Stijve (1), T. Deutsche Lebensm. Rundsch., 76, 119-122 (1980).

Stijve (2), T. Deutsche Lebensm. Rundsch., 76, 234-237 (1980).

Suffet, I.H., J. Agr. Fd. Che., 21, 591-598 (1973).

Tafuri (1), F. et al., Analyst, 95, 675-679 (1970).

Tafuri (2), F. et al., J. Agr. Fd. Chem., 18, 869-871 (1970).

Takimoto (1), Y. and Miyamoto, J., Residue Rev., 60, 84-95 (1976).

Takimoto (2), Y. and Miyamoto, J., Report CG-50-0001, JMPR 1975.

Tanaka, A. and Fujimoto, Y., J. Chromatog., 117, 149-160 (1976).

Telling, G.M. et al., J. Chromatog., 137, 405-423 (1977).

Tjan (1), G.H. and Konter, Th., JAOAC, 54, 1122-1123 (1971).

Tjan (2), G.H. and Jansen, J. Th. A., JAOAC, 62, 769-773 (1979).

Thornton (1), J.S. and Anderson, C.A., J. Agr. Fd. Chem., 16, 895-898 (1968).

Thornton (2), J. et al., J. Agr. Fd. Chem., 25, 573-576 (1977).

Thornton (3), J.S., J.Agr. Fd. Chem., 19, 890-893 (1971).

Vogeler, K., Pflanzensch. Nachr. Bayer, 21, 317-321 (1968).

Voss, G. et al., Residue Rev., 37, 120-132 (1971).

Wagner (1), K. and Frehse, H., Pflanzensch. Nachr. Bayer, 29, 54-66 (1976).

Wagner (2), K. and Thorton, J.S., Pflanzensch. Nachr. Bayer, 30, 1-17 (1977).

Ward, P.M., JAOAC, 60, 673-678 (1977).

Wegman, R.C.C. et al., Meded. Fac. Landb. Gent., 40, 1077-1084 (1975).

Weilenmann, H.R. et al., Lebensm. Wiss. u. Technol., 5, 106-107 (1972).

Westlake, W.E., et al., J. Agr. Fd. Chem., 19, 1191-1195 (1971).

Wijnants, J., Meded. Fac. Landb. Gent., 44, 913-926 (1976).

Williams, I.H. et al., J. Agr. Fd. Chem., 19, 456-458 (1971).

Winell, B., Analyst, 101, 883-886 (1976).

Working Group of the Committee for Analytical Methods, Analyst, 105, 515-517 (1980).

Wright, F.C. and Riner, J.C., J. Agr. Fd. Chem., 26, 1258-1259 (1978).

Zweig (1), G. (edit.), Analytical Methods for Pesticides, Plant Growth and Food Additives, Academic Press, New York-San Francisco-London, Vol. VII (1974).

Zweig (2), G., idem., Vol VIII (1976).

Zweig (3), G., idem, Vol. IX (1977).

Zweig (4), G., idem, Vol. X (1978).

Zweig (5), G., idem, Vol. XI (1980).

B. Simplified Approaches to Residue Analysis

Although sensitive methods of analysis are desirable for research and metabolic studies, selectivity is not usually necessary in such methods. Even the methods used to determine residues in samples from residue trials are not generally required to cope with a range of interference from other pesticides. Investigative methods of analysis can concentrate on sensitivity at the expense of speed and cost. On the other hand, speed and low running costs are very desirable properties of a method used to screen crops or commodities to check if residues of pesticides exceed a legal maximum reside limit.

Since there are no known health risks at or about the levels of Codex maximum residue limits, unnecessary sensitivity and/or precision can be costly and probably a yes/no result is adequate in most situations. Sophisticated equipment requiring stable electricity, supplies of pure solvents and bottled gases and a reliable services and spares supply may be an expensive and frustrating luxury for routine screening.

Methods are available which use technology appropriate to the task undertaken and the IUPAC Commission on Pesticide Chemicstry has reviewed the availability of methods which would meet the following criteria.

These methods should:

1. Show reasonable selectivity, sensitivity, precision, and accuracy comparable to gas chromatographic (GC) or liquid chromatographic (LC) methods.
2. Give reliable information in screening for the parent pesticides and important transformation and degradation products.
3. Be capable of quantitating residue levels using different techniques with an increasing degree of sophistication.
4. Be useful for commodities of importance in international trade or in domestic food supplies with an unknown pesticide history.
5. Should not require compressed gases, large volumes of organic solvents or uncommonly high purity of solvents.
6. Use equipment which is relatively inexpensive compared to GC or LC.

These criteria are fulfilled by only a few methods such as thin-layer chromatography (TLC) or spectrometry in the visible range. Other simple methods may be more convenient under certain specific laboratory conditions.

Suitable Procedures

All pesticide residue analytical methods involve extraction, clean-up, and a subsequent determination step. In each case, the last step dictates the purity required for the extracts and thus the extent of clean-up necessary. Published methods need not be used in their entirety and it is often advantageous to combine individual working steps from different methods. In addition some analytical methods can analyse a much broader range of residues than described in the literature.

TLC appears to be the most convenient procedure for screening and determination of groups of pesticides in multiresidue analysis. It is simple, fast, sensitive, and usually quite specific, being equal to or even surpassing other determinative steps with regard to speed, and cost (1).

TLC is especially valuable for the detection and identification of residues, whereas the quantitative evaluation is currently more limited. Recent development of quantitative TLC for pesticides (2) and automatization of pesticide residue determination (3) has extended the usefulness of TCL for quantitation. The technique has been in widespread use for many years for confirmation of residue identity detected by other procedures, such as GC methods (4).

As multiresidue procedures for organochlorine residues, suitable TLC methods are described in several manuals (5, 6, 7, 8). They are all based on separation of pesticides and metabolites on layers of silica gel or preferably of alumina using non-polar solvent systems such as petroleum ether or mixtures of petroleum ether with acetone, diethyl ether or ethanol. The visualisation is always performed by means of silver nitrate and UV-irradiation allowing detection limits down to 0.1 mg/kg in most cases.

For organophosphorus pesticides and metabolites (e.g. oxons, sulphoxides and sulphones), silica gel is used, the solvent system depending on the polarity of the compounds to be analysed. As chromogenic reagents, 4-(p-nitrobenzyl)pyridine, 2,6-dibromo-N-chloro-p-quinoneimine and other are available. In many cases, however, an enzymatic detection can be recommended, whereby clean-up can be greatly reduced (9, 10). The same enzymatic visulisation is suitable for insecticidal carbamates.

Appropriate TLC methods are also available (11) for the analysis of herbicide residues such as chlorophenoxyalkanoic acids, triazines, ureas and carbamates.

Quantitative determination is usually performed by visual comparison of spot size with standards but more precise results can be obtained by using densitometric evaluation of the spots.

In contrast to TLC, spectrophotometry yields only quantitative results. Except for the

specificity inherent in the colour reaction spectrophotometry often lacks the required selectivity and hence is more susceptible to possible interferences (12). Spectrophotometric methods however, can be useful in conjunction with TLC as a confirmatory technique.

As an alternative or where adequate analytical methods or equipment are not available, biological assay can be used (13, 14, 15). Although these methods are non-specific they can be easily combined with TLC and offer the advantage of fairly rapid analysis.

The IUPAC Commission on Pesticide Chemistry has published a review of the Development and Evaluation of Simplified Appraoches to Residue Analysis (16) and emphasises the continuing need for the development of comprehensive multiresidue methods based on relatively unsophisticated procedures which are rapid and cheap.

References

1. C.E. Mendoza, Residue Rev. 50, 43 (1974).

2. J.D. McNeil, R.W. Frei, J. Chromatogr. Sci. 13, 297 (1975).

3. B.A. Karlhuber, D.O. Eberle, Analyt. Chem. 46, 1094 (1975).

4. M.S. Schechter, Pestic. Monit. J. 2, 1 (1968).

5. Pesticide Analytical Manual, Vol. I, U.S. Department of Health, Education and Welfare, FDA (1977).

6. Analytical Methods for Pesticide Residues in Food Canada Department of National Health and Welfare, Ottawa (1973).

7. Deutsche Forschungsgemeinschaft: Ruckstandsanlytik von Pflanzenschutzmitteln, Verlag Chemie, Weinheim, 1977.

8. Klisenko, M., ed. Methods for Determination of Pesticide Residues in Foodstuffs, and Environmental Materials, Moscow "Kolos", (1977) pp. 368.

9. C.E. Mendoza, J.B. Shields, J. Agr. Food Chem. 21, 1978 (1973).

10. H. Ackermann, J. Chromatogra. 36, 309 (1968).

11. G. Yip, J. Chromatogr. Sci. 13 (5) 225 (1975).

12. G.E. Keppel, J. Assoc. Off. Anal. Chem. 52, 162 (1969).

13. S. Nagasawa, Ann. Rev. Entomol. 4, 319 (1959).

14. W.M. Hoskins, R. Craig, Ann. Rev. Entomol. 7, 437 (1962).

15. R.C.C. Wegman, M.D. Northolt and P.A. Greve, Mededed. Rijksfac. Landb. Gent. 40, 1077 (1975).

16. V. Bâtora, S. Lj. Vitorović, H. Thier, M.A. Klisenko, IUPAC Report on Pesticides (13) Development and Evaluation of Simplified Approaches to Residue Analysis (1981).

Annex 7

GOOD ANALYTICAL PRACTICE IN THE DETERMINATION OF PESTICIDE RESIDUES

These guidelines define good analytical practice in three inter-related parts;

The Analyst
Basic Resources
The Analysis

and then consider the source of error which contribute to the variability in results.

The Analyst

Residue analysis consists of a chain of procedures, most of which are known, or readily understood, by a trained chemist, but because the margin of error is smaller than in most other types of analysis and any mistake can invalidate the whole analysis, attention to detail in these procedures is essential. There should be adequate overlap and continuity of staff and all need to be experienced in residue analysis over a period of years. Staff should be trained in the correct use of apparatus and basic laboratory skills and the basic principles of residue analysis. They must understand the purpose of each stage in the method being used and the importance of following the method exactly as described and of noting any enforced deviations. A clear understanding of the terminology involved is also essential.

Ideally, when a laboratory for residue analysis is set up, the staff should spend some of their training period in a well established laboratory where experienced advice and training is available. If the laboratory is to be involved in the analysis for a wide range of pesticide residues it may be necessary for the staff to gain experience in more than one established laboratory.

Basic Resources

The Laboratory

In ideal circumstances the laboratory and its fittings should be designed to allow tasks to be allocated to well define areas with maximum safety and minimum chance of contamination of samples. Fittings should be of materials resistant to attack by chemicals likely to be used in the are. Thus, in such ideal conditions separate rooms would be available for sample receipt and storage, for sample preparation, for extraction and clean-up and for instrumentation used in the determinative step. The area used for extraction and clean-up would meet solvent laboratory specifications and all fume extraction facilities would be of high quality. The minimum requirements for pesticide residue analysis are that the facilities are adequate to avoid contamination.

Laboratory safety must also be considered in terms of necessary and preferable conditions as it must be recognised that the stringent working conditions enforced in residue laboratories in some parts of the world would be totally unrealistic in others. No smoking, eating, drinking or application of cosmetics should be permitted in the working area. Only small volumes of solvents should be held in the working area and the bulk of the solvents stored separately, away from the main working area. The use of toxic solvents and reagents must be avoided whenever possible. All waste solvents should be stored safetly and disposed of frequently.

The main working area should be treated as a solvent laboratory and all equipment such as lights, macerators and refrigerators should be spark-free. Extractions, clean-up and concentration steps should be carried out in a well ventilated area, preferably in fume cupboards or under fume hoods.

Safety screens should be used when glassware is used under vacuum or pressure. There should be an ample supply of safety glasses, gloves and other protective clothing, emergency washing facilities and spilling treatment kit. All staff should be trained in the use of these facilities and in an appreciation of the hazards involved. Staff must be aware that many pesticides have toxic properties and although little risk is attached to the handling of most samples, great care is necessary in the handling of standard reference compounds.

Adequate fire fighting equipment must be provided. The staff should be given periodic medical checks. If tritium-containing electron capture detectors are used, regular surveys of ^{3}H-excretion in the urine are advisable.

Equipment and Supplies

Supplies

The laboratory will require adequate supplies of electricity and water and various gases, either piped or from gas cylinders of proven quality. Adequate supplies of reagents, solvents, glassware, stationary phases, etc., are essential.

Servicing facilities for gas chromatographs, balances, spectrophotometers, etc., will be required and will probably involve keeping some essential spare parts plus access to a good technical service.

Adequate Equipment

Although, in an ideal situation, equipment should be regularly updated in order to keep up with developments, e.g., gas chromatography with microprocessor controls, the equipment only needs to be sophisticated enough to do the job required. Thus, the demands for monitoring commodities at tolerance levels laid down in the Codex are much less stringent than those required in a research environment.

All laboratories require an adequate range of standard pesticides of known and reasonably high purity. The range should cover all parent species for which the laboratory is monitoring samples as well as their more common metabolites. Most of these standards are now commercially available.

THE ANALYSIS

Avoidance of Contamination

One of the major areas in which pesticide residue analysis differs significantly from macroanalysis is that of the problem of contamination. Trace amounts of contamination in the final samples used for the determination stage of the method can give rise to errors such as false positive results and to a loss of sensitivity that may prevent the residue analyst from achieving the necessary limits of determination. Contamination may arise from either the environment or the procedure.

Contamination from the working environment

Bench polish, barrier creams, soaps containing germicides, fly sprays, perfumes and cosmetics are all commodities that can give rise to laboratory contamination and are especially significant when an electron-capture detector is being used. There is no real solution to the problem other than to ban their use.

Greases, plasticisers, rubber bungs and tubing, oil from air lines, extraction thimbles, filter-papers and cotton wool can also all give rise to contamination of the final test solution.

Pesticide reference standards should always be stored in a roon separate from the main residue laboratory. Field samples, sample preparation and formulation analysis should also be kept separate from the main residue laboratory and from each other.

Contamination from the procedure being used

Contamination of glassware, syringes and gas-chromatographic columns can arise from previous samples. All glassware should be cleaned with detergent, rinsed thoroughly and then rinsed with the solvent to be used. There must be a separate stock of glassware for pesticide residue work. Chemical reagents, absorbents and general laboratory solvents may contain components that interfere in the analysis. It may be necessary to purify reagents and adsorbents by heating and it is generally necessary to use redistilled solvents. Deionised water is often suspect and redistilled water is preferable. In many instances tap

water or well water may be satisfactory.

No apparatus containing PVC should be allowed in the residue laboratory. Other materials containing plasticisers are suspect but PTFE and silicone rubbers are usually acceptable and others may be acceptable in certain circumstances. Sample storage containers can cause contamination and glass bottles with ground glass stoppers should always be used. Instrumentation should always be housed in a separate room. The nature and importance of contamination can vary according to the type of determination technique used and the level of pesticide residue to be determined. These contamination problems, which are important with methods based on gas chromatography or HPLC, may well be less significant if a spectrophotometric finish is used, and vice versa. For relatively high levels of residues the background interference from solvents and other materials may be insignificant in comparison with the amount of residue present, while many problems can be solved by the use of specific detectors. Furthermore, if the contaminant does not interfere with the residue being sought, its presence may be acceptable.

Avoidance of Losses

Losses during storage

In an ideal situation samples should be stored at chill temperature, away from direct sunlight, and analysed within a few days. However, in many instances samples can require storage for an extended period (6-9 months) before analysis and the following precautions should be observed.

Storage temperature should be approximately -20°C, when degradation of residues of pesticides by enzyme action is extremely slow. If any doubts exist, the samples should be compared with fortified samples stored under the same conditions.

All samples should be re-homogenised after freezing as there is a tendecy for water to distil out and to collect as ice crystals, which, if discarded, will affect the analytical results. Alternatively the sample may be divided into analytical units before freezing.

Neither the containers used for storage nor their caps or stoppers should allow migration of the chemical being sought into the container. The containers must not leak. All samples should be labelled clearly with permanent labels and recorded in a sample book.

Losses during analysis

The extracts and final test solutions should not be exposed to direct sunlight.

Validation of Methods

The amount of effort allocated to the validation of methods will vary considerably. In a routine laboratory monitoring for compliance with Codex or national tolerances, standardised methods will be used in most instances and effort expended on validation of methods will be at a minimum.

In all laboratories, regular checks will be made on the effects of variation in sources of supply of chemicals, solvents, etc.

The performance of the method will have to be checked by, for example, the recovery of standards, added at appropriate levels, taken through the method both alone and in the presence of each new substrate.

The effects of light, storage at intermediate stages of the procedure, temperature, etc., on the stability of reagents and samples must be studied.

The evaluation of detection determination systems (e.g., in gas or liquid chromatography) for effects of flow-rate, temperature, etc., is important.

In laboratories where method development and/or modification is undertaken other aspects that may be studied are the effect of variation in sample size, partition ratios, etc., the

efficiency, resolution and column stability of gas- and liquid-chromatographic systems and variations in activity of various column clean-up systems.

Mainteance of Over-All Analytical Performance

In all laboratories engaged in pesticide residue analysis there is a need for regular assessment of the methods in use both at the tolerance level and at the lower limit of determination.

Recovery studies

Recovery of pesticides from "spiked" samples is commonly used as a measure of efficiency of extraction and subsequent steps, but it must be recognised that such studied are of limited value. More emphasis should be placed on checking recoveries where residues are in a "real" state, e.g., in aged samples. It must also be recognised that a method that gives adequate recoveries from samples spiked with parent compounds may be inadequate for the measurement of significant metabolites produced during ageing of the substrate. Recoveries should be within the range 70 - 110% with a mean of greater than 80% after removal of outliers.

Blank responses of interferences

Regular analyses of substrates known to be free of pesticide residues is necessary in order to check that contamination is not occuring.

Stability of standards

Regular injection of standards during the anlaysis of a series of samples allow the performance of the determination step to be checked. In addition, care should be taken that standard solutions of pesticides are not decomposed by the effect of light or heat during storage or become more ccncentrated owing to solvent evaporation. Equal care must be taken to ensure the stability of reference standard compounds.

Analysis of check samples

An excellent means of monitoring the performance of a method (or an analyst) is to introduce check samples at regular intervals. These check samples should be introduced as routine samples without any indication being given as to their special nature.

Participation in collaborative studies/ring tests

Various national and international organisations now organise collaborative studies on particular methods and/or ring tests on particular substrates. These present an ideal way for laboratories to assess their own performance. If possible, collaborative samples should be introduced as routine samples so that the analyst concerned does not attempt to "make a special effort", which would invalidate the samples as a test of laboratory performance.

Confirmatory Tests

For routine control, where the range of resulting values is, at least to a certain extent, known beforehand, confirmatory tests will not normally be necessary. Only if there are doubts as to the reliability of results need confirmatory tests be used. Confirmatory tests can be considered under a number of headings.

Use of solvent partitioning effects such as "p" values.

Use of multiple gas-chromatographic columns. Although this technique is widely used, its value is limited because, in all instances, the basic chromatographic technique is similar.

Use of different chromatographic techniques. In many instances confirmation of gas-chromatographic findings is best achieved by using thin-layer chromatography or high-performance liquid chromatography. Both have considerable advantages over gas chromatography in some circumstances, especially when dealing with substances that are not thermally stable. Whenever possible, confirmatory techniques should be carried out rather than placing

complete reliance of gas-chromatographic columns as a method of identification.

Use of different detectors.

Use of chemical derivatisation techniques. These are widely used techniques and a number of text books are available on the types of derivatisation that can be achieved. A closely linked technique is the use of, for example, ultraviolet light to change the chemical structure of the compound under examination.

Gas chromatography-mass spectrometry is a technique widely used in laboratories with a high level of sophisticated instrumentation, although it is not available in the majority of pesticide residue laboratories.

Pre-gas-liquid chromatographic separation techniques often give an indication of the identity of residues, as they are based on the properties of residues present.

SOURCES OF ERROR WHICH CONTRIBUTE TO VARIABILITY OF RESIDUE DATA

A laboratory method for determining a residue concentration is a sequence of procedures and errors, both systematic and random, may occur in each. Typical procedures following the receipt of the sample in the laboratory are:

- sub-sampling
- extraction
- clean-up steps
- analysis, including the preparation and use of standard solutions
- confirmation
- calculation.

The operating principle is the same for sub-sampling as for sampling, that is, each item or piece must have an equal chance of being chosen for the analytical sample. It is important to take a sub-sample of a suitable size. With modern techniques, it is possible to analyse a very small sample but such analyses will have little practical value. Procedures for achieving representative sub-sampling are given in manuals of residue analysis published in several countries, of which the "Pesticide Analytical Manual of the US Food and Drug Administration" has undergone the most rigorous revision and collaborative testing.

Extraction procedures may be divided into two kins, those which attempt to remove all the residue from the sample however much crop material is also taken into solution, and those which attempt to remove the residue selectively in an effort to minimise the concentration of interfering substances and which allow the efficiency of extraction of residue to be non-quantitative. In general, the first of these choices is to be preferred, especially for pesticides that absorb to or concentrate in particular parts of the foodstuffs or which degrade to compounds with different physical properties.

Studies to establish the completeness of extraction of the pesticide from the substrate should be an indispensable part of the development of a satisfactory method of analysis. The extractability of a residue may be determined by extracting a 'weathered' residue, resulting from the application of a pesticide to a growing crop, with procedures of increasing severity. The application may be made either with radio-labelled or with unlabelled compound. The use of label has the advantage that the total residue can be determined and thus the label remaining unextracted with any particular procedure can be found. In addition, the presence of label means that breakdown products can be identified and the extractability of their residues determined. By contrast, with unlabelled compound, the assumption is made that most rigorous procedure removes the compound completely and the other solvents and procedures are compared with it as standard.

For those compounds which are most difficult to extract, such as root-translocated residues, the important factors are an effective solvent, sufficient contact time between solvent and residue, a polar component if the solvent mixture to desorb the residue, and possibly heat.

If a quantitative extraction procedure is used the subsequent clean-up steps maybe considerable. This is usually the most time consuming part of a method and where systematic errors are most likely to occur. It is very important at this stage that recovery samples are included in each batch of determinations in order that a check may be made on what losses have occurred.

Errors may occur at several stages during the analytical determination itself. For example, with gas chromatography, the basis for most residue methods, injection of a volume of sample extract with a syringe has a small random error which will only be corrected for if similar volumes of external standard solutions are used for calibration. But perhaps the most serious errors occur in chromatographic procedures because co-extracted substances have identical or very similar retention characteristics to the pesticide under the operating conditions of the analysis. This interference mean that any peak present at the 'correct' retention time may consist wholly of the pesticide residue, wholly of interference or be a mixture of the two. That is, the quantity of pesticide determined from any single peak on a chromatograph always represents the maximum possible residue measurable under those conditions, and not necessarily the true residue concentration.

A source of systematic error in the analysis of extracts that may be overlooked is the purity of the material used as the analytical standard and the correctness of the concentrations of primary and working standard solutions. The highest purity is not required in substances used as standards in residue analysis but the purity should be known and the stability of the compound must also be known under the conditions in which it is being stored. This is also true for the standard solutions, their stability must be known and they should be replaced at regular intervals.

Confirmation

Confirmatory methods should be based on procedures which are as different as possible from the original analysis method in their physical chemical principles. Thus a retention time on a second GLC stationary phase offers some confirmatory evidence but the evidence is slight, since for many compounds there is a high degree of correlation between retention times on different phases. However, there are methods which offer powerful evidence of identity, such as mass spectrometry, and the use of quadrupole mass spectrometers as GLC detectors is increasing. Another effective procedure is the chemical conversion of the pesticide residue into a derivative suitable for further chromatography and many derivatisation methods have been published in the last decade.

Calculation

During several collaborative studies when the concentration of a residue has been determined from photocopies of the same chromatographic chart the precision of the results has been surprisingly poor. The establishment of an acceptable base-line and correction for small interfering peaks seems to be operations with a wide variation of individual choice. This is an apparently simple task, but there are calculations which are inherently more difficult, such as the qualification of multi-peak residue mixtures such as chlordane. Calculation against an external standard may be based on normalisation (if that is possible) or on one or two selected peaks, or on the long retention-time, unweathered peaks or on a comparison with the commercial product. Each of these calculations will give a different result and each may be considered 'correct'.

The analyst must decide whether he should apply a correction to the calculated residue concentration to allow for 'recovery' through the clean-up and analysis stages. In the recovery experiments, which are run in parallel with the test samples, the added pesticide may be recovered quantitatively. Allowing for the random errors occurring in the clean-up and analysis steps a recovery may be considered quantitative if the proportion found lies between 70% and 110% of that added. If the recovery is lower than this but precise for a number of experiments, a recovery correction may be applied. If the recovery is low and variable, the analytical method should be examined for some undesirable feature causing irregular losses.

Correction for 'blank' is a difficult question in residue analysis. It is not acceptable to subtract the 'apparent' residue concentration in the untreated control sample (if there is

an untreated sample) from the concentration in the treated sample. There are two considerations. Only if the peak in the untreated sample chromatogram can be shown to be due to interfering co-extracted material is it acceptable to correct for 'blank'. However, it may be difficult to prove this, especially as it is not unusual for the control sample to contain a small concentration of pesticide caused by spray drift or by contamination of the sample. If the peak in the untreated sample chromatogram is, in fact, caused by pesticide, then a correction for 'blank' must not be carried out.

Errors

Thus the variability in results obtained from residue samples may arise from the simultaneous operation of a large number of independent factors, each of which may contribute random error or systematic error or both. The total random error may be calculated from each of the independent random errors by the 'law of the propagation of errors', that is, that the total variance is equal to the sum of the variances arising from the independent factors (the variance being the square of the standard deviation).

The systematic error of a method determines the accuracy of the result, or the closeness of the result to the 'true' value. The greater the error, the poorer the accuracy and the greater the departure from the 'true' result. The 'recovery' experiments are a measure of the systematic error (provided that the method ensures quantitative extraction, since the recovery experiment cannot measure errors in the extraction process). Within a laboratory experienced in residue analysis and using a number of validated methods, the deviation from 100% recovery of the mean of a set of recovery experiments is usually less than 10%. Thus it can be said that many of the commonly-used, collaboratively-studied residue methods are essentially quantitative.

The other component of the overall error is the random error. The random error of a method determines the precision of results, that is, their closeness to one another. The greater the error, the poorer the precision and the farther apart the results are from one another. The usual measures of random error are the standard deviation and the relative standard deviation (the ratio of standard deviation to mean value). The measurement of the random error in one laboratory, where a single operator is obtaining successive results with the same apparatus under constant operating conditions on identical test materia, is called the "repeatability" of the method. For the residue methods in common use, that have been accepted following collaborative studies, the repeatability expressed as relative standard deviation has a maximum value of about 0.1. This value applies to experienced staff in a well-equipped laboratory using the methods over their working concentration range, that is, at concentrations that are not close to the limit of detection nor excessively high.

Reporting Results

This aspect of pesticide residue analysis depends very much on the requirements of the organisation demanding the analytical information and it is difficult to lay down strict rules of reporting, or evn on the accuracy required. It is recommended that both analyst and user of the information fully appreciate the capability of the methods used and the interpretation to be placed upon data prodcued before the work is started.

Valid interpretation of residue data depends on a knowledge of how the various factors contribute to the variability in results. Thus a sufficient number of analyses must be carried out to show the extent of errors involved and the standard deviation should be calculated.

All the analytical data obtained from the analysis of samples, including where relevant, the parent component and the main metabolites, should be provided, and not just a summary or an average figure. It should be clearly stated how the residues are calculated and expressed.

If necessary, explanatory notes for erratic results should be given.

For most commodities the residues of the pesticide and its metabolites will be expressed on the basis of the whole product as it moves in commerce or is prepared for marketing, e.g. certain vegetables without outer leaves, root vegetables after removing aerial parts, etc.

Guidance on the recommended portion of the sample to be prepared for the determination of pesticide residues is given in Annex 5.

Residue data should be supported by:

1. a full description of, or adequate reference to the analytical method used, including apparatus and reagents;
2. data on the specificity of the method used;
3. data on the limits of determination of the analytical method on the commodity in question;
4. adequate recovery data at levels (which should be stated) corresponding to those found in practice;
5. the value of the untreated control and its standard deviation, including the number of observations upon which the standard deviation is based;
6. a statement on whether or not the results presented have been corrected for blanks (untreated controls) or recoveries, or for both;
7. an indication on whether a pre-treatment of the sample, e.g. washing, peeling, making soil free or any other method of preparing has occurred before analysis. This should be stated in expressing the amount of residue found.

FURTHER READING

Burke, J., and McMahon, B. "Analysis of Food for Residues of Pesticides", FDA By-Lines, No. 4, January 1977.

Cochane, W.P., Whitney, W. The Canadian Check Sample Programme on Pesticide Residue Analysis: Reliability and Performance. Pesticide Residues, 1979, Pergamon Press.

Car, M. Internal Laboratory Quality Control in the Routine Determination of Chlorinated Pesticide Residues. Pesticide Residues, 1979 Pergamon Press.

Telling, G.M. Good Analytical Practice in Pesticide Residue Analysis. Proc. Analyt. Div. Chem. Soc. Jan. 1979.

"Guidelines on Analytical Methodology for Pesticide Residues Monitoring", Federal Working Group on Pest Management, Washington, D.C. 20460, June 1975.

Sherma, J. "Manual of Quality Control for Pesticides and Related Compounds in Human and Environmental Samples", USA Environmental Protection Agency, EPA 600/1 76 017. February 1976.

"Pesticide Analytical Manual", Volume 1, US Department of Health, Education and Welfare, Food and Drug Administration.

REPORT ON PESTICIDE RESIDUE TRIAL - PART B ANALYTICAL REPORT (to be used with Part A)
(See Annex 3)

Please type or use block capitals

Person(s) responsible for the analysis.

IDENTITY OF SAMPLE

Crop Commodity		Sample identity or number	
Pesticide(s) used on sample(s)			

CONDITION AND TREATMENT OF SAMPLE(S)

Date(s) of receipt in laboratory		Date(s) of analysis	
Method of storage and condition of sample(s)			
Portion of sample(s) to be analysed			

ANALYSIS

Method of analysis (or reference) and/or modifications Extraction: Clean up Method of determination and expression of residue Recoveries Limit of determination	

RESULTS

Dosage Rate	____	____	____	____	____	____	
Interval (Treatment to sampling)	____	____	____	____	____	____	
Residue* (Not corrected for recovery or control)	____	____	____	____	____	____	
Control (Including standard deviation)	____	____	____	____	____	____	

Other information/ e.g. stability of residues under storage conditions;

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* give mean values, range and number of analyses