

# 农药基础知识与农药残留分析

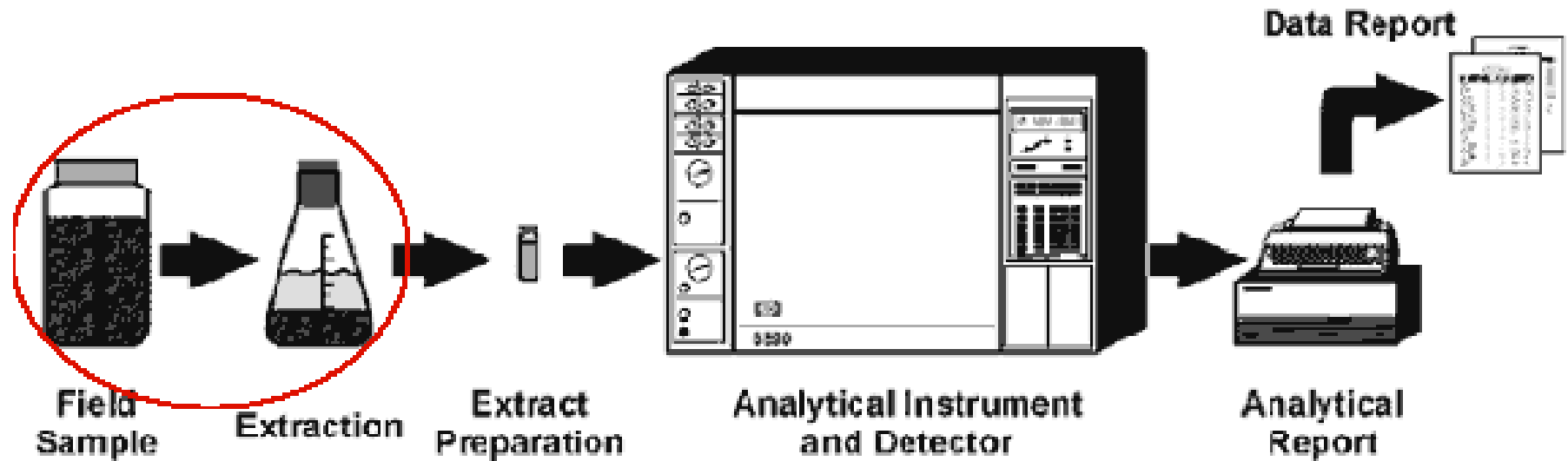
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# 农药残留分析基本流程

取样、实验室样品、分析部位、提取、样品净化、仪器分析、分析报告、结果报告



# Steps in determination of pesticide residues

- **sample preparation** (laboratory sample reception and verification, sample preparation and processing, storage of samples, preparation and handling of reference standards, storage of analytical standards, and procedures for checking stock stability)
- **extraction and clean-up,**
- **quantitative determination** of the analyte (integration and calibration),
- **estimation of uncertainty** of results,
- **confirmation** of the analyte's **identity**, and
- **quality control** procedures for pesticide residue analysis.

# 1、 农药基础知识

## 1) 农药的定义与有关概念

- **Pesticide** 杀虫剂

广义的农药的概念： 农用化学品(Agrochemicals)

- 农药原药与制剂

- 农药的分类

- 不同化学结构的农药

# 农药定义

- 农药定义：引自《农药管理条例》
- 农药主要是指用于预防、消灭或控制危害农业、林业的病、虫、草和其它有害生物以及有目的地调节植物、昆虫生长的化学合成或者来源于生物、其它天然物质的一种物质或者几种物质的混合物及其制剂。

- *Pesticides are chemicals that we use to kill undesirable organisms.*
- When we say *undesireable organisms*, we are referring to organisms (plants, animals, insects, etc.) that are harmful to us. Some of these organisms, or "pests," eat our crops, while others spread diseases. And it doesn't always have to be this serious. Weeds can be considered a pest for just growing in the wrong places (our yards). The point is, if we are using some type of chemical to control these pests, that chemical would be considered a **pesticide**.

# 现代农业中农药的使用不可缺少

- The world population is **5 billion** and growing. Of those, **700 million** are undernourished. Even with the use of pesticides, over **one-third** of our food is lost to pests.
- (Without pesticides, the losses will probably be even higher). Do you think we can afford to feed the world organically?

# 杀菌剂历史

- 杀菌剂是人类历史上最古老的药剂（公元前1000多年），从硫黄、石硫合剂、波尔多液、汞制剂，至今天的多种结构的化合物。有二硫代氨基甲酸酯类、苯并咪唑类、三唑类、吗啉类、酰胺类、嘧啶胺类等。
- 据英国植保协会出版的《The Pesticide Manual》) 介绍杀菌剂品种共200多种，新研发品种共230种左右。



# 除草剂发展历史

- 20世纪40年代，H.B. Tukey和Celia Kirby等成功地合成和生产苯氧乙酸类除草剂，从此，对杂草的防治由人工进入化学防治阶段。
- 50年代，随着氨基甲酸酯类杀虫剂的出现，硫代氨基甲酸酯类除草剂也跟着进入农药市场，如扑草灭、苏达天、野麦畏、毒草胺、西玛津、赛克津等，现在有不少产品仍占有一定的市场。
- 以后又发明了有氟乐灵、敌草快，和二苯醚类除草剂。
- 70年代出现磺酰脲类除草剂甲磺隆、嘧磺隆、醚苯磺隆及氟嘧磺隆。磺酰脲类除草剂活性高，用量少，每公顷只需要15~150克即可，目前仍为销售量最高的除草剂。
- Glyphosate，与转基因作物

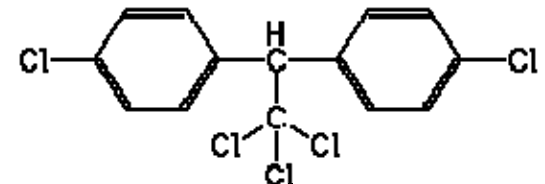
# 杀虫剂的历史

- 20世纪40年代问世的第一代杀虫剂是有机氯、有机磷杀虫剂，其代表化合物为DDT、666、艾氏剂、七氯等有机氯，对硫磷、特丁磷等有机磷。
- 第二代杀虫剂为氨基甲酸酯类农药，如西维因等。
- 第三代杀虫剂为除虫菊酯，它源于植物除虫菊，但光稳定性差。20世纪70年代，化学家们对其结构进行改造，生产出一批在当时为高效低毒的拟除虫菊酯，如：氰氯菊酯、溴氯菊酯、氰戊菊酯等。

# 农药的历史

- 1948年，Hermann Muller因为发明了化学农药DDT而获诺贝尔生理和医学奖

In the past, **malaria** was once a serious disease that killed millions of people globally. (The photo to the right shows the red blood cells of someone with malaria.) To fight this problem, we used the pesticide DDT, to kill the mosquitoes which transmitted the disease. It was successful, and the number of people who died from malaria shrank drastically.



first made in a laboratory in 1873 , found its biological activity in 1939

- At the beginning of World War II (1940), our insecticide selection was limited to several arsenicals, petroleum oils, nicotine, pyrethrum, rotenone, sulfur, hydrogen cyanide gas, and cryolite. It was World War II that opened the *Modern Era of Chemical* control with the introduction of a new concept of insect control --synthetic organic insecticides, the first of which was DDT.

# 有机磷农药发展

- The similarity of OP chemical structures to the "nerve gases," their modes of action are also similar. Their insecticidal qualities were first observed in Germany during World War II in the study of the extremely toxic OP nerve gases *sarin*, *soman*, and *tabun*.
- Initially, the discovery was made in search of substitutes for nicotine, which was heavily used as an insecticide but in short supply in Germany.

# 农药的其他基本概念

- 有效成分 a.i., active ingredient
- 剂型 formulation
- 农药的通用名、商品名、化学名称
- Chemical name \*
- Common name \*
- Product name \*

# Pesticide Names:

- **Chemical Name:**
- The systematic Name of a Chemical Compound according to the rules of nomenclature of the International Union of Pure and Applied Chemistry as adapted for indexing in Chemical Abstracts.
- For example: 3,5,6-trichloro-2-pyridinyloxyacetic acid.. is a chemical name.

# Pesticide Names: Common Name

- A generic name for a chemical compound (see the Weed Science Society of America list of herbicide nomenclature). For example: The common name for 3,5,6-trichloro-2-pyridinoxyacetic acid.. is triclopyr. The common name is the name generally used in discussing pesticidal toxicology and environmental behavior and fate.



# 中英文通用名例子

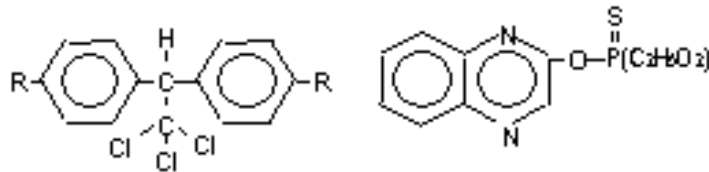
- chlorphoxim 氯辛硫磷
- chlorpropham 氯苯胺灵
- chlorpyrifos 毒死蜱
- chlorpyrifos-methyl 甲基毒死蜱
- chlorquinox 四氯喹噁啉
- chlorsulfuron(草案) 氯磺隆
- chlorthal-dimethyl 氯酞酸甲酯
- chlorthiamid 氯硫酰草胺
- chlorthiophos 虫螨磷
- chlortoluron 绿麦隆
  
- “西维因”， 甲萘威， carbaryl ， “Sevin”

# Pesticide Names: Product Name

- The trade name of a pesticide; that is the name on the container you purchase. It is also the name to which the EPA registration number is applied at the time of registration. Triclopyr alone is sold as: Garlon 3A or Garlon 4.
- 一个农药制剂的商品名可以有多个。

## Active ingredient(s)

### 有效成分



- "The component(s) of a formulation responsible for the direct or indirect biological activity against pests and diseases, or in regulating metabolism/growth, etc.
- A single active ingredient may be comprised of one or more chemical or biological entities which may differ in relative activity.
- A formulation may contain one or more active ingredients."

# Formulation 制剂

- "A pesticide preparation containing technical grade active ingredient(s) and formulant(s) in a form suitable for use."
- The pesticide product offered for sale.

剂型:

**Type of Formulation**



- 农药原药的田间实际用量很少，一般是几克到百余克，为了把这少量的农药均匀地喷撒到农作物上，必须把农药原药加工成某种易于在田间均匀分布的粉剂、粒剂、供加水稀释的喷雾用的可湿性粉剂、浓悬乳剂、乳油等，农药原药必须加工成适宜的剂型才能使用。
- |农药剂型是指具有一定组分和规格的农药加工形态
- |一种剂型可以制成多种不同用途、不同含量的产品，即农药制剂
- 乳油：由原药（一般不溶于水）、有机溶剂（苯、二甲苯、樟脑油等）和乳化剂等经溶解混合而成单相透明油状液体制剂
- 粉剂：|供喷粉用的具有规定细度的粉状农药剂型。一般细度为**95%**通过**200**筛目。
- 可湿性粉剂：不溶于水的农药原药或溶剂中溶解度极低的农药，加工配制成能兑水使用的药剂。
- 还有悬浮剂、油剂、烟剂、微胶囊剂、种衣剂等等

## 2 农药的分类 Classification types

- Pesticides can be classified according to
- the type of pest they control
- their mode of action or
- their chemistry
- Hazard. I, II, III
- Source: 无机、有机合成、天然生物农药

# Compendium of Pesticide Common Names

## Classified Lists of Pesticides

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Acaricides	Algicides	Antifeedants
Avicides	Bactericides	Bird repellents
Chemosterilants	Fungicides	Herbicide safeners
Herbicides	Insect attractants	Insect repellents
Insecticides	Mammal repellents	Mating disrupters
Molluscicides	Nematicides	Plant activators
Plant growth regulators	Rodenticides	Synergists
Virucides	Miscellaneous	Chemical classes

## Compendium of Pesticide Common Names

### Chemical Classes

[A](#) [B](#) [C](#) [D](#) [E](#) [F](#) [G](#) [H](#) [I](#) [J](#) [K](#) [L](#) [M](#) [N](#) [O](#) [P](#) [Q](#) [R](#) [S](#) [T](#) [U](#) [V](#) [W](#) [X](#) [Y](#) [Z](#)

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#### A

[acylalanine fungicides](#) see [acylamino acid fungicides](#)

[acylamino acid fungicides](#)

[aliphatic amide organothiophosphate insecticides](#)

[aliphatic nitrogen fungicides](#)

[aliphatic organothiophosphate insecticides](#)

[amide fungicides](#)

[amide herbicides](#)

[anilide fungicides](#)

[anilide herbicides](#)

[antiauxins](#)

[antibiotic acaricides](#)

[antibiotic fungicides](#)

[antibiotic herbicides](#)

[antibiotic insecticides](#)

[antibiotic nematicides](#)

[aromatic acid herbicides](#)

[aromatic fungicides](#)

[arsenical herbicides](#)

[arsenical insecticides](#)



# Gross Classification of Pesticides by Chemistry

- Inorganic pesticides \*
- Organic pesticides \*
- Biological pesticides \*

# Gross Classification of Pesticides by Chemistry

- Inorganics
  - Molecules do not contain carbon
    - Heavy metals – lead and arsenic
    - Copper products
    - Sulfur products

# Gross Classification of Pesticides by Chemistry

- Organics
  - Molecules contain carbon
    - May be chains or rings

# Gross Classification of Pesticides by Chemistry

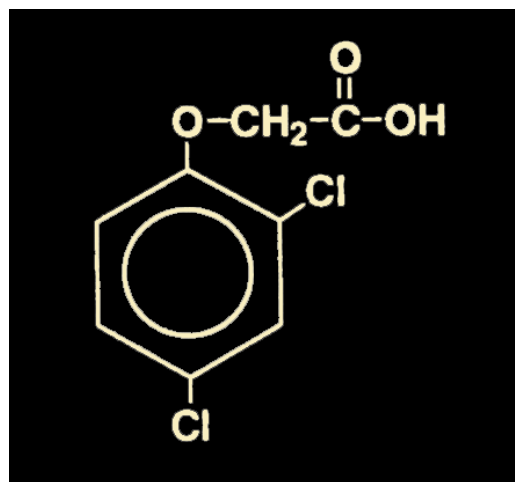
- Biologicals
  - Viruses, bacteria, fungi, and plants
  - Nematodes, insects and other parasites or predators

# Classification of Organic Herbicides by Chemistry

- Phenoxy herbicides \*
- Triazines \*
- Imidazolinone \*
- Sulfonylureas \*

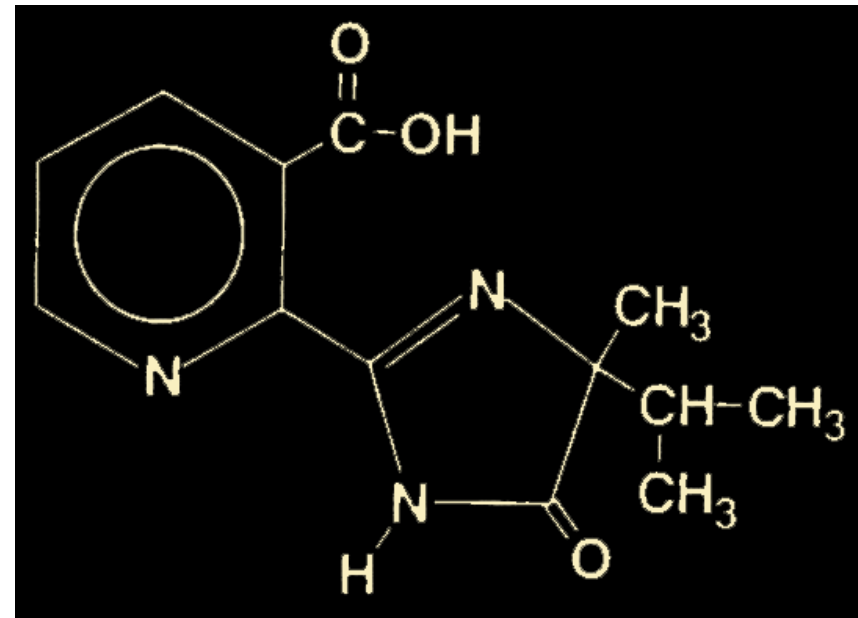
# Classification of Organic Herbicides by Chemistry

- Phenoxy herbicides
  - 2,4-D, 2,4-DP, 2,4,5-T
  - Behaves as an auxin causing hypertrophy
  - Sample structure



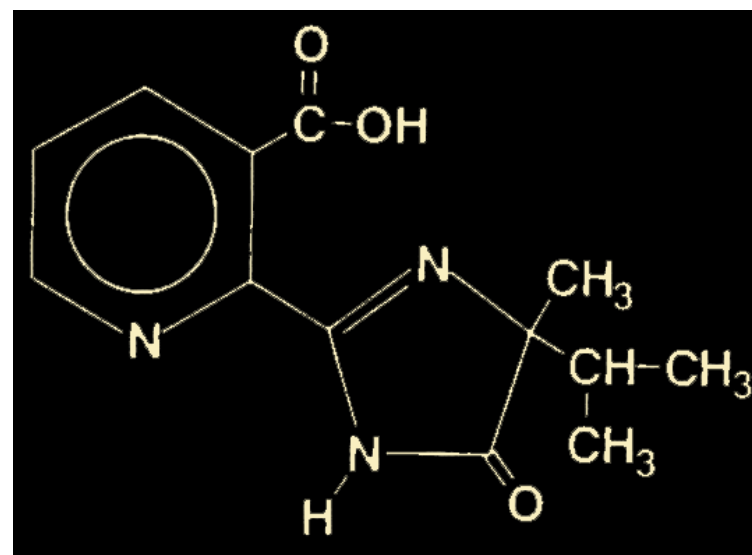
# Classification of Organic Herbicides by Chemistry

- Triazines
  - Hexazinone
  - Have extreme soil mobility
  - Structure



# Classification of Organic Herbicides by Chemistry

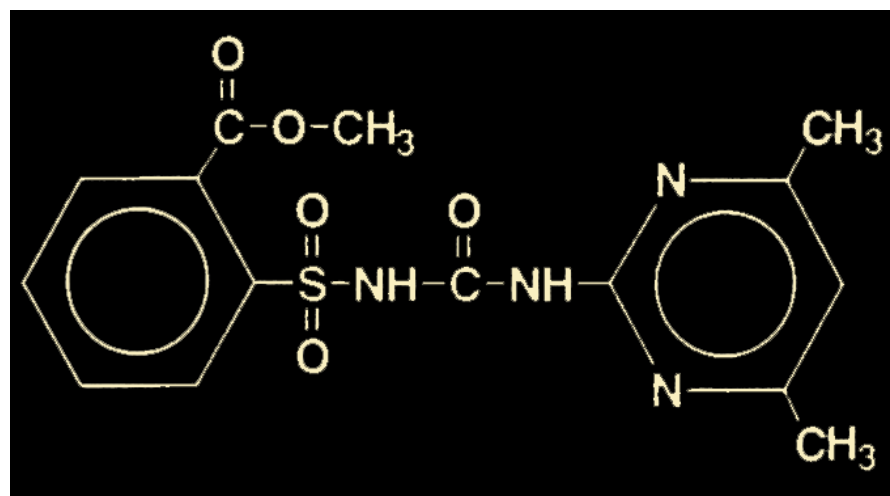
- Imidazolinone
  - Imazapyr
  - Structure





# Classification of Organic Herbicides by Chemistry

- Sulfonylureas
  - Metsulfuron & sulfometuron methyl
  - Sample structure



# Classification of Organic Insecticides by Chemistry

- Chlorinated hydrocarbons \*
- Organophosphates \*
- Carbamates \*

etc

# Insecticides

- Cholinesterase Inhibitors
  - Carbamates
  - Organophosphates
- Pyrethrins & Pyrethroids
- Organochlorines



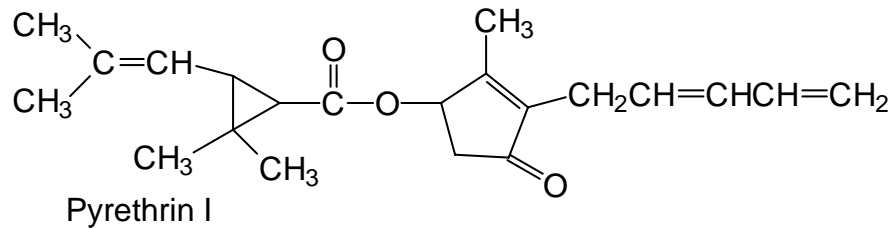
# Insecticides

## Pyrethrins & Pyrethroids

- Pyrethrins
  - Natural insecticidal extract
  - Unstable
- Pyrethroids
  - Synthetic derivatives
  - Used with piperonyl butoxide



# Pyrethrins:



- Low systemic toxicity
- Respiratory sensitization
  - Asthma
- Skin reactions
  - Paresthesia
  - Allergic dermatitis



# Pyrethroid Insecticides

- Use increasing
- Examples of use
  - Structural & agricultural
  - Pet flea control
  - Pediculicide
- Vector control
  - West Nile virus
  - Aircraft “disinsection”



Source: CDC

# Classification of Organic Insecticides by Chemistry

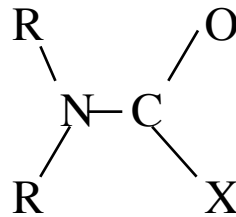
- Chlorinated hydrocarbons
  - Dieldrin, aldrin, DDT, mirex, chlordane
  - Sample structure

# Insecticides

## Cholinesterase Inhibitors

- N-methyl Carbamates

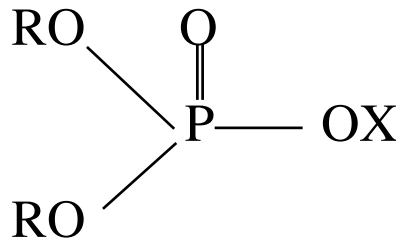
- aldicarb (Temik), carbofuran (Furadan), carbaryl (Sevin)



Generic structure for N—methyl carbamates

- Organophosphates (OPs)

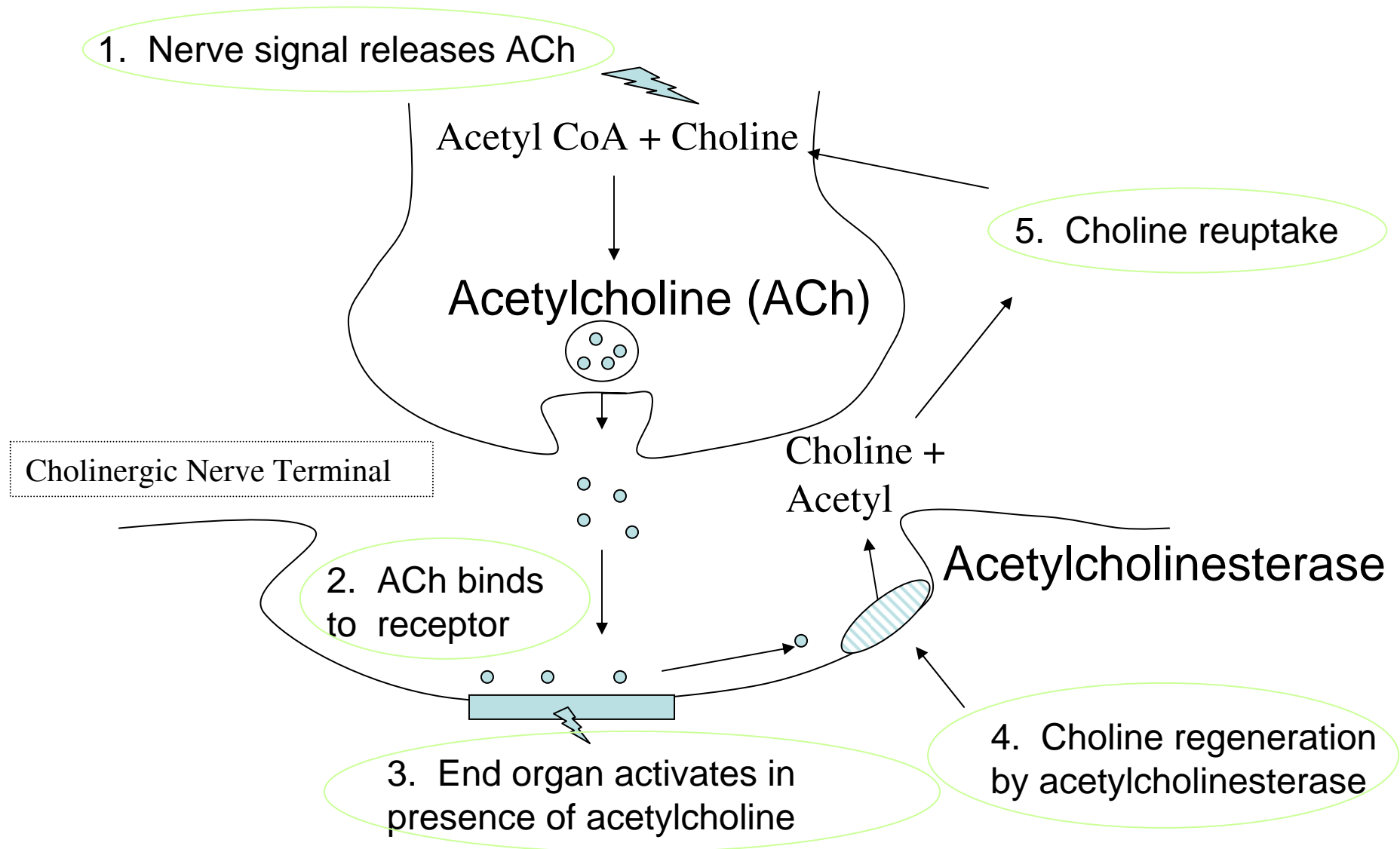
- chlorpyrifos (Dursban, Lorsban), diazinon, malathion



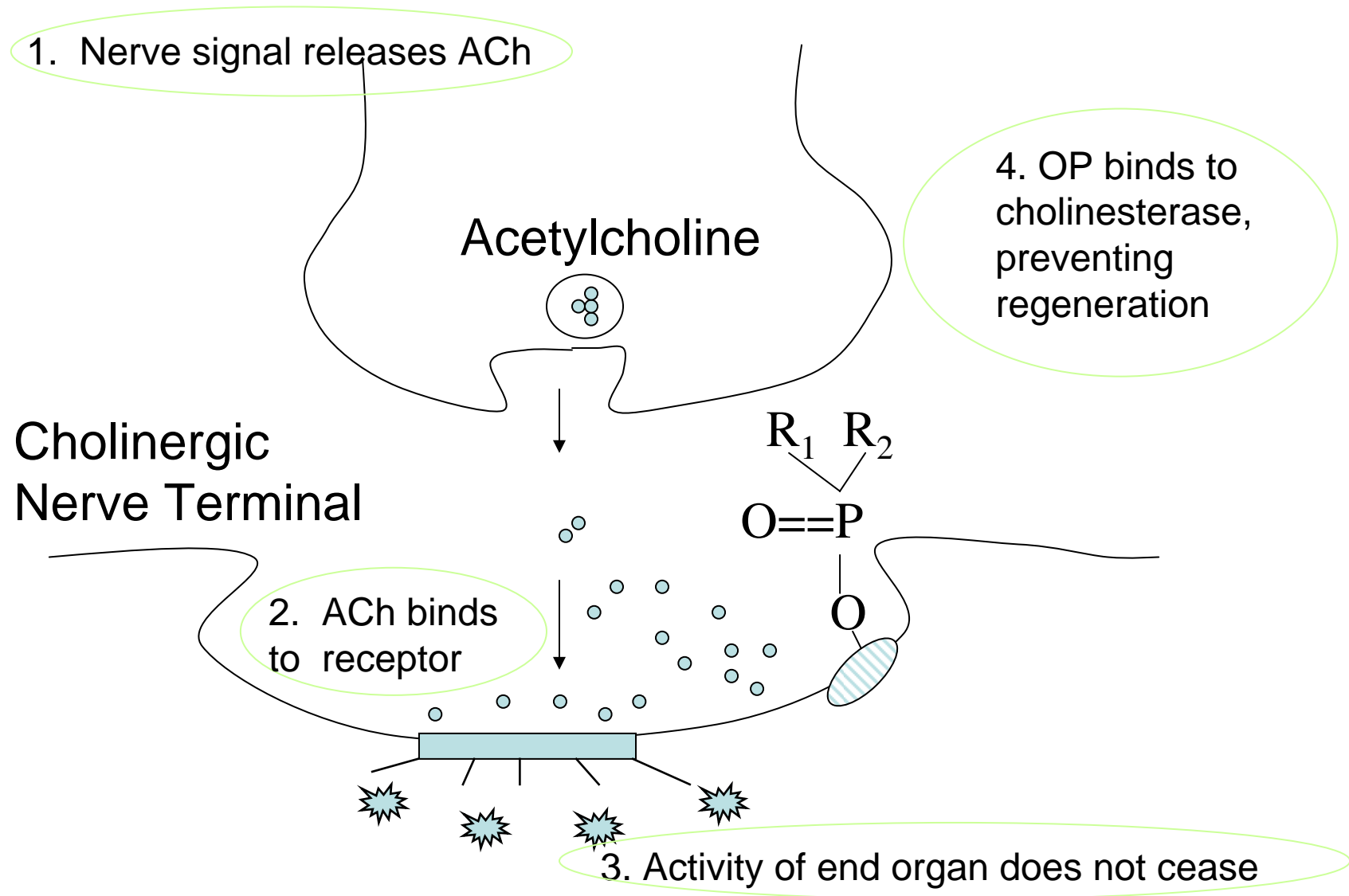
Generic structure for organophosphates



# Cholinesterase Normal Function



# Inhibition of Cholinesterase



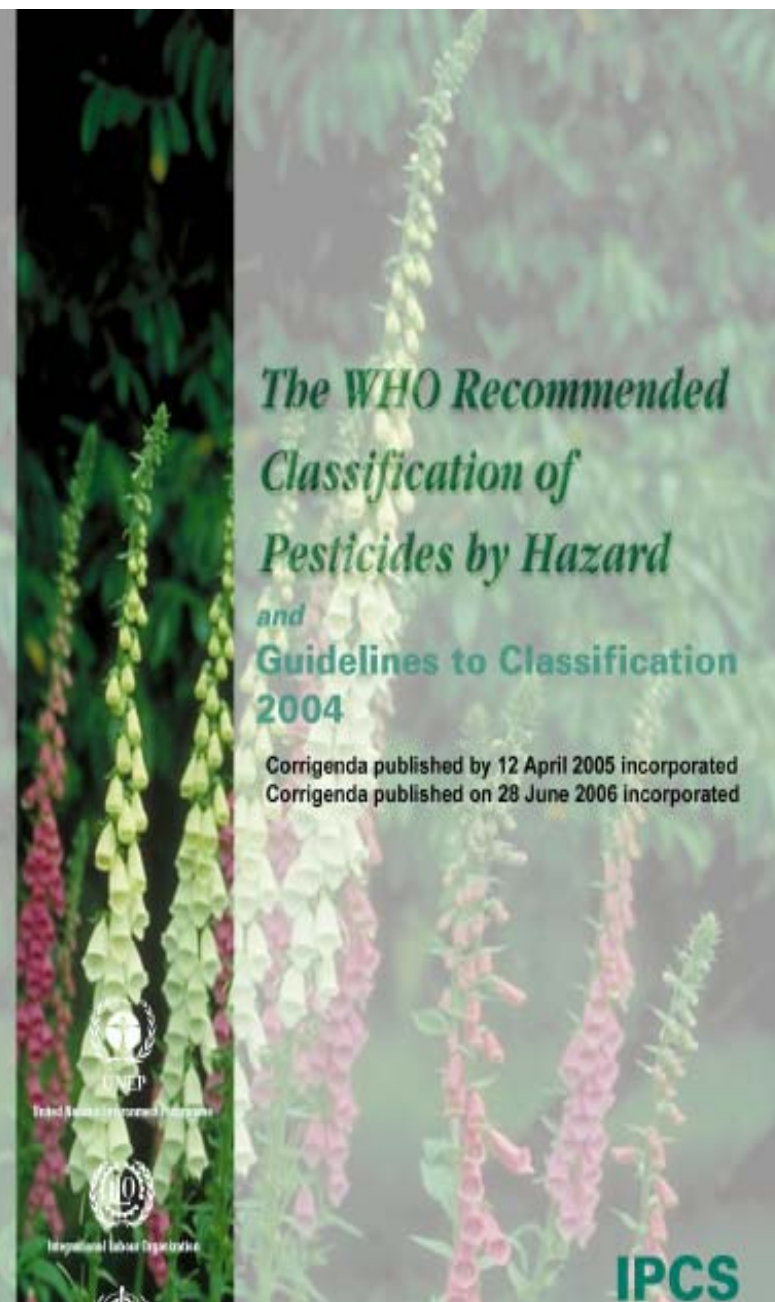
# Classification of Organic Insecticides by Chemistry

- Organophosphates
  - Malathion, azinphos-methyl, naled
  - Sample structure

# Classification of Organic Insecticides by Chemistry

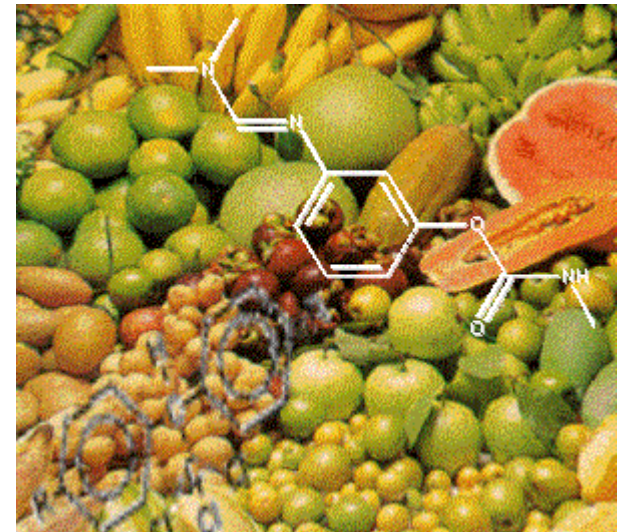
- Carbamates
  - Carbaryl (Sevin)
  - Structure

- THE WHO RECOMMENDED CLASSIFICATION OF PESTICIDES BY HAZARD AND GUIDELINES TO CLASSIFICATION
- PART I RECOMMENDED CLASSIFICATION OF PESTICIDES BY HAZARD
- PART II GUIDELINES TO CLASSIFICATION OF PESTICIDES BY HAZARD
- NOTES ON THE USE OF THE TABLES IN CLASSIFICATION
- ENTRIES AND ABBREVIATIONS USED IN THE TABLES
- REFERENCES
- Table 1. Extremely hazardous (Class IA) technical grade active ingredients in pesticides
- Table 2. Highly hazardous (Class IB) technical grade active ingredients in pesticides
- Table 3. Moderately hazardous (Class II) technical grade active ingredients in pesticides
- Table 4. Slightly hazardous (Class III) technical grade active ingredients in pesticides
- Table 5. Technical grade active ingredients of pesticides unlikely to present acute hazard
- TABLE 6. ACTIVE INGREDIENTS BELIEVED TO BE OBSOLETE OR DISCONTINUED FOR USE
- TABLE 7. PESTICIDES SUBJECT TO THE PRIOR INFORMED CONSENT (PIC) PROCEDURE
- TABLE 8. GASEOUS OR VOLATILE FUMIGANTS NOT CLASSIFIED UNDER THE WHO RECOMMENDED CLASSIFICATION
- ANNEX: How to find the hazard class of a formulation
- CAS NO INDEX
- ALPHABETICAL INDEX. CLASSIFICATION OF ACTIVE PESTICIDE INGREDIENTS



# Pesticide residue

- "Any specified substance in food, agricultural commodities or animal feed resulting from the use of pesticide.
- The term includes any derivatives of a pesticide, such as
  - conversion products,
  - metabolites,
  - reaction products and
  - impurities considered to be of toxicological significance."



# MRL的制定过程

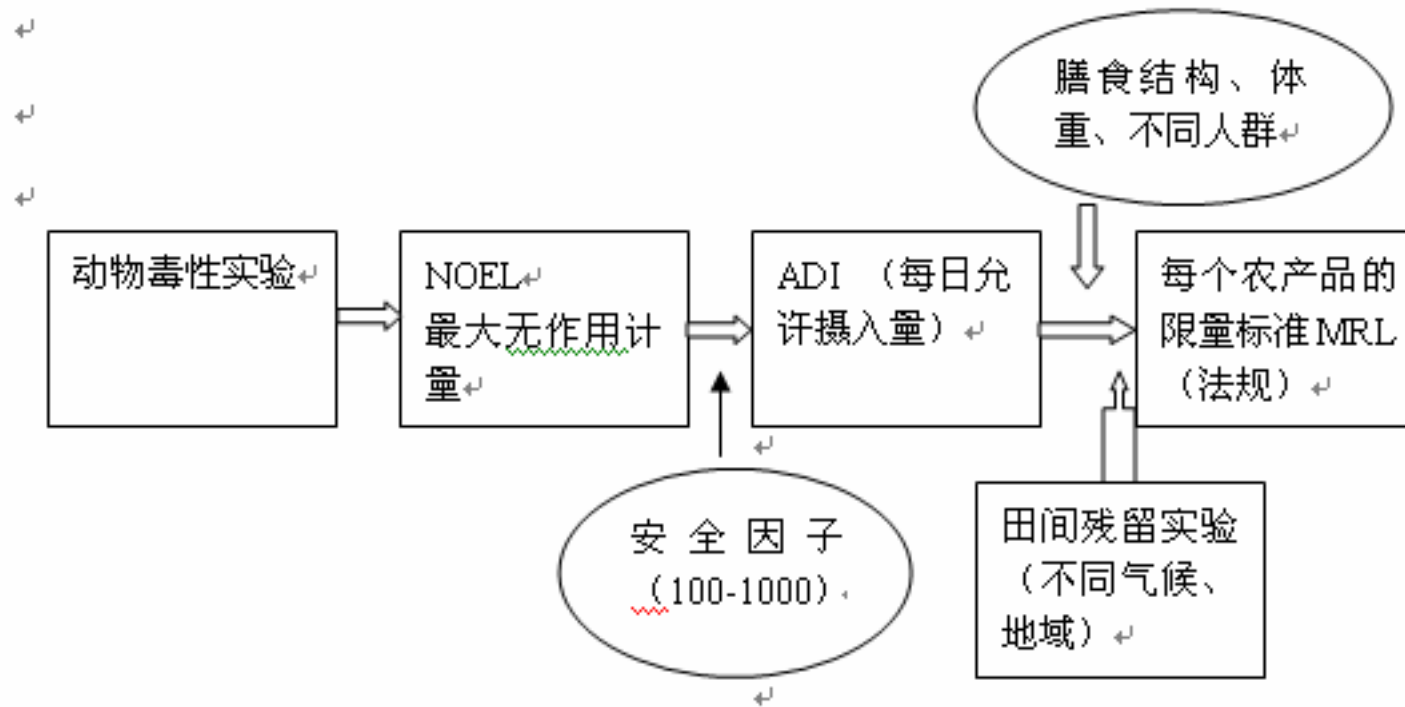
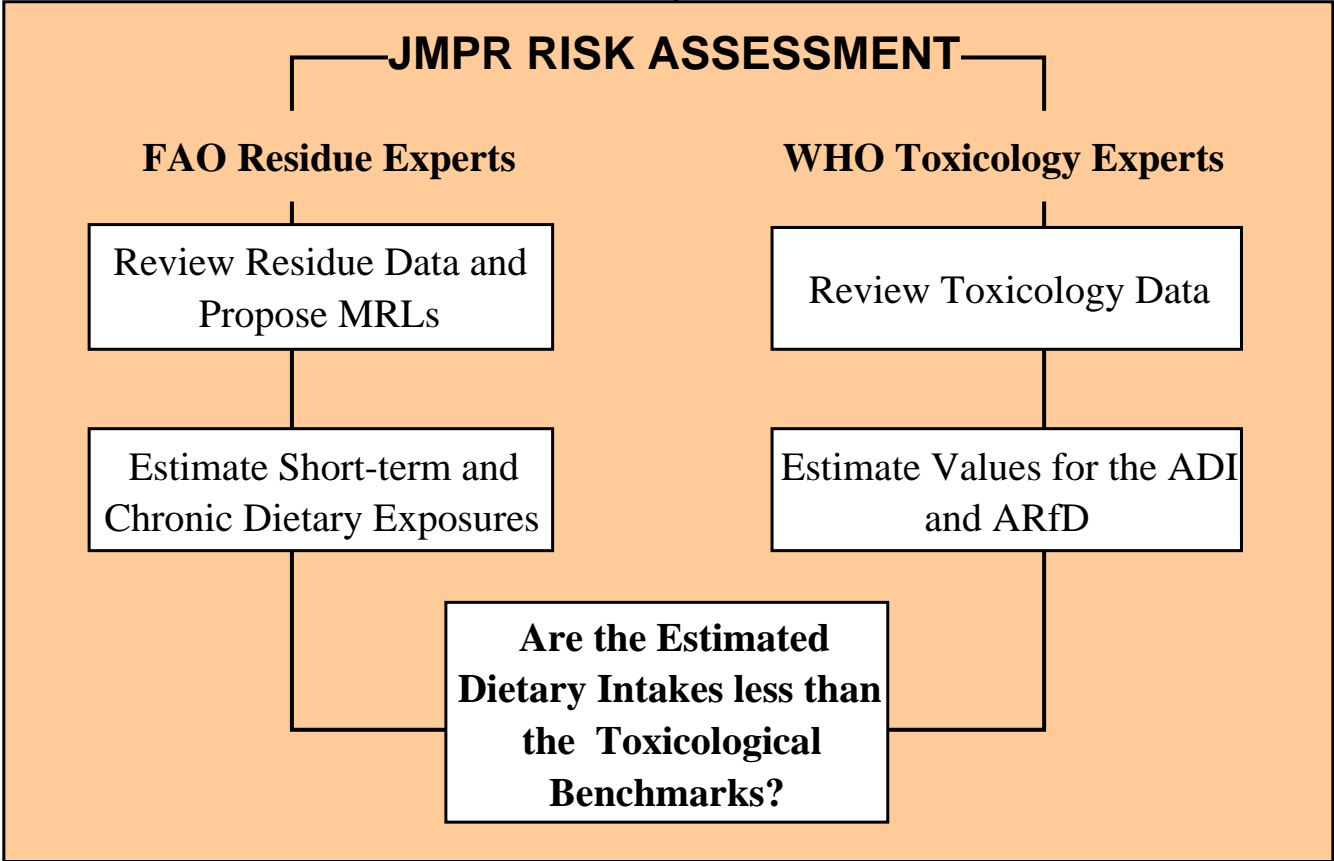


图1 制定MRL的基本流程图

如果农药实测的田间残留数据大于根据慢性毒性算出的可允许的残留量，则此农药不能使用，如杀虫眯。

**CCPR**  
Determine Priorities



**CCPR**  
Consider Proposed MRLs in the context of the Risk Assessment



## **MRLs not advanced for adoption by CAC if;**

- **IESTI potentially > ARfD**
- **IEDI > ADI for any regional diet**

# MRL的设定模型

- TMDI的计算是根据推荐的MRL值，假设人们每日摄入的食品中都含有MRL水平的农药残留，然后根据人们的膳食结构来计算每日理论摄入量，即： $TMDI = \sum F_i \times M_i$  其中 $F_i$ 表示平均每天摄入某种食品的量， $M_i$ 表示相应食品的MRL。
- 由于TMDI比较保守，因此WHO在1997年颁布了比较准确的EDI方法来估算人们的每日摄入量， $EDI = \sum STM R_i \times E_i \times P_i \times F_i$ ；其中， $STM R_i$ 是残留中浓度（STM R）。 $E_i$ 某食品可食部分系数， $P_i$ 为食品的加工系数， $F_i$ 平均每天摄入某种食品的量。

# Results from the 1989, 1990 & 1991 FDA Total Diet Studies

# MRL的主要作用

作为一种法定限量其主要作用是用以检验农作物和食品生产过程**是否严格执行优良农业措施**，帮助经农药处理的农产品在全球进行**进出口贸易**。

MRL可保障食品安全？

MRL不是一个安全限量，**农业残留超标的食品并不一定必须意味着对人体健康有影响**。ADI是通过一系列毒理学研究而得到的一个安全限量，也就是说估计摄入量是否超过由ADI计算的TMDI，才是判断食品是否安全的标准。

ADI反应了长期评价；最近关注急性和慢性毒性方面的安全。(急性参考剂量等)

Questions?

- 肯定列表制度实施后日方对我农产品采取命令检查、监控检查情况
- 银耳、葱：甲胺磷
- 乌龙茶：三唑磷
- 香菇：甲氰菊酯
- 未成熟豌豆：氟硅唑
- 油菜（青梗菜）：茚虫威
- 木耳：联苯菊酯、毒死蜱
- 蒜薹：啞菌胺

- 从2007年全年全国37个城市蔬菜农药残留监测结果看，甲胺磷、氧乐果和水胺硫磷检出次数占农药总超标次数的54.1%
- 从2002年到2005年，甲胺磷、氧乐果超标次数占总超标个数的比例一直在80%左右。但在我国禁止使用的农药，在日本不一定禁止使用

- 禁用农药

- 六六六、滴滴涕、毒杀芬、二溴氯丙烷、杀虫脒、二溴乙烷、除草醚、艾氏剂、狄氏剂、汞制剂、砷、铅类、敌枯双、氟乙酰胺、甘氟、毒鼠强、氟乙酸钠和毒鼠硅



- 不得使用 and 限制使用的农药

- 甲胺磷、甲基对硫磷、对硫磷、久效磷、磷胺、甲拌磷、甲基异柳磷、特丁硫磷、甲基硫环磷、治螟磷、内吸磷、克百威、蝇毒磷、地虫硫磷、灭蝇磷、硫环磷、氯唑磷和苯线磷

- 农业部、发改委、工商总局和检验检疫总局联合发文，2007年1月1日起，停止甲胺磷、甲基对硫磷、对硫磷、久效磷和磷胺五种高毒农药的生产，并禁止在任何农作物上使用