



Supervised residue trials

Purpose:

To establish the MRL or the Guideline for safety application of pesticide in the crop, essential material in registration process.

Designed followed with the guideline of pesticide residue trial, with the similar application dosage, stage, frequency to the field efficacy test, without considering the control of insect, herb, fungi, etc.

Guideline on Pesticide Residue Trials

《农药残留试验准则(试行)》in 1984 NY/T 788-2004 Guideline on pesticide residue trials

Trial for the combination of commodity/pesticide: **continuous** <u>two years</u> at <u>two or three</u> representative <u>sites</u>.

Two parts of the trial <u>Dissipation</u> of pesticide residue in crop, soil or water; <u>half life</u>.

<u>Terminal residue</u> related with different application dosage, frequency, harvest interval.

农药残留试验准则 Gebeline en preticide residue triab

Background information of pesticide residue trial

Active ingredient, common name, chemical name, structure, molecular weight, physical property, chemical property, formulation, solubility, stability, Metabolite or degradate etc

Crop strains, sampling site, growth cycle, crop culture

Application stage, application method, Field Efficacy Test result

Toxicology, LD50, ADI, MRL

Analytical method, half life, terminal residue

Pesticide product

Essential to each combination of pesticide / commodity

different formulation, content

Commodity change, caused to different application: dosage, frequency, stage, target to control.

Exceptions: me-too registration 相同农药产品 Trial is not essential 质量无明显差异的相同制剂 case by case

	Commodity	
In principle, e	the commodity needs the trial.	
A representat	w to contain the highest residues	
is likely to h	be major in terms of production ar	d/or
consumption	is major in terms of production an	u/01
is most like	y similar in morphology(形态学)	growth
1 1	blams and adible portion to the re-	ated
habit, pest pro		aicu

Commodity

Group MRL

稻类: rice、旱稻upland rice

麦类: wheat、大麦barley、燕麦oat、黑麦rye; 旱粮类: maize、高粱sorghum、谷子millet;

其他番茄类: eggplant、pepper、秋葵okra;

梨果类: pear、apple; Minor Crop

Residue extrapolation is the process by which the residue levels on representative commodities are utilized to estimate residue levels on related commodities in the same commodity group or subgroup for which trials have not been conducted.



CAC Crop Classification for MRL Establishment

Class A Primary food commodities of plant origin Type 1 Fruits

- ype I Fruits
- Type 2 Vegetables Type 3 Grasses
- Type 4 Nuts and Seeds
- Type 5 Herbs and Spices

28 Groups

Group 001 Citrus fruits 柑橘类水果(FC0001) subgroup 001A Lemons and Limes柠檬与青柠类(FC0002) subgroup 001B Mandarins 柑橘类(FC0003) subgroup 001C Oranges, sweet, sour 甜橙、酸橙类(FC0004) subgroup 001D Pummelos 柚子类(FC0005)

CAC Crop Classification for MRL Establishment

Class A

Type 1 Fruits

Group 001 Citrus fruits 柑橘类水果(FC0001)

subgroup 001A Lemons and Limes柠檬与青柠类(FC0002)

FC2201 Australian blood lime 澳大利亚红橙

FC2202Australian desert lime 澳大利亚沙漠橙

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Chinese (Crop classification establishment	on for MRL t	
	中华人民共	共和国农业部公告	
1 Cereal grains		第 1490 号	
2 Oilseeds	为适应农药残留标用 类,我部组织制定了《用	注制定工作需要,规范不同类别的作物分 于农药最大或留限量标准制定的作物分	
3 Vegetables	类》,经国家农药残留村	市准审评委员会审议通过,现予公告。	
4 Fruits	附件:用于农药最大	K或留限量标准制定的作物分类	
5 Nuts	7 Beverage	10 Feeds	
6 sugar crop	8 Edible fungi	11 Herbs	
o sugar erop	9 Spices		_
			ł

Cro	p classification for MRL establishment -leafy vegetable
Vegetab	les
leaf	y vegetables
((1) 绿叶类
3	菠菜、普通白菜(小白菜、小油菜、青菜)、苋菜、
蕹菜、	茼蒿、大叶茼蒿、莴苣、莴笋、苦苣、落葵、油麦
菜、叶	芥菜等
1	弋表作物: 菠菜、普通白菜
((2)叶柄类: 芹菜、小茴香、球茎茴香等
,	代表作物: 芹菜
((3) 大白菜

Sites for different commodity

Three sites - crop rice, wheat, cabbage, cucumber, tomato (pepper), orange, pear (apple), soybean, tea, peanut

one site-crop 榴莲、亚麻籽、可可、咖啡、调味品类、香草类等。

Two sites-crop: other crop

Plot arrangement Field sites One plot for each treatment, such as dose, application times, harvest interval. Some plot could be combined. 3 replicates for each treatment. **Representative site** Plot area: 30m² for crop, 15m² for leafy vegetable; 2 trees for Geographical position, climatic conditions, fruit cultural method, soil type. arrangement of the plot: wind direction, water flow direction, No application history of same class pesticide buffer zone before and during the trial. different field in the 2nd year 试验地信息与小区布置图<u>yg11</u>

Application

Recommended dosage from the Field Efficacy test

Normal dosage:

the highest dosage in the Field Efficacy test

High dosage: 1.5 times of the normal dosage, avoiding the phytotoxicity.

Frequency:

one or two times more than recommended times of Field Efficacy test

One application for pesticides used as soil treatment, seed treatment, herbicide, or PGR (plant growth regulator).



Pesticide Application stage Working backward Based on the information of the harvest interval, application interval and application times Different to the Field Efficacy test

Uses of water, normally 30-50L/mu, 15-25L/mu for seedling stage, uses of soil, 40kg/mu

Example:

application to watermelon, not the stem or leaf;

application herbicide to maize plant in dissipation study

application to the target in terminal residue

按照常规方法施药,不需"专门"喷 施土壤或植株。





Pesticide dissipation dynamics

Dissipation Loss of pesticide residues from an environmental compartment due to degradation and transfer to another environmental compartment.

is the ${\bf loss}\ {\bf process}$ of pesticide residue in crop or environment due to degradation, transfer or dilution for growing .

is the **trial** designed to investigate the pesticide residue change in the crop, soil or water

is the criteria to evaluate the **stability or persistent** of pesticides in crop or environment.

Pesticide dissipation dynamics Pesticide dissipation dynamics In the dissipation study application with the highest dosage Half-life (t_{0.5}) one application, several samplings several application, one sampling Time taken for the concentration of a pesticide in a compartment to decline by one half. Usually an estimate based on observed Sampling at 2h, 1, 3, 7, 14, 21, 30, 45, 60d after application. dissipation over several half-lives that can be described by first order kinetics. $C=C_0e^{-KT}$, $T_{0.5}=0.693/k$. (In2/k) It is permitted to increase the dosage in order to obtain the dissipation curve if the initial concentration is too low, however, Dissipation time 50% (DT₅₀) the phytotoxicity (药害) must be avoided. Time required for one-half the initial quantity or concentration of **土壤中如果原始沉积量太低,可按下面规律增加剂量:** 每m²土壤施用100mg(有效成分)农药,土壤中(取样深度10cm)的 原始沉积量为1mg/kg。 a pesticide to dissipate from a system.





Pre-Harvest Interval

PHI

The time interval between the last application of a pesticide to a crop and harvest.

Different PHI for different pesticide, crop and environment.

Different pesticide, more stable, longer PHI; Different commodity ; Different site

Essential to give the PHI for each pesticide in each commodity at different site.



plot	area	dose	time			Appli	cation	1		treatment	Harvest
	m ²		s	1	2	3	4	5	6		interval
1、2、3	3*30	低	3				0	0	0	低三	7
4、5、6	3*30	低	3			0	0	0		低三	14
7、8、9	3*30	低	3		0	0	0			低三	21
10、11、12	3*30	低	4			0	0	0	0	低四	7
13、14、15	3*30	低	4		0	0	0	0		低四	14
16、17、18	3*30	低	4	0	0	0	0			低四	21
19、20、21	3*30	高	3				0	0	0	高三	7
22、23、24	3*30	高	3			0	0	0		高三	14
25、26、27	3*30	高	3		0	0	0			高三	21
28、29、30	3*30	高	4			0	0	0	0	高四	7
31、32、33	3*30	高	4		0	0	0	0		高四	14
34、35、36	3*30	高	4	0	0	0	0			高四	21
37、38、39	3*30	高	1	0						植株动态	0-45
40	30	高	1	0						土壤动态	0-45
41	30				不雇	药		-		空白	施药与收养

Application interval: 7days Dose:

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ξ:	200mg/kg,	用水量50L/亩,	3%含量,	计算制剂量为:	333g/亩
6:	300 mg/kg,	用水量50L/亩,	3%含量,	计算制剂量为:	510g/亩

Guidance amendment?

1 treatment of non cGAP or non-GAP (higher dosage, frequency)

2 environmental samples: dynamic study or terminal residue of soil or water

3 dissipation study or terminal residue of inedible portion

4 storage stability

5 more filed trial sites with QC

Guideline for safety application of pesticide

it is issued nationally and one part of the pesticide management.

The purpose is to guide the pesticide application in **scientific, reasonable, safe** way.

To prevent the crop from the harm of insect, herb or fungi; To ensure the harvested commodity with the pesticide residue lower than MRL.



	Gui	deline	for	safe	ety appli	cat	ion	of p	estic	ide
序号	湖用名	2药 剂型及含量	适用作物	防治 対象	每 657m ² 每次 制刻施用量成 稀释倍数 (有效成分排度)	施药方法	每季作 物最多 使用 次数	最后一次 施药距收 夜的天数 (安全同 稱期)/d	実施要 直说明	最高残 留限量 (MRL) 参考值/ (mg/kg
		10.278	棉花	紅蜘蛛	30mL~40mL		2	21		相村 0.0
		10212201	叶菜	小菜蛾	33mL~50mL		1	7		0.05
		5000 M W	柑桔	潜叶蚊、 红蜘蛛	4000~6000 倍液 (3mg/L~4.5mg/L)		2	14		0.01
1	阿维菌素 abamectin	1.8%乳油	黄瓜	美洲斑 潜蝇	900mL~1200mL	喷雾		2		0,01
			虹豆	美洲斑 潜蝇	900mL~1200mL		3	5.00		0, 01
		No. No.	梨	梨木虱	3000~6000 倍液 (3mg/L~6mg/L)		893	14		0.02

	Comparison of pes formulatio	ticide residue and n analysis
	Pesticide Formulation Analysis	Pesticide Residual Analysis
Target	Active ingredients or impurity in technical or formulation. Quantitative and qualitative analysis	Residue pesticide, toxicological degradate, metabolite or impurity in organism, commodity, environment. Quantitative and qualitative analysis
Appli cation range	Registration, QC in produce, Monitor of quality in market. Research to improve the formulation and application.	Registration, to set MRL, safety use guideline, evaluate the risk, monitoring studies for food safety or bioremediation.
Requi remen t	Higher accuracy, precision, linear Lower sensitivity	Normal accuracy, precision, linear Higher sensitivity

























Sample preparation

Fruiting vegetables (edible peel) 黄瓜、辣椒、茄子、西葫芦、西红柿、黄秋葵 Whole commodity after removal of stems. Collect 6~12 pieces, not less than 3kg.



Fruiting vegetables (inedible peel) 南瓜、冬瓜。 Whole commodity after removal of stems. 测定时**果皮与果肉分别测定**。

Collect 4~6 pieces.





Pome fruits

苹果、梨等 Whole commodity after removal of stems. Collect 12pieces, not less than 3kg

Stone fruit

杏、油桃、樱桃、桃、李子、枣 Whole commodity after removal of stems and stones but the residue calculated and expressed on the whole commodity without stem.



Collect more than 24pieces, not less than 2kg

Sample preparation

Small fruits and berries 葡萄、草莓、黑莓、醋栗、越橘、罗甘 莓、酸果蔓、黑醋栗、覆盆子

whole commodity after removal of caps and stems.

Currants(葡萄干), fruit with stems.

Not less than 3kg.









Classification of the samples

Laboratory sample Sample or subsample(s) sent to or received by the laboratory.

Analytical Sample The material prepared for analysis from the laboratory sample, by separation of the portion of the product to be analysed and then by mixing, grinding, fine chopping, etc., for the removal of analytical portions with minimal sampling error.

Control sample (field) CK Sample from a field test plot to which no pesticide was applied (a zero rate sample) or which received chemical treatments identical to the test plots except for the test chemical.







PR stability in Sample Storage

Pesticide: (polarity, solubility, volatility)

Matrix: soil, crop, vegetable (water, pH, oil, protein, starch)

Condition: temperature, light, humidity, time

State: original, homogenized, extracted (enzyme, solvent)

Homework title?

Analytical method

Official methods, AOAC, GB, NY Method developed by the lab

Method validation

Sensitivity---LOD, LOQ Accuracy----fortified recovery, Precision---- RSD

Analytical method

Repeatability

For an analytical method, the closeness of agreement between results of measurements on identical test material subject to the following conditions: same analyst, same instrumentation, same location, same conditions of use, repetition over a short period of time.

Reproducibility

For an analytical method, the closeness of agreement between results of measurements on identical test material where individual measurements are carried under changing conditions such as: analyst, instrumentation, location, conditions of use, time.

Analytical method

Precision

Closeness of agreement between independent test results obtained under prescribed conditions.

Accuracy (of measurement)

Closeness of agreement between the result of a measurement and the (conventional) true value of the measure.

Note 1. Use of the term precision for accuracy should be avoided. Note 2. True value is an ideal concept and, in general, cannot be known exactly.







limit of reporting

Practical limit of residue quantification at or above the LOQ.

The LOQ for a defined matrix and method may vary between laboratories or within the one laboratory from time to time because of different equipment, techniques and reagents.,

Lower Practical Levels

Analytical method					
LOQ mg/kg	MRL mg/kg	MRL/LOQ			
0.001	0.001	1			
0.005	0.01	2			
0.01	0.02	2			
0.02	0.05	2.5			
0.02	0.1	5			
0.04	0.2	5			
0.1	0.5	5			
0.1	1	10			
0.2	2	10			
0.5	5	10			
1	10	10			



Recovery, analytical

Fraction or percentage of a pesticide residue recoverable following extraction and analysis of a matrix containing the pesticide.

In principle, the fortified level should be at the <u>residue level</u> in samples.

Unknown samples,

fortified at LOQ, MRL, and above MRL or LOQ, 2~5LOQ, 10 LOQ

Fortified recovery and **Relative Standard Deviation** Fortified recovery % Fortified level mg/kg Recovery 70-110% > 0.0170-110 0.001-0.01 60-120 mean recovery>80% < 0.001 50-120 Fortified level (mg/kg) RSD(%) >110 5 replicates >0.1 - ≤1 15 RSD, coefficient of >0.01 - ≤0.1 20 variation >0.001 - ≤0.01 30 ≤0.001 35





Calculation and expression of the result

Fresh weight basis

Pesticide residues are reported on the laboratory sample as it is received, with no allowance for the **moisture content**. MRLs and pesticide residues in **food commodities** are expressed in this way.

Dry weight basis

Pesticide residue concentration reported as if the residue were wholly contained in the dry matter of the sample, i.e. analytical results are **corrected for the water content** of the test sample. Residues in **soils and feeds**, and MRLs for feedstuffs are expressed on a dry weight basis.

P30

Pesticide Standard

Certified Reference Material

Reference material, accompanied by a <u>certificate</u>, whose pesticide concentrations are certified by procedures which establish their <u>traceability</u> and for which each certified concentration is accompanied by an <u>uncertainty</u> at a stated level of confidence. <u>Storage conditions and period</u> for which the certification remains valid may also be included for unstable materials.

P24

Stability of pesticide standard Storage condition for the standard Low temperature, Light-avoiding, Moisture protection, normally stable in a few years Storage condition for the stock solution Low temperature, Light-avoiding, Moisture protection, high concentration, suitable solvent The loss mainly caused by the solvent evaporation. Most compounds are stable. Momework title?





Guidance on Crop Field Trials Questions NY/T 788-2004 Guideline on pesticide residue trials 1. Pesticide Residue Trials and Field Efficacy test OECD Guideline for the testing of chemicals Crop Field Trial, 2009-9 1. Pesticide Residue Trials and Field Efficacy test Guidance Document on Crop Field Trials, 2011-10 2. How to design the field trial for residue? EPA 860 1500 Crop Field Trials 3. The definition of half life How to calculate the LOD and LOQ? 5. Pesticide validation method.