codex alimentarius commission

FOOD AND AGRICULTURE ORGANIZATION OF THE UNITED NATIONS

WORLD HEALTH ORGANIZATION

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Agenda Item 7(a) **CX/PR 10/42/8-Add. 1**
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JOINT FAO/WHO FOOD STANDARDS PROGRAMME

CODEX COMMITTEE ON PESTICIDE RESIDUES
Forty-Second Session
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Comments on the PROPOSED DRAFT REVISION OF THE GUIDELINES ON ESTIMATION OF UNCERTAINTY OF RESULTS FOR THE DETERMINATION OF PESTICIDE RESIDUES at step4,
submitted by Argentina, United States of America, Australia, Cuba and European Union

ARGENTINA

The Delegation of Argentina submitted comments on the Spanish version of the document which will be taken into account in revising the Spanish version.

UNITED STATES OF AMERICA

The U.S.A. is pleased to provide comments of the Guidelines on Estimation of Uncertainty of Results, document CAC/GL 50-2006. The central addition in the document is Table 4: "Typical expected uncertainties of major steps in the sample and analysis of pesticides residues." Of particular interest is the table entry (row 4) "**Analysis"** which addresses ranges of relative uncertainty expressed as within laboratory reproducibility and as average between laboratory reproducibility. It is noted that the typical coefficient of variation (CV) can be conveniently determined by recovery studies on selected pesticide/commodity pairs over different days using the same methods.

The U.S.A fully concurs with this approach. It is simplistic and readily useable by the typical analytical laboratory. The types of calculations express method variability. This is approach has been adopted by U.S. federal and state pesticide laboratories required to determine Uncertainty for their pesticide residue determinations. The U.S.A. last summer provided you actual calculations based on Uncertainty data generated by the U.S. Department of Agriculture's (USDA) Pesticide Data Program. It is our understanding that the many of comments at last year's *ad hoc* Committee on Methods of Analysis and Sampling supported a simplistic approach and real data, so that they can make an informed decision on how they would want to calculate Uncertainty in their laboratories for testing samples for compliance with Maximum Residue Limits (MRLs).

The U.S. suggests that a range in the number of replicates, specification in the number of concentration levels relative to the pesticide/commodity MRL, be added to provide additional guidance. Also, as an appendix, you may want to consider providing actual calculation examples provided by USDA in June 2009. If other countries submitted Uncertainty calculations, they should be included in an Appendix.

CUBA

Cuba approves this document.

AUSTRALIA

General Comments in response to CL 2010/3-PR

If the document is intended as an annex to the current Guideline CAC/GL 59-2006, as noted at 41CCPR (Alinorm 09/32/24, para 159), Australia recommends that the headings and text currently covered under paragraphs 1-15 is revised to only provide a brief introduction to the 'top-down' approaches to the estimation of MU and the corresponding examples that follow. In particular, Australia considers that there is no need to provide a background and justification for development of the additional guidelines

Australia believes the references to 'limited laboratory resources' and the impracticality of estimating MU for the large number of pesticide/commodity combinations, tend to suggest that residue laboratories are a special case where it is not necessary to rigorously estimate MU. In fact, as described by Horwitz (JAOAC International, 86, 109-11, 2003) top-down estimates are equally reliable as bottom-up estimates as per the ISO GUM, perhaps more so. It is recommended the wording be changed to something similar to, 'the complexity of pesticide residue analyses favours 'top-down' estimates of MU based on a combination of available data from validation studies, collaborative studies, intra-laboratory quality control or inter-laboratory proficiency studies.'

After a brief introduction, it is recommended that the document explains such 'top-down' approaches, perhaps presented in order according to their relative rigor, each with a example of how it might be applied to a given situation, using either real or hypothetical data.

A suggested order, starting with the least rigorous approach might be;

- ± 50%
- Horwitz equation, noting the follow-up publication of Thompson and Lowthian (JAOAC, 80,3, 676-679, 1997)
- Twice inter-laboratory standard deviation from collaborative studies or other suitable studies
- Data based on intra-lab reproducibility (im)precision, bias and uncertainty of bias from a combination of studies
    - Intra-lab QC plus results from proficiency studies
    - Intra-lab QC plus results from analysis of a matrix CRM
    - Intra-lab QC plus recoveries from spiked samples
    - Validation data, noting that allowance is necessary if precision is evaluated under repeatability conditions

It is suggested an example, using each approach is provided. The example in the current draft, provides equations suitable for estimating MU based on intra-lab reproducibility data plus data from proficiency studies, but it does not actually apply the equations to real or hypothetical data to estimate MU. It is recommended the example follow the format used in section 2.4.1 of Eurolab Technical Report 1/2007. If this tabular format is followed, it may be simpler to define s_R as the average standard deviation for 'n' proficiency studies, as used in the Eurolab example, rather than present the more complicated formula currently shown for u (C_{ref}).

It is recommended that a similar tabular format be employed for each example shown under the fourth bullet point above.

Australia considers that it would be worthwhile commenting on the limited availability (or non-availability) of suitable collaborative studies, matrix CRMs and on-going inter-laboratory proficiency programs for pesticide residue analyses. This limits the opportunity to apply 'top-down' approaches to estimate MU based on data from such studies for most pesticide residue analyses. In most cases, laboratories will need to

rely on data from analysis of spiked samples (either from validation studies or on-going QC) to estimate bias and the uncertainty of bias, plus intra-lab reproducibility data for a reasonable estimate of MU.

It is suggested that the document makes the point that residue laboratories should have data available from validation and quality control studies to employ one of the more rigorous approaches. If they are forced to use one of the first two listed approaches, it might be assumed that they have not sufficiently validated their test method(s).

As mentioned in the current draft, MU is usually concentration dependent, with the relative MU increasing as concentration decreases. It is suggested the document recommends that MU be estimated at the most critical concentration. In the Codex context, the most critical concentration is the Codex MRL.

European Union

Mixed Competence

European Union Vote

For all the examples it is calculated the combined relative standard uncertainty (u´)

From there, the coverage factor considered is two (k = 2, 95% confidence interval)

Therefore the expanded relative uncertainty (U´) is calculated as:

U' = k x u´

Example 1 (Following 1)

In this example PT scheme data is used to calculate the estimate measurement of uncertainty. In this case the PT data themselves form the basis for an estimate of measurement uncertainty, using the dispersion of the relative differences* of the results given by the laboratories in a number of PTs to provide an approximate estimate of the uncertainty expressed as a relative standard deviation. The laboratory A has participated in the 11 EUPT.

Laboratory A

x_i is the individual concentration reported result by the laboratory

X is the assigned value (the median in the EUPTs)

SD is the standard deviation or global relative standard uncertainty

u´global relative standard uncertainty (SD x 100)

Table 1. Laboratory individual results against the assigned value for EUPT 3-11 for Multiresidue Method for pesticides in fruits and vegetables.

Pesticides	*
EUPT3	$(x_i - X) / X$
Carbendazim	0,071
Deltamethrin	-0,406
Diazinon	0,028
Endosulfan	-0,086
Metalaxyl	-0,175
Permethrin	0,172
Pirimiphos-methyl	0,184
Vinclozolin	-0,174
EUPT4	
Bromopropylate	0,364
Chlorpyriphos-ethyl	-0,068
Chlorpyriphos-methyl	0,128
Cypermethrin	-0,033
Diazinon	-0,026
Methidation	0,054
Parathion	-0,071
EUPT5	
Diazinon	-0,052
Lambda-Cyhalothrin	0,122
Parathion	0,012
Phosmet	-0,226
Propyzamide	-0,133
Tolclofos-methyl	0,127
EUPT6	
Acrinathrin	0,373
Bromopropylate	0,239
Diazinon	0,659
Endosulfan	0,362
Procymidone	0,393
EUPT7	
Cyprodinil	-0,339
Diazinon	-0,063
Iprodione	0,227
Kresoxim-methyl	0,015
Procymidone	-0,236
Pyrimethanil	-0,037
Tetraconazole	-0,250
EUPT8	
Bifenthrin	-0,047
Bromopropylate	0,069
Carbendazim	-0,004
Chlorpyrifos	-0,050
Cyprodinil	0,011
Diazinon	-0,167
Dichlofluanid	-0,020
Lambda-cyhalothrin	-0,033
Myclobutanil	-0,264
Parathion	1,223
Pirimicarb	-0,159
EUPT9	
Bupirimate	0,214
Cyprodinil	-0,027
Diazinon	0,195
Endosulfan I	0,063
Endosulfan II	0,138
Iprodione	0,043
Myclobutanil	0,087
Procymidone	0,000
Pyrimethanil	-0,224
Quinoxyfen	0,058
Tebuconazole	-0,003
Tolylfluanid	0,081
EUPT10	
Chlorpyrifos-methyl	-0,282
Diazinon	-0,317
Endosulfan Sulfate	-0,418
Isofenphos-methyl	-0,126
Phosmet	-0,411
Quinoxyfen	-0,181
Vinclozolin	-0,135
EUPT11	
Deltamethrin	-0,121
Diazinon	-0,088
Isofenphos-methyl	-0,078
Lambda-Cyhalothrin	-0,207
Metalaxyl Sum	-0,011
Parathion-methyl Sum	-0,134
Phosalone	0,041
Procymidone	-0,038
SD	**0,247**
u'	**24.7%**
U´	**49.4%**

Example 2 (Following 3)

This example is referred to the use of PT data to evaluate the bias component of the uncertainty by the following formula:

$U' = k \times u'$ $\qquad u' = \sqrt{u'(R_w)^2 + u'(bias)^2}$

Being:

U' = expanded relative uncertainty

k = coverage factor

u'= combined relative standard uncertainty

$u'(R_w)$ = intermediate precision relative standard uncertainty, based on intra-laboratory validation and/or QC data

u'(bias) = relative standard uncertainty component from method and laboratory bias, based on PT data

How is u'(bias) calculated?

$$u'(bias) = \sqrt{RMS'_{bias}{}^2 + u'(C_{ref})^2}$$

RMS'_{bias} = root mean square of relative bias values

$u'(C_{ref})$ = average relative standard uncertainty of assigned values

$$RMS'_{bias} = \sqrt{\frac{\sum (bias'_i)^2}{m}} \qquad \text{and} \qquad u'(C_{ref}) = \frac{\sum_i \frac{S'_{Ri}}{\sqrt{n_i}}}{m}$$

$bias'_i$ = relative bias of PT i [obtained result$_i$ – assigned value$_i$)/assigned value$_i$]

S'_{Ri} = interlaboratory relative standard deviation of PT I (or Qn)

n_i = number of participants in PT i

m total number of PT schemes

So for Laboratory A, for its GC-MRM

$RMS'_{bias} = \sqrt{\frac{\sum (bias'_i)^2}{m}}$ and $u'(C_{ref}) = \frac{\sum_i \frac{S'_{Ri}}{\sqrt{n_i}}}{m}$ are calculated:

Table 2 Relative bias and average relative standard deviation calculus for EUPT

EUPT3	(bias´)	$(bias')^2$		S'_{Ri}	n_i	$\sqrt{n_i}$	$S'_{Ri} / \sqrt{n_i}$
Deltamethrin	-0.406	0.1652		0.370	116	10.770	0.034
Diazinon	0.028	0.0008		0.220	116	10.770	0.020
Endosulfan	-0.086	0.0074		0.290	116	10.770	0.027
Metalaxyl	-0.175	0.0307		0.320	116	10.770	0.030
Permethrin	0.172	0.0296		0.300	116	10.770	0.028
Pirimiphos-methyl	0.184	0.0337		0.310	116	10.770	0.029
Vinclozolin	-0.174	0.0302		0.280	116	10.770	0.026
EUPT4							
Bromopropylate	0.364	0.1327		0.430	117	10.817	0.040
Chlorpyriphos-methyl	0.128	0.0164		0.430	117	10.817	0.040
Cypermethrin	-0.033	0.0011		0.400	117	10.817	0.037

Diazinon	-0.026	0.0007		0.450	117	10.817	0.042
Methidation	0.054	0.0029		0.310	117	10.817	0.029
Parathion	-0.071	0.0050		0.460	117	10.817	0.043
EUPT5							
Diazinon	-0.052	0.0027		0.240	127	11.269	0.021
Lambda-Cyhalothrin	0.122	0.0148		0.330	127	11.269	0.029
Parathion	0.012	0.0001		0.220	127	11.269	0.020
Phosmet	-0.226	0.0513		0.290	127	11.269	0.026
Propyzamide	-0.133	0.0178		0.210	127	11.269	0.019
Tolclofos-methyl	0.127	0.0162		0.240	127	11.269	0.021
EUPT6							
Acrinathrin	0.373	0.1393		0.340	130	11.402	0.030
Bromopropylate	0.239	0.0570		0.210	130	11.402	0.018
Diazinon	0.659	0.4338		0.210	130	11.402	0.018
Endosulfan	0.362	0.1314		0.220	130	11.402	0.019
Procymidone	0.393	0.1546		0.210	130	11.402	0.018
EUPT7							
Cyprodinil	-0.339	0.1147		0.230	128	11.314	0.020
Diazinon	-0.063	0.0039		0.250	128	11.314	0.022
Iprodione	0.227	0.0516		0.250	128	11.314	0.022
Kresoxim-methyl	0.015	0.0002		0.210	128	11.314	0.019
Procymidone	-0.236	0.0556		0.210	128	11.314	0.019
Pyrimethanil	-0.037	0.0014		0.240	128	11.314	0.021
Tetraconazole	-0.250	0.0625		0.310	128	11.314	0.027
EUPT8							
Bifenthrin	-0.047	0.0022		0.233	129	11.358	0.021
Bromopropylate	0.069	0.0048		0.222	129	11.358	0.020
Chlorpyrifos	-0.050	0.0025		0.220	129	11.358	0.019
Cyprodinil	0.011	0.0001		0.188	129	11.358	0.017
Diazinon	-0.167	0.0280		0.217	129	11.358	0.019
Dichlofluanid	-0.020	0.0004		0.289	129	11.358	0.025
Lambda-cyhalothrin	-0.033	0.0011		0.289	129	11.358	0.025
Myclobutanil	-0.264	0.0695		0.192	129	11.358	0.017
Parathion	1.223	1.4963		0.232	129	11.358	0.020
Pirimicarb	-0.159	0.0253		0.184	129	11.358	0.016
EUPT9							
Bupirimate	0.214	0.0458		0.253	137	11.705	0.022
Cyprodinil	-0.027	0.0007		0.209	137	11.705	0.018
Diazinon	0.195	0.0380		0.260	137	11.705	0.022
Endosulfan I	0.063	0.0040		0.270	137	11.705	0.023
Endosulfan II	0.138	0.0191		0.259	137	11.705	0.022
Iprodione	0.043	0.0018		0.220	137	11.705	0.019
Myclobutanil	0.087	0.0076		0.230	137	11.705	0.020

Procymidone	0.000	0.0000	0.209	137	11.705	0.018
Pyrimethanil	-0.224	0.0501	0.197	137	11.705	0.017
Quinoxifen	0.058	0.0034	0.237	137	11.705	0.020
Tebuconazole	-0.003	0.0000	0.233	137	11.705	0.020
Tolylfluanid	0.081	0.0066	0.305	137	11.705	0.026
EUPT10						
Chlorpyrifos-methyl	-0.282	0.0796	0.260	132	11.489	0.023
Diazinon	-0.317	0.1003	0.240	132	11.489	0.021
Endosulfan Sulphate	-0.418	0.1746	0.290	132	11.489	0.025
Isofenphos-methyl	-0.126	0.0159	0.170	132	11.489	0.015
Phosmet	-0.411	0.1689	0.280	132	11.489	0.024
Quinoxifen	-0.181	0.0328	0.230	132	11.489	0.020
Vinclozolin	-0.135	0.0181	0.240	132	11.489	0.021
EUPT11						
Deltamethrin	-0.121	0.0146	0.250	151	12.288	0.020
Diazinon	-0.088	0.0077	0.260	151	12.288	0.021
Isofenphos-Methyl	-0.078	0.0060	0.240	151	12.288	0.020
Lambda-Cyhalothrin	-0.207	0.0428	0.240	151	12.288	0.020
Metalaxyl Sum	-0.011	0.0001	0.210	151	12.288	0.017
Parathion-Methyl Sum	-0.134	0.0181	0.240	151	12.288	0.020
Phosalone	0.041	0.0017	0.300	151	12.288	0.024
Procymidone	-0.038	0.0015	0.200	151	12.288	0.016
	Sum	4.2552			Sum	1.5662
	m	68			m	68
	RMS'_{bias}	**0.2501**			**$u'(C_{ref})$**	**0.0230**
	RMS'^{2}_{bias}	0.0626			**$u'(C_{ref})^2$**	0.000530
u´(bias) = √(0.0626 + 0.000530) = 0.251212198						

Where going back to $u' = \sqrt{u'(R_w)^2 + u'(bias)^2}$, u´(R_w) is 0.11 (see Annex 1 for intra-laboratory validation and/or QC data) so $u' = \sqrt{(0.11)^2 + (0.251212198)^2} = 0.27$

U´= 54%

Example 3 (Following Horwitz Equation)

Expanded relative uncertainty (U´) may also be calculated using empirical Horwitz formula. This approach is concentration dependency upon the pesticide residues. Therefore only a range of values can be obtained. The formula is:

$$u' = 2^{(1-0.5\log c 10^{-6})}$$

u´= relative interlaboratory standard deviation

c = concentration of the analyte

For different concentration the achieved results are:

For c = 0.01 mg/Kg the u´= 32%, U´= 64%

For c = 1.0 mg/Kg the u´= 16%, U´= 32%

But this formula may give whatever expanded uncertainty. It was design for analysis of other compounds not just pesticides. Ever since the establishment of the Horwitz equation, instrumentation technology has experienced significant advancements both in terms of sensitivity and selectivity, which reduces the uncertainty contribution by the instrumental measurement process. The resulting estimates of uncertainty accordingly are based on the distribution of between-laboratory standard deviations.

Example 4 (Following 2 and EUPTs)

In the last EUPTs a FFP RSD of 25% has been used demonstrating that a variability of 25% can be accepted as a noticeable representation of laboratory performances for MRM in pesticides residues in fruit and vegetables. Therefore is a prerequisite in order to apply this type of uncertainty within a laboratory to participate in PTs and have a successful score. Then, the laboratories will be in a position to use the FFP RSD of 25% as the relative standard uncertainty.

u´= 0.25 U´= 50%

Example 5 (Following 1, 5)

The uncertainty arising from run-to-run variability can be estimated from in-house validation experiments, in which known quantities of representative pesticides are added to representative test materials; these experiments provides three type of uncertainty, the one arising from the estimation of the overall bias, the one coming from the recoveries and the one derived from the preparation of the standards using reference material to be add to the test materials. They also include the effects of changes of sample type and change of pesticide.

The internal calculation of uncertainty within a laboratory based on reproducibility estimations is:

$$u_{c,rel} = \sqrt{\frac{RSD_R^2}{n_m} + u_{mr,REL}^2 + \frac{RSD'^2_R}{n_R}}$$

Where:

$\frac{RSD_R^2}{n_m}$ = the relative standard deviation of 5 replicates at different calibration levels, where nm is the number of replicated.

$u_{mr,REL}^2$ = relative standard deviation uncertainty derive from the use of reference material, volumetric calibration, weighting calibration…; it is considered between 1 and 2%

$\frac{RSD'^2_R}{n_R}$ = is the relative standard deviation of all the recovery data, at different levels, different matrices and different pesticides being n_R the number of data used. Normally laboratories not correcting for recovery does no need to apply this factor.

So for a particular case:

$u' = \sqrt{(0.05)^2 + (0.01)^2 + (0.11)^2} = 0.12$ U´= 24%

Evaluation of uncertainty estimates against PT results (Following 3)

This is not a way to calculate uncertainty, simply is a way to evaluate the different methods described above. Checking the quality of uncertainty, zeta (ζ) score formula is applied

$$\zeta = \frac{x - x_a}{\sqrt{u(x)^2 + u'(x_a)^2}}$$

ζ = zeta score

x= laboratory result

x_a= assigned value

u(x) = standard uncertainty of laboratory results

$u(x_a)$ = standard uncertainty of assigned values

This example is for confirming that your previous u´ (Example 2) are considered correct if $|\zeta|$ is in the range of 0 – 2. It is then compared with u´from Horwitz and FFP RSDs

For Laboratory A for bupirimate pesticide

x	0.959	x	0.959	x	0.959
x_a	0.79	xa	0.79	xa	0.79
From Example 2 u´	0.27	Horwitz RSD	0.16	FFP RSD	0.25
Qn	0.25	Qn	0.25	Qn	0.25
u(x) = x u´	0.259	u(x) = x Horw	0.153	u(x) = x FFP	0.240
$u(xa) = x_aQn$	0.198	u(xa)	0.198	u(xa)	0.198
zeta score	0.52	zeta score	0.68	zetas core	0.54

REFERENCES:

1) EUROLAB Technical Report 1/2007. March 2007. Measurement uncertainty revisited: Alternative approaches to uncertainty evaluation

2) L. Alder et al.: Estimation of Measurement Uncertainty in Pesticide Residue Analysis. JAOAC Int. Vol. 84, No 5, 2001, 1569-1577

3) ALINORM 09/32/24

4) NORDTEST Report 537. Ed 2. 2004. Handbook for Calculation of Measurement Uncertainty in Environmental Laboratories.

5) ISO 5725

6) ISO 13528

Recovery Data for pesticides in the MRM scope for different levels and different matrices - Annex 1

Analytes	% Recov	% Recov	% Recov	% Recov	% Recov	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	% Recov..	DSR
4.4DDE	118.13	103.11	115.62	120.13	115.62	103.52	109.78	118.13	114.36	112.62	108.38	109.99	104.55	119.88	107.12	111.45	100.21	95.39	100.75	93.74	115.89	120.82	8.1
Acrinatrin	16.72	104.71	1825.73	106.36	114.92	102.26	103.81	113.50	120.53	111.03	102.53	98.08	120.26	118.51	96.62	115.53	107.38	95.05	103.02	98.51	106.51	120.61	8.4
Benalaxyl	110.95	113.20	95.92	100.73	101.09	90.36	93.46	101.25	106.64	129.50	101.01	91.73	99.34	121.04	98.67	102.11	87.92	84.05	94.20	92.09	118.03	114.66	11.6
Bifenthrin	110.86	100.32	124.27	127.36	113.29	104.00	107.09	125.07	125.73	114.00	114.43	95.75	105.52	124.69	107.17	106.65	100.39	90.99	113.64	107.45	121.20	119.16	10.3
Bromopropile	106.50	120.10	130.12	114.76	108.24	97.98	115.93	122.77	120.05	109.20	95.10	90.02	115.01	120.54	109.53	105.61	89.53	80.37	86.83	113.32	115.35	105.42	13.0
Bupirimato	104.44	90.86	104.48	72.51	66.55	96.74	89.88	110.00	99.33	94.51	92.64	84.88	92.09	98.63	66.52	95.43	78.05	86.99	77.43	76.36	101.39	106.41	12.8
Cihalotrin-lambda	95.23	101.52	113.04	109.15	105.32	108.81	99.01	110.85	120.90	106.49	108.21	96.30	108.83	121.04	108.93	114.06	100.65	88.77	96.68	100.25	110.39	109.10	8.1
Cipermetrin (+iso)	124.21	109.14	116.47	104.80	100.43	97.61	105.99	121.65	113.23	119.41	106.50	101.53	107.93	120.68	100.73	106.25	106.12	109.44	98.91	107.69	112.47	104.74	7.6
Ciprodinil	103.22	132.25	102.66	90.78	92.97	104.05	91.61	110.22	114.17	122.64	101.63	139.80	92.71	113.53	94.13	100.26	96.10	79.88	86.87	88.22	107.98	108.02	14.8
Clorfenapir	109.88	103.99	107.92	97.77	98.06	106.31	107.22	114.60	107.37	110.92	106.63	88.46	102.23	100.63	92.23	92.52	111.47	103.33	104.30	100.26	109.08	116.78	7.3
Clorfenvinfos E+Z	108.38	108.57	104.57	95.94	100.66	105.30	99.54	113.42	123.57	116.67	107.58	129.46	99.58	121.20	97.74	110.71	96.71	95.38	93.29	103.47	110.47	103.03	9.7
Clorpirifos	115.51	90.76	110.52	104.28	111.15	107.27	123.31	114.90	116.19	108.94	112.40	111.25	108.28	114.24	93.82	99.92	107.52	100.55	95.61	99.02	107.22	111.42	8.1
Clorpirifos-m	89.35	101.35	111.95	105.46	99.39	94.58	110.55	114.57	108.84	106.35	101.86	94.62	98.49	112.85	102.79	105.56	93.37	83.06	88.16	93.25	106.25	104.87	8.6
Clorprofam	105.19	87.29	96.53	88.40	94.57	84.31	98.29	116.11	104.38	97.79	105.48	79.19	86.88	111.76	77.99	84.25	84.81	84.31	81.87	75.03	94.40	97.38	11.2
Clortal-dimetyl	107.19	86.32	109.67	106.12	105.86	94.02	97.99	112.60	112.63	104.15	115.95	131.01	98.14	114.08	109.64	106.48	95.97	92.30	89.03	85.41	100.56	110.03	10.9
Clortiofos	118.74	116.64	2.44	133.70	114.33	116.80	110.79	112.27	86.72	69.83	104.20	106.74	104.20	115.01	109.18	111.12	100.97	97.29	93.92	79.80	114.08	130.93	14.7
Deltametrin	122.04	108.47	132.55	101.30	98.72	98.80	107.01	118.12	114.93	108.88	124.03	105.82	102.36	115.51	106.88	60.99	94.95	70.77	99.62	85.81	107.60	114.99	16.4
Diazinon	110.97	95.34	105.40	105.61	101.58	91.73	104.33	113.59	108.41	107.35	104.35	92.43	103.70	114.82	99.09	101.16	97.51	103.39	93.98	98.23	103.88	109.66	6.5
Diclofluanida	114.47	92.43	101.37	91.03	93.42	90.55	93.17	106.08	108.25	90.97	114.10	105.55	91.97	93.28	84.69	61.69	86.77	88.83	81.03	93.16	105.95	101.70	11.9
Difenilamina	89.33	89.41	89.29	91.12	100.08	93.36	97.91	96.30	92.74	95.42	88.55	76.76	85.78	94.83	86.44	90.73	88.35	69.00	79.24	98.67	92.99	85.62	4.0
Diflufenican	97.76	71.11	106.34	132.94	92.25	106.76	98.34	97.31	117.40	107.01	101.51	98.08	95.31	107.49	81.24	76.24	78.11	75.30	92.43	86.18	80.54	95.14	14.9
Endosulfan a	92.58	66.01	97.68	112.91	99.71	106.64	100.50	118.12	113.57	100.87	100.46	90.93	102.05	116.80	97.55	103.75	101.93	84.84	96.03	89.58	118.67	108.97	12.15
Endosulfan b	93.56	109.71	124.27	106.98	102.83	99.29	96.31	113.43	106.92	112.44	101.31	95.04	107.58	112.11	104.86	103.53	86.04	93.78	86.54	105.03	114.58	105.81	9.33
Endosulfan Sulf.	94.33	107.84	91.25	80.73	76.53	99.40	85.81	111.32	113.80	133.19	97.19	82.98	92.68	102.58	93.47	106.73	94.99	72.67	79.96	97.25	96.81	95.11	13.8
Esfenvalerate	98.78	104.08	116.46	101.98	98.79	101.78	100.84	114.42	110.97	104.52	109.81	94.55	104.81	119.58	104.47	108.17	93.83	77.65	91.64	92.85	108.24	103.83	9.3
Etion	118.00	111.41	97.48	124.57	106.21	99.43	107.61	117.61	117.67	104.86	111.67	110.02	104.07	112.70	107.45	111.55	91.99	97.15	102.29	95.80	117.91	125.80	9.2
Etofenprox	120.59	110.41	125.87	119.09	113.58	98.75	113.88	117.84	116.57	111.95	121.99	108.67	103.30	126.14	113.96	98.06	99.14	104.53	107.94	97.20	117.28	125.64	9.3
Etoprofos	95.95	93.06	96.12	94.57	100.77	65.87	108.95	111.52	106.85	104.58	102.25	92.47	88.40	106.76	102.00	93.58	84.64	74.27	79.04	89.20	103.08	102.50	11.6
Fenpropatrin	115.76	104.03	105.84	115.65	101.79	93.75	92.38	121.12	127.06	102.07	114.21	100.94	102.68	134.62	109.31	92.48	79.75	101.41	85.36	93.22	116.30	109.83	13.4
Fention	86.12	96.78	111.06	111.88	108.55	110.87	90.49	94.85	100.52	99.13	113.13	108.13	110.48	79.47	97.27	100.20	89.47	95.93	88.16	101.94	104.77	110.33	9.6
Fipronil	110.83	72.82	252.23	73.10	62.15	89.99	67.15	116.85	72.31	96.86	101.39	135.30	95.53	76.30	81.54	108.38	85.01	82.78	80.05	99.99	70.06	63.53	16.4
Fluvalinato (+iso)	126.56	102.07	125.10	100.64	95.71	101.78	98.15	116.55	118.49	109.45	119.62	104.40	116.12	121.13	97.94	127.12	99.85	95.52	104.68	102.13	107.39	116.78	10.6
Fosalone	91.84	118.22	118.13	91.85	91.83	105.48	122.02	114.27	118.15	106.62	95.42	87.86	101.55	106.76	99.13	90.66	92.11	78.86	91.92	104.24	107.80	114.32	12.0

Iprodione	95.67	108.02	73.36	94.66	84.88	95.83	90.45	114.94	108.66	115.30	99.29	63.02	93.33	99.26	95.36	111.81	83.71	67.09	87.33	91.03	107.00	79.83	14.5
Isofenfos-metil	116.58	107.47	112.48	110.40	109.27	107.58	105.65	117.68	114.12	103.35	104.19	107.83	95.65	105.29	96.94	103.70	94.73	91.89	95.36	93.00	115.41	117.63	8.3
Lindano	96.03	69.35	96.75	100.89	102.72	87.12	94.67	122.11	84.65	84.10	102.40	134.87	97.03	100.27	80.83	88.48	102.83	87.95	85.07	90.40	88.42	99.21	13.8
Metalaxil	81.80	57.60	107.26	93.81	83.65	101.74	98.20	111.64	104.79	102.23	94.66	89.04	93.79	109.02	87.92	106.66	78.48	77.34	84.48	102.47	106.60	100.62	13.2
Metidation	103.43	65.63	94.46	96.12	91.20	86.99	107.17	112.97	104.65	102.26	106.15	107.40	110.56	105.70	90.35	105.86	82.27	91.69	79.78	93.95	109.62	107.04	11.9
Miclobutanil	84.76	101.95	90.17	87.42	66.90	100.68	91.36	111.55	116.70	99.82	90.44	78.01	97.32	99.32	93.39	130.83	81.49	74.36	84.60	90.41	101.12	90.32	14.2
Nuarimol	115.59	98.88	106.08	94.92	79.58	90.61	83.55	100.95	110.02	94.33	89.92	82.81	84.72	105.98	87.88	108.61	79.34	72.88	78.19	83.99	111.32	106.54	12.7
0rtofenilfenol	75.94	80.96	90.30	82.16	90.33	78.10	89.42	95.30	88.74	91.45	82.04	76.96	78.37	89.18	77.50	86.18	78.64	71.38	77.05	92.92	88.27	81.80	6.6
Paration-metil	118.70	62.57	98.15	90.24	84.04	99.77	101.36	105.76	115.47	102.41	107.46	83.13	120.31	102.53	77.96	102.92	63.64	88.13	81.09	92.93	97.12	105.53	15.6
Permetrin	105.00	103.11	125.58	113.62	111.72	102.27	105.73	108.10	109.57	111.90	110.43	95.95	116.93	123.61	113.62	100.33	95.14	89.07	100.24	100.75	115.39	115.47	9.1
Piridaben	94.26	91.59	127.78	93.06	99.05	108.22	109.13	123.37	99.36	96.31	115.06	108.91	105.10	107.32	95.63	91.65	60.72	77.51	99.77	83.32	117.17	91.03	15.1
Pirimetanil	90.87	103.02	104.44	93.84	88.59	106.40	88.38	103.19	119.24	139.43	103.04	92.61	103.51	115.57	94.73	105.32	92.81	88.68	85.38	84.84	115.56	98.23	13.1
Pirimicarb	63.58	62.32	82.78	71.61	67.25	87.55	87.77	82.91	74.19	63.02	69.85	61.74	72.88	62.37	69.04	69.66	65.68	70.83	60.58	74.04	92.69	81.53	9.5
Pirimifos-metil	92.44	105.37	109.10	106.96	94.44	106.93	103.45	109.22	113.19	108.53	103.04	91.44	105.37	99.58	93.88	114.88	94.62	83.52	90.57	98.00	107.21	102.41	8.2
Piriproxifen	113.23	101.73	119.30	91.42	98.97	94.91	106.92	111.42	117.12	103.76	101.72	102.68	93.92	121.60	93.60	113.48	103.33	105.55	92.53	109.31	105.92	124.08	9.6
Procimidona	91.72	98.61	115.12	106.07	100.82	99.16	95.64	101.18	105.47	104.19	100.17	106.61	94.66	120.33	105.20	105.00	89.18	80.31	85.71	99.74	119.22	103.16	9.8
Profenofos	117.41	105.93	64.96	107.86	104.26	104.13	127.17	119.92	116.16	109.87	108.79	100.68	110.71	136.79	98.67	84.39	84.28	102.93	98.39	108.00	106.29	129.56	15.7
Propiconazol (+iso)	107.78	105.09	112.44	94.29	85.48	93.42	110.09	106.12	92.36	96.91	98.39	80.07	106.33	130.19	83.35	96.24	87.74	98.25	76.73	97.12	87.01	122.50	13.3
Propizamida	110.81	100.18	93.23	96.79	89.36	105.32	90.24	114.90	111.02	101.97	103.16	79.38	111.14	100.72	95.49	109.17	87.02	82.30	83.63	111.77	117.22	108.33	11.3
Protiofos	118.95	107.26	115.18	117.42	116.66	108.06	115.73	112.01	112.02	106.09	109.07	109.51	100.29	122.18	111.74	113.27	88.16	98.07	97.54	91.05	121.44	118.87	9.4
Pyrifenox I	101.37	64.64	102.12	74.37	100.85	98.00	85.65	110.93	101.50	80.34	83.73	116.36	77.98	93.99	78.60	97.08	72.30	70.95	77.09	73.65	95.53	95.71	13.5
Pyrifenox II	103.32	89.39	102.42	76.33	88.55	91.71	82.72	107.11	109.47	88.08	84.49	80.53	77.90	87.54	80.96	101.98	83.51	76.98	79.86	76.70	101.47	96.66	10.7
Quinalfos	124.87	91.84	110.80	103.66	104.69	103.80	108.89	116.13	123.06	103.52	106.89	92.67	109.56	106.91	96.77	98.60	95.34	102.54	94.68	98.01	113.50	110.00	9.0
Quinoxyfen	106.37	88.64	113.57	99.00	79.81	104.58	83.32	108.41	113.74	97.85	103.28	74.27	109.40	114.25	92.22	99.02	96.50	100.31	92.04	93.28	105.21	111.98	11.2
Tebuconazol	112.87	93.75	114.59	96.97	92.29	96.96	90.39	107.85	118.27	100.55	103.38	94.05	97.26	104.62	96.59	105.22	96.43	92.51	82.62	87.42	101.93	108.77	9.0
Tebufenpirad	126.00	91.60	113.05	107.96	104.54	116.10	104.96	120.03	115.63	109.28	114.88	99.15	95.88	113.64	96.38	87.26	100.64	85.87	97.85	101.84	122.65	117.84	11.4
Terbufos	103.22	79.38	98.55	105.89	100.96	81.63	97.30	108.97	106.56	102.95	98.40	92.06	93.26	102.70	101.51	98.28	91.99	83.36	81.65	83.97	93.54	105.27	9.1
Tetraconazol	94.31	65.31	86.19	88.83	68.95	92.90	82.19	95.50	99.06	97.45	109.95	96.51	80.76	89.08	99.68	104.97	64.47	81.30	77.90	82.94	109.25	110.51	13.6
Tetradifon	115.99	97.44	110.77	99.30	92.85	105.08	96.96	117.19	115.52	108.15	104.75	88.52	104.34	107.12	95.14	98.10	96.53	94.02	90.34	98.81	95.87	109.68	8.4
Tolclofos -metil	117.38	73.52	104.43	102.47	100.95	98.57	105.85	106.51	121.18	99.93	102.47	90.28	94.91	119.93	92.84	107.79	100.34	95.67	90.30	102.26	106.06	109.88	10.6
Tolifluanida	112.29	95.63	107.22	100.04	99.33	103.44	94.22	111.88	107.61	107.10	99.90	89.32	104.02	107.58	94.71	90.04	99.40	90.66	88.32	101.43	107.43	107.53	7.4
Trifluralina	101.84	105.13	97.29	104.99	103.21	91.68	113.35	120.60	100.04	104.12	100.26	99.49	88.05	103.54	95.75	100.13	119.08	80.00	87.25	90.37	101.01	105.00	9.7
Vinclozolin	108.52	91.62	111.58	103.94	94.02	100.05	95.89	112.72	113.59	104.34	104.27	89.31	104.77	107.38	92.29	108.06	89.25	90.79	91.49	94.13	103.08	106.59	8.1
Mean																							**11.0**