Recovery Correction and its impact on measurement uncertainty: Data from QuEChERS Verifications

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Introduction

In pesticide residue analysis, most laboratories use the pragmatic approach for measurement uncertainty (MU) estimation given in the SANCO document 10684/2009 [1a]: based on the experiences from EUPTs [2], "*a default expanded uncertainty figure of 50% (corresponding to a 95% confidence level and a coverage factor of 2), in general covers the inter-laboratory variability between the European laboratories and is recommended to be used by regulatory authorities in cases of enforcement decisions (MRL-exceedences).*" As prerequisite to be allowed to use this default expanded MU, laboratories have to prove that their own (within laboratory) expanded MU is smaller than 50% [1a]. This is done using data obtained from method validation, quality controls, and/or PT results, i.e. data sources with a limited number of representative analytes.

Since the Turkish Accreditation Body, TÜRKAK, does not accept the use of representative analytes for method validation, two within-laboratory verifications of the QuEChERS method for a total of 546 pesticides analyzed by LC-MS/MS and GC-MS were carried out using the approach of the IUPAC/AOAC/ISO "Harmonized Guidelines for Single-Laboratory Validation of Methods of Analysis" [3] with ANOVA calculation of the results. With this multitude of data, individual MU estimations were calculated for all analytes considering the effects of a possible recovery correction.

Sources of uncertainty in QuEChERS

Based on the work flow of the QuEChERS method, an Ishikawa diagram was drawn to find the contributing standard uncertainties (Figure 1 step 1). Since balances, volumetric measuring devices and environmental conditions were under regular control, and the verification studies were carried out over a longer period of time with variations in analysts, laboratory tools, and calibrations, it can be assumed, that the influences of the variability of most sources on the measurement uncertainty are covered by the within-laboratory precision. The only source exempted from this assumption is the purity of the standard materials, which were used for the preparation of the calibration standard solutions as well as for spiking the samples in the precision and trueness studies. While their average content was compensated during initial weighting, the uncertainty in content must be considered twice, as possible errors might occur in both, standard solutions and spiked samples. Taking these assumptions into consideration, the Ishikawa diagram could be simplified as shown in step 2. During the evaluation of the individual results, it could be seen, that the effect of standard purity was negligible for all analytes. Thus, the Ishikawa diagram could be further simplified by reducing the important sources of measurement uncertainty to precision and trueness, i.e. intermediate (or within-laboratory) reproducibility and recovery (step 3).

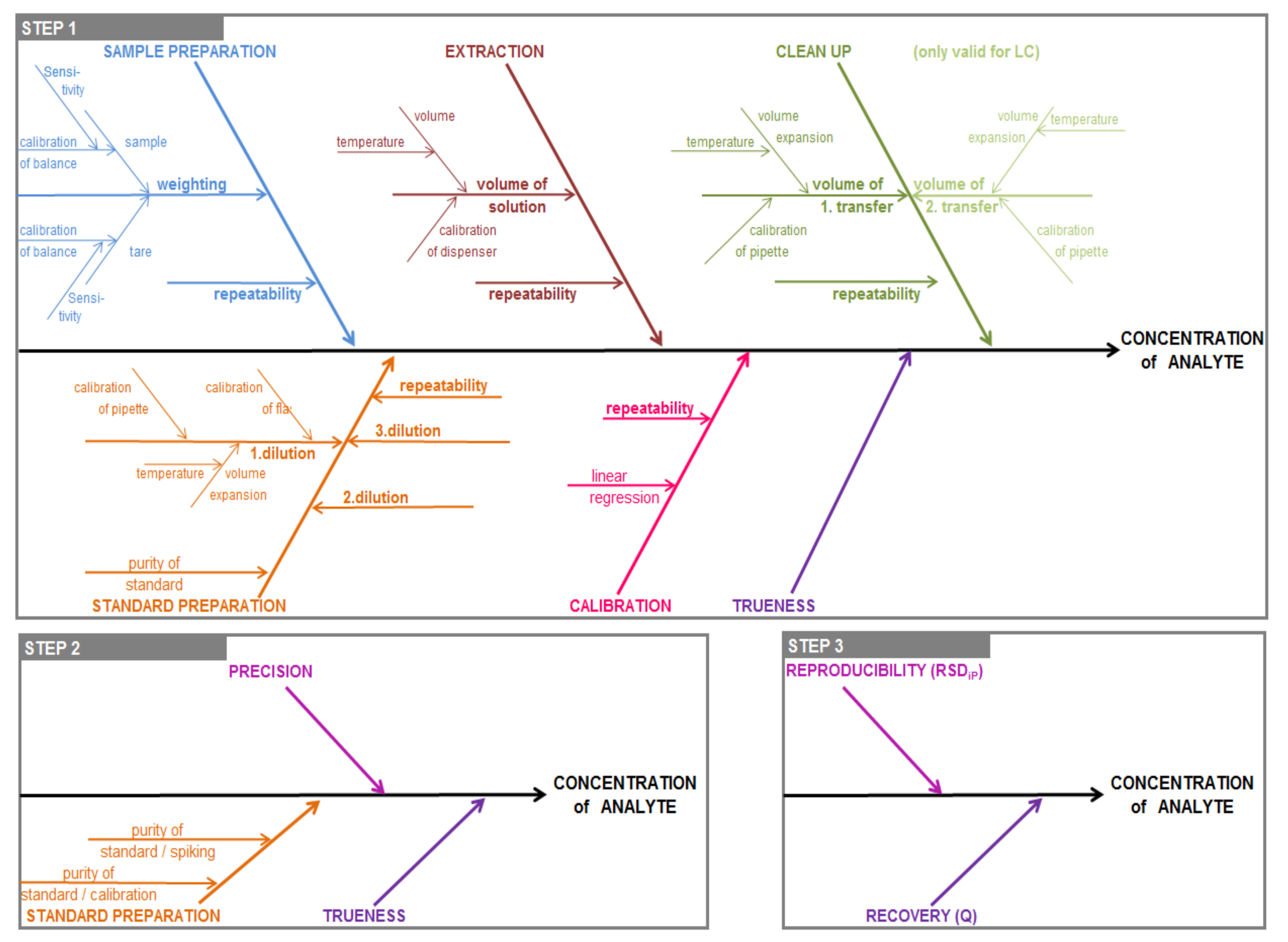

Fig. 1: Ishikawa diagrams for the QuEChERS method

Calculating uncertainty from recovery and combined uncertainty

Whether to correct the result of an analysis for recovery or not, and how this decision influences the MU estimation, was calculated according to the "*Protocol for uncertainty evaluation from validation data*" [4]. Recovery correction is not necessary, if the recovery value is not significantly different from 1 when compared to the precision for the individual analyte. This comparison is done by means of a t Test (Formula 1).

In case the recovery value is not significantly different from 1 (which was true for 59 out of 546 analytes, i.e. 10,8%) or the recovery is significantly different from 1, but is corrected using a correction factor derived from the average recovery obtained in method validation studies, the uncertainty from trueness can be estimated as the uncertainty of the average recovery value via formula 2. Thus, the combined MU for an individual analyte can be calculated from formula 3.

In case the recovery value is significantly different from 1 (shown by a negative t Test), but is not corrected, an additional term must be included to calculate the uncertainty from trueness (Formula 4). Thus, the combined MU for an individual analyte must be calculated from formula 5.

$$t = \frac{|1-Q|}{RSD_{iP}/\sqrt{n}} \quad (1)$$

$$\frac{u(Q)'}{Q} = \frac{RSD_{iP}}{\sqrt{n}\times Q} \quad (2)$$

$$\frac{u(y)'}{y} = \sqrt{RSD_{iP}^2 + \left(\frac{RSD_{iP}}{\sqrt{n}\times Q}\right)^2} \quad (3)$$

$$\frac{u(Q)''}{Q} = \sqrt{\left(\frac{RSD_{iP}}{\sqrt{n}\times Q}\right)^2 + \left(\frac{1-Q}{t_{crit}}\right)^2} \quad (4)$$

$$\frac{u(y)''}{y} = \sqrt{RSD_{iP}^2 + \left(\frac{RSD_{iP}}{\sqrt{n}\times Q}\right)^2 + \left(\frac{1-Q}{t_{crit}}\right)^2} \quad (5)$$

Theoretical Approach

With the above mentioned assumption of precision and trueness being the only important sources of uncertainty accepted, values for the MU can be calculated for each combination of reproducibility and recovery values acceptable according to the SANCO criteria [1b] (Figure 2 left). Using n = 100 (means a quite thoroughly method verification), the "worst case" (i.e. reproducibility = 20% and recovery = 70%) yields an expanded MU of 50,2 %, while the other extreme (reproducibility = 20% and recovery = 120%) adds up to 45,0 % for uncorrected results. Recovery correction would cease the influence of trueness nearly completely and improve expanded MU to a constant value of approx. 40% for poorest acceptable precision values (Figure 2 right).

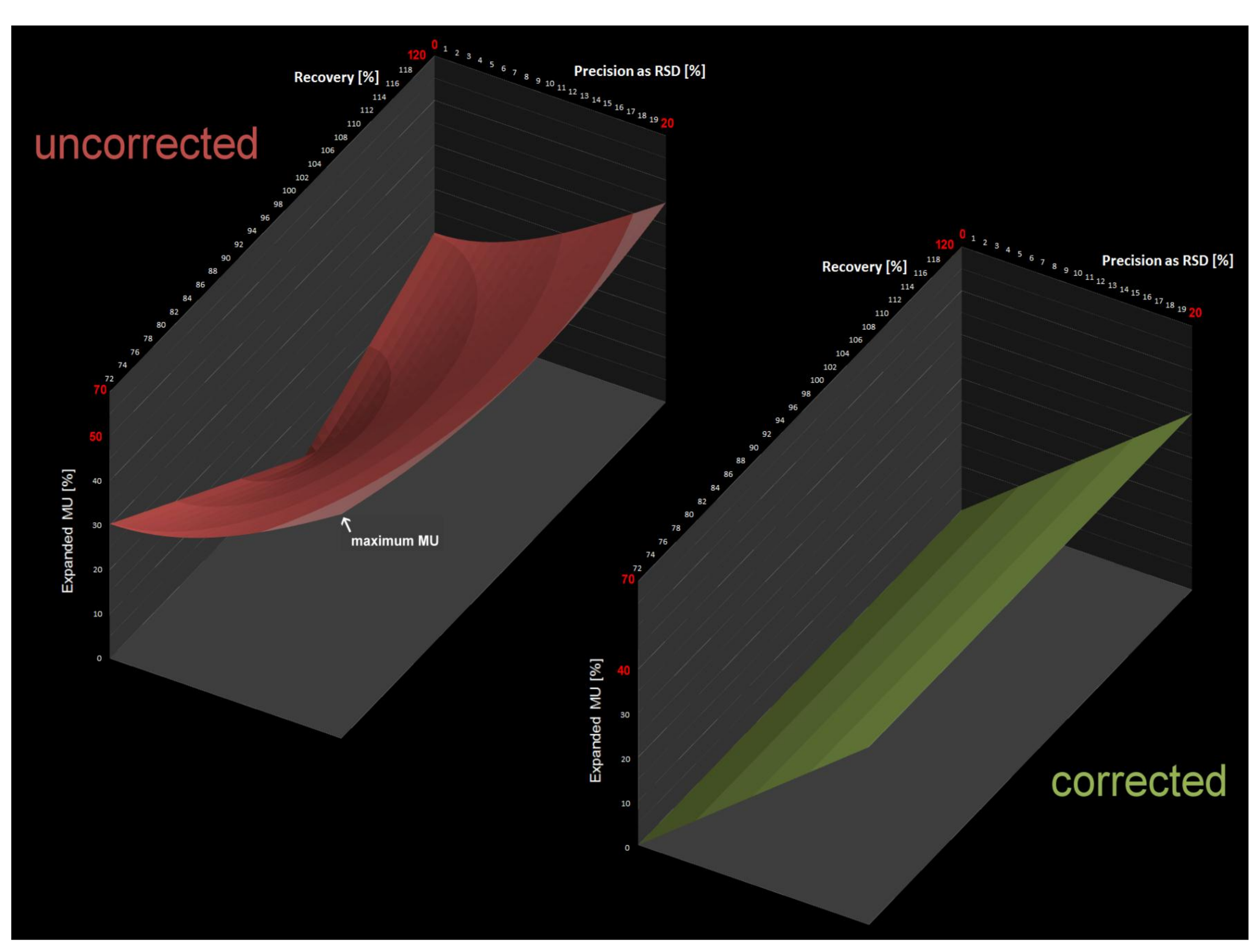

Fig. 2: Theoretical approach using RSD and Q values acceptable according to the SANCO criteria

Calculations from Verification Data

The same calculations were used for the results of each of the 546 analytes (Table 1). For uncorrected results, all expanded MUs were better than 46%, even for three analytes, which were included although they slightly failed the SANCO recovery criterion: Deltamethrin (69%), Dichlorvos (68%), and Bentazone (65%) (Figure 3 left). Again, recovery correction would yield a significant gain in the calculated uncertainty (Table 2): all expanded MUs would be better than 35% (Figure 3 right).

Tab. 2: Comparison of expanded MUs

uncorrected			corrected		
	no of analytes	portion		no of analytes	portion
MU < 25%	254	46,5%	MU < 25%	384	70,3%
25% < MU < 40%	282	51,6%	25% < MU < 35%	162	29,7%
40% < MU < 46%	10	1,8%			

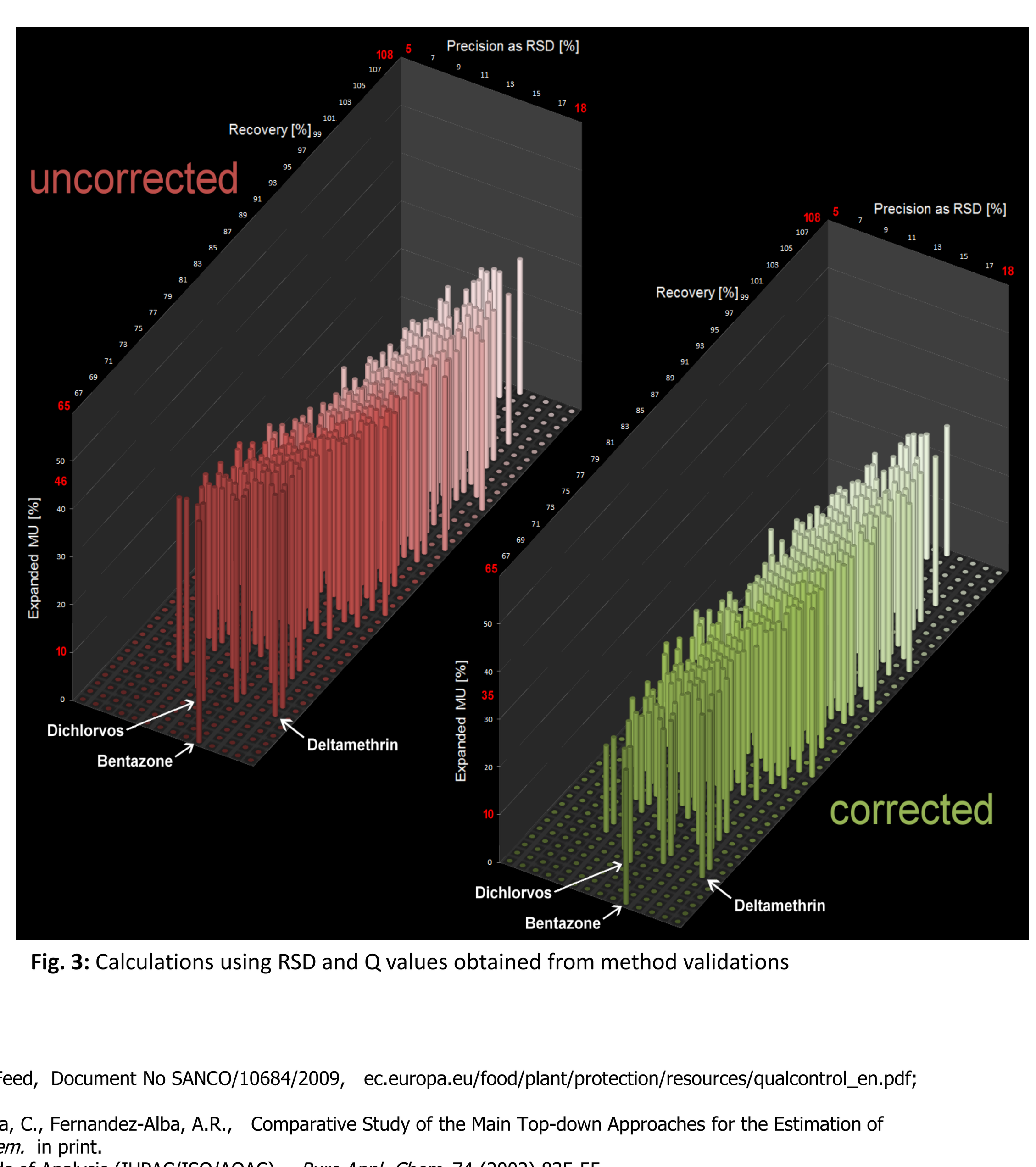

Fig. 3: Calculations using RSD and Q values obtained from method validations

Conclusion

For MRMs in pesticide analysis, the long lasting dispute on the advisability of recovery correction [5,6] was settled with the harmonization of Codex [7] and SANCO [8] recommendations on MU estimation. For laboratories involved in pesticide analysis, this consensus implied a remarkable facilitation: too huge efforts are required to create a sufficient data base for the recovery correction of each analyte within the scope of an up-to-date application of the MRM like QuEChERS during method validation/verification. (The values given in this poster are based on more than 86.000 measurements.) This, is hardly counterbalanced by the gain in MU. But applying the calculative principle of the "Harmonized Guidelines for Single-Laboratory Validation" on the results of ongoing quality controls using a rolling program covering all analytes [1c] in combination with convenient software solutions might offer an alternative approach with little extra expenses. Thus, the discussion on recovery correction in MRMs for pesticide analysis might be revived in near future.

Tab. 1: Verification data and expanded MUs for individual analytes (sorted by uncorrected expanded MUs)

No	Analyte	Validation results: RSD$_{iP}$	Validation results: Q	expanded MU: uncorr.	expanded MU: corrected
529	Triazamat	0,047	1,000	9,5	9,5
171	Dinotefuran	0,063	0,970	13,0	12,6
476	Silthiofam	0,067	1,000	13,6	13,6
229	Fenthion-oxon	0,046	0,895	14,1	9,3
92	Chlorthal-dimethyl	0,075	0,999	15,0	15,0
277	Fuberidazol	0,074	1,025	15,2	15,0
356	Methiocarb-Sulfoxide	0,073	1,040	15,2	14,7
247	Fluazifop-p-butyl	0,052	0,890	15,3	10,5
38	Bifenthrin	0,051	0,887	15,3	10,2
48	Bromopropylate	0,056	0,894	15,5	11,2
280	Halfenprox	0,078	1,008	15,8	15,7
62	Carbofuran-3-hydroxid	0,078	1,025	15,9	15,7
421	Pirimicarb-desmethyl	0,079	0,987	16,0	15,9
337	Mefenpyr diethyl	0,052	0,881	16,0	10,5
236	Fipronil	0,071	0,925	16,1	14,1
26	Beflubutamid	0,079	0,973	16,2	16,0
359	Methoxychlor	0,066	0,904	16,3	13,1
95	Chromafenozid	0,077	0,947	16,4	15,5
180	Disulfoton-sulfoxide	0,081	1,027	16,4	16,2
384	Nitrothal isopropyl	0,083	1,004	16,7	16,7
21	Azaconazole	0,081	0,965	16,7	16,3
209	Fenamiphos	0,082	0,972	16,7	16,5
177	Dipropetryn	0,077	0,934	16,8	15,4
422	Pirimicarb-desmethyl formamido	0,082	1,030	16,8	16,5
363	Metolcarb	0,083	0,997	16,8	16,8
514	Thiofanox-Sulfoxide	0,082	0,963	16,9	16,5
147	Dichlofenthion	0,084	0,991	16,9	16,9
278	Furalaxyl	0,073	0,914	16,9	14,6
543	Uniconazole	0,079	0,939	17,0	15,8
63	Carbophenothion	0,085	1,015	17,1	17,0
57	Cadusafos	0,080	0,942	17,1	16,1
361	Metobromuron	0,085	1,021	17,1	17,0
135	DDT, p-p	0,069	0,899	17,2	13,8
365	Metoxuron	0,083	0,950	17,3	16,6
513	Thiofanox-Sulfone	0,086	1,014	17,4	17,4
237	Fipronil-desulfinyl	0,050	0,857	17,6	10,0
197	Ethion	0,084	1,050	17,6	16,8
402	Pencycuron	0,081	0,933	17,6	16,3
291	Heptenophos	0,088	0,991	17,6	17,6
506	Thiabendazole	0,084	0,946	17,7	16,8
423	Pirimiphos-methyl	0,071	0,897	17,7	14,3
313	Isofenphos	0,086	0,957	17,9	17,4
232	Fenthion-Sulfoxide	0,089	1,005	17,9	17,9
504	Tetramethrin TOTAL	0,087	0,959	18,0	17,6
532	Trichloronat	0,089	0,965	18,3	18,0
312	Isodrin	0,088	0,952	18,4	17,7
98	Climbazol	0,090	0,967	18,4	18,1
498	Terbumeton	0,091	0,999	18,4	18,4
234	Fenuron	0,087	1,059	18,4	17,4
392	Oxadixyl	0,080	0,911	18,4	16,1
483	Spiroxamine	0,083	0,923	18,4	16,7
167	Dimetilan	0,092	0,990	18,5	18,5
453	Pyrazophos	0,073	0,887	18,5	14,6
428	Profluralin	0,091	0,972	18,6	18,4
489	Tebufenozid	0,083	0,916	18,6	16,6
224	Fenpropimorph	0,084	0,921	18,7	16,8
473	Secbumeton	0,093	0,997	18,7	18,7
79	Chlorfenvinphos	0,066	0,869	18,8	13,3
276	Fosthiazat	0,093	0,988	18,8	18,7
274	Formethanat	0,093	0,982	18,8	18,7
377	Napropamide	0,092	0,961	18,8	18,4
71	Chlorbenzilate	0,059	0,854	18,9	11,8
386	Norflurazon	0,088	1,066	19,0	17,7
400	Pebulat	0,091	0,949	19,0	18,3
501	Tetrachlorvinphos	0,090	0,936	19,1	18,0
355	Methiocarb-Sulfone	0,094	0,964	19,1	18,8
46	Bromophos-ethyl	0,065	0,860	19,3	13,0
160	Diflufenican	0,088	0,923	19,3	17,7
192	Etaconazole TOTAL	0,093	0,950	19,3	18,6
398	Parathion-ethyl	0,078	0,886	19,4	15,5
212	Fenbuconazole	0,095	0,964	19,4	19,0
172	Dioxacarb	0,095	1,040	19,5	19,1
155	Dicrotophos	0,093	0,941	19,6	18,7
486	Sulprofos	0,097	0,973	19,6	19,4
243	Florasulam	0,086	0,907	19,7	17,3
396	Paraoxon-Ethyl	0,098	0,980	19,7	19,6
32	Benoxacor	0,097	1,030	19,8	19,6
195	Ethiofencarb-Sulfone	0,097	0,963	19,9	19,5
357	Methomyl	0,099	1,005	19,9	19,9
510	Thiobencarb	0,095	0,942	19,9	19,0
36	Bifenazate	0,097	0,959	19,9	19,5
118	Cyhalofop-butyl	0,078	0,877	19,9	15,5
430	Promecarb	0,099	0,981	19,9	19,8
2	Acephat	0,080	0,882	19,9	16,0
14	Allethrin	0,095	0,937	20,0	19,0
149	Dichlofop-methyl	0,072	0,863	20,1	14,5
22	Azadiractrin	0,098	0,958	20,1	19,6
409	Perthan	0,091	0,919	20,1	18,3
218	Fenobucarb	0,098	0,962	20,1	19,7
306	Iprobenfos	0,100	1,007	20,1	20,1
373	Monocrotophos	0,097	0,948	20,2	19,5
389	Ofurace	0,093	0,922	20,2	18,6
322	Isoxathion	0,100	0,971	20,2	20,0
52	Butacarboxim Sulfoxide	0,087	0,898	20,3	17,5
169	Diniconazole	0,098	0,948	20,4	19,7
496	Terbacil	0,097	0,941	20,4	19,5
245	Fluazifop-butyl	0,093	0,917	20,5	18,7
490	Tebufenpyrad	0,098	0,945	20,5	19,7
519	Tolfenpyrad	0,094	0,921	20,5	18,9
153	Dicloran	0,102	0,989	20,5	20,5
103	Cloquintocet-mexyl	0,097	0,933	20,5	19,4
231	Fenthion-Sulfone	0,102	0,975	20,6	20,5
465	Quinoxyfen	0,059	0,833	20,6	11,7
219	Fenoxaprop-p-ethyl	0,092	0,911	20,6	18,6
196	Ethiofencarb-Sulfoxide	0,099	0,944	20,6	19,8
295	Hexazinone	0,101	0,961	20,7	20,3
310	Isocarbamid	0,103	1,000	20,7	20,7
494	Tefluthrin	0,097	0,933	20,7	19,6
380	Nitenpyram	0,083	0,879	20,7	16,8
481	Spirodiclofen	0,101	0,957	20,8	20,3
446	Prosulfocarb	0,091	0,900	20,8	18,2
226	Fenson	0,102	0,959	20,8	20,4
102	Clopyralid	0,099	0,935	20,8	19,8
42	Bromacil	0,100	0,946	20,9	20,1
416	Picolinafen	0,089	0,892	20,9	17,8
350	Methabenzthiazuron	0,100	0,942	21,0	20,2
88	Chlorpropylat	0,099	0,931	21,0	19,8
242	Flonicamid	0,095	0,912	21,1	19,1
308	Iprovalicarb	0,100	0,938	21,1	20,1
168	Dimoxystrobin	0,105	0,998	21,1	21,1
104	Clothianidin	0,101	0,944	21,1	20,4
35	Benthiavalicarb-isopropyl	0,103	0,953	21,1	20,6
407	Pentachlorphenol	0,096	0,913	21,2	19,3
266	Flusilazole	0,102	0,946	21,2	20,5
53	Butafenacil	0,100	0,930	21,2	20,0
258	Fluometuron	0,100	1,066	21,3	20,2
417	Picoxystrobin	0,100	0,932	21,3	20,1
451	Pyraclostrobin	0,106	0,982	21,3	21,2
15	Ametryn	0,102	1,055	21,3	20,6
330	Linuron	0,106	1,006	21,4	21,3
28	Bendiocarb	0,105	0,967	21,4	21,2
338	Mepanipyrim	0,102	0,937	21,4	20,5
264	Fluprimidol	0,096	0,906	21,4	19,2
282	Haloxyfop-2-etoxy-ethyl	0,100	0,924	21,4	20,0
360	Methoxyfenozid	0,106	0,973	21,4	21,3
439	Propetamphos	0,106	0,968	21,5	21,2
290	Heptachlorepoxide, cis (exo)	0,107	0,998	21,6	21,6
375	Monuron	0,107	0,976	21,6	21,4
408	Permethrin TOTAL	0,068	0,835	21,6	13,6
334	Mandipropamid	0,105	0,956	21,6	21,1
61	Carbofuran	0,104	0,947	21,6	20,9
262	Fluoxastrobin	0,104	0,942	21,6	20,8
176	Diphenylamine	0,099	0,910	21,8	19,8
152	Diclobutrazol	0,103	0,928	21,8	20,6
283	Haloxyfop-p-methyl	0,109	1,013	21,9	21,8
471	Rotenon	0,105	0,942	21,9	21,1
372	Monalid	0,090	0,877	21,9	18,0
261	Fluotrimazol	0,107	0,963	21,9	21,6
259	Fluopicolid	0,109	0,983	22,0	21,9
474	Sethoxydim	0,100	0,911	22,0	20,1
45	Bromocyclen	0,107	0,956	22,0	21,5
6	Acibenzolar-S-Methyl	0,108	0,965	22,1	21,8
424	Primiphos-ethyl	0,110	0,979	22,1	22,0
150	Dichlorbenzofenon-4,4'	0,097	0,896	22,1	19,5
464	Quinoclamine	0,107	0,945	22,1	21,5
340	Mepronil	0,097	0,895	22,2	19,5
117	Cyfluthrin gamma+delta	0,101	0,907	22,3	20,2
190	EPTC	0,109	0,954	22,3	21,8
29	Benfluralin	0,103	0,917	22,3	20,7
78	Chlorfenson	0,108	0,946	22,3	21,7
72	Chlorbromuron	0,092	0,877	22,4	18,6
383	Nitrofen	0,111	0,975	22,4	22,2
463	Quinalphos	0,081	0,848	22,4	16,3
440	Propham	0,110	0,967	22,4	22,2
336	Mecarbam	0,108	0,938	22,5	21,6
109	Cyanofenphos	0,111	1,031	22,5	22,3
299	Imazethapyr	0,111	0,967	22,5	22,3
256	Flufenoxuron	0,110	0,953	22,5	22,0
523	Transfluthrin	0,105	0,922	22,5	21,1
205	Etrimfos	0,099	0,894	22,5	19,8
378	Neburon	0,087	0,858	22,6	17,5
522	Tralkoxydim	0,102	0,906	22,6	20,5
111	Cyazofamid	0,112	0,988	22,6	22,6
339	Mepiquat	0,112	0,967	22,7	22,4
31	Benodanil	0,107	1,070	22,7	21,5
370	Mirex	0,104	0,911	22,7	20,8
37	Bifenox	0,108	0,934	22,7	21,7
534	Tricyclazol	0,112	1,033	22,7	22,5
253	Flucythrinate TOTAL	0,083	0,846	22,8	16,6
450	Pymetrozin	0,109	0,934	22,8	21,8
530	Triazophos	0,093	0,869	22,9	18,7
181	Ditalimfos	0,091	0,863	22,9	18,3
86	Chloroxon	0,109	0,930	22,9	21,8
391	Oxadiazon	0,107	0,919	23,0	21,4
484	Sulfentrazon	0,112	0,956	23,0	22,5
23	Azinphos-ethyl	0,091	0,863	23,0	18,3
404	Pentachloranilin	0,095	0,874	23,0	19,1
161	Dimepiperat	0,110	0,934	23,0	22,0
30	Benfuracarb	0,112	0,954	23,0	22,6
314	Isofenphos-Methyl	0,111	0,937	23,1	22,2
139	Demeton-S-methyl sulfone	0,100	0,887	23,1	20,1
309	Isazophos	0,094	0,867	23,1	18,8
491	Tebutam	0,102	0,894	23,2	20,6
125	Cyproconazole TOTAL	0,113	0,954	23,2	22,7
395	Paclobutrazol	0,110	0,930	23,2	22,1
344	Metalaxyl	0,112	0,939	23,4	22,5
250	Flubendiamid	0,116	1,020	23,4	23,3
203	Etoxazol	0,113	0,942	23,4	22,6
179	Disulfoton-Sulfon	0,111	1,074	23,5	22,2
127	Cyromazin	0,108	0,909	23,5	21,6
108	Cyanazin	0,108	0,912	23,5	21,8
202	Ethoxyquin	0,115	0,955	23,5	23,1
358	Methoprothryn	0,117	1,001	23,5	23,5
527	Triamiphos	0,116	1,027	23,5	23,4
82	Chlormephos	0,114	0,946	23,5	22,9
16	Aminocarb	0,108	0,909	23,6	21,7
114	Cyflufenamid	0,106	0,898	23,6	21,2
298	Imazaquin	0,116	0,969	23,6	23,4
472	S421	0,115	0,951	23,6	23,1
157	Diethofencarb	0,114	0,940	23,6	22,9
405	Pentachloranisol	0,107	0,900	23,7	21,4
394	Oxyfluorfen	0,084	0,835	23,7	16,8
140	Demeton-S-methyl sulfoxide	0,088	0,844	23,7	17,6
351	Methacrifos	0,117	0,977	23,7	23,6
452	Pyrafluofen-ethyl	0,112	0,926	23,7	22,5
385	N-naphtylacetamide	0,116	0,956	23,8	23,3
67	Carfentrazon-ethyl	0,118	1,005	23,8	23,8
343	Metaflumizon	0,117	0,955	23,9	23,4
426	Procymidone	0,071	0,810	23,9	14,1
319	Isoxaben	0,118	0,969	23,9	23,7
7	Aclonifen	0,119	0,998	24,0	24,0
40	Bitertanol TOTAL	0,071	0,809	24,0	14,2
252	Fluchloralin	0,119	0,976	24,0	23,9
332	Malaoxon	0,111	0,912	24,0	22,3
410	Phenmedipham	0,120	0,988	24,1	24,0
24	Azinphos-methyl	0,118	0,958	24,1	23,7
101	Clomazon	0,116	0,940	24,1	23,3
107	Crimidin	0,120	0,987	24,1	24,1
467	Quizalofop free acid	0,107	0,892	24,1	21,5
341	Mesosulfuron-Methyl	0,120	0,980	24,1	24,0
419	Piperonyl-butoxid	0,114	0,924	24,2	22,9
388	Nuarimol	0,112	0,910	24,2	22,4
255	Flufenacet	0,117	0,947	24,2	23,6
435	Propanil	0,116	0,936	24,3	23,4
223	Fenpropidin	0,112	0,910	24,3	22,5
124	Cyphenothrin	0,116	0,933	24,3	23,3
485	Sulfotep	0,117	1,064	24,4	23,5
304	Iodosulfuron-Methyl	0,109	0,893	24,5	22,0
528	Triasulfuron	0,116	0,928	24,5	23,4
479	Spinosad A	0,112	0,904	24,5	22,5
268	Flutolanil	0,118	0,939	24,5	23,7
105	Coumaphos	0,104	0,871	24,5	20,8
136	Deet	0,111	0,896	24,6	22,2
540	Triflusulfuron-methyl	0,108	0,885	24,6	21,7
499	Terbutryn	0,119	1,059	24,6	23,9
77	Chlorfenapyr	0,120	0,948	24,7	24,1
345	Metalaxyl-M	0,108	0,882	24,7	21,6
461	Pyrimidifen	0,105	0,873	24,7	21,2
415	Phosphamidone TOTAL	0,104	0,868	24,8	20,9
346	Metalochlor	0,082	0,817	24,8	16,5
459	Pyrifenox	0,117	0,916	24,9	23,4
397	Paraoxon-Methyl	0,110	0,886	24,9	22,1
269	Flutriafol	0,120	0,933	24,9	24,0
211	Fenazaquin	0,104	0,865	24,9	20,9
317	Isoprothiolane	0,119	0,925	25,0	23,9
315	Isofenphos-oxon	0,120	0,930	25,1	24,1
432	Prometryn	0,121	1,063	25,2	24,4
131	DDD, p-p	0,077	0,803	25,2	15,4
178	Disulfoton	0,125	0,986	25,2	25,2
134	DDT, o-p	0,094	0,834	25,2	18,8
20	Atrazine	0,114	0,892	25,3	22,8
99	Clodinafop-propargyl	0,126	0,988	25,3	25,3
47	Bromophos-methyl	0,069	0,791	25,3	13,8
433	Promopocarb	0,085	0,816	25,3	17,1
84	Chloroneb	0,108	0,872	25,3	21,7
130	DDD, o-p	0,073	0,796	25,4	14,7
141	Desmedipham	0,120	0,921	25,4	24,1
241	Flamprop-methyl	0,123	0,946	25,4	24,8
367	Metrofenon	0,110	0,876	25,4	22,1
502	Tetraconazole	0,122	0,937	25,4	24,6
19	Anthraquinone	0,120	0,917	25,4	24,0
300	Imazosulfuron	0,120	0,918	25,5	24,1
342	Mesotrione	0,112	0,880	25,5	22,4
146	Dichlobenil	0,115	0,891	25,6	23,1
163	Dimethanamid	0,115	0,890	25,6	23,0
133	DDE, p-p	0,073	0,793	25,6	14,6
320	Isoxadifen-Ethyl	0,127	0,999	25,6	25,6
420	Pirimicarb	0,085	0,811	25,7	17,0
187	Endosulfan sulfate	0,070	0,788	25,7	14,1
121	Cypermethrin alpha	0,089	0,818	25,7	17,9
521	Topramezon	0,121	0,915	25,7	24,3
221	Fenpiclonil	0,123	0,925	25,8	24,7
447	Prosulfuron	0,124	0,933	25,9	24,9
535	Tridemorph	0,085	0,806	25,9	17,0
538	Triflumuron	0,127	0,957	26,0	25,6
227	Fensulfothion	0,128	1,030	26,0	25,8
265	Fluquinconazole	0,124	0,928	26,0	25,0
500	Terbutylazine	0,092	0,818	26,1	18,5
412	Phenylphenol, o-	0,111	0,863	26,2	22,2
162	Dimethachlor	0,130	0,983	26,2	26,2
352	Methamidophos	0,097	0,826	26,2	19,4
239	Fipronil-Sulfon	0,122	0,906	26,3	24,5
25	Azoxystrobin	0,123	0,911	26,3	24,7
89	Chlorpyriphos	0,084	0,801	26,3	16,8
260	Fluorochloridone	0,078	0,792	26,3	15,7
271	Fonofos	0,123	0,910	26,3	24,7
64	Carbophenthion-methyl	0,131	0,973	26,4	26,3
8	Acrinathrin	0,107	0,848	26,4	21,4
301	Imibenconazole	0,127	0,932	26,5	25,5
249	Fluazuron	0,130	0,960	26,5	26,2
505	Tetrasul	0,095	0,817	26,5	19,0
431	Prometon	0,114	0,868	26,5	23,0
267	Fluthiacet-methyl	0,130	0,954	26,5	26,1
362	Metolachlor	0,123	0,905	26,5	24,7
96	Cinosulfuron	0,110	0,855	26,6	22,2
294	Hexaflumuron	0,115	0,869	26,6	23,1
144	Diazinon	0,105	0,839	26,6	21,0
230	Fenthion-oxon Sulfoxide	0,066	0,771	26,6	13,2
90	Chlorpyriphos-methyl	0,093	0,812	26,6	18,6
445	Proquinazid	0,129	0,938	26,7	25,9
349	Metconazole	0,121	0,889	26,7	24,2
273	Forchlorfenuron	0,133	1,007	26,7	26,7
333	Malathion	0,108	0,845	26,8	21,6
475	Silafluofen	0,121	0,888	26,8	24,3
145	Dicamba	0,128	0,923	26,8	25,6
213	Fenbutatin-oxid	0,131	0,948	26,8	26,3
93	Chlorthiophos	0,134	0,981	26,9	26,8
509	Thifensulfuron-Methyl	0,117	0,871	27,0	23,6
66	Carboxin	0,117	0,870	27,0	23,5
5	Acetochlor	0,093	0,809	27,0	18,7
302	Imidacloprid	0,110	0,847	27,0	22,1
123	Cypermethrin gamma+delta	0,110	0,847	27,0	22,1
43	Bromfenvinphos	0,133	1,037	27,0	26,7
11	Aldicarb sulfone	0,116	0,864	27,0	23,3
94	Chlozolinat	0,109	0,841	27,1	21,8
263	Fluoxypyr-1-methylheptyl	0,129	0,918	27,1	25,9
27	Benalaxyl	0,087	0,795	27,2	17,4
374	Monolinuron	0,109	0,841	27,2	21,8
456	Pyridaben	0,121	0,878	27,3	24,3
281	Haloxyfop	0,132	0,936	27,3	26,6
54	Butocarboxim	0,136	0,979	27,3	27,3
455	Pyrethrins 2	0,136	1,003	27,3	27,3
210	Fenarimol	0,131	1,078	27,3	26,2
174	Diphenamid	0,073	0,772	27,4	14,7
9	Alachlor	0,127	0,901	27,4	25,5
122	Cypermethrin beta	0,102	0,821	27,4	20,5
542	Triticonazole	0,136	0,972	27,4	27,3
443	Propoxycarbazone	0,097	0,808	27,4	19,4
454	Pyrethrins 1	0,136	0,979	27,4	27,4
414	Phosmet	0,120	0,870	27,5	24,1
132	DDE, o-p	0,072	0,770	27,5	14,5
198	Ethirimol	0,137	1,010	27,5	27,4
248	Fluazinam	0,124	0,883	27,5	24,8
214	Fenchlorphos	0,089	0,794	27,5	17,9
311	Isocarbophos	0,136	0,972	27,5	27,4
448	Prothioconazole	0,137	0,990	27,5	27,5
487	Tau-Fluvalinate TOTAL	0,100	0,813	27,5	20,0
437	Propargite	0,136	0,956	27,6	27,2
220	Fenoxycarb	0,134	0,934	27,6	26,8
429	Profoxydim (Clefoxydim)	0,137	1,008	27,6	27,6
468	Quizalofop-ethyl	0,127	0,893	27,6	25,4
478	Simetryn	0,131	0,913	27,7	26,3
289	Heptachlor endo epoxide	0,100	0,812	27,7	20,1
418	Pinoxaden	0,129	0,902	27,7	25,9
194	Ethiofencarb	0,104	0,820	27,8	20,9
515	Thiometon	0,138	0,977	27,8	27,7
206	Famophos (Famphur)	0,138	0,973	27,8	27,7
512	Thiofanox	0,138	0,976	27,8	27,7
279	Furathiocarb	0,135	0,934	27,8	27,0
303	Indoxacarb	0,139	0,996	27,8	27,8
191	Esfenvalerate	0,105	0,819	27,9	21,0
531	Trichlorfon	0,125	0,877	28,0	25,1
296	Hexythiazox	0,138	0,959	28,0	27,7
427	Profenofos	0,105	0,817	28,1	21,1
113	Cycloxydim	0,120	0,856	28,1	24,0
238	Fipronil-Sulfid	0,129	0,891	28,1	25,9
325	Lambda-Cyhalothrin	0,112	0,832	28,1	22,3
368	Metsulfuron-Methyl	0,126	0,876	28,2	25,3
518	Tolclofos-methyl	0,101	0,805	28,3	20,1
462	Pyriproxifen	0,139	0,947	28,4	27,9
545	Vinclozolin	0,094	0,791	28,4	18,9
425	Prochloraz	0,115	0,834	28,5	23,0
116	Cyfluthrin beta	0,099	0,799	28,5	19,8
533	Triclopyr	0,134	0,906	28,5	26,9
272	Foramsulfuron	0,108	0,816	28,5	21,7
200	Ethofumesate	0,132	0,896	28,6	26,5
406	Pentachlorbenzol	0,126	0,867	28,6	25,2
184	Emamectin Total	0,134	0,904	28,6	26,9
222	Fenpropathrin	0,140	0,943	28,6	28,0
390	Omethoate	0,105	0,809	28,6	21,1
411	Phenthoate	0,139	0,938	28,6	27,9
175	Diphenyl (Biphenyl)	0,121	0,849	28,7	24,3
497	Terbufos	0,135	0,906	28,7	27,1
348	Metazachlor	0,095	0,787	28,7	18,9
438	Propazine	0,123	0,853	28,8	24,6
393	Oxamyl	0,123	0,852	28,8	24,6
189	Epoxiconazole	0,142	0,949	28,9	28,4
353	Methidathion	0,101	0,796	28,9	20,3
541	Triforine	0,138	0,917	29,0	27,7
182	Diuron	0,113	0,823	29,0	22,7
115	Cyfluthrin alpha	0,104	0,800	29,0	20,8
470	Rimsulfuron	0,139	0,921	29,0	27,9
173	Dioxathion	0,137	0,910	29,0	27,6
13	Aldrin	0,116	0,824	29,2	23,2
208	Fenamidone	0,146	1,001	29,3	29,3
516	Thionazin	0,146	1,016	29,3	29,2
321	Isoxaflutole	0,122	0,840	29,3	24,5
371	Molinate	0,114	0,818	29,3	22,8
59	Carbaryl	0,109	0,807	29,3	21,9
204	Etridiazol	0,137	0,899	29,4	27,6
326	Landrin	0,144	0,947	29,4	28,9
254	Fludioxonil	0,144	0,940	29,5	28,8
74	Chlordane, cis	0,089	0,769	29,5	17,9
307	Iprodione	0,120	0,831	29,6	24,1
441	Propiconazole	0,142	0,920	29,6	28,5
235	Fenvalerate	0,112	0,809	29,6	22,4
503	Tetradifon	0,090	0,767	29,7	18,0
457	Pyridaphenthion	0,147	0,955	29,7	29,4
251	Flubenzimin	0,130	0,857	29,8	26,0
460	Pyrimethanil	0,097	0,777	29,8	19,3
305	Ioxynil	0,143	0,922	29,8	28,8
81	Chloridazone	0,132	0,862	29,9	26,5
347	Metamitron	0,140	0,897	30,0	28,1
55	Buturon	0,147	0,953	30,0	29,6
159	Diflubenzuron	0,127	0,842	30,0	25,4
158	Difenoconazole	0,136	0,878	30,0	27,3
128	D, 2,4-	0,133	0,863	30,0	26,7
199	Ethofenprox	0,133	0,861	30,1	26,6
51	Buprofezin	0,150	1,002	30,1	30,1
376	Myclobutanil	0,149	0,961	30,1	29,9
324	Kresoxim-methyl	0,150	0,981	30,2	30,1
80	Chlorfluazuron	0,150	0,975	30,2	30,0
507	Thiacloprid	0,114	0,805	30,2	22,8
288	Heptachlor	0,107	0,790	30,2	21,4
544	Vamidation	0,109	0,793	30,3	21,8
166	Dimethomorph TOTAL	0,151	0,995	30,3	30,3
525	Triadimenol	0,150	0,960	30,4	30,1
33	Bensulfuron-methyl	0,129	0,840	30,4	25,8
76	Chlordane-oxy	0,140	0,883	30,4	28,1
244	Fluazifop free acid	0,152	0,987	30,5	30,5
12	Aldicarb sulfoxide	0,113	0,798	30,6	22,7
170	Dinocap	0,139	0,877	30,6	28,0
183	Dodine	0,151	0,951	30,7	30,2
49	Bromoxynil	0,107	0,783	30,7	21,6
434	Propachlor	0,153	1,021	30,8	30,7
4	Acetamiprid	0,121	0,813	30,8	24,3
60	Carbendazim	0,117	0,803	30,8	23,4
56	Butylate	0,130	0,837	30,9	26,1
91	Chlorsulfuron	0,121	0,808	31,0	24,2
217	Fenitrothion	0,110	0,785	31,0	22,0
508	Thiamethoxam	0,127	0,822	31,1	25,4
69	Chlorantranilipol	0,142	0,874	31,1	28,4
18	Amitraz TOTAL	0,093	0,752	31,2	18,6
188	Endrin	0,087	0,745	31,2	17,5
524	Triadimefon	0,143	0,877	31,2	28,7
240	Flamprop-isopropyl	0,156	0,973	31,4	31,3
442	Propoxur	0,123	0,807	31,4	24,6
444	Propyzamide	0,149	0,901	31,5	29,8
10	Aldicarb	0,116	0,789	31,5	23,1
156	Dieldrin	0,096	0,754	31,6	19,2
399	Parathion-methyl	0,113	0,783	31,6	22,6
335	MCPA	0,152	0,920	31,6	30,6
316	Isoprocarb	0,157	0,985	31,7	31,6
520	Tolyfluanid	0,112	0,780	31,7	22,5
511	Thiodicarb	0,146	0,877	31,8	29,3
154	Dicofol	0,093	0,744	31,9	18,5
185	Endosulfan alpha	0,097	0,749	32,0	19,4
517	Thiophanate-methyl	0,123	0,798	32,0	24,6
246	Fluazifop-p	0,148	0,880	32,1	29,7
318	Isoproturon	0,158	0,962	32,1	31,8
126	Cyprodinil	0,153	0,905	32,1	30,6
469	Rabenzazole	0,154	0,913	32,1	30,9
83	Chlormequat chloride	0,086	0,733	32,2	17,3
165	Dimethoate	0,125	0,800	32,2	25,0
546	Zoxamid	0,152	0,897	32,2	30,5
436	Propaquizafob	0,158	0,944	32,2	31,7
17	Amitraz	0,128	0,806	32,3	25,6
327	Lenacil	0,136	0,830	32,3	27,3
216	Fenhexamid	0,144	0,855	32,4	28,8
186	Endosulfan beta	0,119	0,783	32,5	23,9
526	Tri-allate	0,152	0,885	32,6	30,5
382	Nitrapryn	0,161	0,948	32,7	32,2
41	Boscalid	0,154	0,892	32,7	30,8
142	Desmethryn	0,159	0,922	32,8	31,9
354	Methiocarb	0,160	0,926	32,8	32,0
233	Fentin Acetate	0,153	0,885	32,9	30,7
3	Acequinocyl	0,150	0,867	32,9	30,0
477	Simazine	0,138	0,823	32,9	27,6
366	Metribuzin	0,144	0,842	33,0	28,8
413	Phosalone	0,150	0,865	33,0	30,1
75	Chlordane, trans	0,097	0,735	33,2	19,5
285	HCH beta	0,104	0,746	33,2	20,8
120	Cymoxanil	0,128	0,792	33,2	25,6
493	Teflubenzuron	0,155	0,881	33,4	31,1
207	Famoxadone	0,166	0,963	33,4	33,2
466	Quintozene	0,118	0,765	33,5	23,6
193	Ethalfluralin	0,126	0,781	33,6	25,1
387	Novaluron	0,158	0,891	33,6	31,7
329	Lindane (HCH gamma)	0,131	0,794	33,6	26,3
364	Metosulam	0,147	0,840	33,7	29,6
495	Tepraloxydim	0,143	0,825	33,7	28,7
381	Nitralin	0,162	0,911	33,8	32,5
1	Abamectin	0,163	0,918	33,8	32,8
70	Chlorbenside	0,089	0,718	33,8	17,9
112	Cycloate	0,114	0,754	33,8	22,8
73	Chlorbufam	0,152	0,857	33,8	30,6
50	Bupirimate	0,150	0,846	33,9	30,1
164	Dimethipin	0,117	0,757	34,0	23,4
129	Dazomet	0,157	0,870	34,0	31,4
328	Leptophos	0,161	0,891	34,1	32,3
106	CPA, 4-	0,155	0,858	34,2	31,0
201	Ethopropos	0,123	0,765	34,3	24,6
449	Prothiophos	0,126	0,772	34,3	25,3
536	Trifloxystrobin	0,161	0,884	34,4	32,3
110	Cyanophos	0,112	0,742	34,5	22,4
215	Fenfluthrin	0,132	0,781	34,5	26,5
379	Nicosulfuron	0,134	0,784	34,5	26,8
323	Jodfenphos	0,171	0,959	34,5	34,3
482	Spiromesifen	0,167	0,920	34,6	33,6
148	Dichlofluanid	0,145	0,810	34,8	29,0
492	Tecnazene	0,129	0,769	34,9	25,9
292	Hexachlorobenzene	0,118	0,746	35,0	23,7
480	Spinosad D	0,155	0,838	35,1	31,0
228	Fenthion	0,139	0,790	35,1	27,9
286	HCH delta	0,089	0,702	35,1	17,8
138	Demeton-S-methyl	0,133	0,773	35,2	26,7
44	Bromoconazole	0,161	0,852	35,5	32,2
87	Chlorpropham	0,155	0,829	35,5	31,0
284	HCH alpha	0,129	0,759	35,6	25,9
257	Flumioxazin	0,172	0,908	35,7	34,5
58	Captan	0,126	0,748	35,9	25,2
275	Formothion	0,112	0,724	35,9	22,5
458	Pyridate	0,155	0,822	35,9	31,1
65	Carbosulfan	0,128	0,750	36,0	25,6
488	Tebuconazole	0,149	0,788	36,7	29,8
401	Penconazole	0,155	0,806	36,7	31,1
97	Clethodim	0,156	0,809	36,8	31,3
403	Pendimethalin	0,158	0,813	36,9	31,6
68	Chinomethionate	0,104	0,697	37,1	20,8
369	Mevinfos	0,124	0,727	37,2	24,8
39	Binapacryl	0,124	0,726	37,3	24,8
225	Fenproximate	0,169	0,846	37,4	33,9
119	Cyhexatin	0,164	0,810	38,1	33,0
331	Lufenuron	0,170	0,826	38,4	34,1
100	Clofentezine	0,169	0,821	38,5	33,9
293	Hexaconazole	0,160	0,780	39,0	32,0
151	Dichlorvos	0,118	0,680	40,2	23,7
270	Folpet	0,147	0,729	40,4	29,5
287	HCH epsilon	0,139	0,703	40,9	27,8
85	Chlorothalonil	0,135	0,696	41,0	27,0
539	Trifluralin	0,154	0,732	41,1	30,9
143	Diafenthiuron	0,159	0,742	41,3	31,9
297	Imazalil	0,157	0,728	41,8	31,5
537	Triflumizole	0,164	0,703	44,6	32,9
34	Bentazone	0,138	0,645	45,5	27,7
137	Deltamethrin	0,165	0,692	45,6	33,1

acc. SANCO	MU<25	MU<25
acceptable	25<MU<40	25<MU<35
not acceptable	40<MU<46	

Literature

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