Analysis of Acidic Pesticides using CEN-QuEChERS and FA-QuEChERS

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Changes to previous version are highlighted in yellow

Subject: Analytical observations report concerning the following…

- **Compound(s)**: Pesticides and metabolites entailing acidic functions (e.g. carboxy- or phenolic groups)
- **Commodities**: Cucumber, Grapes, Maize (exemplary)
- **Extractions Method(s)**: CEN-QuEChERS (EN-15662), FA-QuEChERS (using 1% formic acid, no citrate salts)
- **Measurement Technique:** LC-MS/MS (mostly ESI-neg. and in a few cases ESI-pos. mode)
- **Cleanup**: None

Brief description:

Two methods, the CEN-QuEChERS method (EN 15662) and the formic acid acidified QuEChERS (FA-QuEChERS) were tested for the analysis of acidic pesticides. FA-QuEChERS involved extraction with acetonitrile containing 1% formic acid and the use of partitioning salts composed of NaCl and $MgSO_4$ only. Recovery experiments were conducted on cucumber, grapes and maize. No alkaline hydrolysis step was conducted and thus the focus was on free acids only. Most compounds showed satisfactory recovery figures by both methods. There were some pesticides, however, whose average recoveries were unsatisfactory (< 70%) using CEN-QuEChERS but satisfactory using FA-QuEChERS.

Apparatus and Consumables:

Refer to EN 15662. For mechanical shaking the GenoGrinder by Spex was used. Extracts were filtered through disposable polyester syringe filters of 0.45 µm pore size.

QuEChERS (EN 15662):

The procedure as described in EN 15662 was followed. Shaking was conducted for 15 minutes using the GenoGrinder. No cleanup step was conducted.

Acidified QuEChERS (FA-QuEChERS):

The method corresponds to the EN 15662 procedure with the only difference being the use of 10 mL acetonitrile containing 1% formic acid instead of pure acetonitrile for extraction and of 4g $MgSO_4$ and 1g NaCl (no citrate buffer salts) for partitioning. Shaking was conducted for 15 minutes using the GenoGrinder. The raw extracts were directly injected (no cleanup performed).

Measurement:

Table 1: LC details for Acidic Pesticides (exemplary)

Instrument	Waters Acquity, ABSciex API 4000 QTrap			
Ionisation mode	ESI neg. / pos. (in separate runs)			
Column	Acquity UPLC BEH C18,1.7 µm; 2.1 x 100 mm			
Pre-column	Van Guard BEH C18, 1.7 µm			
Eluent A	0.01 % acetic acid in water (with 5% acetonitrile)			
Eluent B	0.01 % acetic acid in acetonitrile			
Gradient	Time [min]	flow [µL/min]	A [%]	B [%]
	0	400	80	20
	4	400	70	30
	7	400	10	90
	8.5	400	10	90
	8.6	400	80	20
Internal Standard	BNPU (Bis-Nitrophenyl Urea) (ESI neg.) Propyzamide-D_3 (ESI pos., and neg.) Chlorpyrifos-D_{10} (ESI pos.)			

Table 2: MS/MS details for Acidic Pesticides (ESI-negative or -positive mode, Tune-data ABSciex 4000Q)

Compound	Sensitivity Ranking (1= best)	Parent Mass	Daughter Mass	DP	CE	CXP	Note
1-Naphthylacetic acid	1	185	141	-11	-10	-7	ESI neg.
2,4,5-T	3	253	159	-50	-40	-7	ESI neg.
	1	253	195	-50	-18	-9	ESI neg.
	2	255	197	-55	-18	-11	ESI neg.
2,4,5-TP (Fenoprop)	3	267	159	-50	-40	-9	ESI neg.
	1	267	195	-50	-16	-9	ESI neg.
	2	269	197	-50	-18	-9	ESI neg.
2.4.6-Trichlorophenol	1	195	35	-70	-44	-3	ESI neg.
	2	197	35	-70	-42	-3	ESI neg.
	3	199	37	-70	-40	-3	ESI neg.
2.4-D	3	219	125	-50	-38	-7	ESI neg.
	1	219	161	-50	-18	-9	ESI neg.
	2	221	163	-50	-18	-9	ESI neg.
2.4-DB	3	247	125	-50	-38	-5	ESI neg.
	1	247	161	-50	-12	-9	ESI neg.
	2	249	163	-35	-14	-9	ESI neg.
2.4-DP (Dichlorprop)	3	233	125	-50	-38	-5	ESI neg.
	1	233	161	-50	-18	-9	ESI neg.
	2	235	163	-50	-18	-7	ESI neg.
2-Naphthoxyacetic acid	2	201	115	-55	-54	-7	ESI neg.
	1	201	143	-55	-22	-7	ESI neg.
	3	201	157	-55	-14	-7	ESI neg.
4-CPA	1	185	127	-55	-20	-7	ESI neg.
	2	187	129	-55	-20	-7	ESI neg.
Acifluorfen	2	360	286	-45	-22	-7	ESI neg.
	1	360	316	-45	-12	-9	ESI neg.
Aminopyralid	1	205	161	-50	-14	-7	ESI neg.
	2	207	163	-50	-14	-7	ESI neg.

Compound	Sensitivity Ranking (1= best)	Parent Mass	Daughter Mass	DP	CE	CXP	Note
Bentazon	1	239	132	-75	-38	-7	ESI neg.
	2	239	175	-75	-28	-9	ESI neg.
	3	239	197	-75	-28	-11	ESI neg.
Bromacil	1	259	203	-46	-26	-11	ESI neg.
	3	261	205	-46	-28	-11	ESI neg.
	2	261	81	-41	-46	-5	ESI neg.
Bromoxynil	1	274	79	-60	-48	-1	ESI neg.
	2	276	81	-70	-42	-3	ESI neg.
	3	278	81	-60	-50	-3	ESI neg.
BTS 9608 (Metabolite of prochloraz)	2	253	195	-45	-18	-9	ESI neg.
	1	255	197	-45	-16	-11	ESI neg.
	3	257	199	-50	-18	-9	ESI neg.
Clopyralid	2	190	146	-35	-14	-7	ESI neg. similar MRM and RT as TFNA (metabolite of flonicamid)
	3	190	35	-35	-35	-3	ESI neg.
	1	192	148	-35	-14	-7	ESI neg.
	4	192	37	-35	-32	-5	ESI neg.
Dalapon	3	141	105	-30	-10	-10	ESI neg.
	1	141	97	-30	-12	-12	ESI neg.
	2	143	99	-30	-12	-5	ESI neg.
Dicamba	1	219	175	-25	-8	-8	ESI neg.
	2	221	177	-25	-8	-11	ESI neg.
Diflufenzopyr	2	333	134	-20	-22	-2	ESI neg.
	1	333	160	-20	-18	-2	ESI neg.
	3	333	204	-20	-12	-2	ESI neg.
Dikegulac	2	273	55	-45	-62	0	ESI neg.
	1	273	83	-45	-32	0	ESI neg.
Fenoxaprop-P	3	334	262	-70	-18	-1	ESI neg.
	2	332	152	-70	-32	-7	ESI neg.
	1	332	260	-70	-18	-13	ESI neg.
Fluazifop	3	326	108	-65	-56	-5	ESI neg.
	2	326	226	-65	-38	-11	ESI neg.
	1	326	254	-65	-22	-5	ESI neg.
Fluroxypyr	1	253	195	-50	-20	-9	ESI neg.
	3	253	233	-50	-10	-1	ESI neg.
	2	255	197	-55	-20	-11	ESI neg.
Gibberellic acid	1	345	143	-50	-42	0	ESI neg.
	2	345	221	-50	-34	0	ESI neg.
	3	345	239	-50	-22	-2	ESI neg.
Haloxyfop	3	360	196	-70	-52	-9	ESI neg.
	1	360	288	-70	-20	-15	ESI neg.
	2	362	290	-75	-20	-15	ESI neg.
Imazamox	3	304	186	-40	-44	-9	ESI neg.
	2	304	217	-40	-28	-9	ESI neg.
	1	304	260	-40	-18	-11	ESI neg.
Imazapyr	1	260	173	-50	-30	-9	ESI neg.
	2	260	216	-50	-18	-11	ESI neg.
Imazethapyr	3	288	186	-55	-50	-9	ESI neg.
	2	288	201	-55	-32	-11	ESI neg.
	1	288	244	-55	-20	-1	ESI neg.
Inabenfide	1	337	122	-75	-24	-7	ESI neg.

Compound	Sensitivity Ranking (1= best)	Parent Mass	Daughter Mass	DP	CE	CXP	Note
	3	337	231	-75	-30	-11	ESI neg.
	2	339	122	-75	-24	-7	ESI neg.
Ioxynil	1	370	127	-60	-44	-7	ESI neg.
	2	370	215	-60	-50	-13	ESI neg.
	3	370	243	-60	-32	-13	ESI neg.
MCPA	1	199	141	-55	-20	-7	ESI neg.
	2	201	143	-55	-20	-7	ESI neg.
MCPB	1	227	141	-50	-18	-7	ESI neg.
	2	229	143	-55	-16	-7	ESI neg.
MCPP	1	213	141	-55	-20	-7	ESI neg.
	3	213	71	-55	-14	-1	ESI neg.
	2	215	143	-55	-18	-7	ESI neg.
Pentachlorophenol	2	263	35	-80	-50	-3	ESI neg.
	1	265	35	-80	-52	-3	ESI neg.
	3	267	35	-80	-56	-3	ESI neg.
Picloram	1	241	197	-50	-14	-11	ESI neg.
	2	239	195	-45	-14	-9	ESI neg.
Quinmerac	1	222	204	36	21	14	ESI pos.
	2	224	206	41	23	12	ESI pos.
	3	222	149	41	47	10	ESI pos.
BH 518-2 (Quinmerac-metabolite)	1	250	162	-50	-22	-7	ESI neg.
	2	250	206	-50	-16	-9	ESI neg.
	1	252	234	46	23	12	ESI pos.
	2	254	236	46	23	14	ESI pos.
BH 518-4 (Quinmerac-metabolite)	1	236	192	-55	-10	-9	ESI neg.
	2	236	35	-55	-30	-3	ESI neg.
	3	238	37	-55	-28	-3	ESI neg.
	1	238	220	51	23	12	ESI pos.
	2	238	162	51	43	8	ESI pos.
	3	240	222	46	23	12	ESI pos.
Quizalofop	1	343	271	-36	-22	-15	ESI neg.
	2	345	273	-41	-22	-13	ESI neg.
TFNA (Flonicamid-metabolite)	4	190	119	-35	-36	-5	ESI neg.
	3	190	126	-35	-34	-5	ESI neg.
	2	190	69	-35	-46	-1	ESI neg.
	1	190	146	-35	-16	-7	ESI neg.
TFNG (Flonicamid-metabolite)	2	247	146	-55	-24	-7	ESI neg.
	3	247	163	-55	-24	-7	ESI neg.
	1	247	183	-55	-18	-9	ESI neg.
Triclopyr	1	254	196	-50	-16	-11	ESI neg.
	3	254	218	-50	-8	-11	ESI neg.
	2	256	198	-50	-16	-9	ESI neg.
2,4-D-D3 (IS)	1	222	164	-50	-18	-7	ESI neg.
BNPU (IS)	1	301	137	-45	-16	-7	ESI neg.
Propyzamide-D3	1	257	231	-70	-20	-1	ESI neg.
Chlorpyrifos D10	1	360	199	86	23	12	ESI pos.

Theoretical Background

The QuEChERS method involves a phase separation induced by adding partitioning salts. In CEN-QuEChERS, the pH of the aqueous phase after partitioning typically ranges around 4.3 and is influenced by the sample's pH and buffering capacity as well as the added citrate and $MgSO_4$ salts. In solution, citrate and Mg^{2+} ions form complexes, which cause a release of protons and thus a lower pH than what would have resulted in absence of $MgSO_4$ (pH~5-5.5). This pH-drop favors partitioning of acidic analytes into the acetonitrile phase but is not low enough for some highly polar ones. For such compounds, acidification during QuEChERS is needed. The FA-QuEChERS approach presented here employs formic acid.

Depending on their affinity towards the aqueous or organic phase, analytes partition between the two phases formed during QuEChERS. Polarizable and ionizable functional groups increase the affinity of analytes towards the aqueous phase. In presence of ionizable groups (e.g. amino- and carboxy-groups) the distribution of compounds between the phases will strongly depend on the pH, which defines the position of the acid/base-equilibrium and the share of microspecies. The larger the share of the ionized (charged) form, the higher the affinity of a molecule towards the aqueous phase. In the case of acidic analytes, decreasing the pH during extraction shifts the equilibrium towards the more lipophilic, non-protonated form thus promoting partitioning into the organic phase. With basic analytes it is vice versa. In the distribution of the anionic and the neutral forms (microspecies) at various pH levels (as computed by chemicalize.com) are exemplarily shown for 4-CPA, 2,4-D and 2,4,5-T. When it comes to simple acids (or bases), computed physicochemical figures (e.g. pKa and logD) often match with experimental values, and a certain correlation with QuEChERS recovery rates can be seen. As a rough orientation, a logD[1] value of -0.2 and above will lead to CEN-QuEChERS recovery rates exceeding 80% on average.

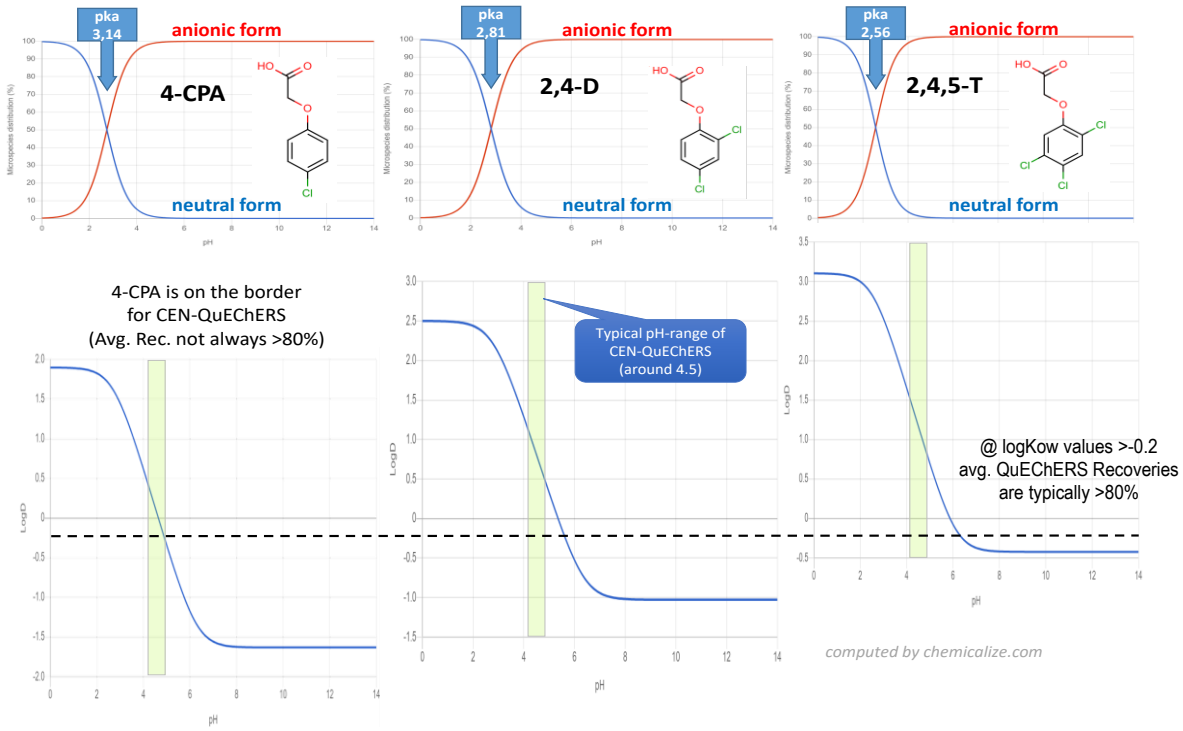


Figure 1: LogD and microspecies across the pH range and pKa values of 4-CPA, 2,4-D and 2,4,5-T

[1] The term LogD is used to express the theoretical logP (synonym to logKow) at a certain pH. LogD values are typically computed based on the theoretical share of microspecies at a given pH and their computed polarities

The examples in furthermore visualize that the lipophilic rest also contributes to the overall “polarity” and partitioning behavior of molecules. The logD values of 4-CPA are lower than those of the other two compounds at any pH value and close to the border for achieving QuEChERS recoveries >80%. In turn, the logD values of 2,4,5-T, despite it being more acidic, are the highest among the three compounds (at any pH) due to the higher lipophilicity of the rest.

Some further examples of the computed distribution of microspecies are shown in **Figure 2** for dalapon, in **Figure 3** for dikegulac, and in **Figure 4** for 2,4-D.

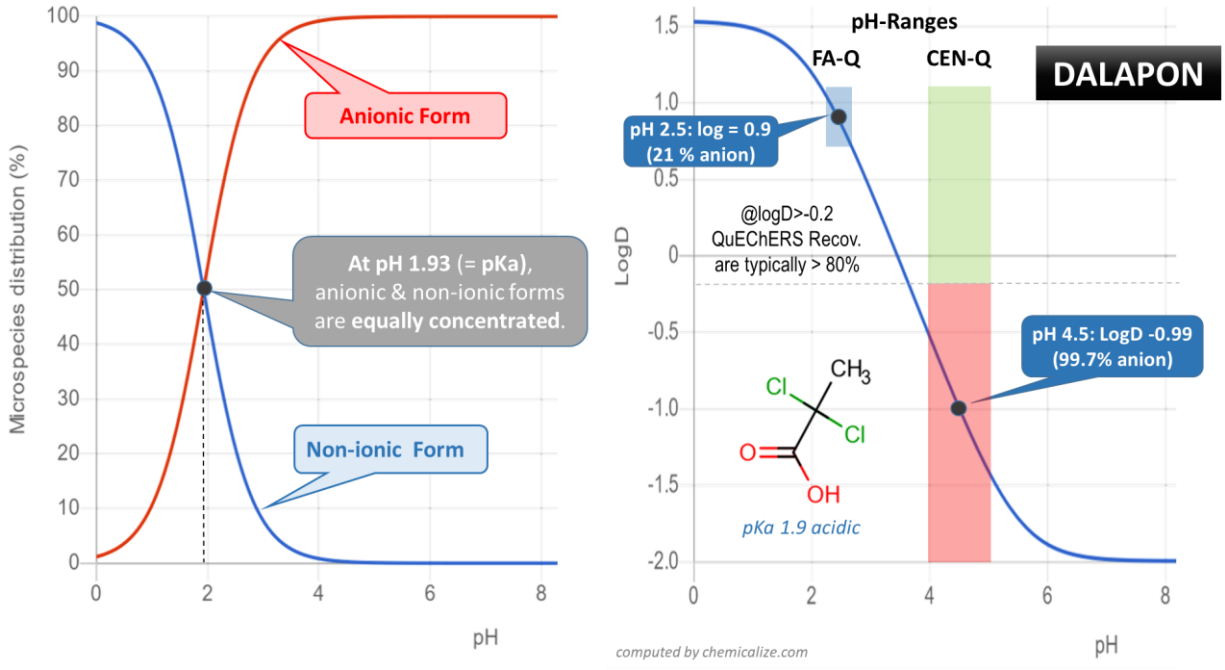


Figure 2: Shares of microspecies and logD values of dalapon (computed by chemicalize.com)

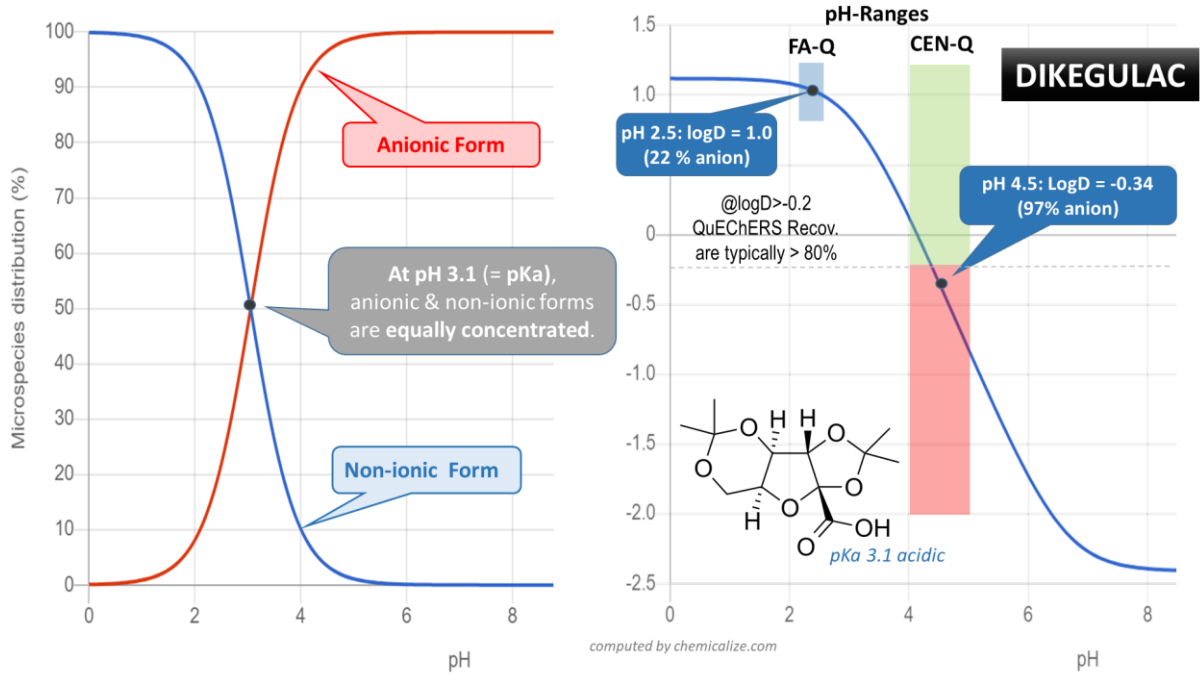


Figure 3: Shares of microspecies and logD values of dikegulac (computed by chemicalize.com)

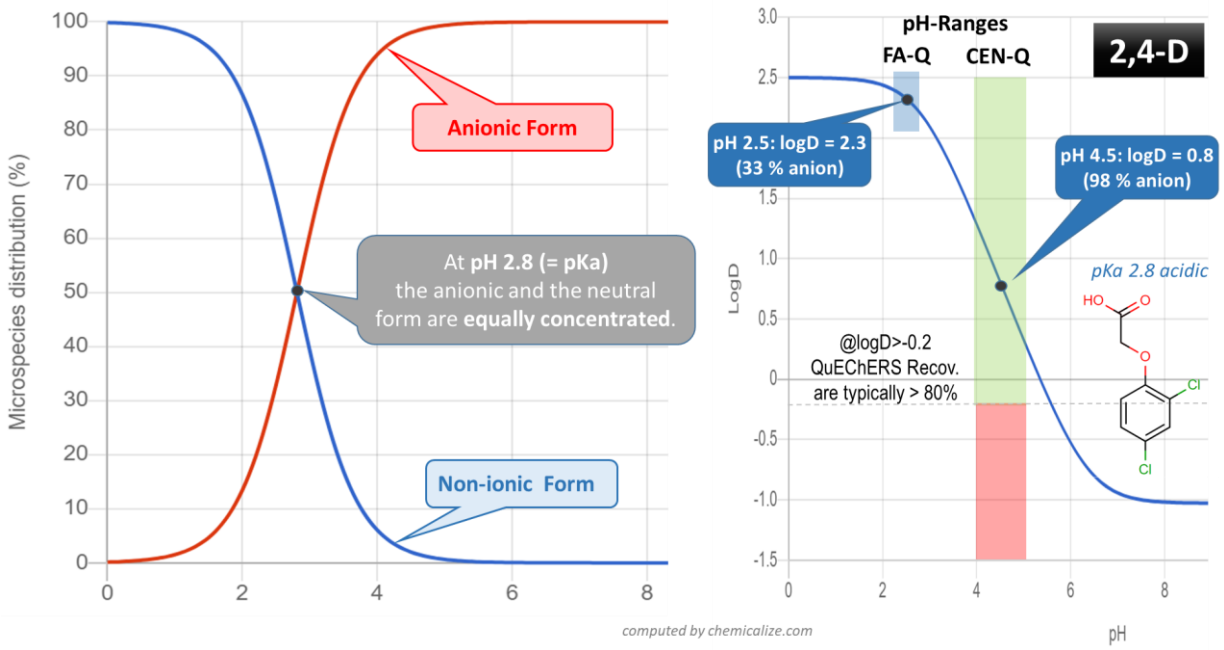


Figure 4: Shares of microspecies and logD values of 2,4-D (computed by chemicalize.com)

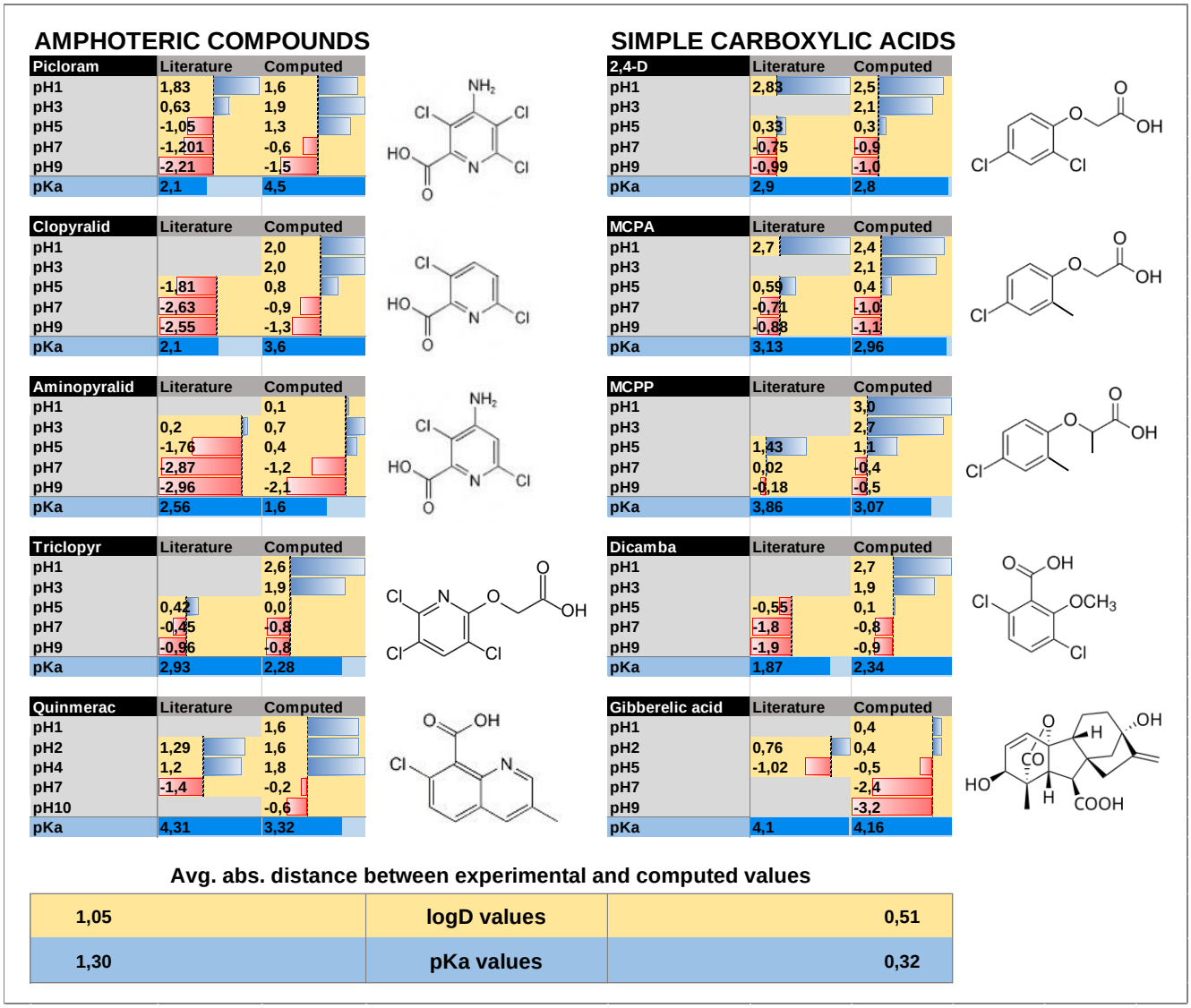
The pH range of the FA-QuEChERS variant (around pH 2.5) is also highlighted. Dalapon combines strong acidity with a small lipophilic rest and thus exhibits very high polarity over a large pH-range. Strong acidification is required to shift the logKow to levels allowing satisfactory partitioning. Dikegulac is just on the border for achieving satisfactory CEN-QuEChERS recoveries, and good recoveries are, in fact, achieved in acidic commodities (see also **Table 3**). In contrast, 2,4-D is well within the CEN-QuEChERS range.

Figure 5 compares the logD and pKa values computed by chemicalize.com with experimental data collected from literature. For simple carboxylic acids, experimentally generated and software computed figures seem to match well with each other in most cases. When it comes to complex (amphoteric) molecules, however, the pKa and logD figures often deviate significantly. Especially affected in this respect are picolinic acid derivatives (pyridine-2-carboxylic acids), such as picloram (see **Figure 6**), aminopyralid (see **Figure 7**) and clopyralid. The average absolute deviation between computed logD and experimental logKow values was 0.51 in the case of carboxylic acids and 1.05 in the case of amphoteric molecules. The pKa values deviated by 0.32 versus 1.30 on average, respectively.

The discrepancy between the computed and the experimental data may have different reasons. The algorithm used might for example not be well suited/adjusted to conduct accurate predictions for complex compounds, e.g. by not considering intramolecular interactions between polar moieties. It should be noted, however, that experimental results also deviate much, either because of using different methodologies or because external factors affecting it, such as precipitations and complexations. Especially in the case of amphoteric compounds, complexation with metals may shift equilibria not only during the determination of logKow and pka figures but also during extractions via CEN-QuEChERS. Picolinic acids are known to undergo complexations with metals.

Overall, it was observed that experimental logKow data are better suited to explain the QuEChERS recovery rates than the figures computed by chemicalize.com. The discrepancies are much more pronounced with amphoteric compounds, while for simple carboxylic acids, computed and experimental data are roughly comparable with some exceptions. Dicamba is such an exception, where the computed data would suggest good recoveries, whereas experimental data suggest difficulties (see **Figure 5**).

Nevertheless, despite the bias of computed logD/pH diagrams, software programs conducting simulations of physicochemical properties are still very useful for recognizing trends and for understanding how a pH shift will influence the partitioning behavior of a molecule.



Picloram	Literature	Computed
pH1	1,83	1,6
pH3	0,63	1,9
pH5	-1,05	1,3
pH7	-1,201	-0,6
pH9	-2,21	-1,5
pKa	2,1	4,5

Clopyralid	Literature	Computed
pH1		2,0
pH3		2,0
pH5	-1,81	0,8
pH7	-2,63	-0,9
pH9	-2,55	-1,3
pKa	2,1	3,6

Aminopyralid	Literature	Computed
pH1		0,1
pH3	0,2	0,7
pH5	-1,76	0,4
pH7	-2,87	-1,2
pH9	-2,96	-2,1
pKa	2,56	1,6

Triclopyr	Literature	Computed
pH1		2,6
pH3		1,9
pH5	0,42	0,0
pH7	-0,45	-0,8
pH9	-0,96	-0,8
pKa	2,93	2,28

Quinmerac	Literature	Computed
pH1		1,6
pH2	1,29	1,6
pH4	1,2	1,8
pH7	-1,4	-0,2
pH10		-0,6
pKa	4,31	3,32

2,4-D	Literature	Computed
pH1	2,83	2,5
pH3		2,1
pH5	0,33	0,3
pH7	-0,75	-0,9
pH9	-0,99	-1,0
pKa	2,9	2,8

MCPA	Literature	Computed
pH1	2,7	2,4
pH3		2,1
pH5	0,59	0,4
pH7	-0,71	-1,0
pH9	-0,88	-1,1
pKa	3,13	2,96

MCPP	Literature	Computed
pH1		3,0
pH3		2,7
pH5	1,43	1,1
pH7	0,02	-0,4
pH9	-0,18	-0,5
pKa	3,86	3,07

Dicamba	Literature	Computed
pH1		2,7
pH3		1,9
pH5	-0,55	0,1
pH7	-1,8	-0,8
pH9	-1,9	-0,9
pKa	1,87	2,34

Gibberelic acid	Literature	Computed
pH1		0,4
pH2	0,76	0,4
pH5	-1,02	-0,5
pH7		-2,4
pH9		-3,2
pKa	4,1	4,16

Figure 5: Discrepancies between literature and computed logKow/logD and pKa values of various acidic pesticides (chemicalize.com). To the left are amphoteric compounds and to the right are simple carboxylic acids. Experimental data was collected from various sources including BVL (DE), EPA (US), and FAO/WHO/JMPR (UN).

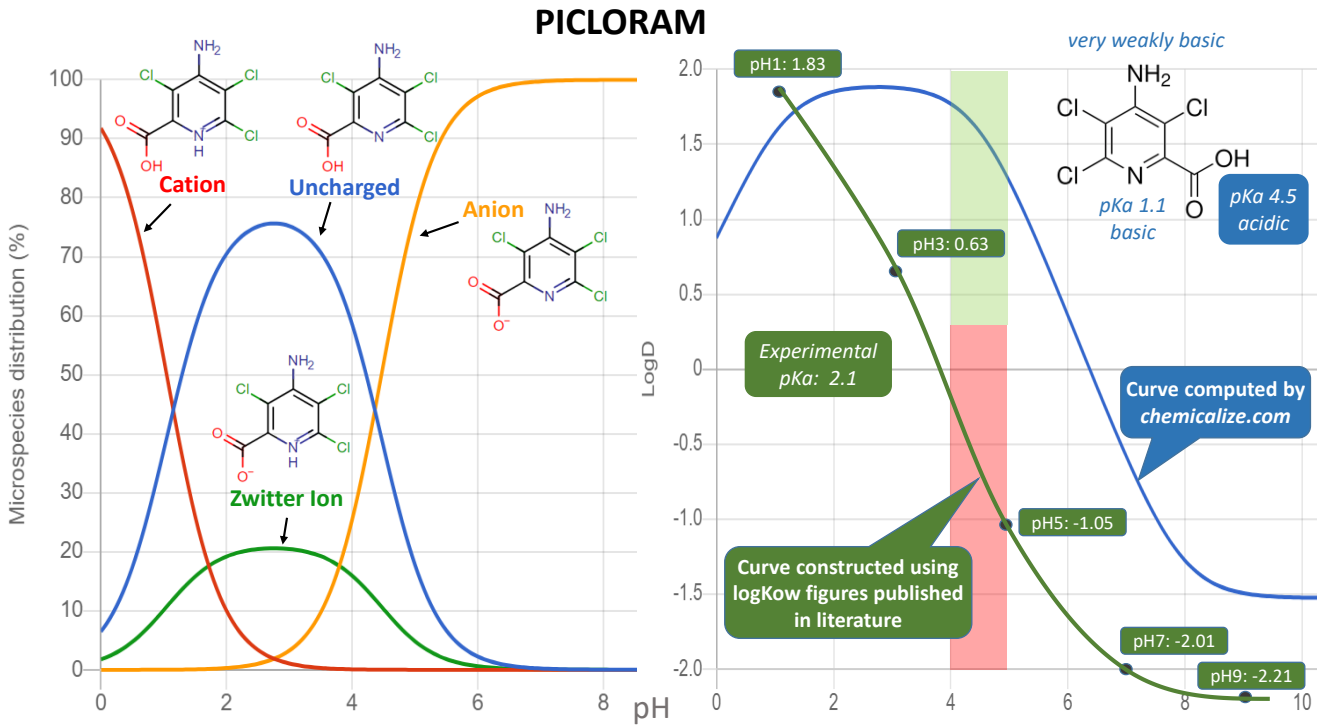


Figure 6: Computed share of microspecies of picloram over the pH range and comparison of computed and experimental logKow and pKa values (computations by chemicalize.com)

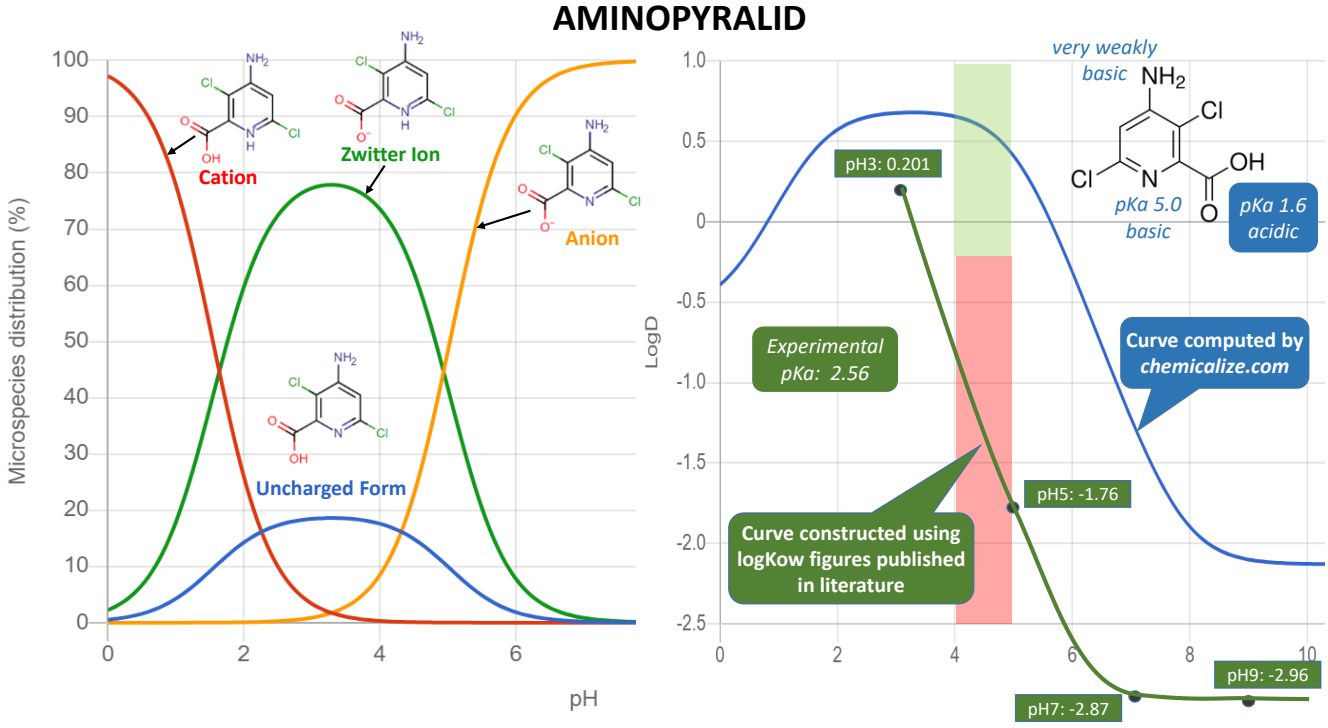


Figure 7: Computed share of microspecies of aminopyralid over the pH range and comparison of computed and experimental logKow and pKa values (computations by chemicalize.com)

Experiments conducted and observations:

Recovery studies of acidic pesticides from cucumber, grapes and maize were conducted using both the CEN-QuEChERS method (which is widely used by routine laboratories) and the FA-QuEChERS method (which employs formic acid for acidification). In both cases, no cleanup was conducted. The recovery experiments were run in quintuplicate at a spiking level of 0.01 mg/kg in all cases. LC-MS/MS analysis was performed in ESI-negative and, partially in ESI positive mode.

Using FA-QuEChERS, the average recovery rates were >90% in all cases except for aminopyralid and BH 518-2 (quinmerac-metabolite) in wheat flour, which both showed a recovery rate of 79%.

Using standard QuEChERS (EN 15662), however, the average recovery rates were significantly lower and for certain compounds even < 70%. In the case of aminopyralid, dalapon, imazapyr, TFNA and TFNG as well as the two quinmerac-metabolites BH 518-2 and BH 518-4, recoveries from all 3 commodities were <70%. In the case of dicamba and dikegulac, recoveries <70% were, only observed in maize. For clopyralid and picloram in cucumber and quinmerac in wheat flour the recoveries obtained using standard QuEChERS were also <70 %. Further experiments are pending. Reduced recovery rates between 70 and 80% were observed for 4-CPA, BTS-9608 and gibberellic acid in maize; for dicamba, dikegulac and quinmerac in cucumber and for imazamox and imazethapyr in grapes.

Validation data

Table 3: Recovery figures for Acidic Pesticides in different commodities (n=5 in all cases)

Substance	Extraction Method	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Corn flour 0.01 mg/kg	
		Rec (%)	*RSD (%)*	Rec (%)	*RSD (%)*	Rec (%)	*RSD (%)*
1-Naphthylacetic acid	CEN-QuEChERS	98	*4*	98	*3*	91	*3*
	FA-QuEChERS	**102**	***4***	**104**	***5***	**101**	***5***
2.4.5-T	CEN-QuEChERS	92	*6*	99	*6*	85	*3*
	FA-QuEChERS	**102**	***2***	**102**	***4***	**99**	***3***
2.4.5-TP (Fenoprop)	CEN-QuEChERS	96	*3*	99	*3*	91	*2*
	FA-QuEChERS	**99**	***2***	**104**	***5***	**95**	***8***
2.4.6-Trichlorophenol	CEN-QuEChERS	95	*10*	104	*4*	105	*5*
	FA-QuEChERS	**106**	***6***	**100**	***5***	**107**	***5***
2.4-D	CEN-QuEChERS	90	*4*	106	*6*	82	*3*
	FA-QuEChERS	**101**	***3***	**108**	***3***	**98**	***5***
2.4-DB	CEN-QuEChERS	85	*8*	98	*8*	92	*7*
	FA-QuEChERS	**101**	***6***	**90**	***6***	**98**	***12***
2.4-DP (Dichlorprop)	CEN-QuEChERS	95	*4*	100	*3*	87	*4*
	FA-QuEChERS	**99**	***2***	**102**	***3***	**99**	***3***
2-Naphthoxyacetic acid	CEN-QuEChERS	93	*4*	99	*3*	81	*3*
	FA-QuEChERS	**102**	***2***	**106**	***5***	**101**	***5***
4-CPA	CEN-QuEChERS	90	*3*	96	*4*	76	*2*
	FA-QuEChERS	**101**	***1***	**103**	***6***	**100**	***5***
Aminopyralid	CEN-QuEChERS [1)]	25	*5*	32 [3)]	*9*	13 [4)]	*15*
	FA-QuEChERS [2)]	**92**	***7***	**88 [5)]**	***1***	**79 [4)]**	***12***
Bentazon	CEN-QuEChERS	100	*4*	100	*6*	88	*2*
	FA-QuEChERS	**105**	***3***	**105**	***4***	**98**	***3***
Bromacil	CEN-QuEChERS	100	*4*	99	*5*	95	*4*
	FA-QuEChERS	**102**	***2***	**109**	***4***	**102**	***4***
Bromoxynil	CEN-QuEChERS	94	*3*	105	*7*	91	*2*
	FA-QuEChERS	**104**	***2***	**106**	***4***	**103**	***2***

Substance	Extraction Method	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Corn flour 0.01 mg/kg	
		Rec (%)	RSD (%)	Rec (%)	RSD (%)	Rec (%)	RSD (%)
BTS 9608 (Metabolite of prochloraz)	CEN-QuEChERS	91	2	97	5	78	2
	FA-QuEChERS	**103**	***2***	**101**	***5***	**98**	***3***
Clopyralid	CEN-QuEChERS [6]	39	1	n.a.	n.a.	n.a.	n.a.
	FA-QuEChERS	**95**	***10***	**95** [5]	***7***	**100** [4]	***7***
Dalapon	CEN-QuEChERS	38	13	31	8	26	10
	FA-QuEChERS	**103**	***4***	**97**	***5***	**82**	***7***
Dicamba	CEN-QuEChERS	78	4	88	2	60	4
	FA-QuEChERS	**102**	***4***	**103**	***4***	**96**	***2***
Diflufenzopyr	CEN-QuEChERS	97	6	97	3	91	5
	FA-QuEChERS	**99**	***3***	**94**	***9***	**98**	***8***
Dikegulac	CEN-QuEChERS	72	6	84	6	65	1
	FA-QuEChERS	**106**	***3***	**92**	***7***	**97**	***3***
Fenoxaprop-P	CEN-QuEChERS	95	5	96	4	92	5
	FA-QuEChERS	**99**	**4**	**99**	**8**	**96**	**6**
Fluazifop	CEN-QuEChERS	94	4	102	4	98	2
	FA-QuEChERS	**100**	**2**	**106**	**3**	**100**	**5**
Fluroxypyr	CEN-QuEChERS	95	4	102	5	82	2
	FA-QuEChERS	**102**	**1**	**106**	**6**	**101**	**3**
Gibberellic acid	CEN-QuEChERS	90	3	89	4	79	3
	FA-QuEChERS	**103**	**1**	**107**	**6**	**99**	**4**
Haloxyfop	CEN-QuEChERS	97	5	101	4	94	3
	FA-QuEChERS	**103**	**2**	**105**	**3**	**106**	**7**
Imazamox	CEN-QuEChERS	86	3	72	3	83	3
	FA-QuEChERS	**103**	**2**	**101**	**5**	**95**	**3**
Imazapyr	CEN-QuEChERS	67	5	45	6	67	2
	FA-QuEChERS	**102**	**4**	**104**	**5**	**99**	**7**
Imazaquin	CEN-QuEChERS	97	4	101	4	93	2
	FA-QuEChERS	**102**	**2**	**103**	**5**	**105**	**3**
Imazethapyr	CEN-QuEChERS	98	4	78	4	88	4
	FA-QuEChERS	**102**	**1**	**98**	**4**	**99**	**4**
Inabenfide	CEN-QuEChERS	102	3	103	5	106	3
	FA-QuEChERS	**102**	**2**	**113**	**7**	**104**	**3**
Ioxynil	CEN-QuEChERS	90	4	105	4	79	2
	FA-QuEChERS	**102**	**4**	**104**	**4**	**99**	**4**
MCPA	CEN-QuEChERS	98	3	103	4	85	2
	FA-QuEChERS	**105**	**2**	**100**	**2**	**97**	**4**
MCPB	CEN-QuEChERS	94	3	98	5	99	10
	FA-QuEChERS	**95**	**6**	**94**	**7**	**100**	**3**
MCPP (Mecoprop)	CEN-QuEChERS	102	4	105	3	88	2
	FA-QuEChERS	**104**	**2**	**103**	**3**	**102**	**3**
Pentachlorophenol	CEN-QuEChERS	90	5	108	7	76	8
	FA-QuEChERS	**111**	**3**	**108**	**6**	**102**	**5**
Picloram	CEN-QuEChERS [6]	52	3	n.a.	n.a.	n.a.	n.a.
	FA-QuEChERS	**106**	**10**	**90** [3]	**13**	**86** [4]	**15**
Propoxycarbazone	CEN-QuEChERS	98	3	102	4	91	2
	FA-QuEChERS	**105**	**1**	**104**	**5**	**104**	**5**
Quinmerac	CEN-QuEChERS	74 [7]	5	89 [8]	2	66 [4]	4
	FA-QuEChERS	**107**	**3**	**n.a.**	**n.a.**	**n.a.**	**n.a.**
Quinmerac-metab. BH 518-2	CEN-QuEChERS [1]	16	12	29 [3]	9	n.m. [4]	-
	FA-QuEChERS [2]	**97**	**6**	**98** [5]	**7**	**79** [4]	**10**
Quinmerac-metab. BH 518-4	CEN-QuEChERS	35	10	37 [3]	13	33 [4]	10
	FA-QuEChERS [2]	**94**	**7**	**87** [5]	**7**	**82** [4]	**14**
Quizalofop	CEN-QuEChERS	94	5	101	5	97	3

Substance	Extraction Method	Cucumber 0.01 mg/kg		Grape 0.01 mg/kg		Corn flour 0.01 mg/kg	
		Rec (%)	*RSD (%)*	Rec (%)	*RSD (%)*	Rec (%)	*RSD (%)*
	FA-QuEChERS	**102**	**2**	**105**	**4**	**96**	**4**
TFNA (Flonicamid-Metabolite)	CEN-QuEChERS	37	4	39	6	34	6
	FA-QuEChERS	**105**	**3**	**105**	**5**	**94**	**2**
TFNG (Flonicamid-Metabolite)	CEN-QuEChERS	53	6	58	5	43	6
	FA-QuEChERS	**104**	**3**	**111**	**5**	**96**	**3**
Triclopyr	CEN-QuEChERS	96	5	101	4	84	2
	FA-QuEChERS	**99**	**2**	**102**	**4**	**98**	**2**

1) The spiking level here was 0.1 mg/kg (to match for very poor recoveries and/or limited sensitivity)
2) The spiking level here was 0.05 mg/kg (to match for very poor recoveries and/or limited sensitivity)
3) The data shown were divergently derived from an experiment on orange juice
4) The data shown were divergently derived from an experiment on wheat flour (with BH 518-2 the signal was too low to measure)
5) The data shown were divergently derived from an experiment on grape juice (not grapes)
6) The data shown divergently refer to a spiking level of 0.5 mg/kg (n=2)
7) The data shown were divergently derived from an experiment on iceberg lettuce
8) The data shown were divergently derived from an experiment on kiwi fruit

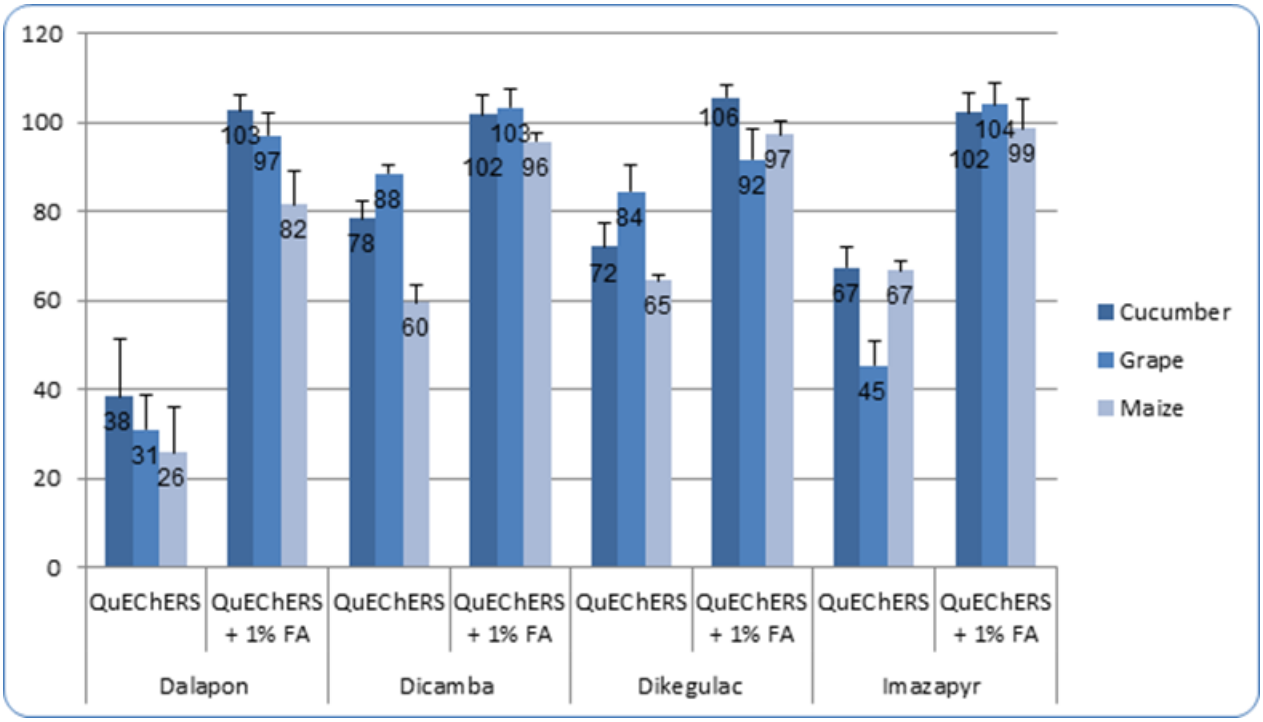


Figure 8: Comparison of recoveries of selected acidic pesticides using QuEChERS or FA-QuEChERS

Document History

Date	Action	Changes
May. 2015	Publication of V1	
Dec. 2024	Publication of V2	- Further compounds with validation data were introduced: Aminopyralid, Clopyralid, Picloram, Quinmerac and the Quinmerac metabolites BH518-2 and BH518-4. - A chapter with the theoretical background was introduced, including a critical assessment of the reliability of computed physicochemical properties - Certain sentences were revised (not always marked)