

COOPERATIVE STUDY

CERTIFIED STANDARD SOLUTIONS

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EURL-FV





The use of certified standard solutions leads to savings in time and laboratory work. However, there is not enough evidence of the quality of these solutions.

The present cooperative study is aimed at verifying the comparability of different certified standard solutions.

Seven participants analysed the same solutions and reported their results.



PARTICIPANT LABORATORIES

NRL. NVWA - Netherlands Food and Consumer Product Safety Authority

NRL. National Food Agency (Livsmedelsverket)

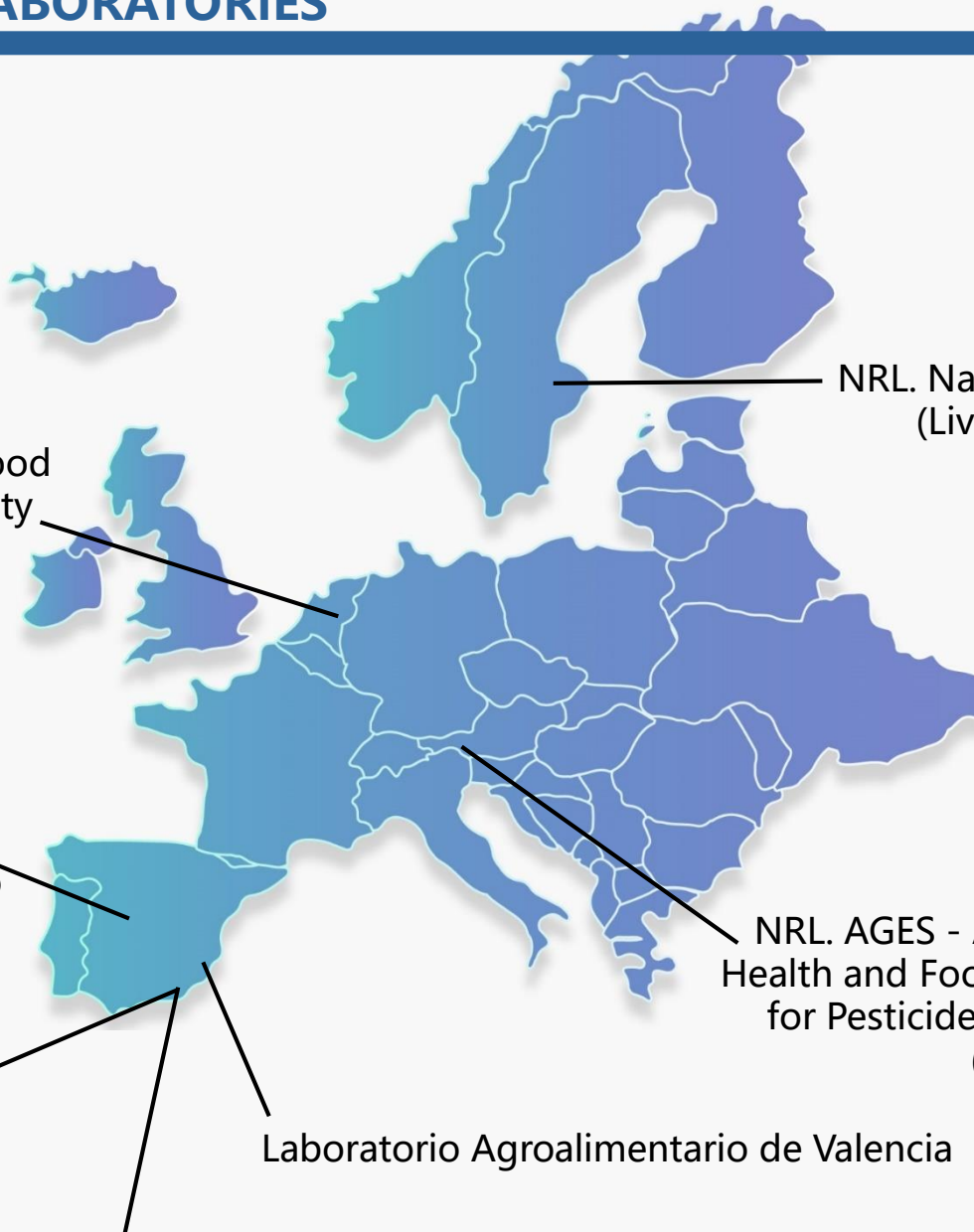
NRL. Laboratorio Arbitral Agroalimentario

NRL. AGES - Austrian Agency for Health and Food Safety. Department for Pesticide and Food Analysis (PLMA)

Eurofins SiCA AgriQ SLU

Laboratorio Agroalimentario de Valencia

EURL for Pesticide Residues in Fruits and Vegetables
University of Almería



4 certified standard solutions prepared by external specialised firms

All of them containing 28 LC-amenable pesticides included in the scope of the EU-MACP

2,4-D	Emamectin benzoate
Abamectin	Fenamiphos-sulfoxide
Acephate	Fenthion
Acetamiprid	Fipronil
Ametoctradin	Haloxypop
Benomyl	Kresoxim methyl
Bromuconazole	Malathion
Bupirimate	Methiocarb sulfone
Carbaryl	Omethoate
Carbendazim	Procymidone
Carbosulfan	Protioconazole-desthio
Cyromazine	Spinosad
Demeton-S-methylsulfoxide	Thiobencarb
Diuron	Triadimefon



Certified concentration
50 mg/L

LabStandard[®]



SPEX CertiPrep.[®]

December

S	M	T	W	T	F	S
					1	2
3	4	5	6	7	8	9
10	11	12	13	14	15	16
17	18	19	20	21	22	23
24	25	26	27	28	29	30
31						

January

S	M	T	W	T	F	S
	1	2	3	4	5	6
7	8	9	10	11	12	13
14	15	16	17	18	19	20
21	22	23	24	25	26	27
28	29	30	31			

February

S	M	T	W	T	F	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28			

March

S	M	T	W	T	F	S
				1	2	3
4	5	6	7	8	9	10
11	12	13	14	15	16	17
18	19	20	21	22	23	24
25	26	27	28	29	30	31

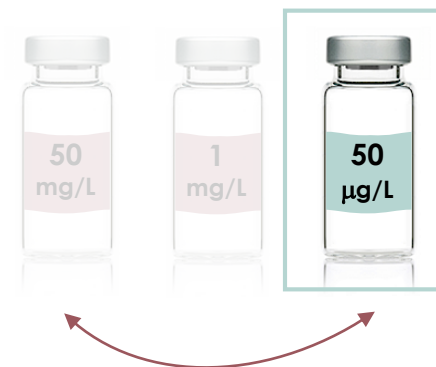
April

S	M	T	W	T	F	S
1	2	3	4	5	6	7
8	9	10	11	12	13	14
15	16	17	18	19	20	21
22	23	24	25	26	27	28
29	30					

December 2017 – February 2018 Preparation of solutions

Diluted to 1 mg/L in acetonitrile

Stored at -20 °C



April 2018

Shipment of solutions

Diluted to 50 µg/L

Analysed 6 times in pure solvent by liquid chromatography

Concentrations calculated by comparison with their own standards

SOLUTION D

Concentrations reported by each laboratory (µg/L)

	Lab 1	Lab 2	Lab 3	Lab 4	Lab 5	Lab 6	Lab 7
2,4-D	51	56	49	47	54	66	55
Abamectin	12	62	70	25	45	54	66
Acephate	48	55	54	50	47	52	60
Acetaminrid	55	52	57	57	45	56	59
Ametoctradin	52	57	56	61	85	58	62
Bromuconazole	48	51	51	46	44	52	NA
Bupirimate	52	61	55	58	44	57	61
Carbaryl	54	53	53	50	54	56	61
Carbosulfan	11	NA	52	NA	42	63	51
Cyromazine	63	NA	60	54	27	53	56
Demeton-S-methylsulfoxide	58	69	59	59	57	60	64
Diuron	56	55	58	56	59	58	53
Emamectin benzoate	7	24	32	6	NA	27	26
Fenamiphos – sulfoxide	54	63	58	59	49	58	59
Fenthion	47	52	51	45	50	62	65
Fipronil	53	59	48	51	52	59	59
Haloxifop	51	57	49	49	56	55	62
Kresoxim methyl	53	56	64	59	49	50	56
Malathion	51	58	60	59	51	61	60
Methiocarb sulfone	2	22	20	4	22	22	52
Omethoate	36	44	48	35	36	51	54
Procymidone	45	NA	51	77	NA	59	NA
Prothioconazole-Desthio	58	60	60	66	62	62	67
Spinosad	27	50	52	28	58	55	57
Thiobencarb	50	NA	NA	49	54	57	NA
Triadimefon	59	59	58	60	59	63	69

Inter-laboratory results

Average	CV (%)	
52	7	2,4-D
59	17	Abamectin
52	8	Acephate
54	8	Acetaminrid
58	6	Ametoctradin
49	6	Bromuconazole
57	6	Bupirimate
55	6	Carbaryl
52	16	Carbosulfan
57	7	Cyromazine
61	7	Demeton-S-methylsulfoxide
56	4	Diuron
20	55	Emamectin benzoate
57	8	Fenamiphos – sulfoxide
49	6	Fenthion
55	9	Fipronil
54	9	Haloxifop
55	9	Kresoxim methyl
57	7	Malathion
36	26	Methiocarb sulfone
43	18	Omethoate
58	24	Procymidone
62	5	Prothioconazole-Desthio
54	6	Spinosad
52	7	Thiobencarb
61	7	Triadimefon

Solution D

Criteria to discard differing results

- At least 5 results per pesticide ($n \geq 5$)
- Deleted data must be at least 20% different from the average result

Inter-laboratory results for all solutions

Average	CV (%)	Average	CV (%)	Average	CV (%)	Average	CV (%)	
46	9	46	6	45	5	52	7	2,4-D
53	14	59	12	56	37	59	17	Abamectin
48	9	48	8	51	7	52	8	Acephate
48	10	48	9	50	10	54	8	Acetamidrid
57	4	29	10	35	6	58	6	Ametoctradin
48	7	47	5	51	8	49	6	Bromuconazole
47	10	46	9	46	9	57	6	Bupirimate
48	7	52	7	51	7	55	6	Carbaryl
43	41	35	44	38	42	52	16	Carbosulfan
48	31	50	13	47	26	57	7	Cyromazine
56	8	51	10	62	7	61	7	Demeton-S-methylsulfoxide
49	5	50	9	52	3	56	4	Diuron
29	49	24	57	36	53	20	55	Emamectin benzoate
52	9	49	10	36	9	57	8	Fenamiphos – sulfoxide
49	8	47	9	47	9	49	6	Fenthion
46	10	48	8	46	8	55	9	Fipronil
49	9	51	10	48	9	54	9	Haloxifop
51	9	51	6	48	8	55	9	Kresoxim methyl
49	7	47	10	46	6	57	7	Malathion
49	26	46	31	57	52	36	26	Methiocarb sulfone
50	9	55	19	53	17	43	18	Omethoate
50	25	51	27	46	24	58	24	Procymidone
48	4	49	9	47	4	62	5	Prothioconazole-Desthio
47	20	36	33	41	21	54	6	Spinosad
48	10	51	8	46	7	52	7	Thiobencarb
50	6	52	7	50	6	61	7	Triadimefon
Solution A		Solution B		Solution C		Solution D		

Selection of pesticides for the assessment of solutions

- Inter-laboratory CV ≤ 10%

28 PESTICIDES

- 18 Used for the assessment of solutions
- 8 Individual study
- 2 Not for quantification purposes

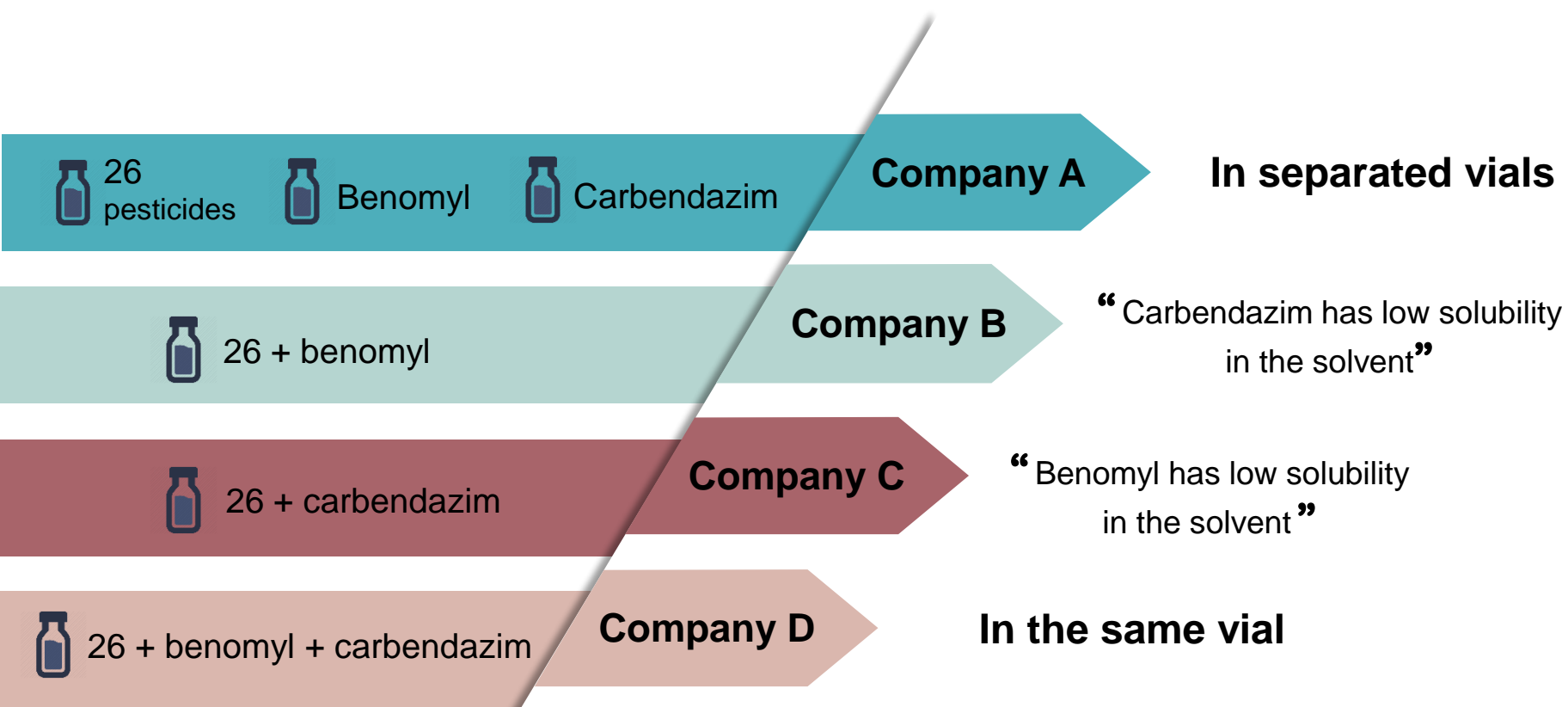
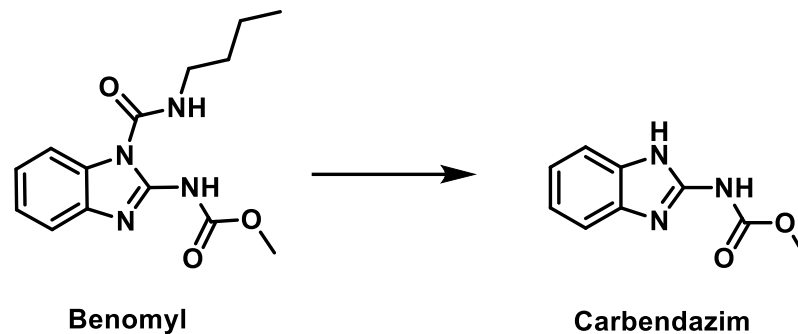
2,4-D	Emamectin benzoate
Abamectin	Fenamiphos-sulfoxide
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Carbendazim	Procymidone
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Demeton-S-methylsulfoxide	Thiobencarb
Diuron	Triadimefon

Benomyl and carbendazim



Benomyl is very unstable and decomposes into carbendazim

Both pesticides were included in the request of solutions A, B, C, D



Assessment of the concentrations in the solutions

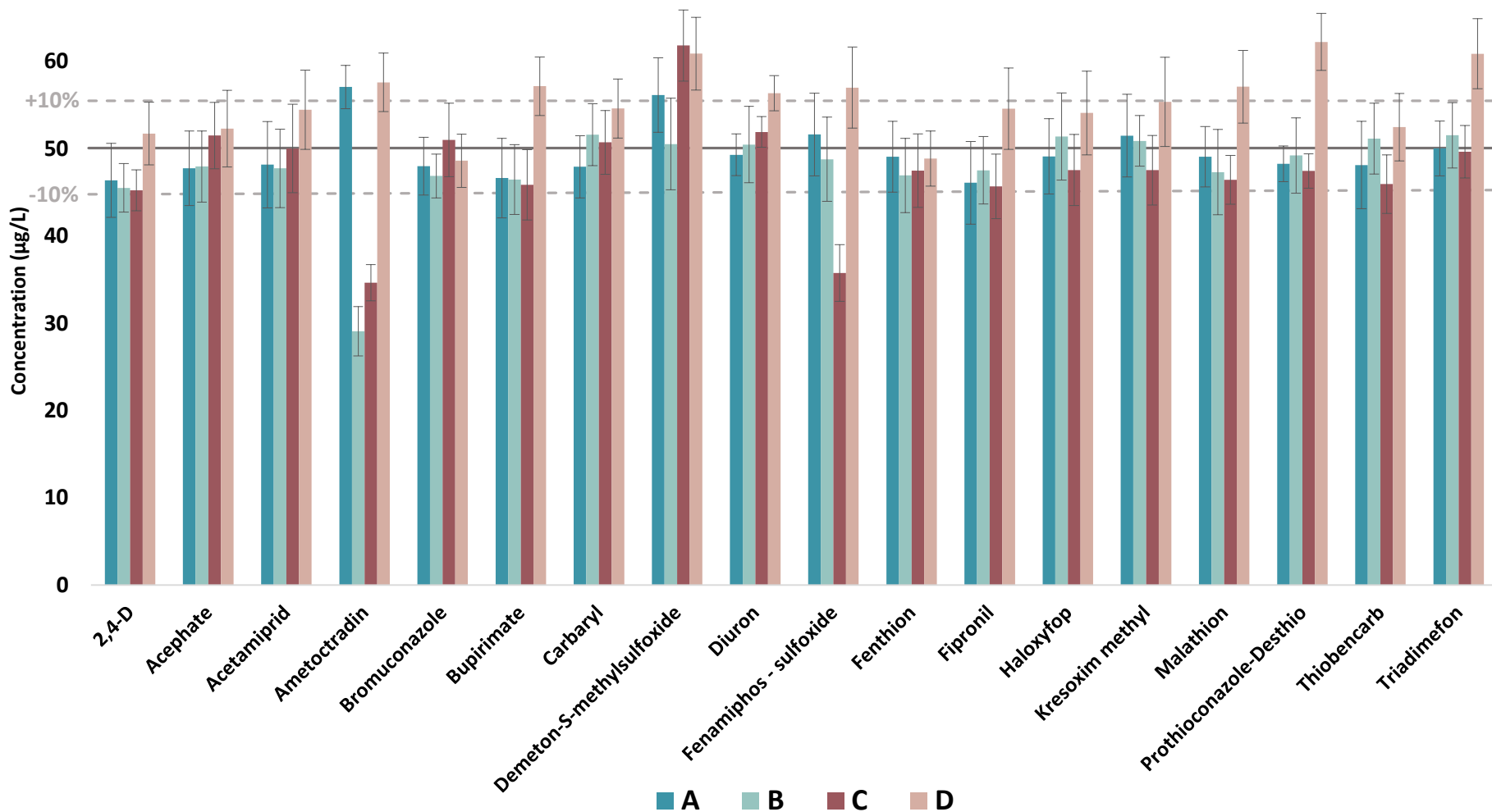


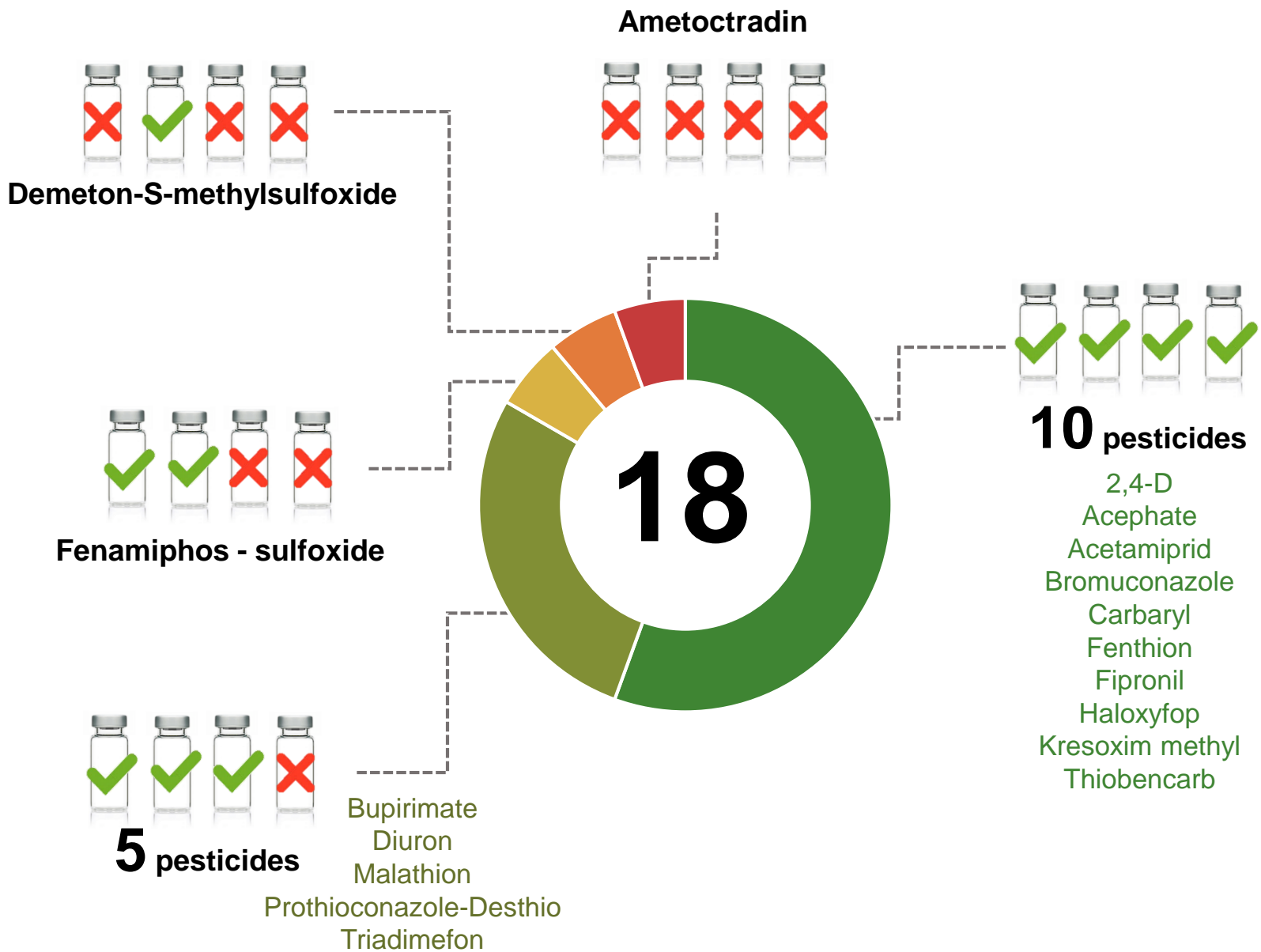
Inter-laboratory CV $\leq 10\%$ ($n \geq 5$)

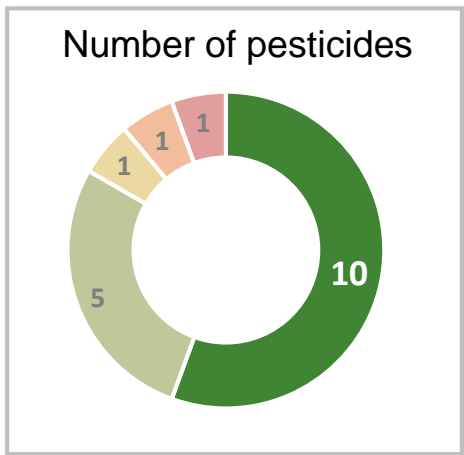


- 18 pesticides for which at least 5 participants reported similar concentration (CV \leq 10%)
- Each bar represents the average of 5-7 results (one per laboratory)

Acceptable concentration of a certain pesticide in a solution: $50 \pm 5 \mu\text{g/L}$ (10% deviation)

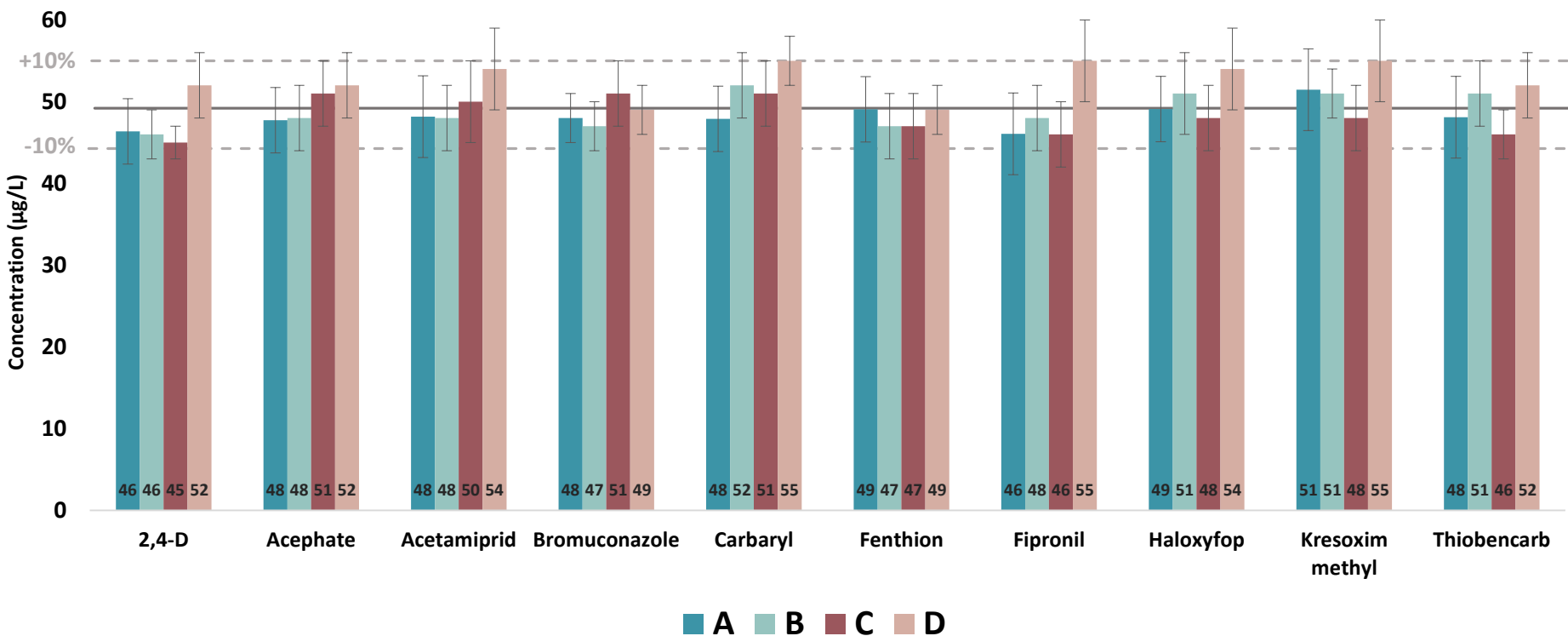


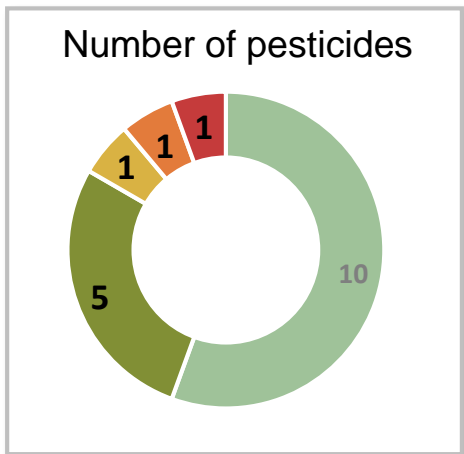




All solutions meet the acceptance criteria

- ✓ Inter-laboratory CV $\leq 10\%$ ($n \geq 5$)
- ✓ Concentrations = $50 \pm 5 \mu\text{g/L}$ (10% dev)

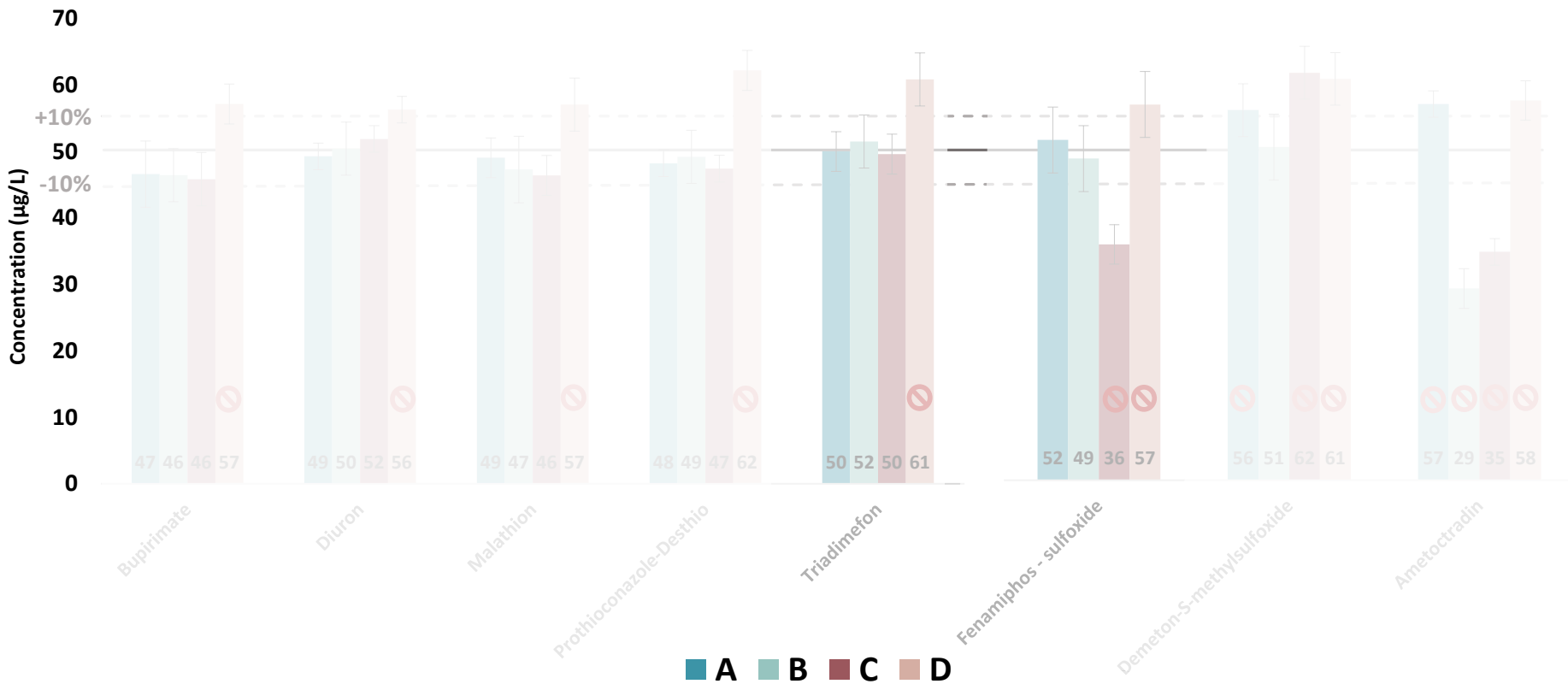


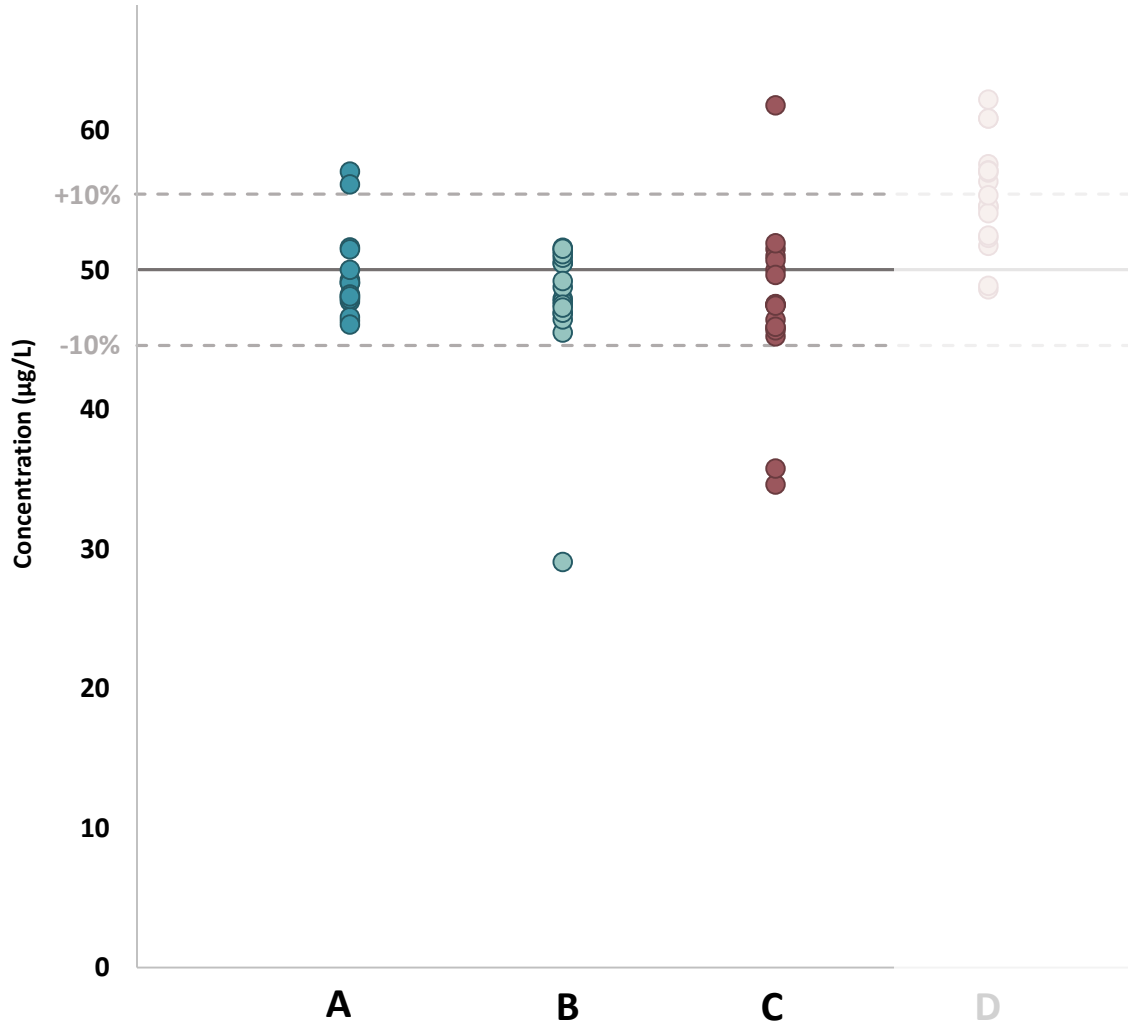


⊘ Results that do not meet the acceptance criteria

✓ Inter-laboratory CV $\leq 10\%$ ($n \geq 5$)

✗ Concentrations = $50 \pm 5 \mu\text{g/L}$ (10% dev)





18 pest. x 4 solutions =

72 RESULTS (A, B, C, D)

58 correct

14 incorrect

80% correct concentrations

18 pest. x 3 solutions =

54 RESULTS (A, B, C)

48 correct

6 incorrect

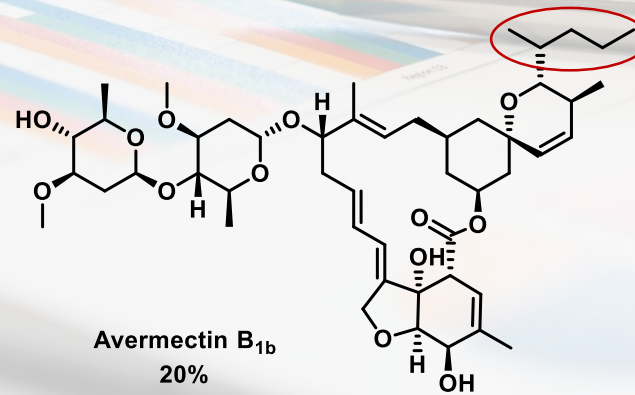
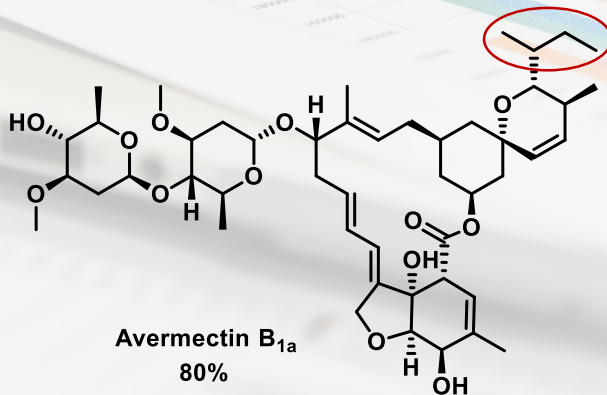
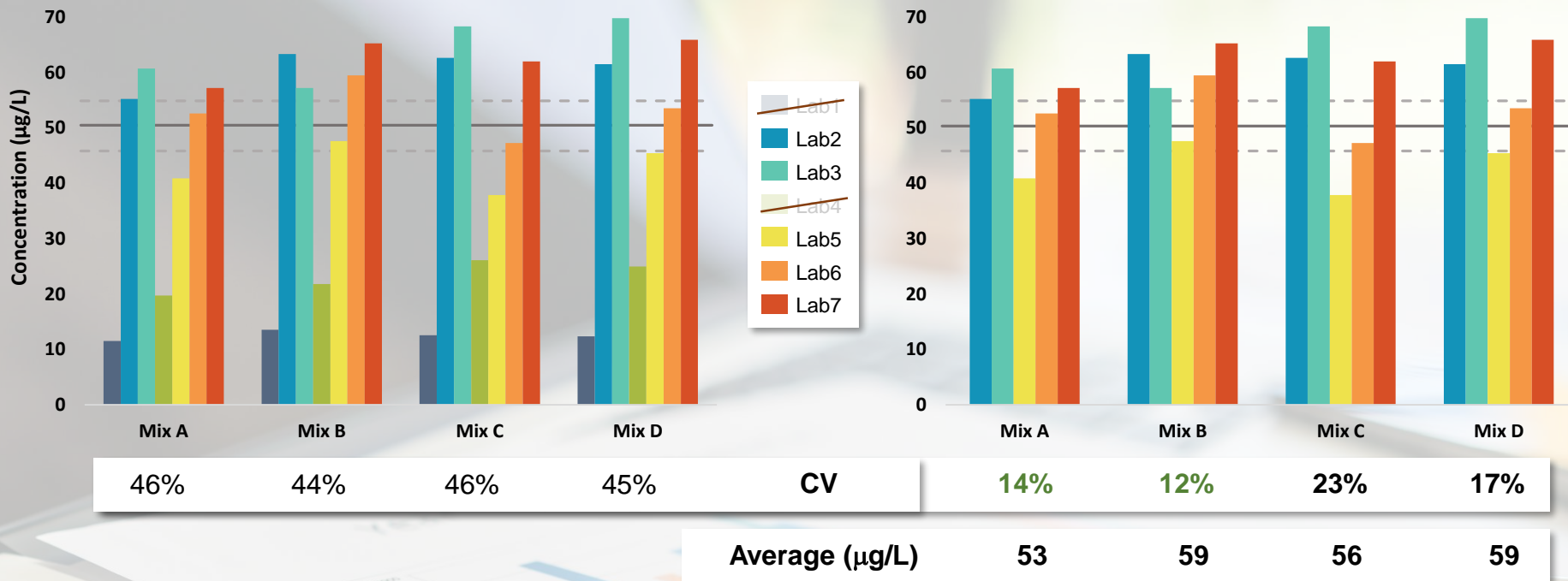
88% correct concentrations

Individual studies

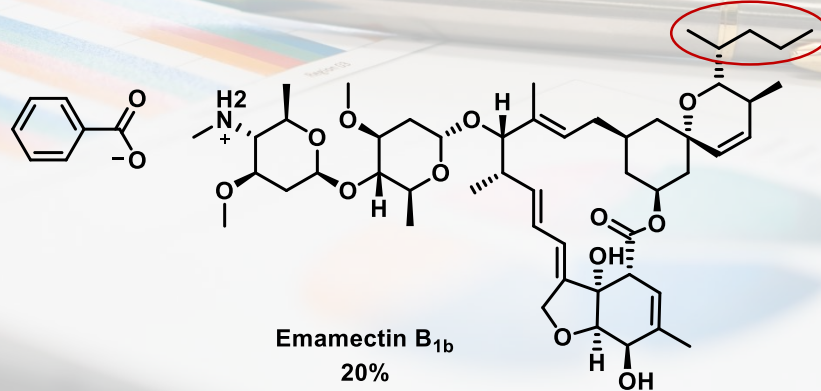
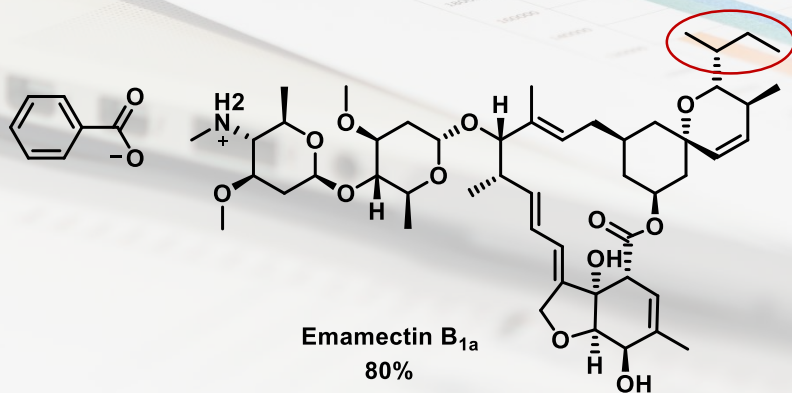
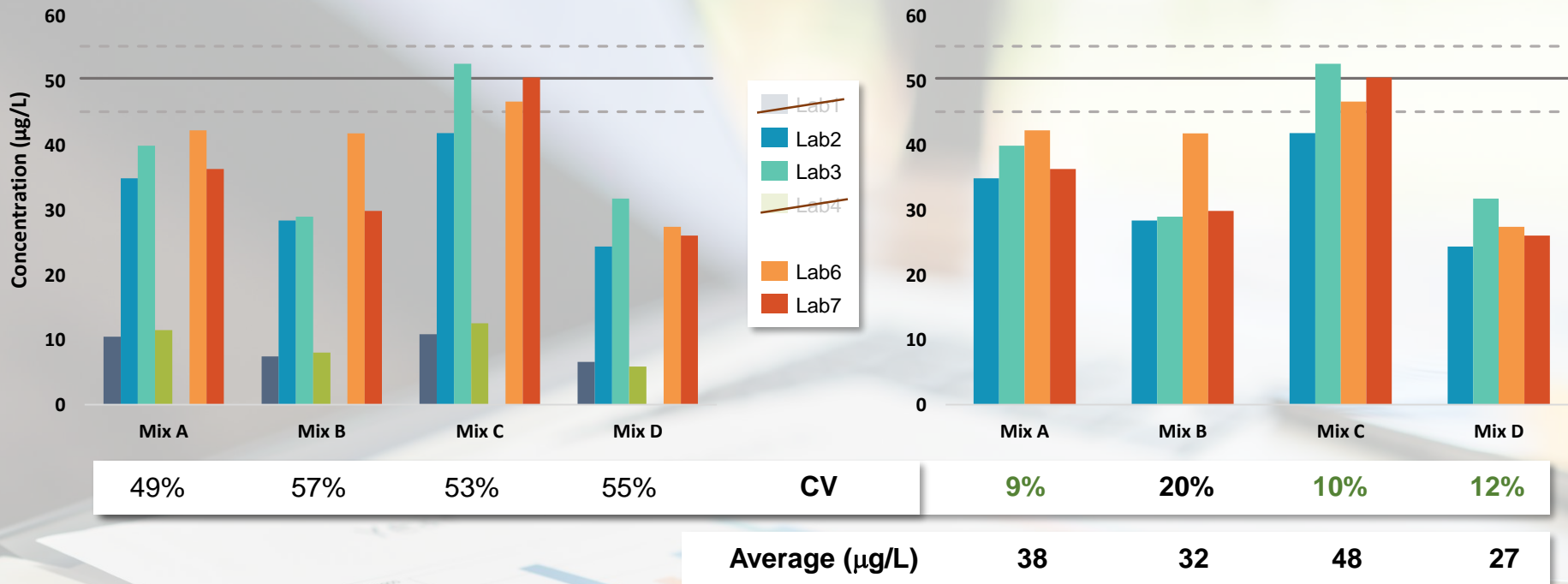
X Inter-laboratory CV $\leq 10\%$ ($n \geq 5$)

Inter-laboratory CV $\leq 15\%$ ($n \geq 4$)

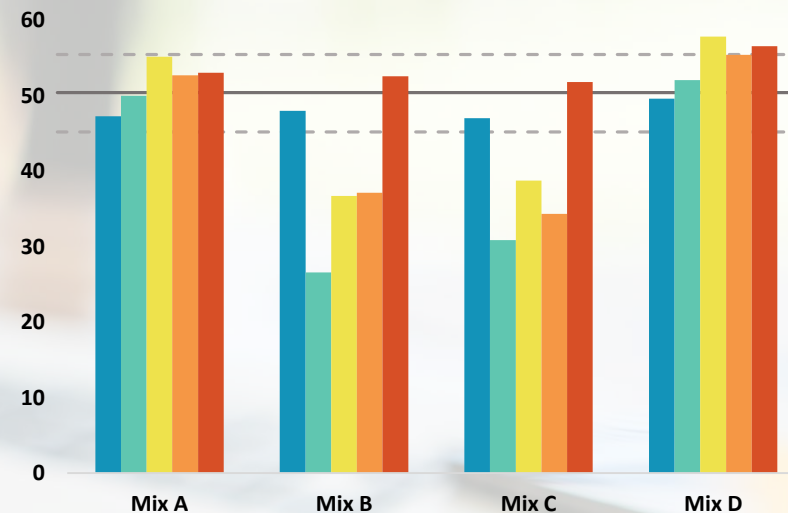
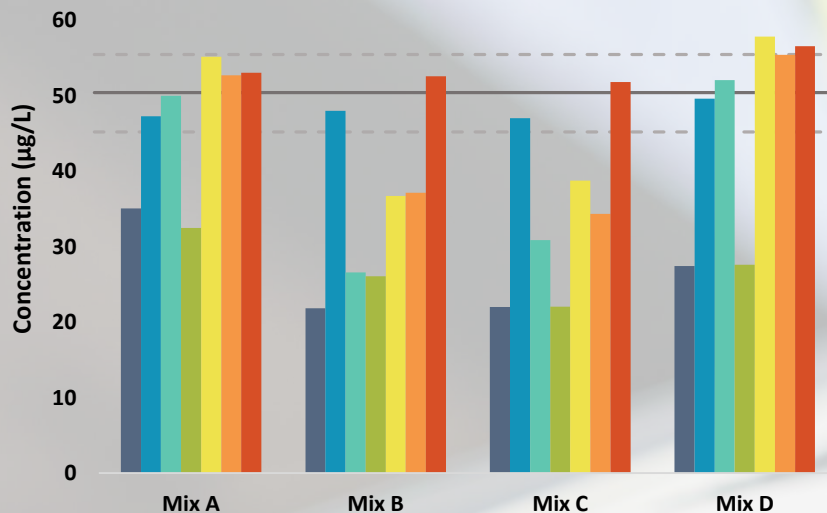
Abamectin



Emamectin benzoate

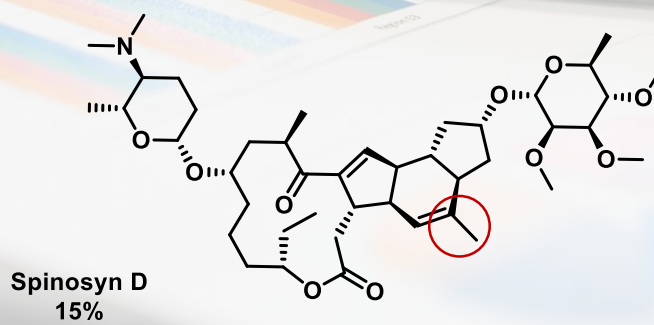
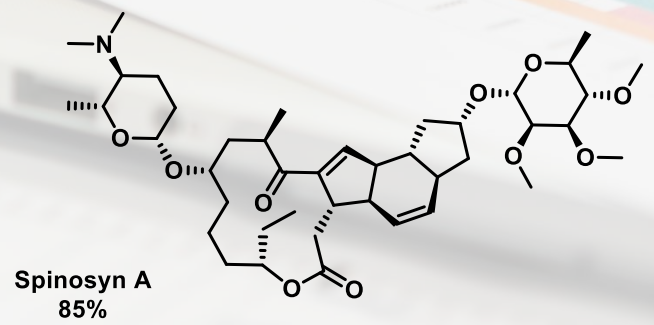


Spinosad

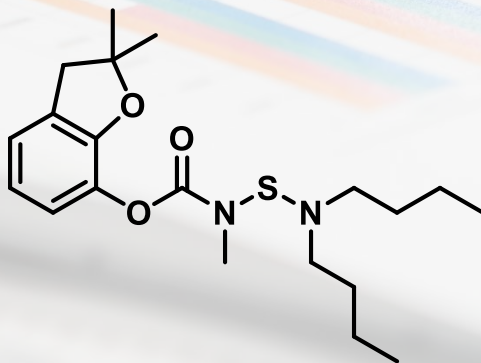
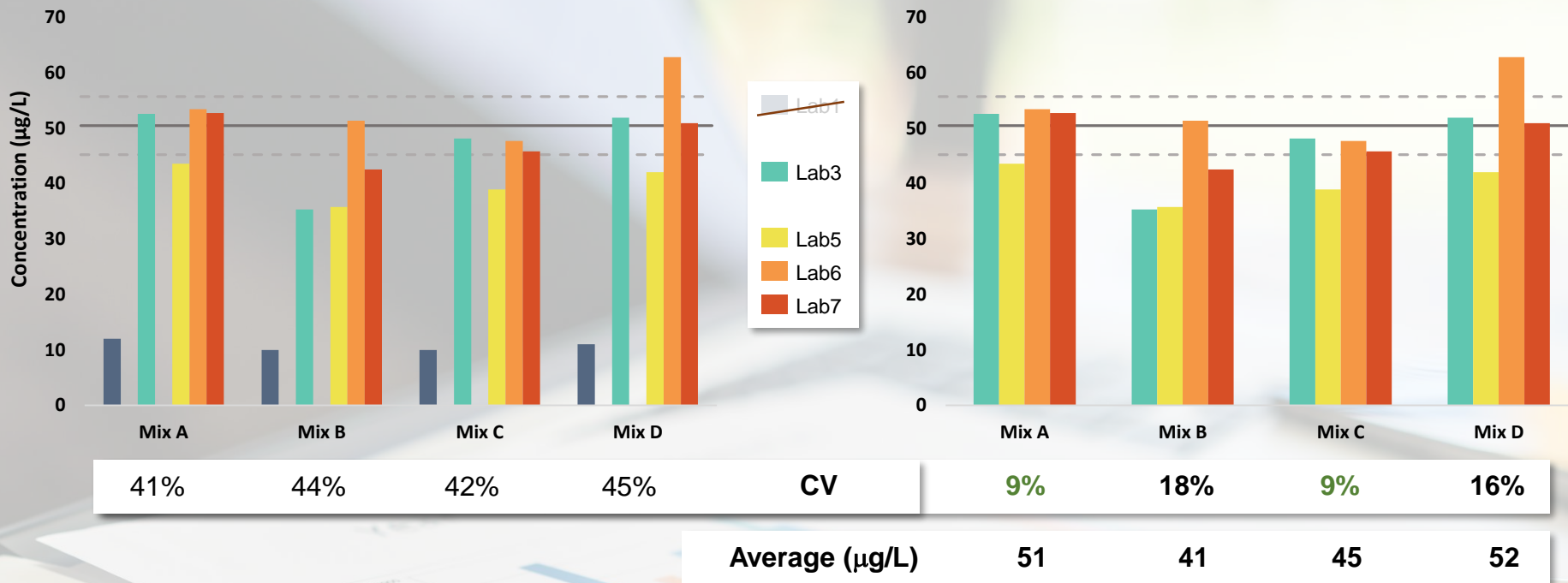


Mix	Mix A	Mix B	Mix C	Mix D	CV
CV	20%	33%	33%	29%	
CV	6%	25%	21%	6%	

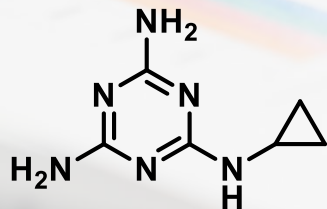
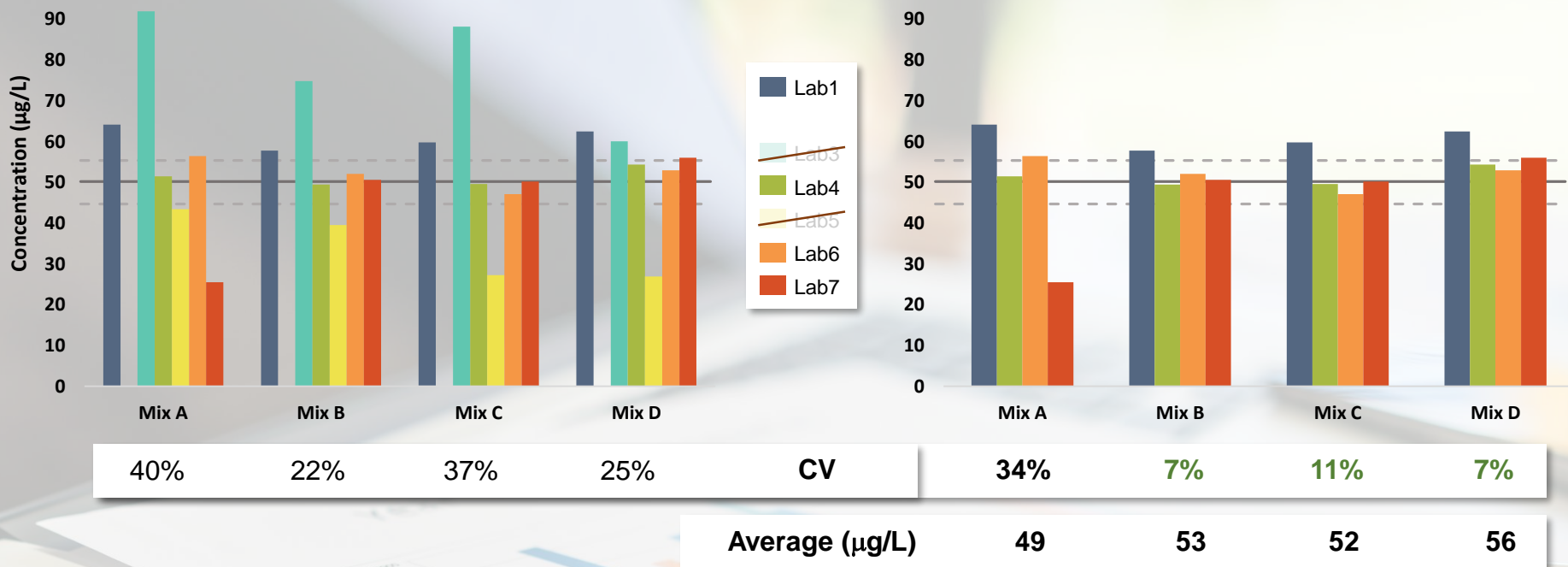
Mix	Mix A	Mix B	Mix C	Mix D
Average (µg/L)	52	40	41	54



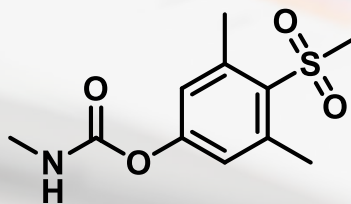
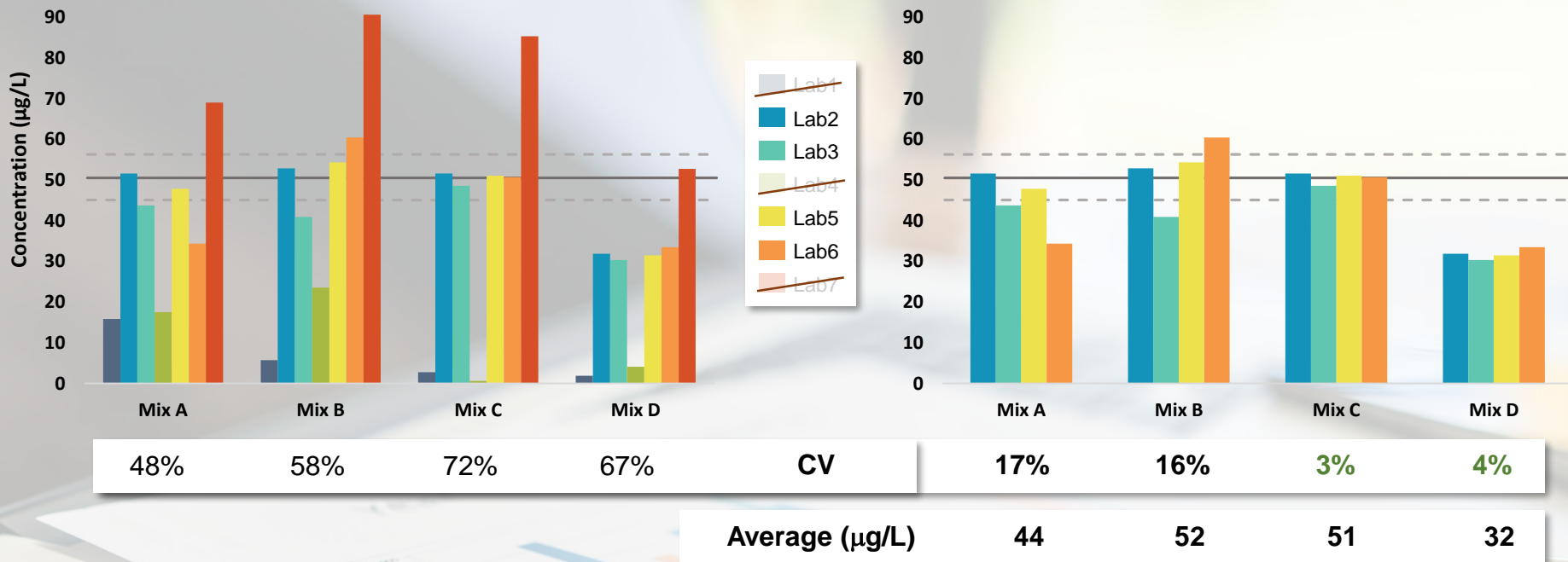
Carbosulfan



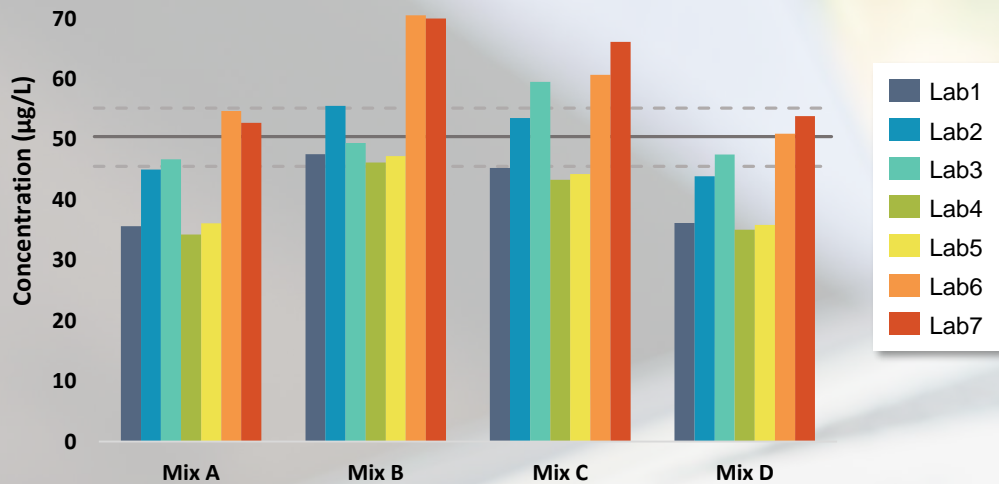
Cyromazine



Methiocarb sulfone



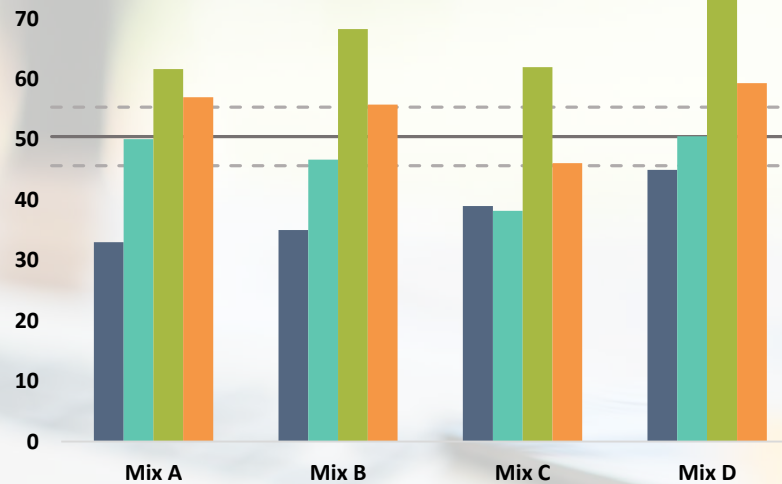
Omethoate



19% 19% 17% 18% CV

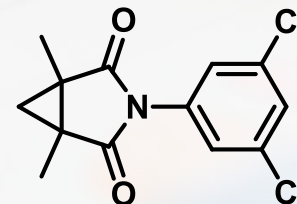
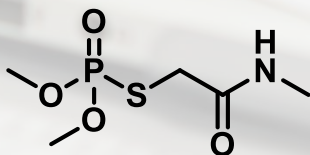
44 55 53 43 Average (µg/L)

Procymidone



25% 27% 24% 24%

50 51 46 58



Certified standard solutions

At least 80% of pesticides showed a deviation $\leq 10\%$ from the certified concentration.

In some cases, the companies do not have enough knowledge of the behaviour of some pesticides in solution.

One of the solutions was clearly unsatisfactory, with several concentrations higher than 55 ppm (more than 10% deviation).

Laboratories

The deviation of the standard solutions prepared by the laboratories contained a considerable error in at least 5% of the results.





EURL-FV Team

May 2018



**THANK YOU
FOR YOUR ATTENTION**



European
Commission

EURL-FV

