



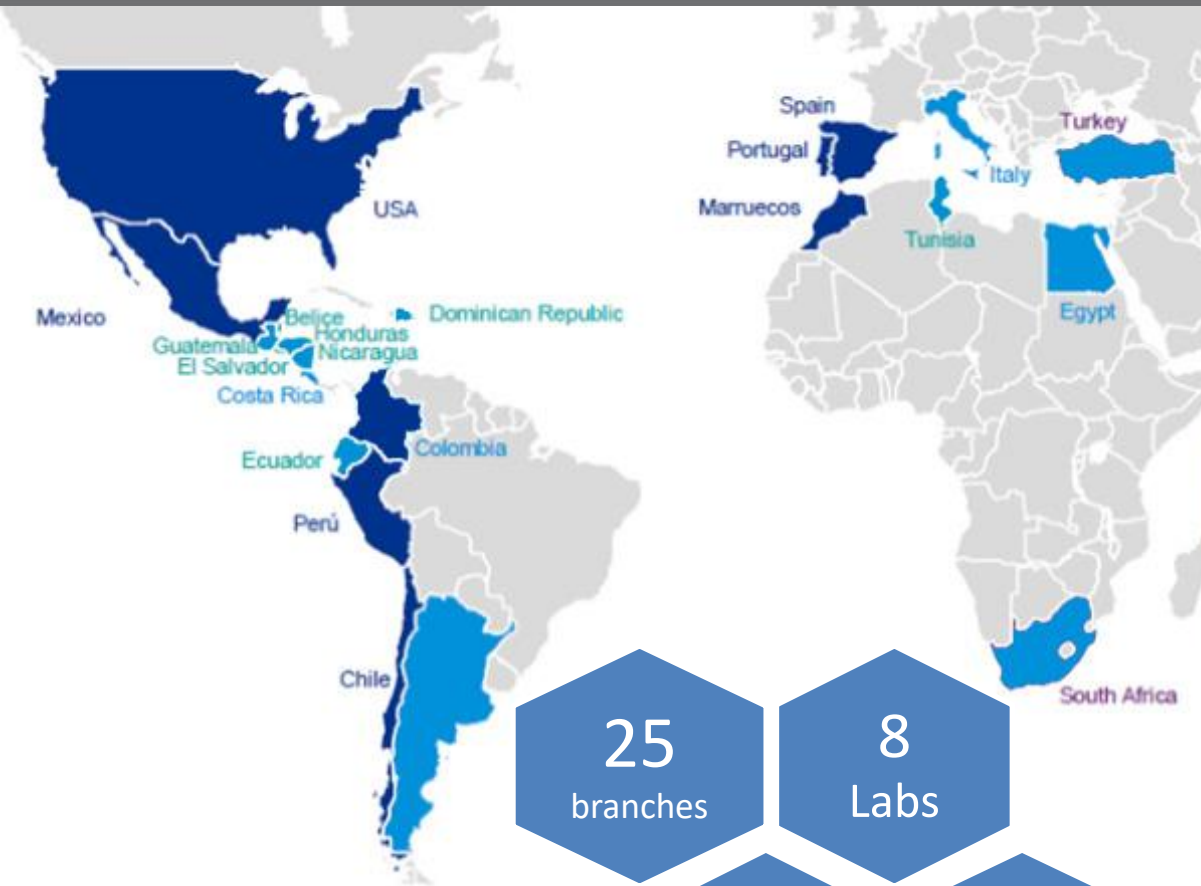
Pesticide Residue Analysis and Global MRL Compliance

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**for a
better
and safer
world**





25
branches

8
Labs

+600
staff

+500 k
samples a
year



Notes:

- Subsidiary entities and laboratories.
- Subsidiaries entities with commercial and technical structures. Operations centre.

agenda

MRL Harmonization and Pesticide Residue Analysis

Strategies for MRL Compliance

Residue Data and MRL Compliance Trends

Pesticide Metabolites and Residue Definitions Challenges

The Never Ending Story: MRL Harmonization

- **New uses of existing chemicals (Ex:Pre-harvest vs post-harvest use)**
- **New studies leading to reduction and/or removal of existing MRLs**
- **New chemicals with limited # of MRLs established**
- **New invasive pest issues**
- **Abrupt new dietary trends**
- **Costly and time consuming to establish new MRLs**
- **Differences in data interpretation and registration policies**

MRL Harmonization: Multiple Fronts

- **Differences in residue definitions**
Ex: US Fosetyl-al = Fosetyl-al vs EU Foestyl-al= Fosetyl + Phosphonic Acid
- **Differences in corresponding MRL values**
Ex: Sweet Potato TBZ MRLs: US- 10 ppm / EU- 0.01 ppm / JP- 0.05 ppm
- **Lack of MRLs established (missing MRLs)**
Ex: China, Hong Kong, other emerging markets
Ex: 16 US MRLs established for Quinoa vs 141 US MRLs established for Rice
- **Policies for residues with no corresponding MRL**
EX: Default, Deferral, both, or neither

Pesticide Residues: Additional Challenges

- **Secondary Standards**
Ex: LIDL US
- **Food Additive Regulations**
Ex: Post-harvest fungicides in Japan
- **International Organic Compliance (in regards to pesticide residues)**
Ex: Taiwan Organic certifier black list
- **The few misleading the many**
Ex: 100 ppb vs 0.1 ppm of glyphosate

Common Reasons for Residue Testing

- **Certification Requirements**
Ex: Global Gap
- **Customer Requirements**
Ex: One residue test at beginning of season vs per lot testing
- **Internal Pre-Export Testing Programs**
Ex: test, hold, ship
- **Verification of Post-Harvest residue concentrations**
Ex: Desired residues to reduce decay
- **Residue Degradation and process studies**
Ex: Develop export market PHI or raw material residue specifications

Pesticide Residue Analysis: Sampling Considerations

- **Residue results are a reflection of application and sampling techniques**
- **Specific Sampling SOPs**
 - Every commodity is different
 - Sampling location/methods: Field vs Packinghouse vs FDA DWPE
 - Proper Labeling and traceability
 - Consistency: do what you say and say what you do
- **Poor sampling leads to useless results and more money/time lost**

Pesticide Residue Analysis: Laboratory Considerations

- **Residue results are also a reflection of the lab analyzing the sample**
- **Technical Capabilities**
 - ISO-17025 Accredited? → Yes
 - Scope of the screen? → 300-400 chemicals including metabolites
 - Limits of Quantitation? → 0.010 ppm for every chemical
 - Instrumentation? → GC-MS/MS + LC-MS/MS
- **Practical Considerations**
 - Turnaround times?
 - Informative Report Format?
 - Additional tools?
 - Cost per chemical? Total cost per sample?

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MRLs: Opportunity Cost vs Non-Compliance Cost

- **2 types of trade disruptions due to of MRL differences**
 1. Not being able to export product due to residues being over export MRL
 2. Unknowingly exporting product with residues over destination MRL
- **1 is more common but 2 is more impactful to industry**
 - EX: Korea detected Piperonyl Butoxide on US export over Korean MRL
 - Impacts:
 - US export industry lost preferential status (only random testing)
 - To regain preferential status there must be zero violations for 5 years
 - Increased surveillance testing increases chances of second violation
- **How to reduce lost opportunities?**
- **How to avoid more significant impacts of non-compliance?**

MRL Compliance Strategy: Plan Ahead!!!

- **Communication is the key to success**
 - Sales picks export markets
 - PCAs/Applicators choose the chemicals
 - Food Safety/QA conducts the testing to determine compliance
- **Export market MRL risk assessments**
 - ID alternative chemicals which have less risk to exceed export market MRL
 - Compare application records to ID high risk product for pre-export testing
- **Degradation and Process Studies to increase likelihood of MRL compliance**
- **Finished product sample for Multi-Residue Analysis prior to exporting**

MRL Risk Assessment by Active Ingredient

Blueberry, highbush

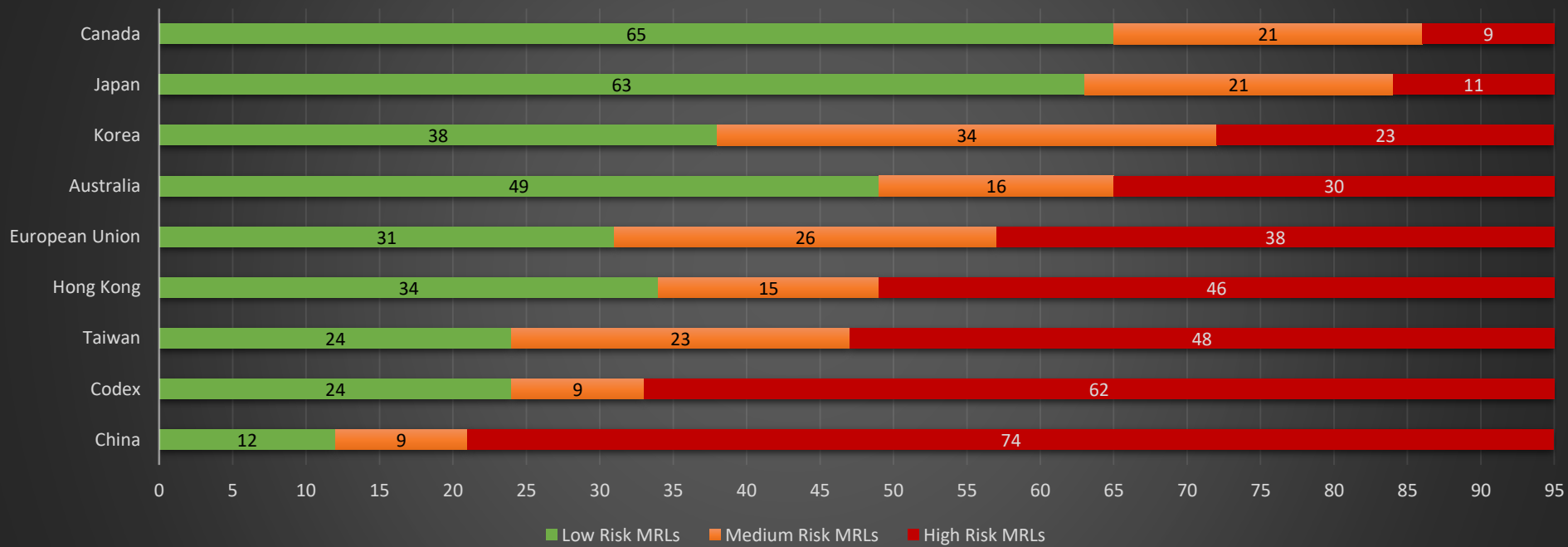
Legend:

Low Risk	Medium Risk	High Risk
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Active Ingredient	Origin	Export Markets								
		United States	Canada	European Union	Japan	Korea	Taiwan	China	Codex	Hong Kong
2,4-D	0.2	0.01	0.1	0.1	0.05	0.1	0.1	0.1	0.1	
Acetamiprid	1.6	1.6	2	2	0.5	1	2	2		1.6
Aldrin	0.05	0.1	0.01	0.05	0.01	0.01	0.05		0.05	0.05
Azoxystrobin	5	3	5	5	1	5		5	5	5
Benoxacor	0.01	0.1		0.01						
Bifenthrin	1.8	0.1	0.01	2	0.3	1		3		3
Boscalid	13	6	15	10	10	10		10	10	15
Captan	20	5	30	20	20	20	20	20	20	20
Carbaryl	3	7	0.01	7	0.5	0.5				
Carfentrazone-ethyl	0.1	0.1	0.01	0.1	0.1	0.1			0.1	0.05
Chlorantraniliprole	2.5	0.35	1.5	3	1	2	1	1	1	3
Chlordane	0.1	0.1	0.01	0.02	0.02	0.01	0.02	0.02	0.02	
Chlorothalonil	1	0.6	0.01	1	1	1			10	10
Clethodim	0.2	0.2	0.1	0.01	0.05	0.01				0.2
Clopyralid	0.5	0.1	0.5	0.01						0.5
Cryolite	7	0.1	0.01	0.01					7	
Cyantraniliprole	4	4	4	4	4			4		4
Cyprodinil	3	4	3	5	1	3		10		3
DDT (DDE, DDD)	0.1	0.1	0.05	0.5	0.05	0.01	0.05		0.05	1
Diazinon	0.5	0.1	0.01	0.1	0.05	0.5			0.5	0.5
Dichlobenil	0.15	0.5	0.01	0.01	0.05					1
Dichlormid	0.05	0.1	0.01	0.01						
Dieldrin	0.05	0.1	0.01	0.05	0.01	0.01	0.02		0.05	0.05
Difenoconazole	4	4	0.1	4	0.5	1				
Dimethoate	1	1	0.01	1	1	0.01				5
Diquat dibromide	0.05	0.1	0.01	0.03	0.02					0.05
Diuron	0.1	0.1	0.01	0.05	1	0.01			0.1	0.5

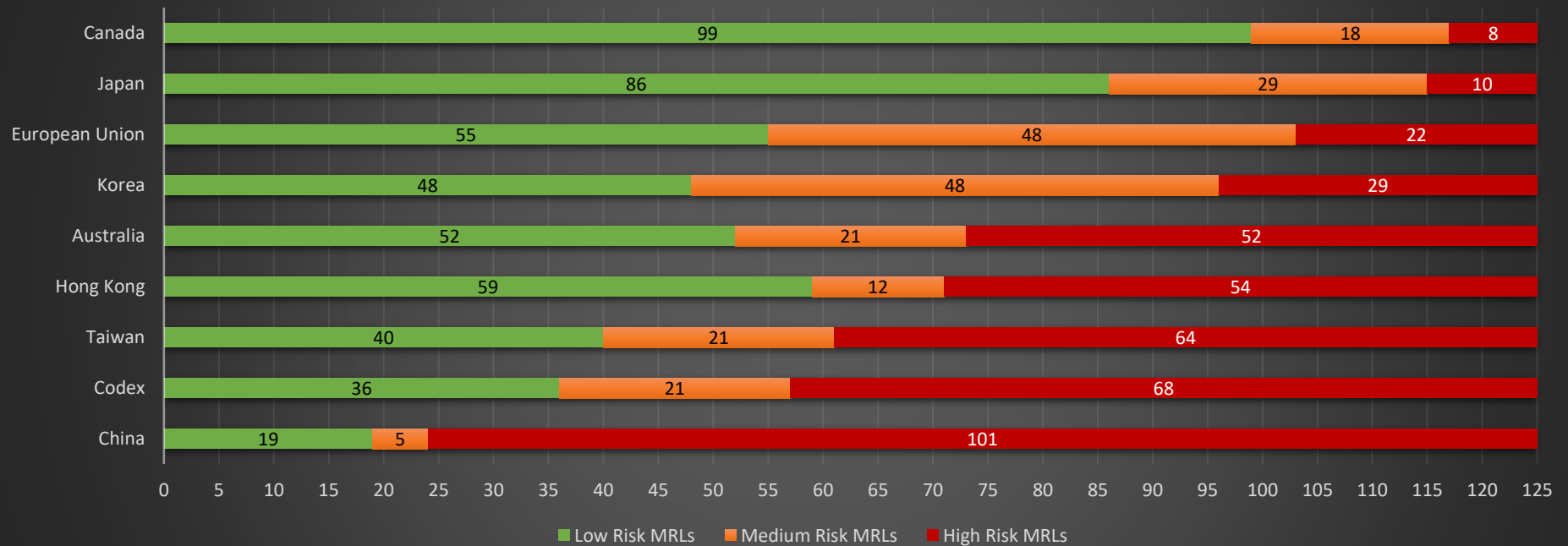
US Origin: Highbush Blueberry MRL Risk Summary

- 95 US MRLs for Highbush Blueberries**



US Origin: Almond MRL Risk Summary

- 125 US MRLs for Almonds

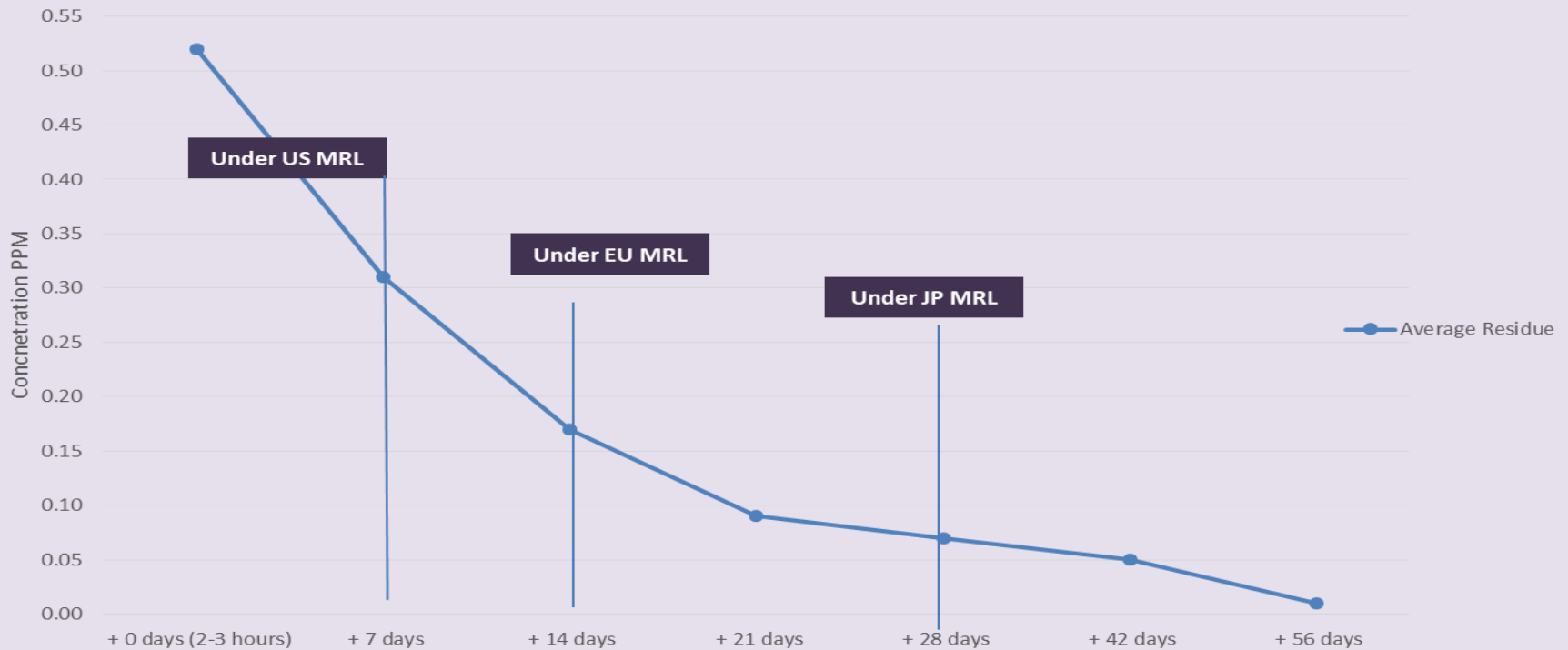


Pesticide Degradation and Process Studies

- Degradation studies can be designed to establish custom PHI's to meet export Market MRLs
- Process studies designed to establish pesticide residue specifications on raw materials in order for processed commodity to be within MRLs
 - EX: Useful for oils, concentrates, dehydrated products, etc...

Pesticide Residue Degradation Curve: Basic Theoretical Example

Example Degradation Curve



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Pesticide Metabolites and Residue Definitions Challenges

Pesticide Residue Metabolites: Contradicting Definitions

- Issues arising due to residue definitions and pesticide metabolites are not easy to overcome
- Degradation and Process studies not as effective
- More advanced MRL risk assessment will help identify areas of risk due to metabolite issues to perform pre-export residue testing
- Long Term Solution:
 - harmonizing definitions and enforcement policy to reduce lost opportunities and MRL exceedances due to residue metabolites
- Short term solution:
 - Avoid use of chemicals with metabolite issues in targeted export markets

Contradicting Definitions: Thiamethoxam and Clothianidin

- US and Canadian definition summary:
 - Thiamethoxam= Thiamethoxam+ metabolite Clothianidin
 - Clothianidin= Clothianidin
- 15 commodities have higher US MRLs for the metabolite Clothianidin than they do for the parent molecule Thiamethoxam
- Consequently the use of clothianidin can result in product exceeding US and Canadian Thiamethoxam MRLs
- Issue for domestic growers but also for producers exporting to the US and Canada

Contradicting Definitions: Thiamethoxam and Clothianidin

List of Commodities with Higher Clothianidin MRLs than Thiamethoxam MRLs in US and/or Canada:

1. Table Grape
2. Wine Grape
3. Potato
4. Apple
5. Pear
6. Nectarine/peach
7. Sweet potato
8. Bell pepper (just US)
9. non bell pepper
10. Carrot
11. Tea leaves
12. Ginger
13. Ginseng
14. Turmeric
15. Wheat straw (just US)

Example: Table Grapes

- Clothianidin US/CA MRL- 0.6 ppm
- Thiamethoxam US/CA MRL- 0.2 ppm

AGQ Reporting Format:

- Clothianidin=Clothianidin
- Thiamethoxam=Thiamethoxam
- Thiamethoxam (Sum)=
Thiamethoxam+Clothianidin

Contradicting Definitions: Thiamethoxam and Clothianidin

The following results were higher or equal to the LOQ:

Parameter	Result	Units	MRL US
Boscalid	0.52	mg/kg	5.00
Clothianidin (SP)	0.33	mg/kg	0.60
Cyprodinil	0.76	mg/kg	3.00
Fludioxonil	0.30	mg/kg	2.00
Iprodione	0.02	mg/kg	60.0
Myclobutanil	0.25	mg/kg	1.00
Pendimethalin	0.01	mg/kg	0.10
Pyraclostrobin	0.27	mg/kg	2.00
Tebuconazole	0.54	mg/kg	5.00
Thiamethoxam (Sum)	0.33	mg/kg	0.20
			NO

Total Table Grape Samples Per Year/Country

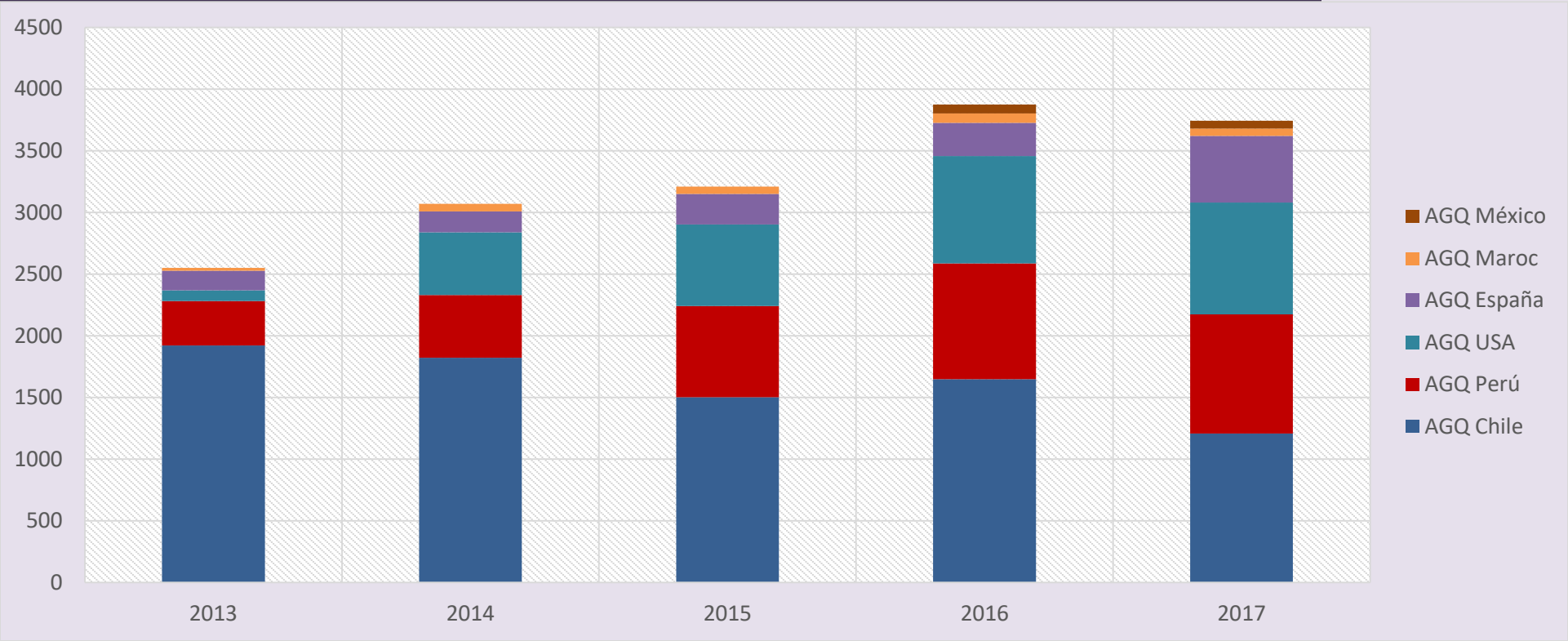
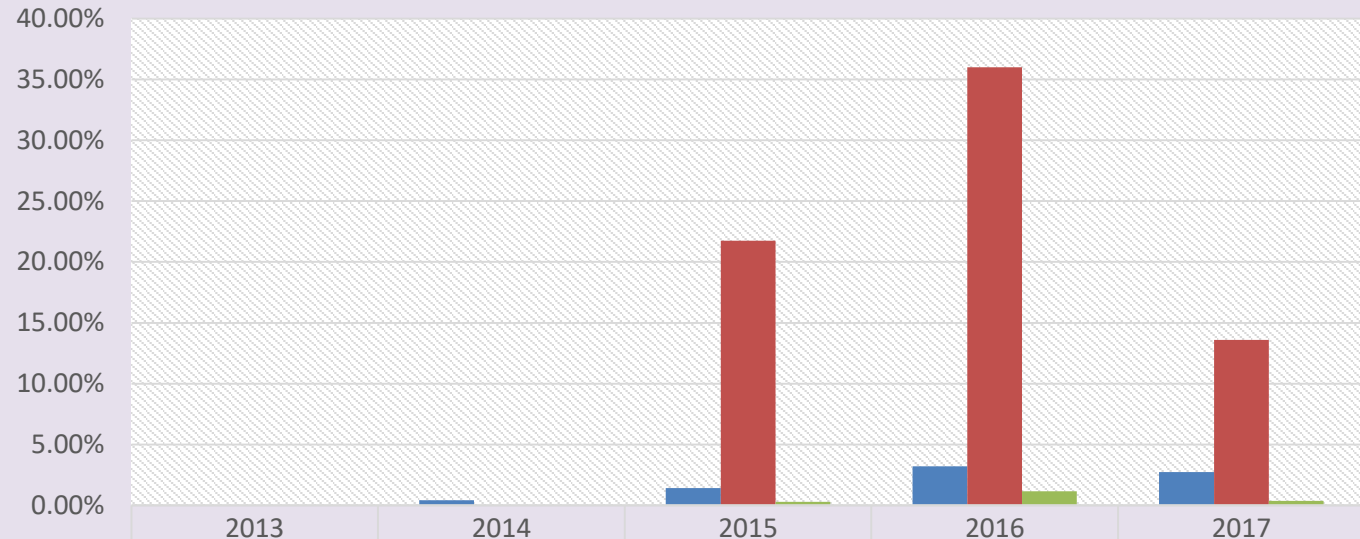


Table Grapes: US/CA Thiamethoxam MRL exceedance due to Clothianidin residues



■ % Samples with Clothianidin	0.0%	0.4%	1.4%	3.2%	2.8%
■ % Clothianidin Positives > US/CA Thiamethoxam MRL	0%	0%	22%	36%	14%
■ % Samples > US/CA Thiamethoxam MRL due to Clothianidin	0.0%	0.0%	0.3%	1.2%	0.4%

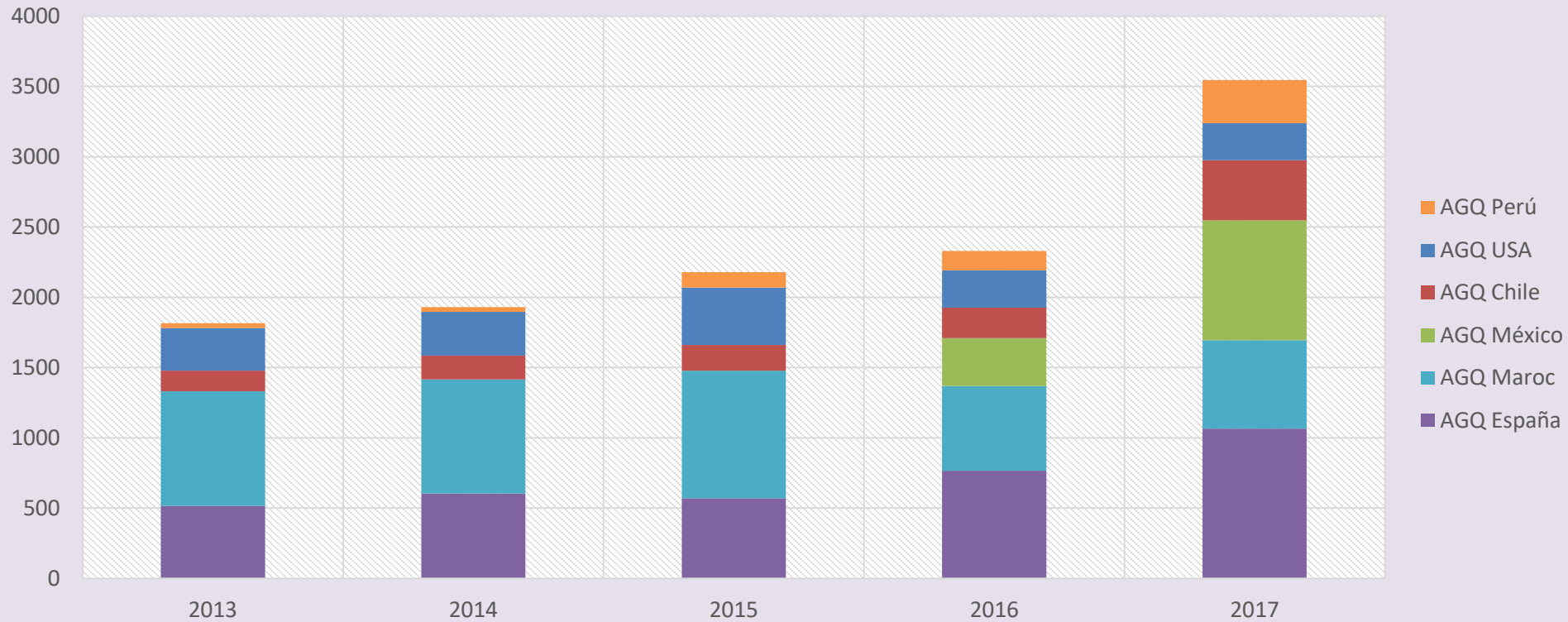
Contradicting Definitions: Thiophanate Methyl, Benomyl and Carbendazim

- Residue Definitions for these 3 chemicals vary greatly between Markets
- **US**
 - Thiophanate Methyl= Thiophanate Methyl including its metabolite carbendazim
 - Benomyl= NO US MRLs
 - Carbendazim= NO US MRLs
- **Japan**
 - Carbendazim= Thiophanate Methyl+Benomyl+Carbendazim
- **EU**
 - Thiophanate Methyl= Thiophanate Methyl
 - Carbendazim= Carbendazim+Benomyl

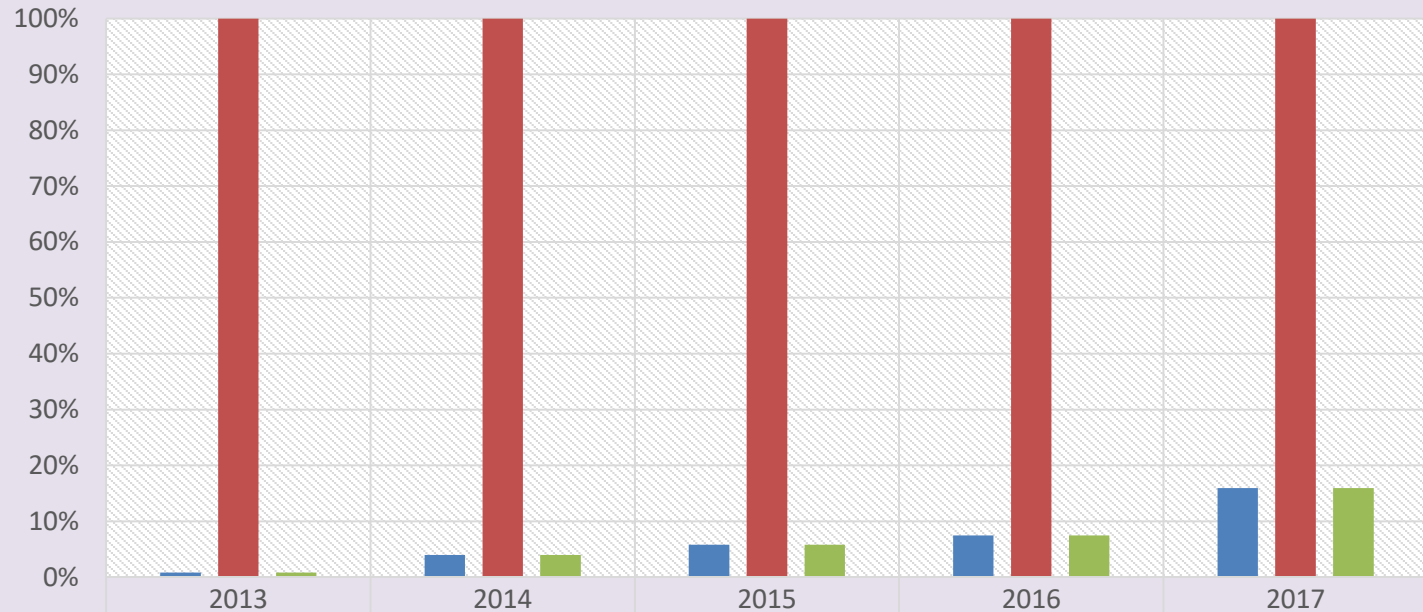
Contradicting Definitions: Thiophanate Methyl, Benomyl, and Carbendazim US Scenarios

- Carbendazim residues can be present as a result of the following:
 - Metabolite of Thiophanate Methyl application
 - Metabolite of Benomyl application
 - Direct Application of Carbendazim
- Benomyl residues can be present as a result of:
 - Direct application of Benomyl
- Thiophanate Methyl residues can be present as a result of:
 - Direct Application of Thiophanate Methyl

Total Strawberry Samples per Year/Country



Strawberries: US MRL Violations due to Benomyl+Carbendadizim



■ % Samples with Ben+Carb

■ % of Ben/Carb Positives > US MRL

■ % of Samples > US MRL due to Ben+Carb

2013

2014

2015

2016

2017

1%

100%

1%

4%

100%

4%

6%

100%

6%

7%

100%

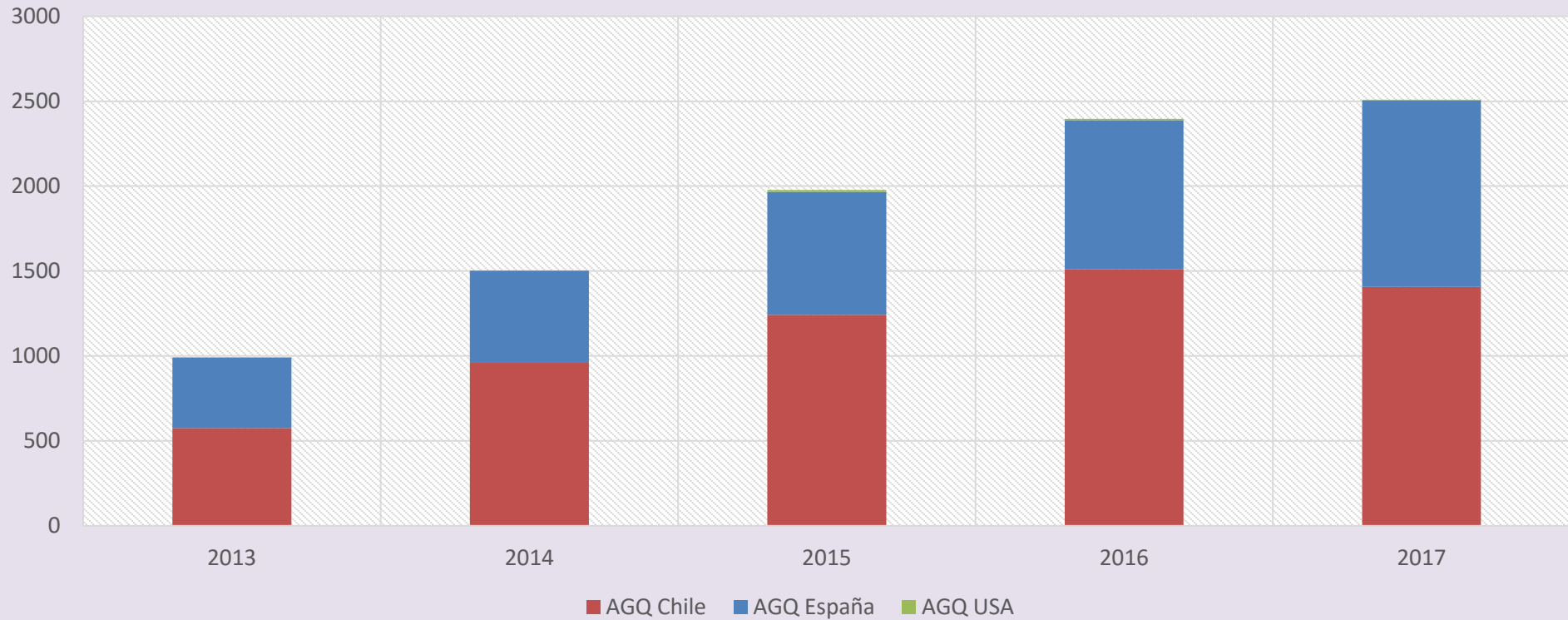
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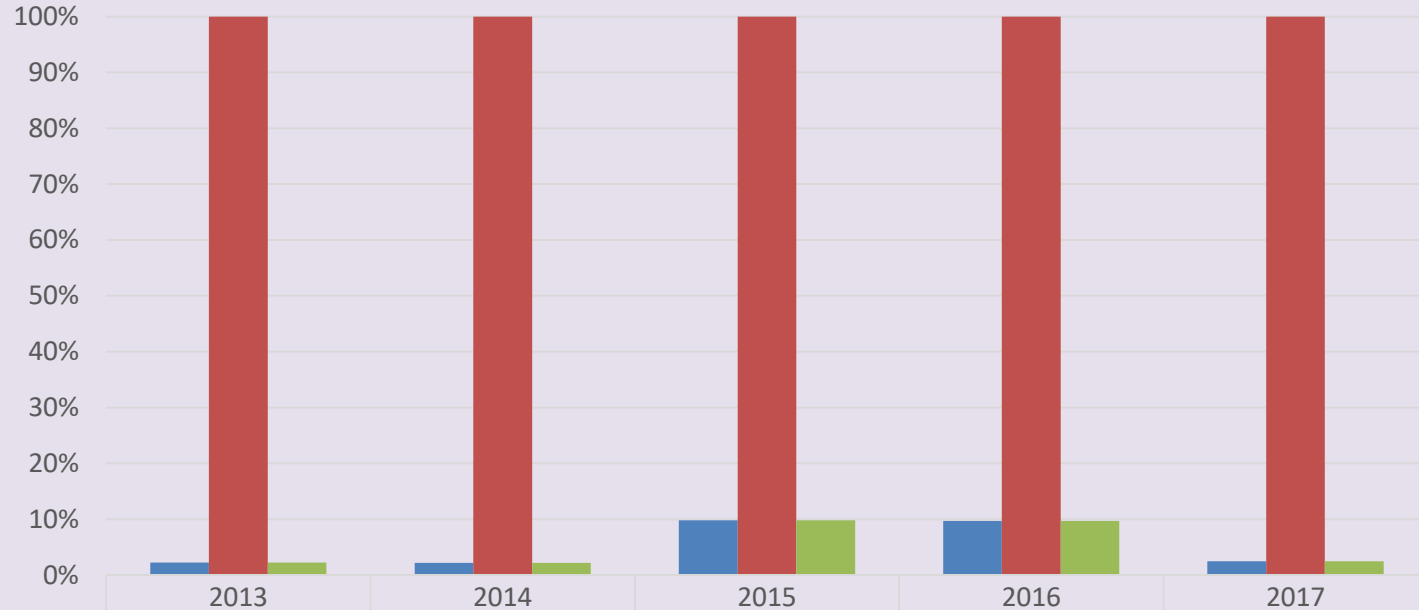
100%

16%

Total Wine Samples per Year/Country



Wine: US MRL Violations due to Benomyl+Carbendazim



■ % Samples with Ben+Carb	2%	2%	10%	10%	2%
■ % of Ben+Carb Positives > US MRL	100%	100%	100%	100%	100%
■ % of Samples > US MRL due to Ben+Carb	2%	2%	10%	10%	2%

Conclusions

- **Companies who master managing export MRL compliance have competitive advantage and help maintain good reputation for their respective industry**
- **Important for trade associations to protect their industry's by educating on the impacts MRL non-compliances and encouraging pre-export testing**
- **Results are only as good as the samples taken and the laboratory analyzing them**
- **Help from regulatory bodies, registrants and agrochemical industry to minimize impacts due to contradictory residue definitions**

Sources

All MRLs sourced from globalmrl.com



THANKS !!

Questions? contact Patrick Brennan at

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