



Inorganic & Organic Certified Reference Materials



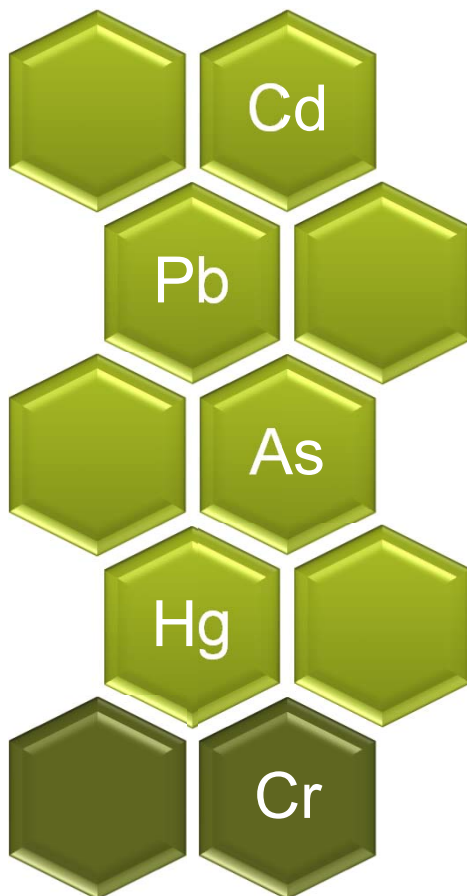
Your Science is Our Passion.™

Contamination, Adulteration and Counterfeiting: An Examination of Sources and Concentrations of Heavy Metals Present in Food, Spices, Beverages and Drinking Water

Patricia Atkins

Senior Applications Specialist, SPEX CertiPrep

Heavy Metals Routes of Exposure



Injection

- Drugs & Pharmaceutical
- Accidental Exposure



Inhalation

- Air Quality: Indoor & Outdoor
- Drugs & Pharmaceutical
- Smoking



Transdermal

- Cosmetics, Health & Beauty Products
- Drugs & Pharmaceuticals
- Accidental Exposure



Ingestion

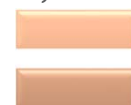
- Food
- Water
- Drugs & Pharmaceuticals
- Accidental Exposure

Dust

Known Oxidation States											
		-3	-2	-1	0	1	2	3	4	5	6
As		X	X	X	X	X	X	X	X	X	
Cd			X		X	X	X				
Hg			X		X	X	X				
Pb	X		X	X	X	X	X	X	X		
Cr	X		X	X	X	X	X	X	X	X	X

Contamination by particles by charge transfer from friction

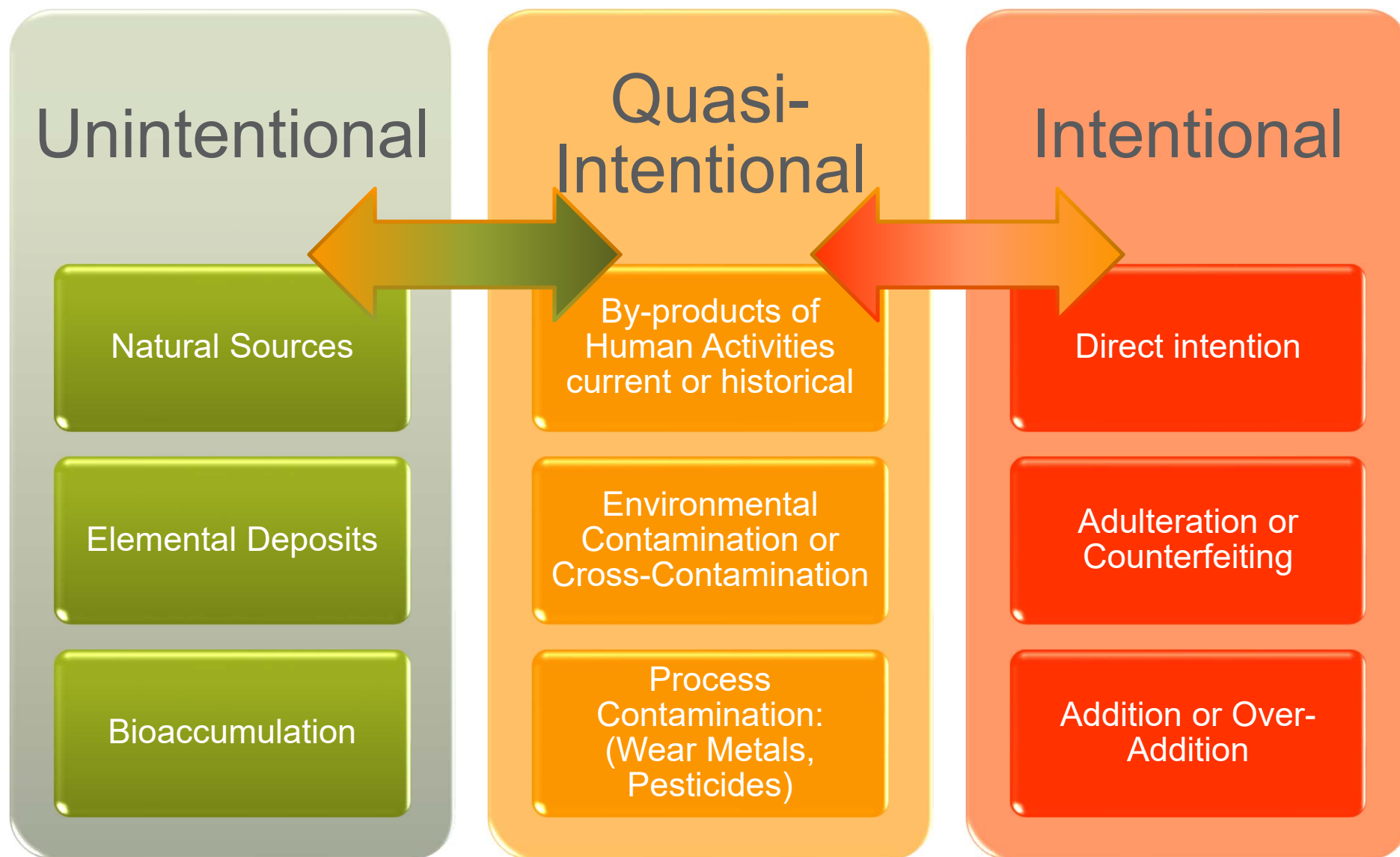
- Opening container –
- Tribology –



Extreme Positive
Charge

Extreme
Negative Charge

Wool	Lead	Heavy Metals	Human Hair	Paper	Cotton	Wood	Rubber	Polyester & Rayon	PS	Tape	PU	PE	PP	PVC	Silicon	Teflon	Silicone Rubber
------	------	--------------	------------	-------	--------	------	--------	-------------------	----	------	----	----	----	-----	---------	--------	-----------------



Heavy Metal Limits - Adults

	FDA Bottled Water	EPA Drinking water	WHO Drinking water	EPA	FDA	WHO/ JECFA	ATSDR	NSF/ANSI 173	CNHP (2008)	AHPA (2012)	USP <2232>
	Action Level (ug/L)	Action Level MDL (ug/L)	Action Level (ug/L)	Oral Rfd (ug/day)	PTTDI (ug/day)	PTDI (ug/day)	Oral MRL (ug/day)	Finished Product (ug/day)	Oral Finished Product (ug/day)	Oral Finished Product (ug/day)	Oral Finished Product (ug/day)
As (Total)	10	-	10	21 (chronic)	-	150	21 (chronic)	10	9.8	-	
As (Inorg)	-	10	-	-	130	-	-	-	-	10	15
Cd	5	5	3	70	?	70	14	6	6.3	4.1	5
Hg (Total)	2	2		-	-	-	-	20	20.3		15
Hg (MeHg)	-	-	-	7	-	16	21	-	-	2	2
Hg (Inorg)	-	-	6	-	-	-	-	-	-	-	-
Pb	5	15	10	-	6 or 75 ug	250	-	20	20.3	6	10

■ Lead

- FDA: 75 ug/day adults; 6 ug/day children
- California Prop 65: 0.5 ug/day; naturally occurring up to 1 ug more per 100 mg

Heavy Metal Sources

Natural Sources

- Found in fertilizer
- Bioaccumulation organic materials and seafood

Natural Sources

- Bioaccumulation: Rice, Bacteria, Seaweed
- Nutrient
- Elemental Deposits (India, Western US, South America)

By-Products

- Colorants
- Stabilizer: Glass & Plastics
- Coatings Iron & Steel
- By-product of Zinc production

By-Products

- Historical As Pesticides
- By-product of Lead production

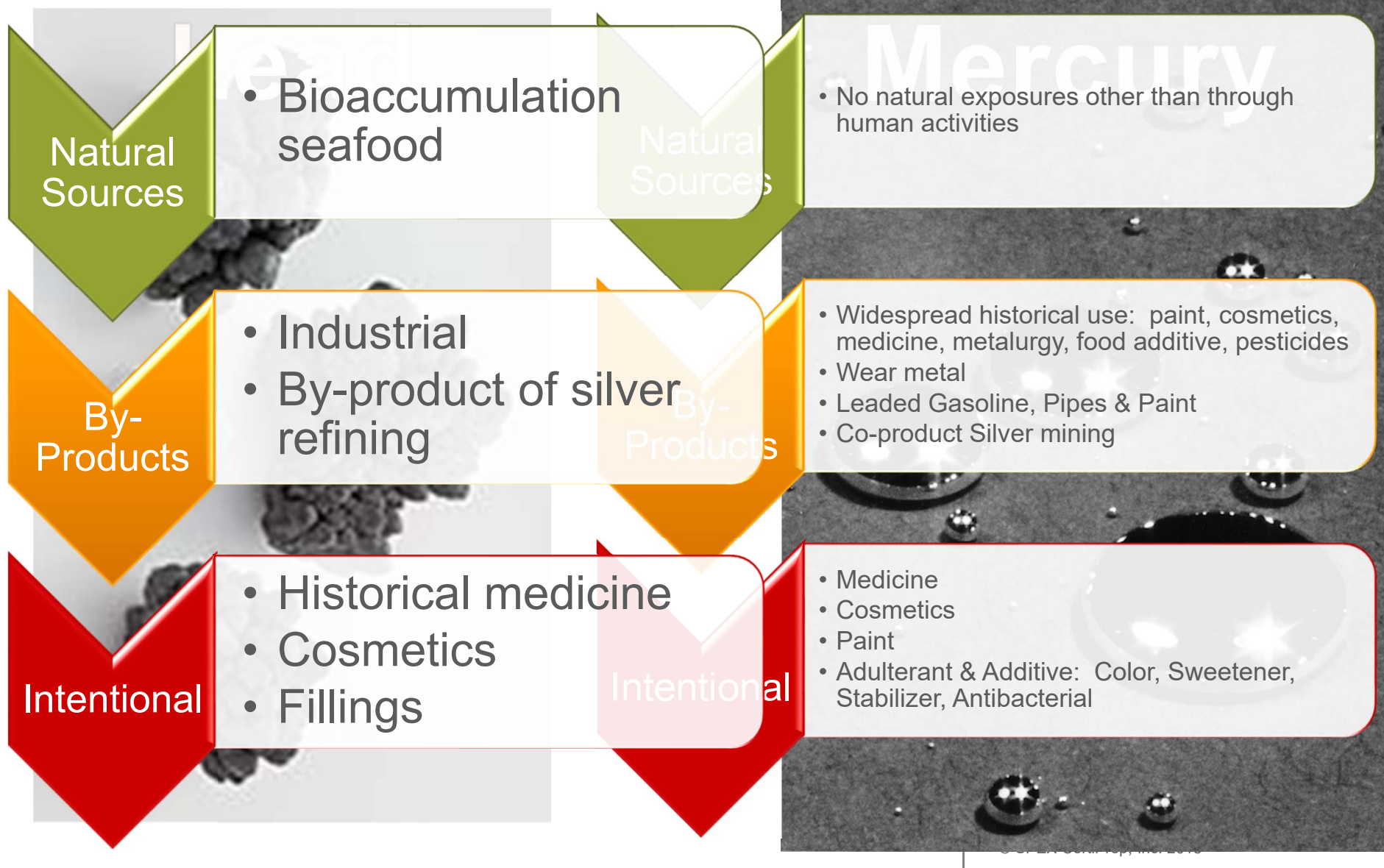
Intentional

- Colorants for counterfeit printing
- Illegal use as stabilizer colorant

Intentional

- Small amounts used in traditional and modern medicine

Heavy Metal Sources



Two Cases of Natural Sources/By-Products



14 Salts
All price ranges
Gourmet to
Laboratory
Dissolved
ICP-MS

13 Ca Supplements
All price ranges
Natural and
Formulated
Dissolved
ICP-MS

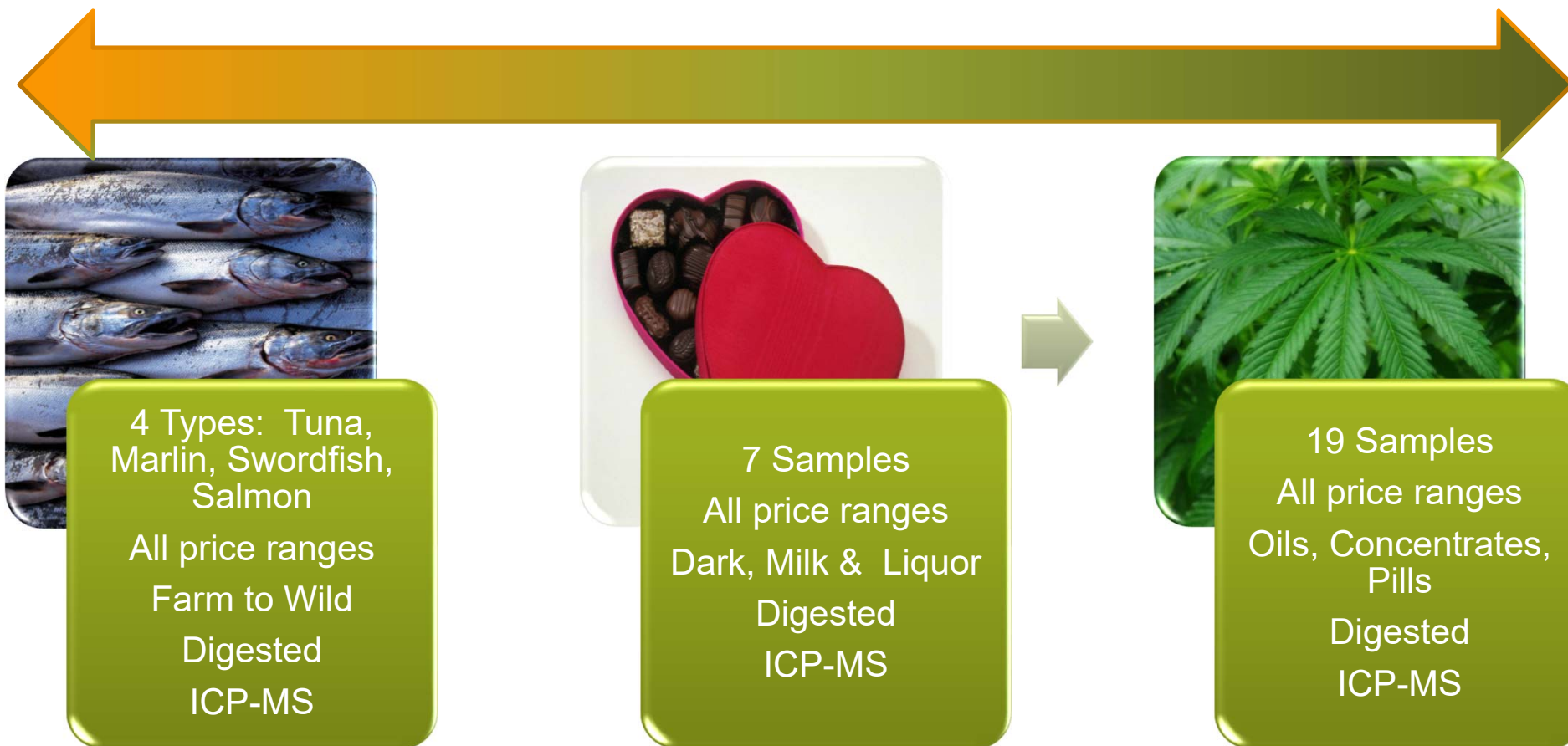
Gourmet Salts

	Cy			A		P		S	Pl	K	Fun	Hin				
ug/1 tsp (6 gm)	Finished Product limit (ug)			Daily Limit (ug)			Cyprus Black		Sel Gris		Kai Black		Himalyan		Fumee Sel Oak	
Pb (in 1 tsp)	10			75			5.46			8.04			5.28			6.6
% Daily limit							7.28			10.72			7.04			8.8
Hg	0.12	0.01	0	0.16	0.11	0.07	0.07	0.04	0.12	0.18	0	0.04	0	0		
Pb	0.91	0.56	1.34	0.47	0.88	0.51	0.94	0.46	0.4	0.58	1.1	0.46	0.44	0.39		

Calcium Supplements

Pb in Calcium Supplements (µg)					#	Description	
					14.4	A	Natural Oyster Shell
						B	Natural Oyster Shell
% Daily allowable Limit of Pb (75 ug)	Oyster 1	Oyster 2	Oyster 3	Bone Meal	Nat'l Ca 1	Nat'l Ca 2	Chelate d Ca
1 capsule	2.8	2.3	2.1	3.9	6.4	3.1	4.3
2 capsules	5.6	4.5	4.3	7.7	12.8	6.1	8.5
3 capsules	8.4	6.8	6.4	11.6	19.2	9.2	12.8
						K	Natural Ca Citrate
Pb in Calcium Supplements (ug/g)						L	National Chelated Ca+Mg

Three Cases of Bioaccumulation/By-Products



Mercury in Fish

Fish	Hg in 4 oz serving (ug)	% of Week Limit (7 ug of MeHg) EPA
		in Serving
Wild Alaska Salmon	5.1	72.86%
Farm Raised Salmon	4.9	70.00%
Black Peal Salmon	3.5	50.00%
Fresh Tuna	6.1	87.14%
Frozen Tuna	21.8	311.43%
Swordfish Steaks	110.8	1582.86%
Marlin Steaks	329.1	4701.43%

Heavy Metals in Chocolate

Toxic metals

late (in µg, per 40 g serving)

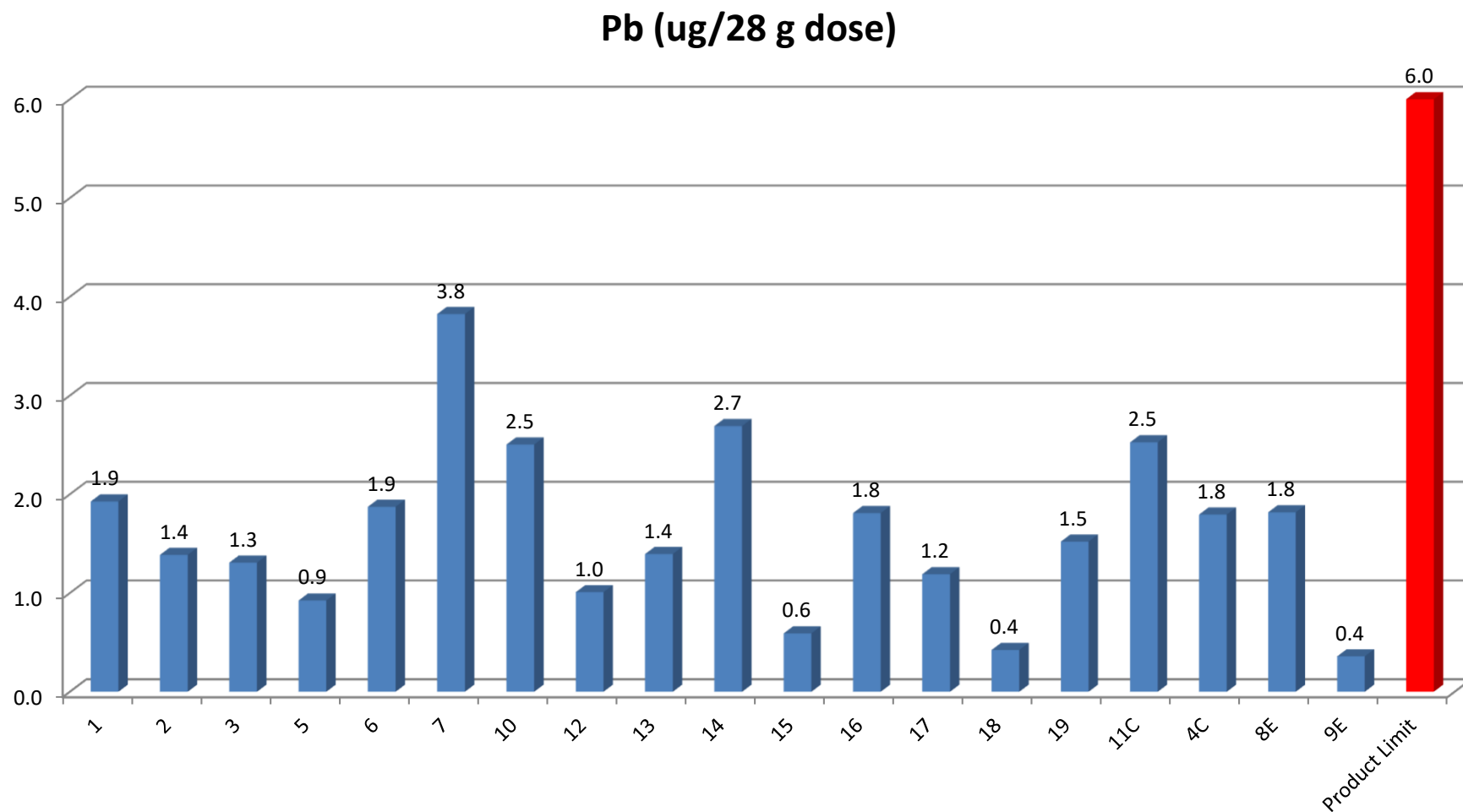
	Dark 1	Dark 2	Dark 3	Milk 1	Daily Limit	Product Limit	% Daily Limit Highest Result
As	0.39	0.98	2	0.4	21	10	4.7
Cd	3	3.8	5.3	0.9	70	6	7.6
Hg	2	0.1	<0.04	4	7*	20	? 50%
Pb	3	2.8	0.87	1	75 or 6	20	4% adult or 50% child

Dark, Milk & Liquor
Digested
ICP-MS

Hemp Oils/Supplements: $\mu\text{g}/28\text{ g}$ dose

#	As	Cd	Pb
1	0.5	0.0	1.9
2	0.7	0.2	1.4
3	0.6	0.1	1.3
5	0.8	0.4	0.9
6	0.9	0.4	1.9
7	1.1	0.4	3.8
10	0.7	0.3	2.5
12	0.7	0.2	1.0
13	0.7	0.4	1.4
14	0.8	0.0	2.7
15	0.0	0.7	0.6
16	0.6	0.7	1.8
17	0.9	0.2	1.2
18	0.8	0.0	0.4
19	1.0	0.0	1.5
11C	0.6	0.7	2.5
4C	0.6	0.3	1.8
8E	1.2	0.2	1.8
9E	3.8	0.1	0.4

Hemp Oils: Pb ($\mu\text{g}/28\text{ g Daily Dose}$)



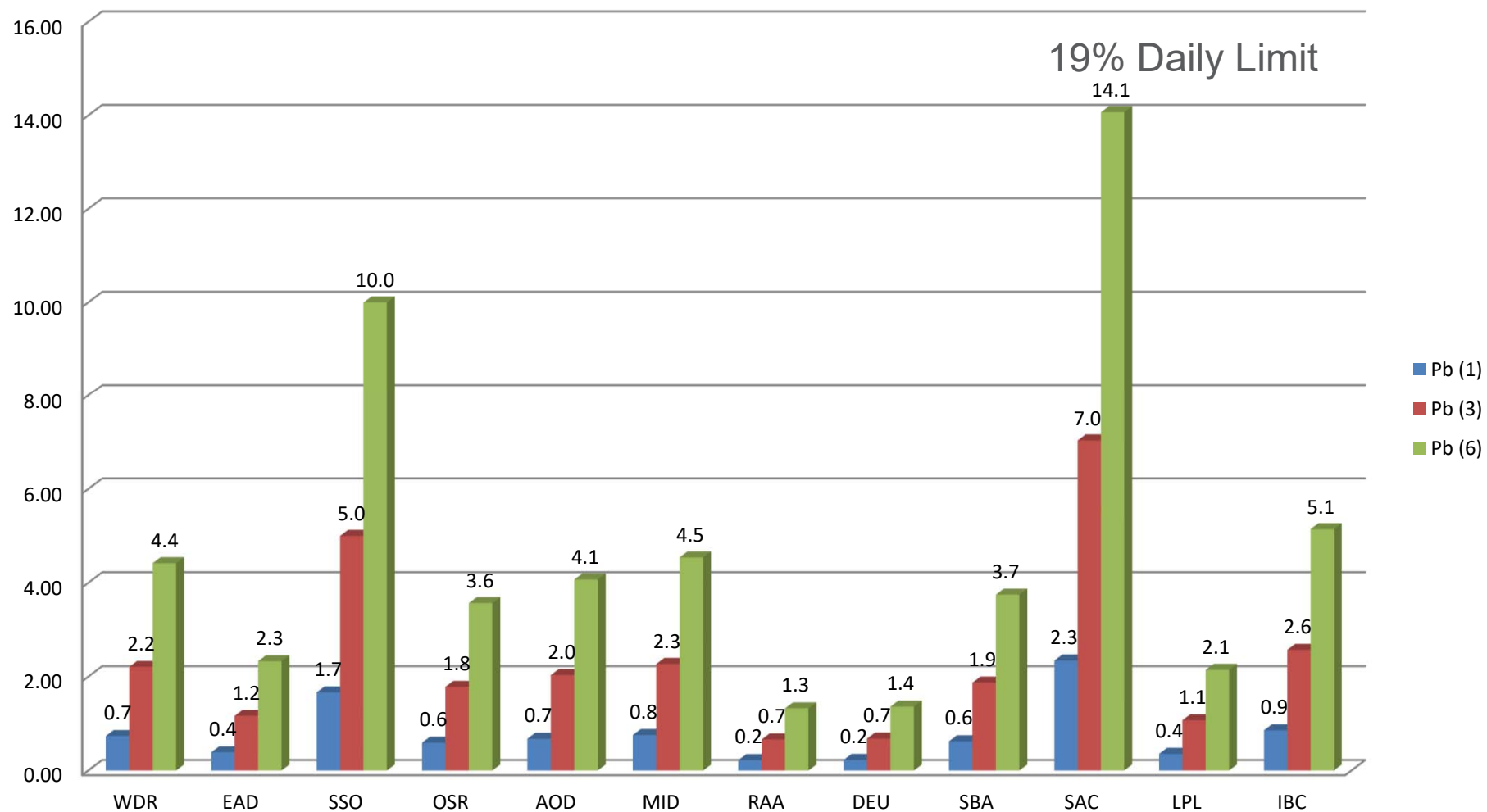
A Case Study of Environmental Contamination/By-Products



13 Alcoholic Ciders
All price ranges
American &
European
Digested
ICP-MS

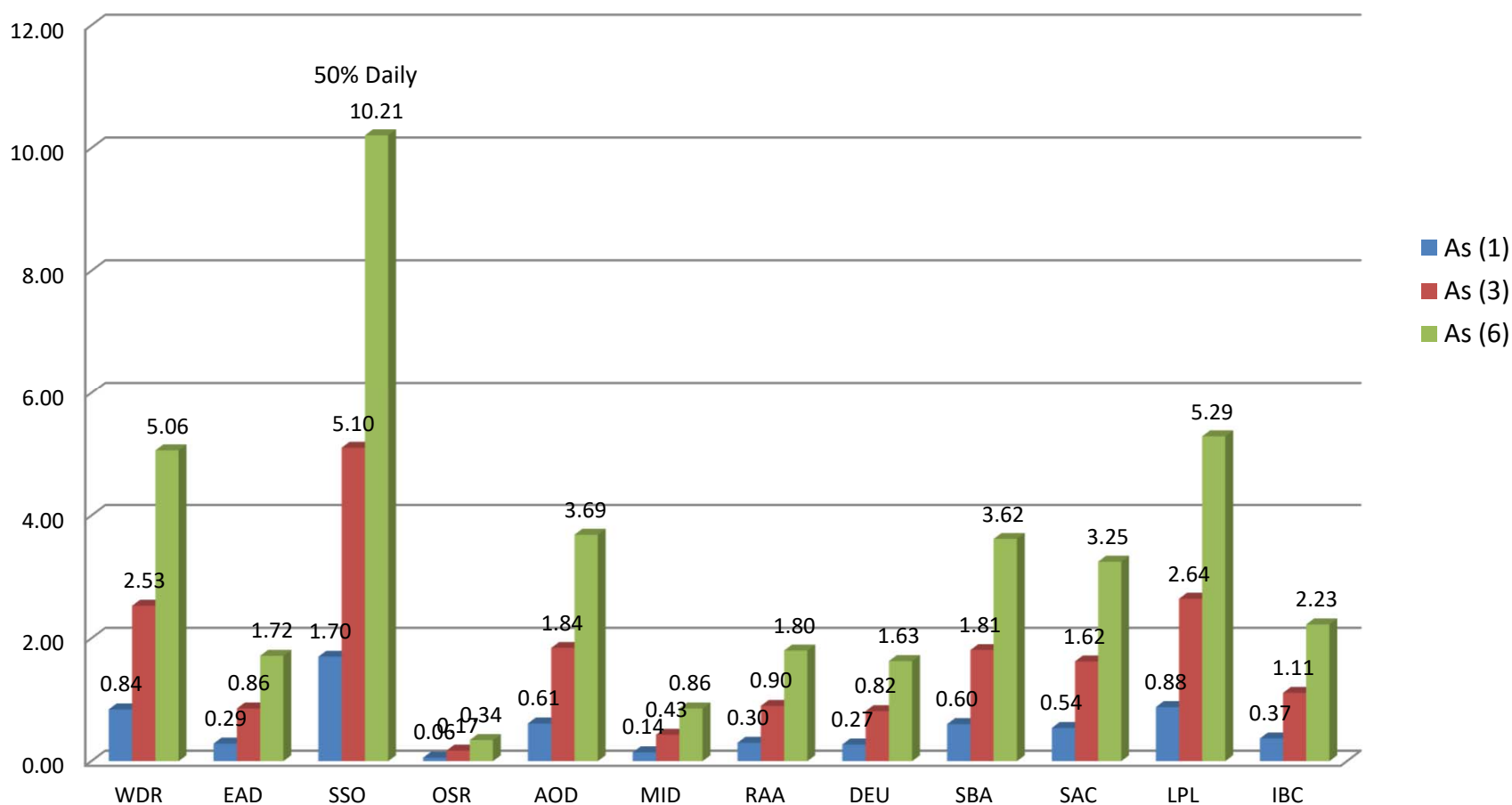
SPEX CertiPrep®
Inorganic & Organic Certified Reference Materials

Pb (μg) in multiple 12 oz servings



As in Cider

As (μg) in multiple 12 oz servings



A Case of Adulteration, Counterfeiting & By-Products

SPEX CertiPrep
Inorganic & Organic Certified Reference Materials



7 Spice Groups & Products

BP, RP, Cinn, Ginger, Cumin, Mustard, Turmeric

All price ranges

Whole & Ground

Digested

ICP-MS

Spice Samples

- 8 Spice Groups & Products
(Supplements, Teas, Sauces & Condiments)
 - *Black Pepper*
 - *Red Pepper: Spice, Hot Sauce, Chili Powder*
 - *Cinnamon: Spice, Supplement, Tea*
 - *Ginger: Spice, Supplement, Tea*
 - *Cumin: Spice, Curry Powder*
 - *Mustard Seed: Spice, Condiment*
 - *Turmeric: Spice, Supplement*
 - *Salt: Gourmet, Table & NaCl*
- Whole & Ground Spices
- Range of Prices:
 - *Dollar store*
 - *Farmer's Market*
 - *Grocery*
 - *Retail Chain*
 - *Name Brand*
 - *Organic*



Common Ground Spice Adulterants

SPEX CertiPrep
Inorganic & Organic Certified Reference Materials



Sawdust or
Bran Powder



Sand or
Silica



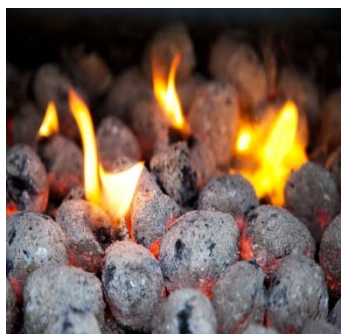
Starch or
Flour



Salts:
Na, Mg



Chalk or
Talc



Charcoal



Brick Powder



Illegal Dyes:
Pb, Azodyes,
Metanil Yellow

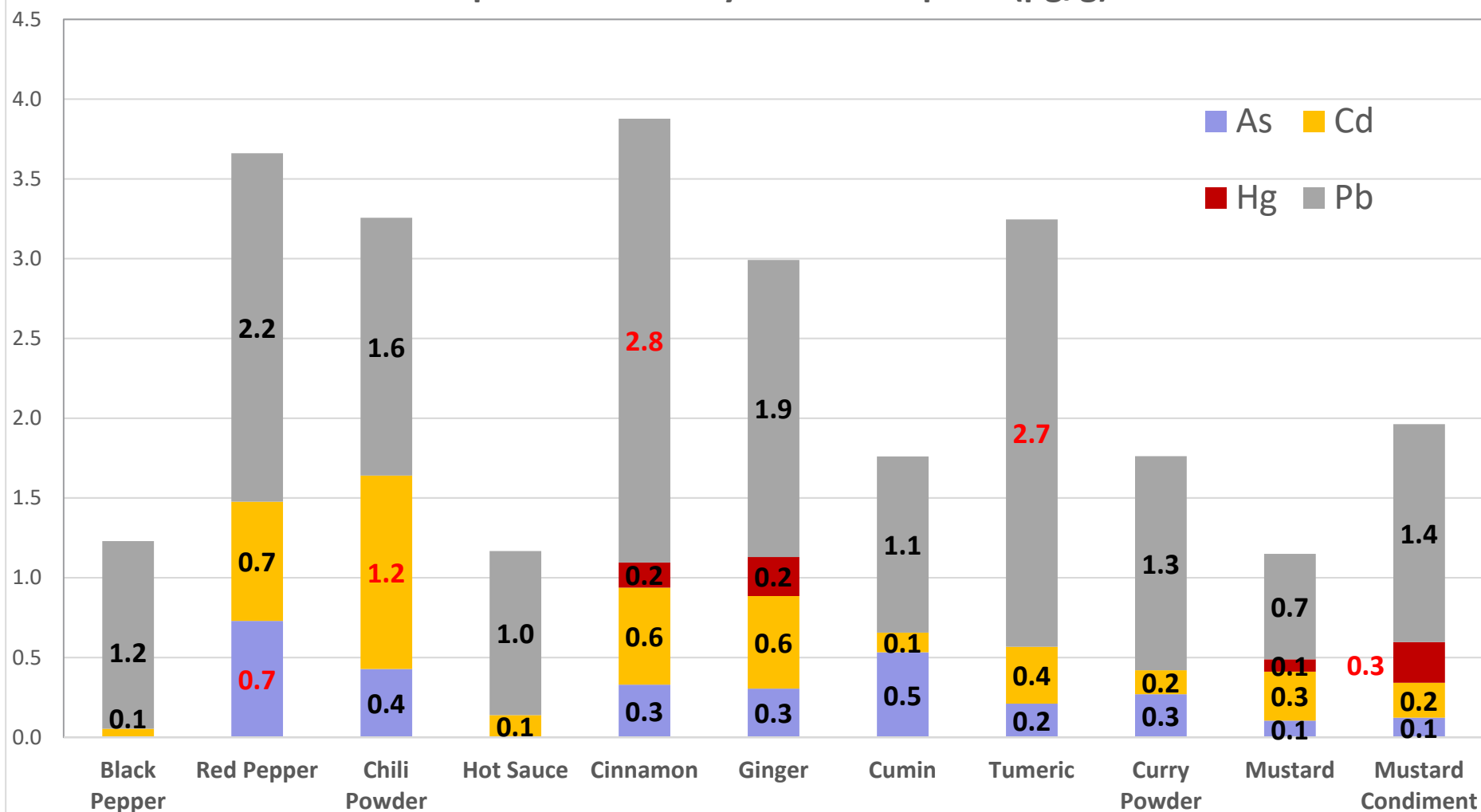


Illegal
Preservatives

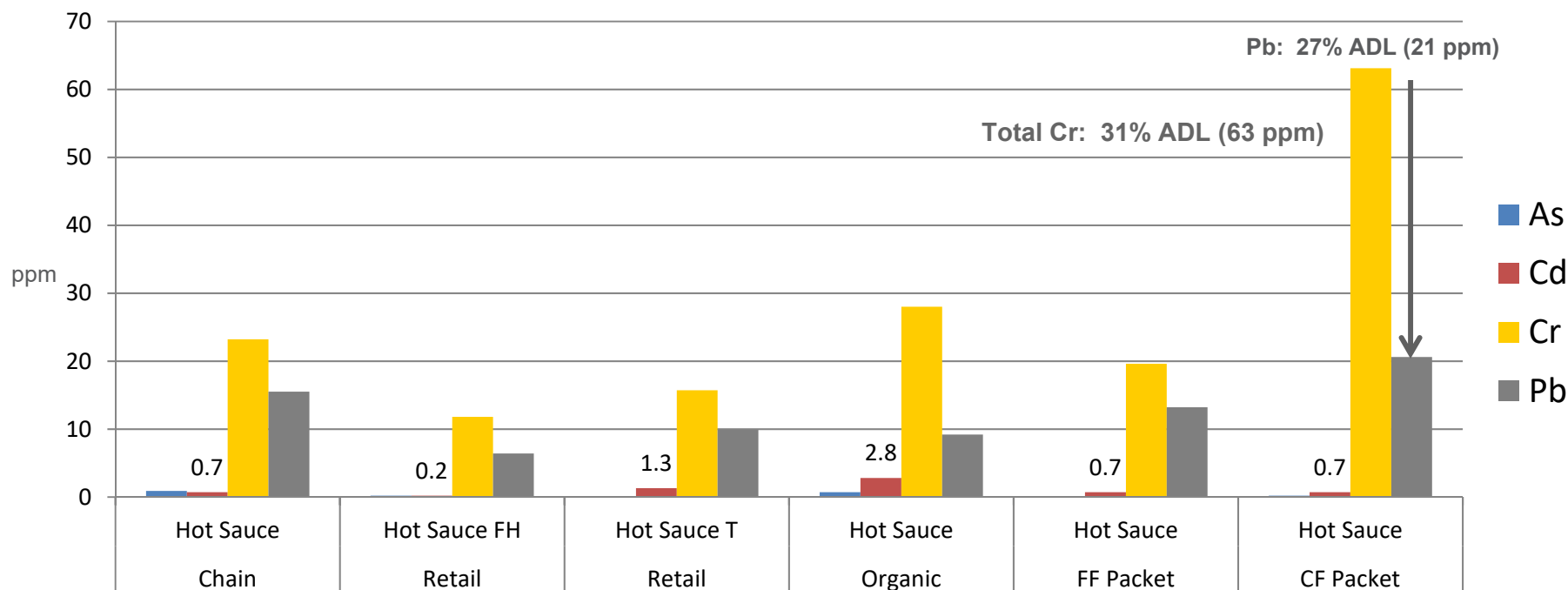


Illegal
Pesticides

Comparison of Heavy Metals in Spices (µg/g)



Heavy Metals in Hot Sauce (ug/serving)



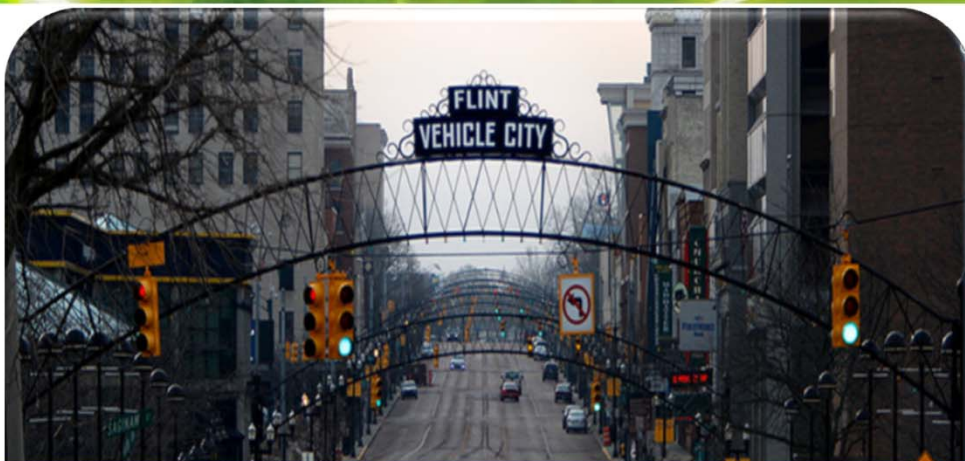
- Packet – 10 g
- Average Use: 1-2 packets (20 g)
- Pb levels, Total Cr level increase to about 30% ADL
- Ingredients:

Water, Salt, Food Starch, Cayenne Pepper, Vinegar, Spices, Colorings & Preservative



A Case of By-Products & Intentional Contamination

SPEX CertiPrep
Inorganic & Organic Certified Reference Materials



Flint, Michigan
Lead in Drinking Water
2014-2016

Flint & Water

2014		April 2014			2014- 2015		2016		
Comparison of Established Regulatory Limits for Lead in Water and Results from Flint Michigan Water Samples									
Source	FDA	EPA	EU/WHO	Cited References	Detroit Lake Huron	Flint	Flint	Flint	EPA
Form	Bottled Water	Drinking Water Action Level	Drinking Water Action Level	Concentration of Concern for Lead exposure	90th Percentile Results	90th Percentile Results	High Result (VT Sample)	Highest Recorded Sample	Designation for Toxic Waste Concentration
Pb (µg/L)	5	15	10	5	2.3	27	158	13000	5000

Contamination measured by the 90th percentile level of lead exposure
90% of homes below that threshold and 10% above it.

The action level for drinking water is 15 µg/L

Flint isn't the only problem

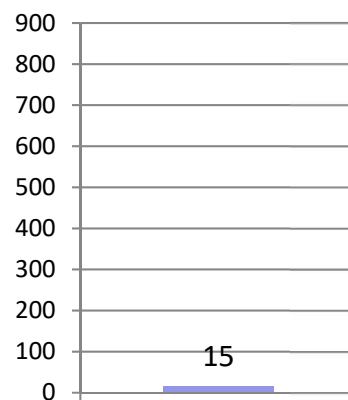
- At end of Flint = Newark, NJ Pb in s
- Another NJ elementary school ha



Only 9 states routinely report safe Pb levels in water

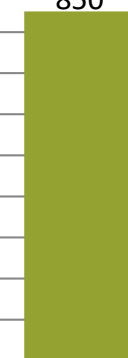
41 States have exceeded state action levels in last 3 years

3000 areas of US have Pb levels higher than Flint (up to 2x)



EPA Drinking Water
Action Level

850



Central, NJ
Elementary School
Water Sample (2016)

Comparison of Lead Levels Found in Flint Water Samples and NJ School Water Sources in 2015-2016 ($\mu\text{g/L}$)



Most Dangerous Meal

- Individual products not necessarily the danger
- Combined Daily Exposure



	As	Cd	Hg	Pb
Rx	5.600	10.133	0.831	24.290
Breakfast	1.368	3.464	0.210	3.252
Lunch	4.246	5.594	0.340	23.380
Dinner	15.058	61.114	332.114	14.864
Snacks	2.492	4.388	2.000	3.084
Drinks	5.304	0.000	0.000	61.000
Total	34.068	84.693	335.495	129.870
Daily Limit	21.0	70.0	7.0	75.0

Toxic food components (ug)

Supplements		As	Cd	Hg	Pb
Hemp dose	2 tsp	3.800	0.700	0.000	3.800
Ca Dose	3 capsules				19.200
Multivitamin	Dose	1.800	9.433	0.831	1.290
Total		5.600	10.133	0.831	24.290
Breakfast		As	Cd	Hg	Pb
Milk	8 oz glass	0.000	0.023	0.000	0.068
Coffee	8 oz cup	0.000	0.023	0.000	0.000
French Toast	2 slices	0.614	2.614	0.010	0.100
Cinnamon	sprinkle 1 g	0.300	0.600	0.200	2.800
Bacon	2 slices	0.000	0.114	0.000	0.057
Apple Juice	8 oz glass	0.454	0.091	0.000	0.227
Total		1.368	3.464	0.210	3.252
Lunch		As	Cd	Hg	Pb
Chinese Carryout	1 serving	4.046	4.760	0.340	0.340
Hot Sauce	2 packets	0.200	0.700	0.000	21.000
Beer	2 beers	0.000	0.134	0.000	2.040
Total		4.246	5.594	0.340	23.380
Snacks		As	Cd	Hg	Pb
Chocolate Bar	1 bar	0.980	3.800	2.000	3.000
Granola Bar	1 bar	1.512	0.588	0.000	0.084
Total		2.492	4.388	2.000	3.084
Drinks		As	Cd	Hg	Pb
Water	2L				54.000
Ciders	3 Ciders	5.100	0.000	0.000	7.000
Soda	2 sodas	0.204	0.000	0.000	0.000
Total		5.304	0.000	0.000	61.000
Dinner		As	Cd	Hg	Pb
Salad	228	4.560	15.504	0.000	1.368
Spinach	1/2 c	0.034	20.862	0.034	0.456
Rice	1/2 c	7.524	0.798	0.000	0.000
Marlin Steak	4 oz	0.000	19.380	329.000	2.850
Salt	tsp	0.600	0.600	1.080	6.000
Wine	glass	1.360	0.170	0.000	1.190
Chocolate Bar	bar	0.980	3.800	2.000	3.000
Total		15.058	61.114	332.114	14.864

Data from FDA TDS & SPEX & Independent Studies; simulates worse case senario for the study products and average for TDS



Inorganic & Organic Certified Reference Materials



Your Science is Our Passion.™

Thank You!

Visit us online at

www.spexcertiprep.com

***View our webinars on our
Utube Channel***