Pesticide Residues in Drinking Water

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[Federal Register: September 27, 2002 (Vol 67, # 188)] [Notices] [Page 61099-61102]

ENVIRONMENTAL PROTECTION AGENCY

Caffeine; Receipt of Application for Emergency Exemption, Solicitation of Public Comment.

SUMMARY: EPA has received a quarantine exemption request from the USDA APHIS to use the pesticide caffeine (1H-purine-2,6-dione,3,7-dihydro-1,3,7- trimethyl-) (CAS No. 58-08-2) to treat up to 200 acres of floriculture and nursery crops, parks, hotels and resort areas, and forest habitats to control Coqui and Greenhouse frogs.

USDA's Pesticide Data Program

- Residue data from 1991 to the present
- Focused on foods consumed by children
- Data are representative of exposure in the US diet.

Commodities

1991	1992	1993	1994	1995	1996
apples	apples	apples	apples	apples	apple juice
bananas	bananas	bananas	bananas	bananas	apples
grapefruit	celery	carrots	broccoli	carrots	can/frz grnbns
grapes	grapefruit	grapes	carrots	grapes	carrots
lettuce	grapes	green beans	celery	green beans	grapes
oranges	green beans	oranges	grapes	oranges	oranges
potatoes	lettuce	peaches	green beans	peaches	peaches
	oranges	peas	lettuce	potatoes	spinach
	peaches	potatoes	oranges	spinach	sweet corn
	potatoes	spinach	peaches	sweet corn	sweet peas
		sweet corn	potatoes	sweet peas	sweet pot.
		wheat	sweet corn	wheat	tomatoes
			sweet peas		wheat
					whole milk

1997	1998	1999	2000	2001	2002
apple juice	apple juice	apples	apples	apples	apples
can peach	cantaloupe	cantaloupe	cantaloupes	bananas	apple juice
can peach	cn/frz grnbns	corn syrup	carrots	broccoli	apple sauce
can spinach	corn syrup	cucumbers	cherries	carrots	asparagus
can/frz grnbns	grape juice	grape juice	cucumbers	celery	bananas
frz w squash	milk	lettuce	grapes	cherries	barley
orange juice	orange juice	oats (roll/brn)	green beans	grapes	beef
pears	pears	pears (frsh/cn)	lettuce	grn bns	broccoli
potat spec.	soybeans	spinach, frozen	nectarines	lettuce	carrots
potatoes	spinach	strwbrs (frsh/frz)	oranges	mushrooms	celery
soybeans	strawberries	sweet bell peppe	peaches	nectarines	cucumbers
spinach	sweet pot.	tomatoes (fr/can)	peanut butter	oranges	mushrooms
sweet pot.	tomatoes	w. squash (fr/frz)	pears (can)	peaches	onions
tomatoes	wnt squash		pineapples	pineapples	peaches
wheat			potatoes	potatoes	pineapples
whole milk			poultry	can swt.corn	potatoes
winter squash			rice	can set peas	rice
			strwbrs (frsh/frz)	can tom.paste	spinach
			swt bll peps	rice	sweet bell peppers
			tomatoes (can)	water, drnk	sweet corn, can
				beef, fat	sweet corn, frozen
				beef, liver	sweet peas, can
				beef, muscle	sweet peas, frozen
				poultry, fat	water, fin. drnk.
				poultry, liver	
				poultry, muscle	

2003	2004	2005
Apples	Apples	Apples
Asparagus, canned	Cantaloupe	Cantaloupe
Asparagus, fresh	Cauliflower	Cauliflower
Barley	Cucumbers	Cream, heavy
Butter	Grapes	Eggplant
Cantaloupe	Green Beans, canne	Grapefruit
Cucumgers	Green Beans, fresh	Grapes
Green Beans, canned	Lettuce	Green Beans, fresh
Mushrooms	Milk	Green Beans, frozen
Onions	Orange Juice	Lettuce
Peaches, canned	Oranges	Milk
Peaches, fresh	Peaches, canned	Orange Juice
Pear Juice, conc/pure	Pears	Oranges
Pears, fresh	Soybean Grain	Pears
Spinach	Spinach, canned	Plums, Fresh
Sweet Bell Peppers	Strawberries	Plums, dried (prunes
Sweet Corn, frozen	Sweet Bell Peppers	Pork, adipose/muscl
Sweet Peas, frozen	Sweet Potatoes	Soybean Grain
Sweet Potatoes	Tomatoes	Strawberries
Tomatoes	Water, finished	Water, bottled
Water, fin. drnk.	Water, untreated	Water, finished
Wheat Flour	Wheat Flour	Water, untreated
	Winter Squash	Watermelon
		Wheat Grain
		Winter Squash

Pesticides in Fruits & Vegetables

Year	# pest. test.	# comm.	# samples	% detect.	# viol.
1991	34	7	1,963	22	4
1992[a]	42	10	2,859	58	19
1993	58	12	7,328	70.6	110
1994	71	13	7,589	61.5	98
1995	69	12	6,924	65	263
1996	91	14	4,856	71.8	196
1997	96	15	6,321	57	383
1998	113	14	7,017	61.2	320
1999	104	13	8,637	67	345
2000	134	20	8,912	66.6	125
2001	152	26	9,903	64.1	251
2002	158	24	10,056	47	387

2003		12,316		
f&v's		9,732	43	
barley		452	8	
butter		732	99	
wheat flour		606	45	
drinking water		794	54	0
2004		13,208		
f&v's (fresh)		8,881	76	
f&v's (processed)		1,485	40	
soybean		616	42	
wheat flour		725	57	
milk		739	100	
drinking water		762		
2005		14,749		
f&v's (fresh)		8,702	73	
f&v's (processed)		1,452	61	
Cream		369	99	
Milk		746	99	
Bottled Water		378	16	
drinking water		750		
soybean		974	22	
Pork		704	8	

PDP 2002

- **Participating labs monitored 158 pesticides plus 48 metabolites, degradates, and isomers using multiresidue methods.**
- **Accepted samples are prepared emulating the practices of the average consumer to more closely represent actual exposure to residues.**

PDP 2002

- **Data from 2002**
  - **10,056 samples of fruits and vegetables**
  - **725 barley samples**
  - **495 rice samples**
  - **924 beef samples**
  - **699 drinking water samples**

PDP Summary 2002
Pesticide Detections

Commodity	%w/o
Fruits & Vegs	53
Barley	85
Rice	82
Beef	85
Overall	58

PDP Summary 2002
Residue Detections

Residues	Percent	Cum. Percent
0	58	58
1	19	77
>1	23	100

Finished Drinking Water Monitoring Survey

- Coordinated with EPA and the AWWA*
- Water treatment facilities are solicited
- Facility personnel collect samples
- Analysis at PDP laboratories
- PDP provides data to facilities in quarterly updates

* American Water Works Association

Finished Drinking Water Monitoring Survey

- **Unlike data collected on f&v, not representative.**
- **Reflects the unique characteristics of the watersheds sampled.**
- **Collected just before distribution to consumers.**

Drinking Water

- 2001: Samples from NY (11), CA (10)
  - Two highly populated regions
  - Different hydrological settings
  - Samples collected bimonthly
- 2002: Five new sites in KA (2), CO (2), TX (1) added
  - Rural areas (<50,000 pop.)
  - Samples collected weekly

Change in Criteria

- 2001-2003 sites selected to represent diversity of land use
- 2004 and 2005, criteria for site selection changed.
  - Service to more than 50,000 people
  - Use of surface water as primary source
  - Location in regions of heavy agriculture where it was known that pesticides heavily applied.

Table 9. Sampling summary; 2001-2005.

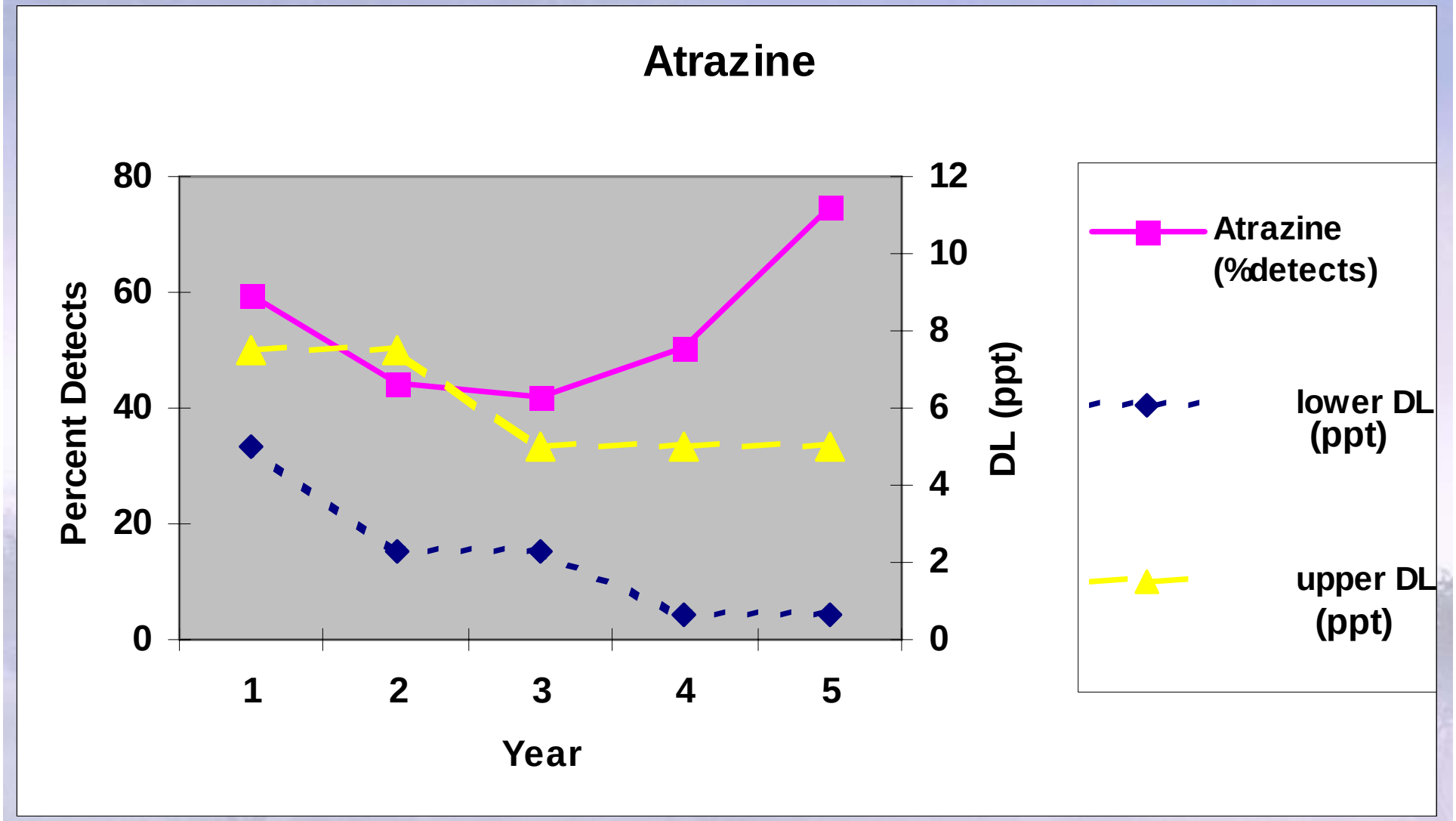
	2001	2002	2003	2004	2005
No. of Samples	297	699	794	762	750
No. of residues assayed	170	212	230	233	222
No. pesticides detected	17	28	33	38	43
Per cent of pesticides det.	10	13.2	14.35	16.31	19.37
Total samples	3173	11640	18663	11028	13187
Total samples w/ detects	455	1503	1857	2415	3528
% of samples w/ detects	**14.34**	**12.91**	**9.95**	**21.9**	**26.8**

Table 8. Summary of selected drinking water pesticide data from 2001-2005.

	%Samples with detects					
Pesticide	**2001**	**2002**	**2003**	**2004**	**2005**	**Trend[a]**
Atrazine	59.6	44.3	41.7	50.3	74.6	+
Desethyl atrazine	48.7	48.6	34.7	46.8	66	+
Desisopropyl atrazine	41.6	40.1	20	33.4	40.1	N/A
Hydroxy atrazine	ND	ND	ND	66	66.7	N/A
Metolachlor	50.2	40	41.2	40.2	43	N/A
Metolachlor ethanesulfonic acid	22.9	51.9	41.9	48.5	74.1	+
Metolachlor oxanilic acid	10.1	37.6	36.7	43.8	62.8	+
Simazine	15.3	21.1	17.5	41.1	47.9	+
Alachlor	0	0	0.7	0.8	0	N/A
Alachlor ethanesulfonic acid	3.8	32.6	18.6	39.1	50.3	+
Alachlor oxanilic acid	0.7	5.1	5.1	27.7	38	+
2,4-D	ND	16.5	24.3	35.4	58.8	+
Imazapyr	0	1.5	0.7	45.2	59.3	+
Prometon	0	4.7	5.4	51.6	53.2	+
Bentazon	1	7.5	9.3	40.3	44.7	+
Acetochlor	0	0	3.1	2.9	2.4	N/A
Acetochlor ethanesulfonic acid	0	1.3	3.8	80.9	40.1	+
Acetochlor oxanilic acid	0	0	1.7	39.6	38.5	+
Tebuthiuron	1.9	5.7	4.8	33	37.7	+

[a] Trend symbols: (-) declining; (+) increasing; (N/A) trend not applicable

ND: Not Determned; was not included in the pesticide analysis.


Atrazine
Percent Detects
80
60
40
20
0
12
10
8
6
4
2
0
DL (ppt)
1
2
3
4
5
Year
Atrazine (%detects)
lower DL (ppt)
upper DL (ppt)

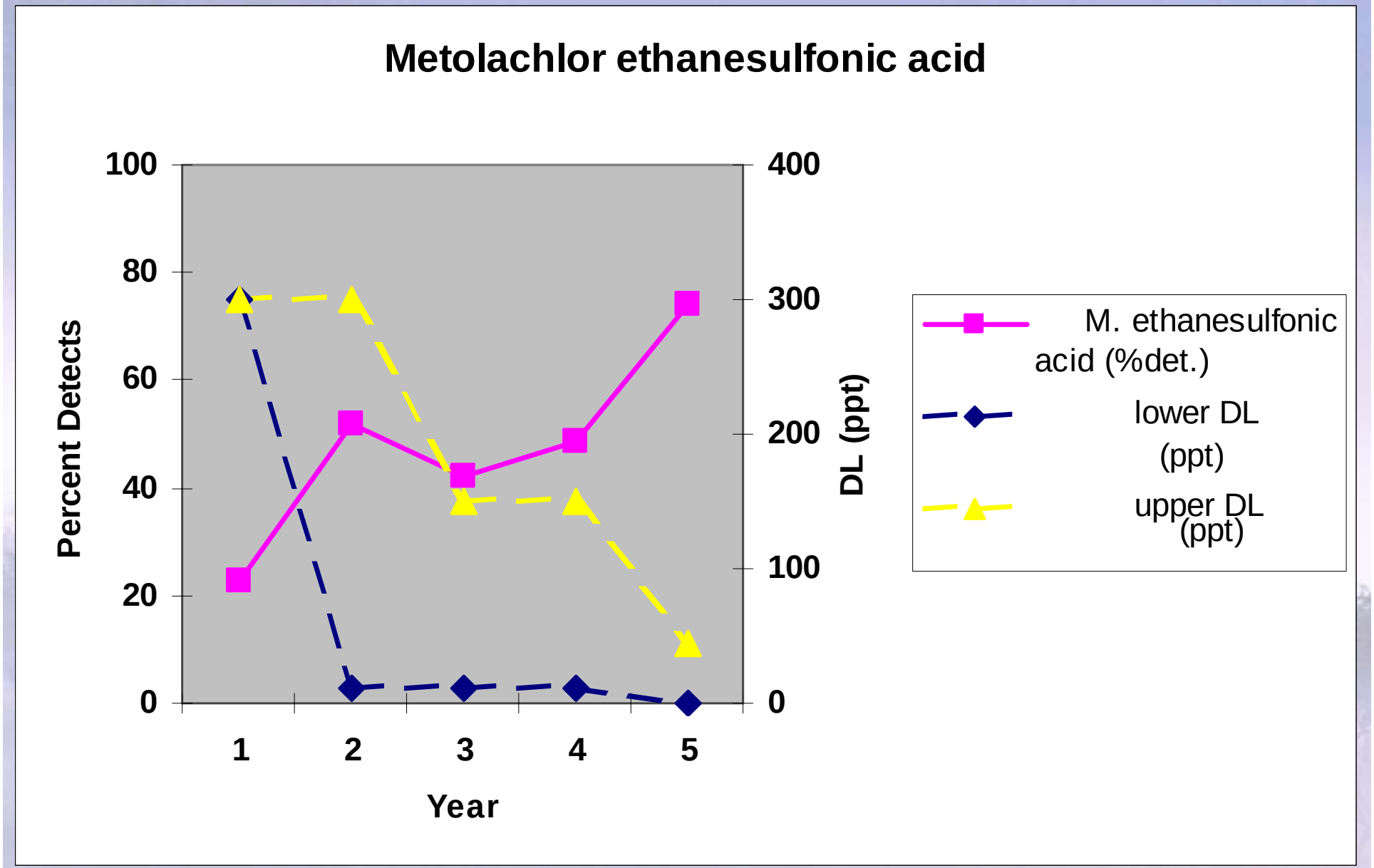

Metolachlor ethanesulfonic acid
Percent Detects
100
80
60
40
20
0
DL (ppt)
400
300
200
100
0
1
2
3
4
5
Year
M. ethanesulfonic acid (%det.)
lower DL (ppt)
upper DL (ppt)

Table 10. Detection Limit Values and Detection percentages for selected pesticides in drinking water. 2001-2005.

	% Detects Detection Limit Values (ppt)					%Detects	Change
Pesticide	**2001**	**2002**	**2003**	**2004**	**2005**	**%Change[a]**	**in DL[b]**
Atrazine (%detects)	**59.6**	**44.3**	**41.7**	**50.3**	**74.6**	**25.2**	
lower DL	5	2.3	2.3	0.66	0.66		7.6
upper DL	7.5	7.5	5	5	5		1.5
Desethyl atrazine (% detects)	**48.7**	**48.6**	**34.7**	**46.8**	**66**	**35.5**	
lower DL	24.8	25	24.8	0.43	0.43		57.7
upper DL	24.8	25	25	25	25		0
Desisopropyl atrazine (% det.)	**41.6**	**40.1**	**20**	**33.4**	**40.1**	**-3.6**	
lower DL	9.8	9.8	9.8	1.6	1.6		6.1
upper DL	32.5	50	50	50	50		0.7
Hydroxy atrazine (% dets.)	**-**	**-**	**-**	**66.0**	**66.7**	**0.0**	
Metolachlor (% dets.)	**50.2**	**40**	**41.2**	**40.2**	**43**	**-14.3**	
lower DL	5	3	3	1.5	1.5		3.3
upper DL	6	6	5	5	45		0.1
M. ethanesulfonic acid (%det.)	**22.9**	**51.9**	**41.9**	**48.5**	**74.1**	**223.6**	
lower DL	300	12	12	12	0.36		833.3
upper DL	300	300	150	150	45		6.7
M. oxanilic acid (% dets.)	**10.1**	**37.6**	**36.7**	**43.8**	**62.8**	**521.8**	
lower DL	300	12	12	12	3.2		93.8
upper DL	300	300	100	100	45		6.7
Simazine (% detects)	**15.3**	**21.1**	**17.5**	**41.1**	**47.9**	**213.1**	
lower DL	7.5	3.8	3.8	0.71	0.71		10.6
upper DL	50	15	15	15	15		3.3
Alachlor (% detects)	**-**	**-**	**0.7**	**0.8**	**-**	**0.0**	
A. ethanesulfonic acid (% dets)	**3.8**	**32.6**	**18.6**	**39.1**	**50.3**	**1223.7**	
lower DL	300	12	12	12	1.7		176.5
upper DL	300	300	823	823	45		6.7
Alachlor oxanilic acid (% det.)	**0.7**	**5.1**	**5.1**	**27.7**	**38**	**5328.6**	
lower DL	300	24	12	12	0.61		491.8
upper DL	300	300	100	100	45		6.7
2,4-D (% detects)		**16.5**	**24.3**	**35.4**	**58.8**	**256.4**	
lower DL		7.2	2.6	3.6	0.65		11.1
upper DL		7.2	1700	264	90		-11.5

[a] To calculate % Change in the % Detections the % of detects in 2001 were subtracted from the in 2005; the remainder was then divided by the % Detects in 2001 (baseline) and the result mu 100 to give a percentage change from 2001.

[b] Detection Limits are express and a "fold" decrease relative to detection limits in 2001. For inst the Lower DL for Atrazine, the Lower DL for 2001 (5.0) was divided by the Lower DL for 2005 (0 resulting in a 7.6 fold decrease in the Lower DL from 2001 to 2005.

Okay, so what does it all mean?

We need some…

…perspective!

Atrazine, 2005

- **Max. conc. Detected?**
  - 1.5 ppb or 1.5 ug/L
  - EPA says 2 L/day
  - So; 3 ug/day
- **What is the Risk?**
  - RfDc = 0.018 mg/kg/day
  - Ave. person in US = 70 kg
  - Thus, 1.26 mg/day
  - 3 ug = 0.003 mg
  - Thus, drinking worse case scenario water gives you **0.24% of the RfDc**.
  - Not much…

A Simple Comparison

- **Average American consumes 4.5 cups of coffee per day. That's about 238 mg of caffeine per person per day.**
- **Average exposure to atrazine in finished drinking water is 0.003 mg/person/day.**
- **So, average American is exposed to about 80,000 times more caffeine than atrazine.**

A Simple Comparison, pt. 2

	Daily Exposure	$\%LD_{50}$
• Caffeine	238 mg	2.7
• Atrazine	0.003 mg	0.0001
• Malathion	0.42 mg	0.000002

So, is Caffeine killing us?

- **What we know.**
  - **Caffeine can increase blood pressure but only for a short time. There is no other biologically plausible reason why coffee should cause heart or other vascular effects.**

Still Concerned?

How about bottled water?

Table 6. Distribution of Residues by Pesticide in Bottled Water in 2005

Pesticide	Pest Type	No. of Samples	Samples with Detects	% of Samples with Detects
Hydroxy atrazine	HM	211	22	10.4
Met. ethanesulfonic acid	HM	211	18	8.5
Desethyl atrazine	HM	378	26	6.9
Ala. ethanesulfonic acid	HM	211	9	4.3
Met. oxanillic acid	HM	211	6	2.8
Atrazine	H	378	10	2.6
Desethyl -desisopropyl atrazine	HM	211	4	1.9
Imazethapyr	H	211	2	0.9
Desisopropyl atrazine	HM	378	3	0.8
Picloram	H	211	1	0.5
Alachlor oxanillic acid	HM	211	1	0.5
Acetochlor oxanillic acid	HM	211	1	0.5
Tetraconazole	F	378	1	0.3
Acetochlor	H	378	1	0.3

Table 7. Comparison of pesticide residues in bottled water and in public drinking water for selected pestides in 2005.

	% of Samples with Detects		
Pesticide	**Drinking Water**	**Bottled Water**	**% Difference**
Atrazine	74.6	2.6	72
Met. ethanesulfonic acid	74.1	8.5	65.6
Hydroxy atrazine	66.7	10.4	56.3
Desethyl atrazine	66	6.9	59.1
Met. oxanillic acid	62.8	2.8	60
Ala. ethanesulfonic acid	50.3	4.3	46
Desisopropyl atrazine	40.1	0.8	39.3
Acetochlor oxanillic acid	38.5	0.5	38
Alachlor oxanillic acid	38	0.5	37.5
Imazethapyr	20.6	0.9	19.7
Acetochlor	2.4	0.3	2.1
Picloram	0	0.5	-0.5
Tetraconazole	0	0.3	-0.3

Cheers for Beers

- **Beer has been found to be protective against heart attacks among middle aged men in the Czech Republic. Over 900 men who drank only beer were studied. Those who drank 5 to 9 liters per week were less than half as likely to have a heart attack than those who drank no beer (British Med. J., May 20, 2000).**

Acute Toxicity (LD_{50})

oral exposure in rats

Chemical	LD_{50}[1] (mg/kg)
Botulinum toxin	0.00001
Dioxin (TCDD)	0.001
Strychnine sulfate	2
CARBOFURAN	5
Vitamin D3[2]	43
Rotenone[2]	70
Nicotine[2]	95
Caffeine	127
DDT	450
Copper sulfate[2]	472
Solanine	590

Chemical	LD_{50}[1] (mg/kg)
Borax[2]	596
2,4-D	690
Lime/Sulfur[2]	820
Aspirin	891
Boric acid[2]	1,350
Ferrous sulfate[2]	1,500
ATRAZINE	3,000
MALATHION	4,000
NaCl (salt)	4,000
GLYPHOSATE	5,600
Ethyl alcohol[2]	10,000

[1]Oral Lethal Dose 50% in rats

[2] Approved organic pesticides.

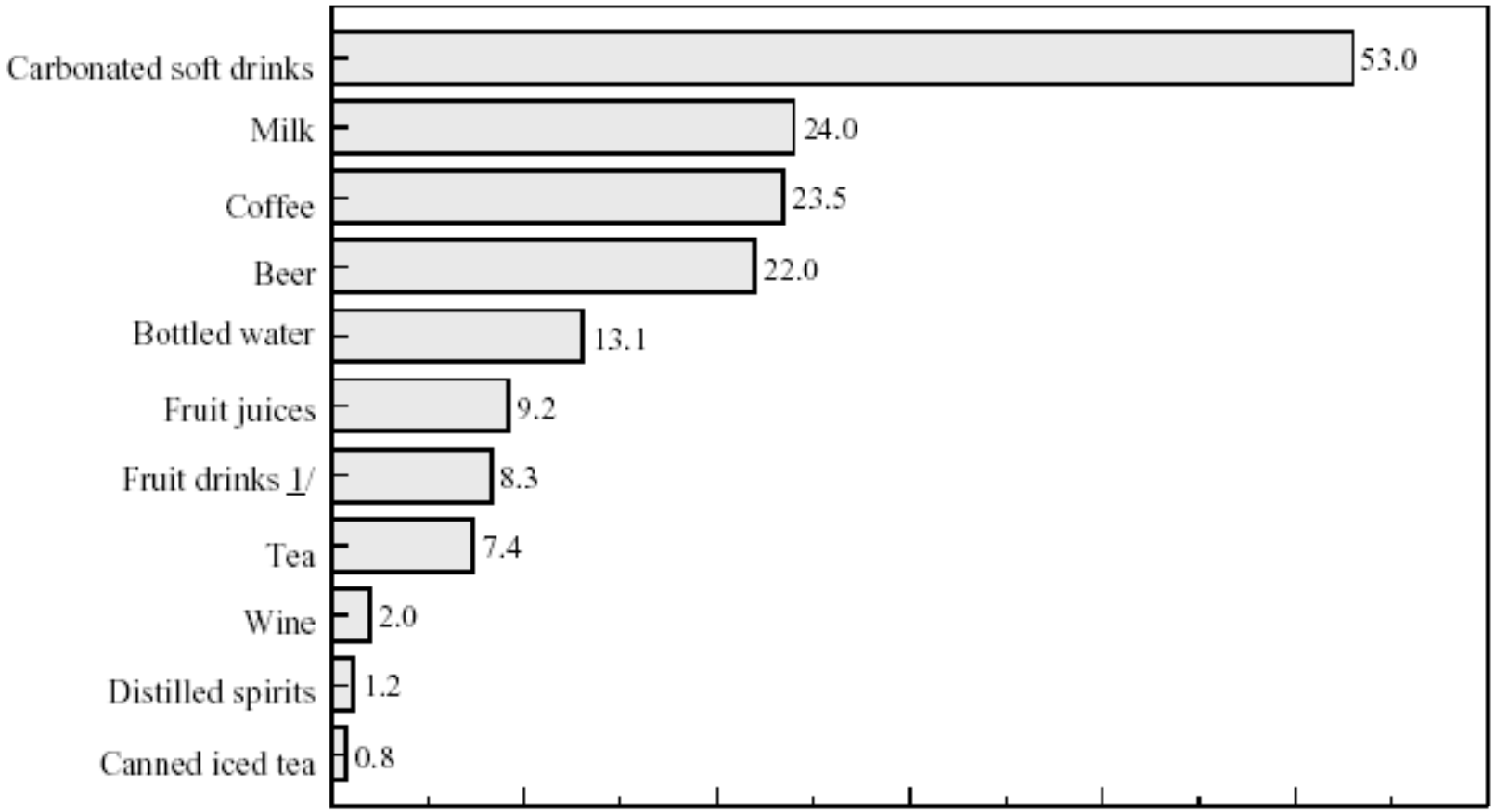
Drinking Water

- **372 of 699 samples (53.2%) had detectable levels of pesticides.**
  - **28 different pesticides out of 150 tested for.**
  - **59% were at or below LOQ (usually 3X LOD).**
  - **Only 16 detected above the LOQ.**
  - **None exceeded MCLs.**

- **Most common pesticides (699 total samples)**
  - **Atrazine (258)**
  - **Metolachlor (233)**
  - **Metolachlor ESA (198)**
  - **Atrazine desethyl (154)**
  - **Metolachlor (152)**
  - **Simazine (141)**
  - **Atrazine disospropyl (127)**
  - **Alachlor ESA (76)**

Figure 21

Per capita beverage consumption, gallons in 1997



1/ Includes fruit cocktails and ades.

Source: USDA/Economic Research Service.