

**Organophosphorous Insecticide Exposure Assessment:  
Human Urine Biomarkers Are More  
Persistent In Produce Than Their Toxic  
Precursors**

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# Overall goals...

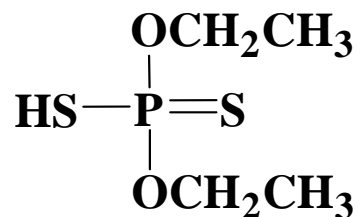
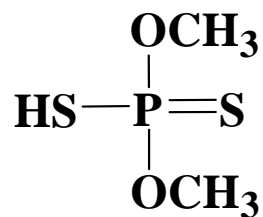
- Describe the occurrence of pesticides and biomarkers in produce
- Measure the relative persistence of pesticides and their biomarkers under field conditions
- Promote recognition of background levels of biomarkers in the diet and potential influence on misclassification of 'body burden'

# DAPs in 153 California Fruit and Vegetable Samples, 2003-2004

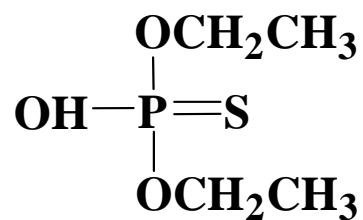
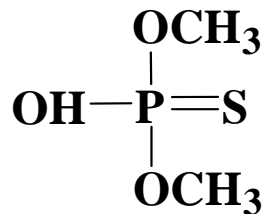
Acephate  
Azinphos-methyl  
Chlorpyrifos  
Diazinon  
Dimethoate  
Malathion  
Methamidophos  
Oxydemeton-methyl  
Phosmet

Zhang et al 2008

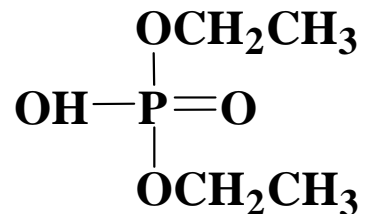
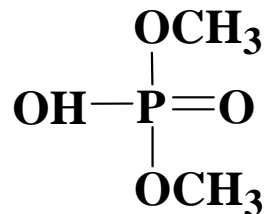
## STRUCTURES OF ALKYLPHOSPHATE



**dialkyldithiophosphate**



**dialkylthiophosphate**



**dialkylphosphate**

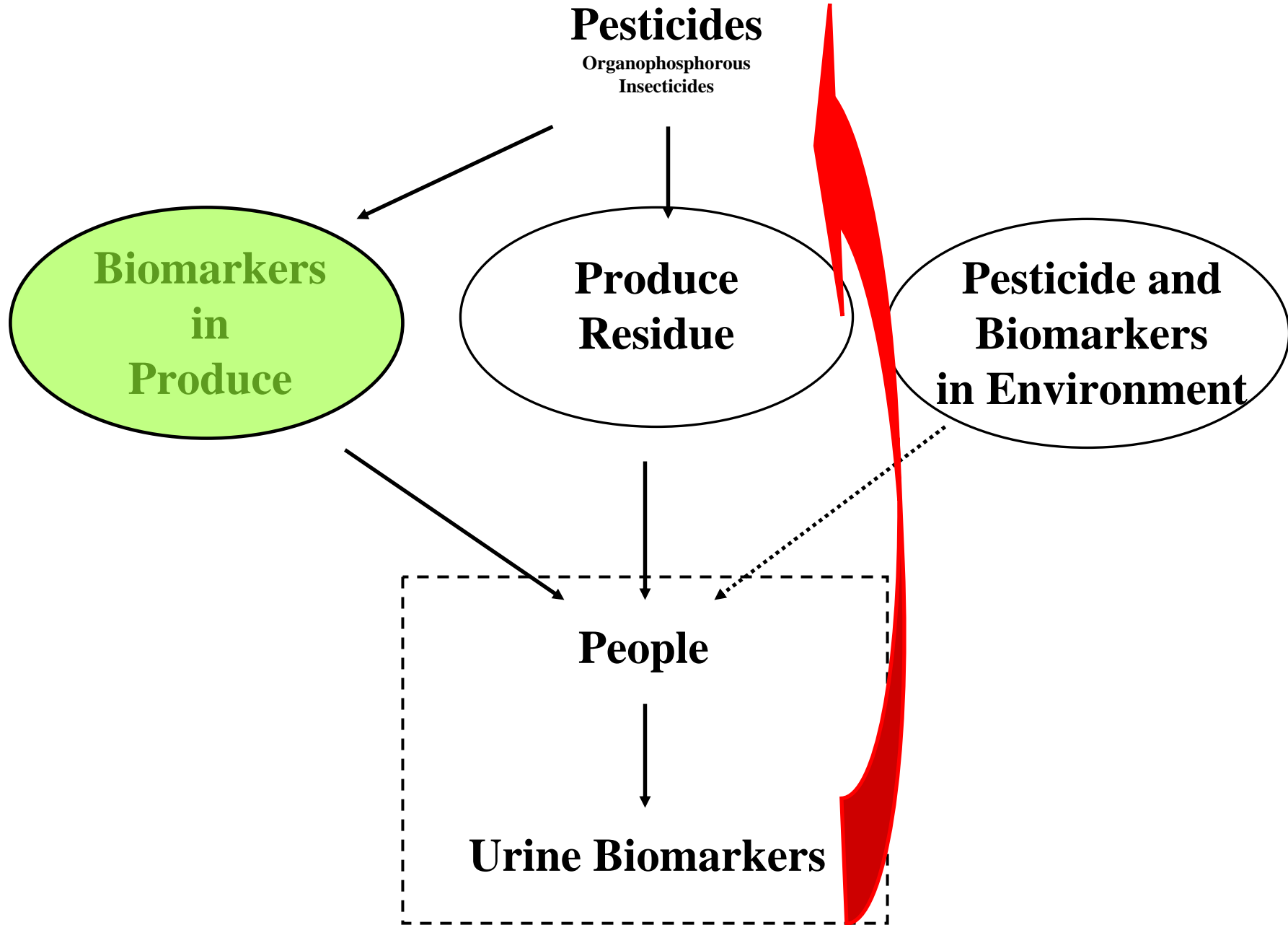
# Summary Data From the California Fruit and Vegetable Residue Survey, 2003-2004

- DAP/OP mole ratio 0.02 to 73
- Arithmetic mean DAP/OP mole ratio 5.2
- Geometric mean DAP/OP mole ratio 1.4
- 60% of fruits and vegetables had mole ratios >1
- Samples without measurable OP contained measurable DAPs<sup>a</sup>

Zhang et al 2008

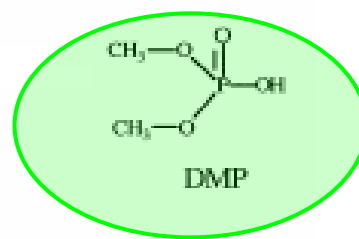
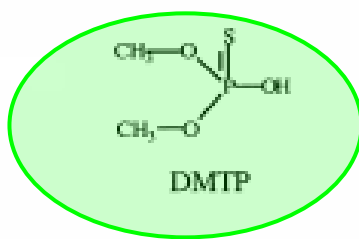
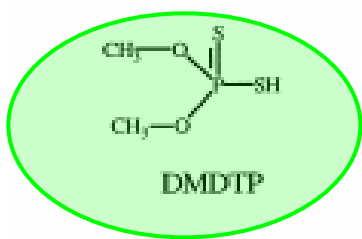
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<sup>a</sup> A 2009 survey of produce without measurable OPs has confirmed this observation, but sampling is compromised by analysis of produce without known history of OP exposure. Sankaran et al.

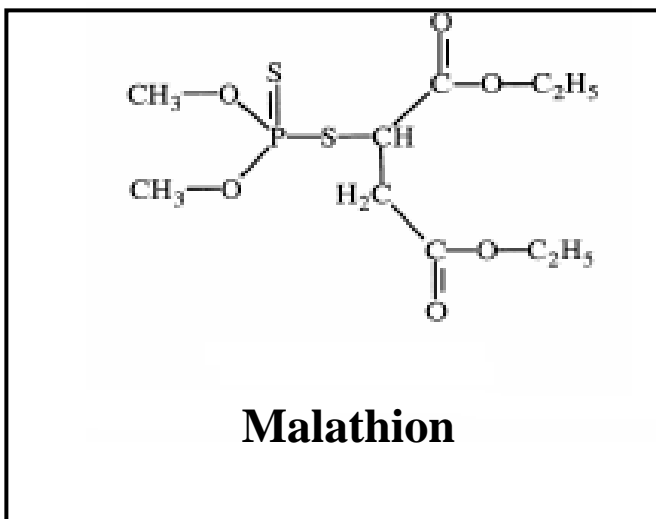


**Biomarkers Used to Estimate Pesticide Exposure**

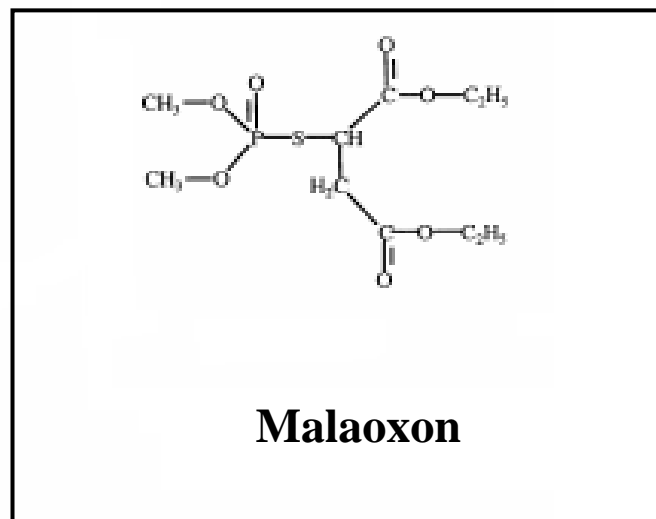




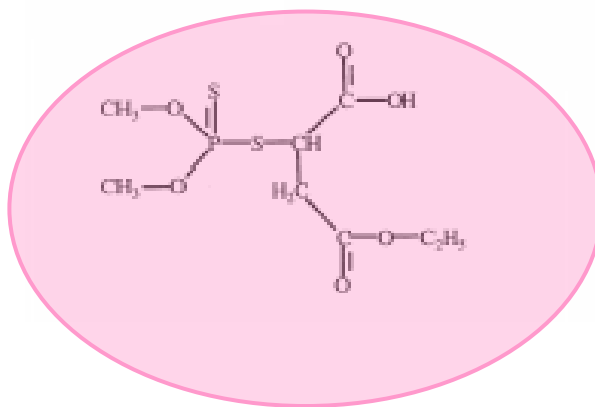
## Dialkylphosphates (DAPs)



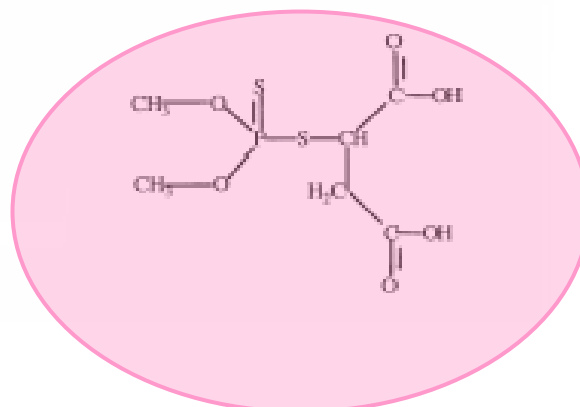
**Malathion**



**Malaoxon**



**Malathion Monoacid**



**Malathion Diacid**

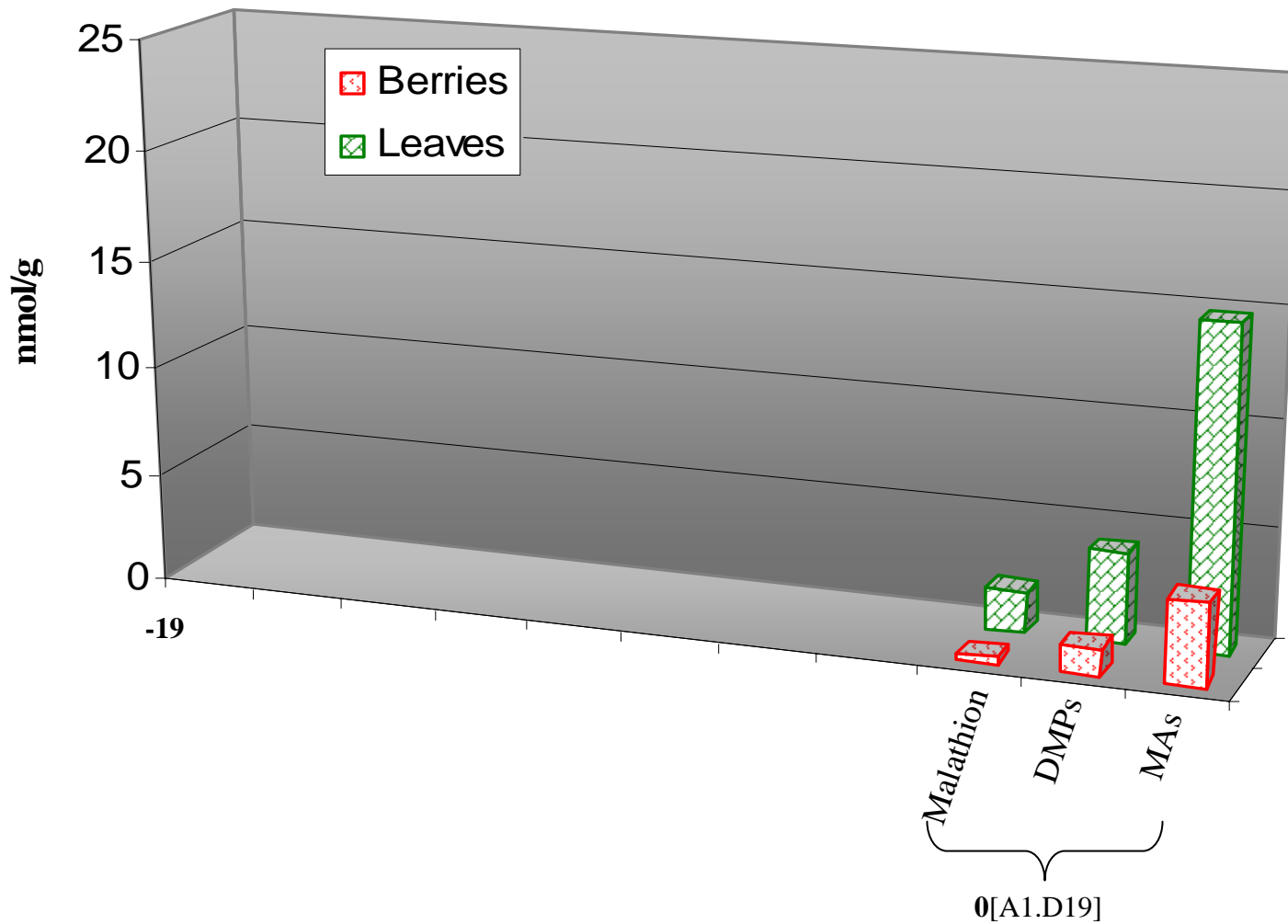
# Malathion and Biomarkers



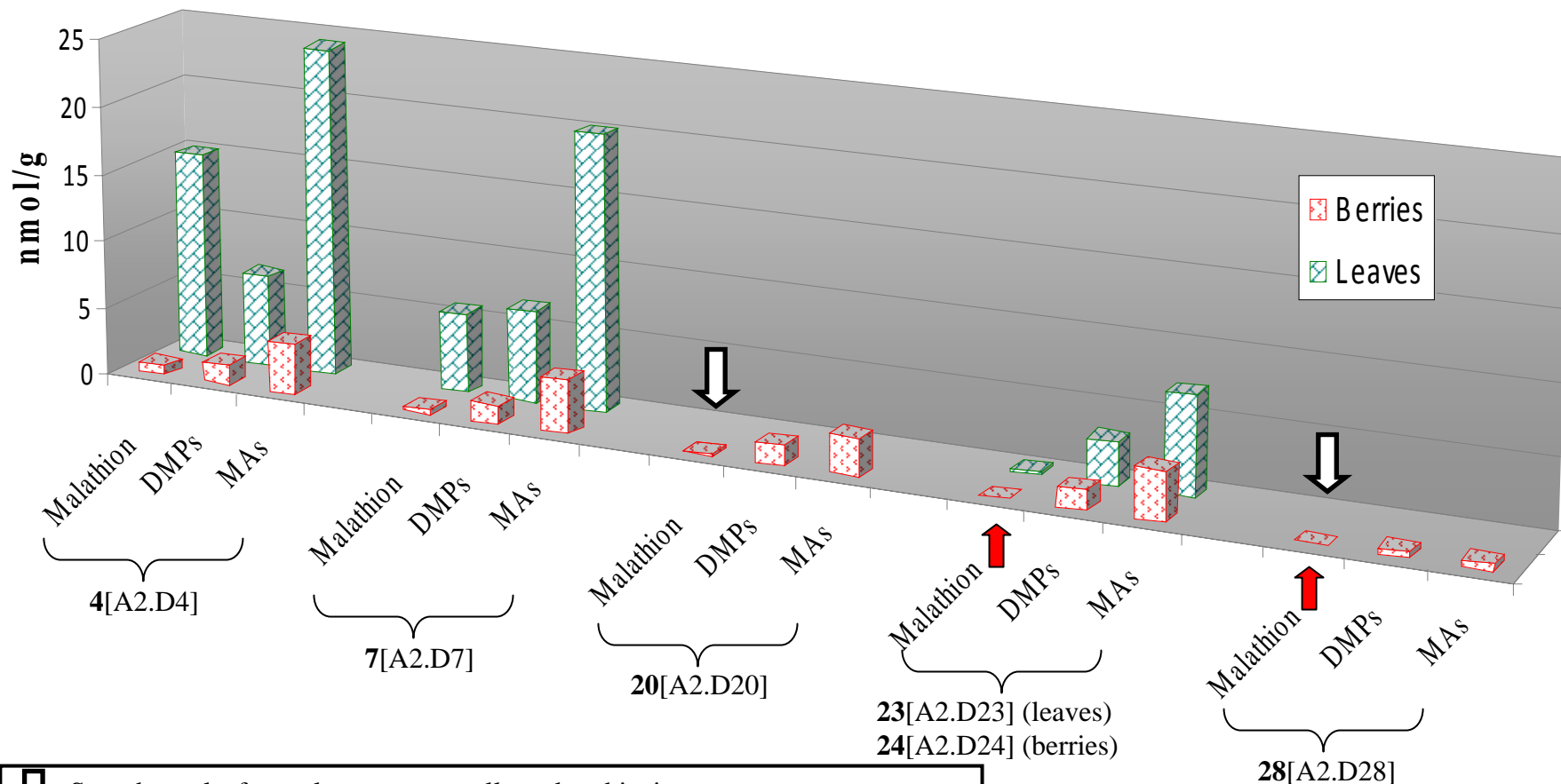
# Dialkylphosphate and MA Analysis



- Samples from channels of trade
- Acetone:water extracts of produce *positive* for organophosphorous insecticide residues
- 5-10 ppb as benzyl tolyl triazine DAPs  
2-4 ppb diazomethane MAs  
analyzed using GC-FPD
- 70-110% DAPs; 80-120% MAs recovery

# First Malathion Application at -D19 (32 oz /acre)

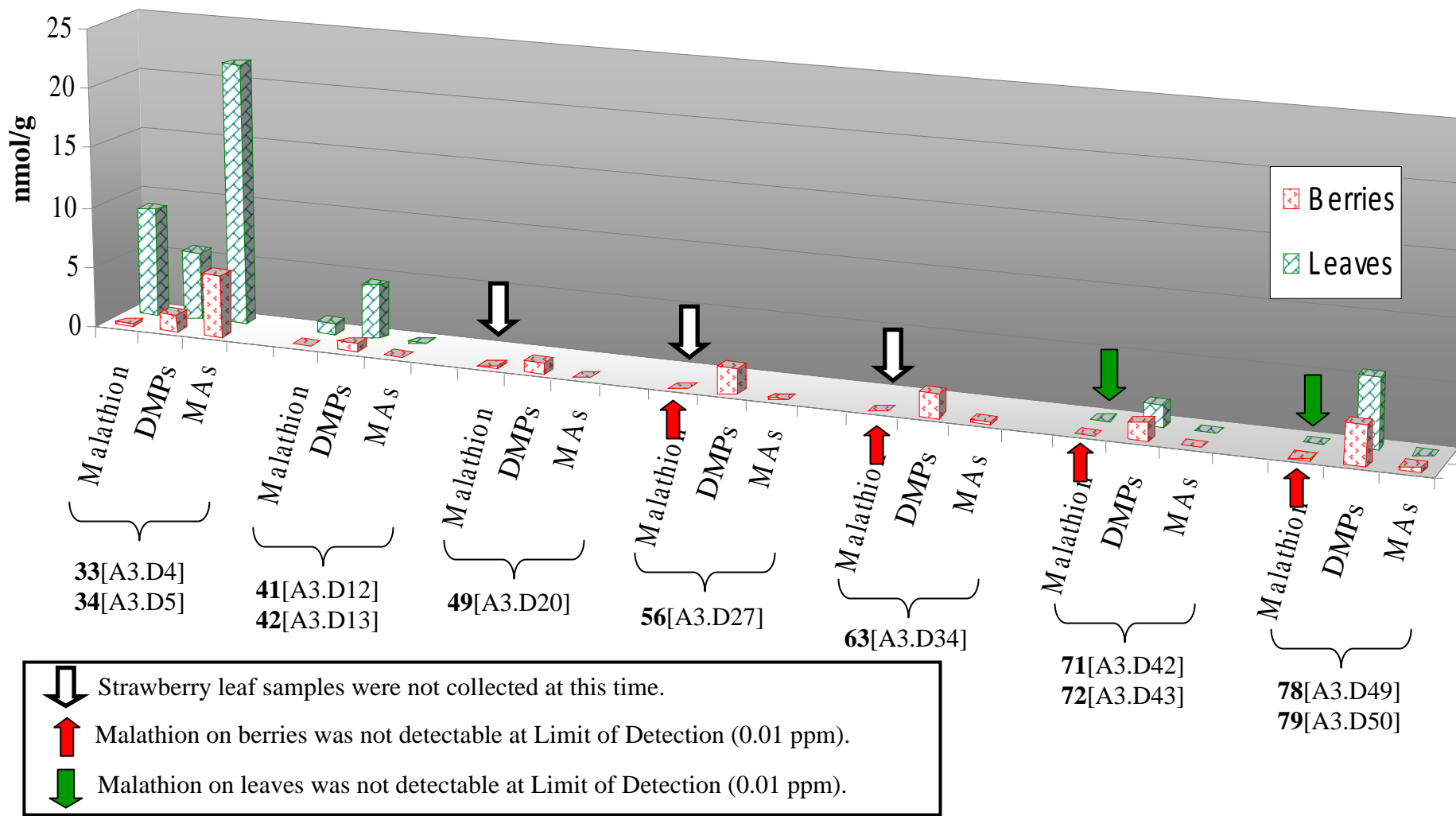


# Second Malathion Application at D0 (16 oz /acre)

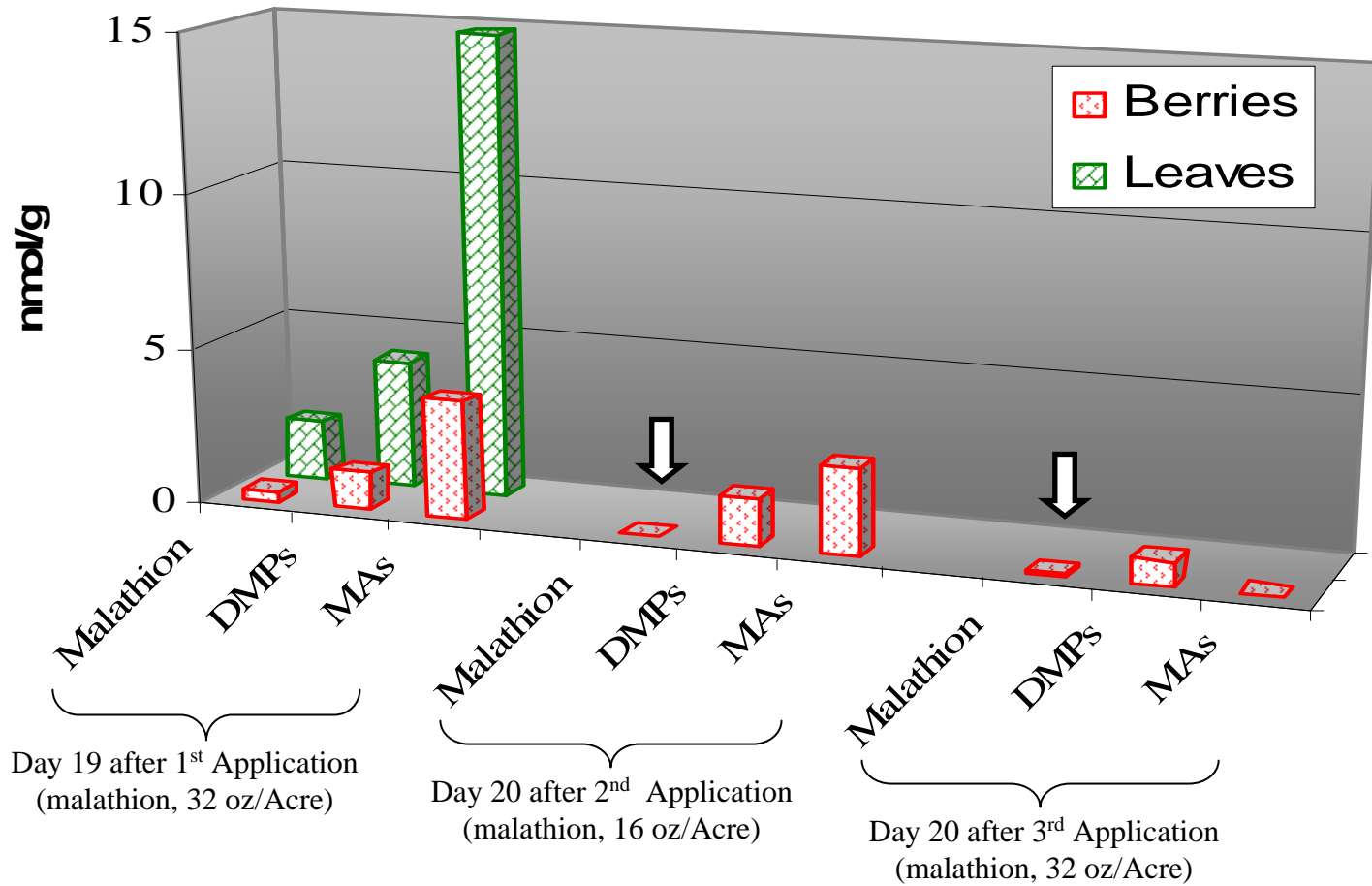


 Strawberry leaf samples were not collected at this time.  
 Malathion on berries were not detectable at Limit of Detection (0.01 ppm)

# Third Malathion Application at D33 (32 oz /acre)



# Malathion Residues After 19/20 Days Following Each Application

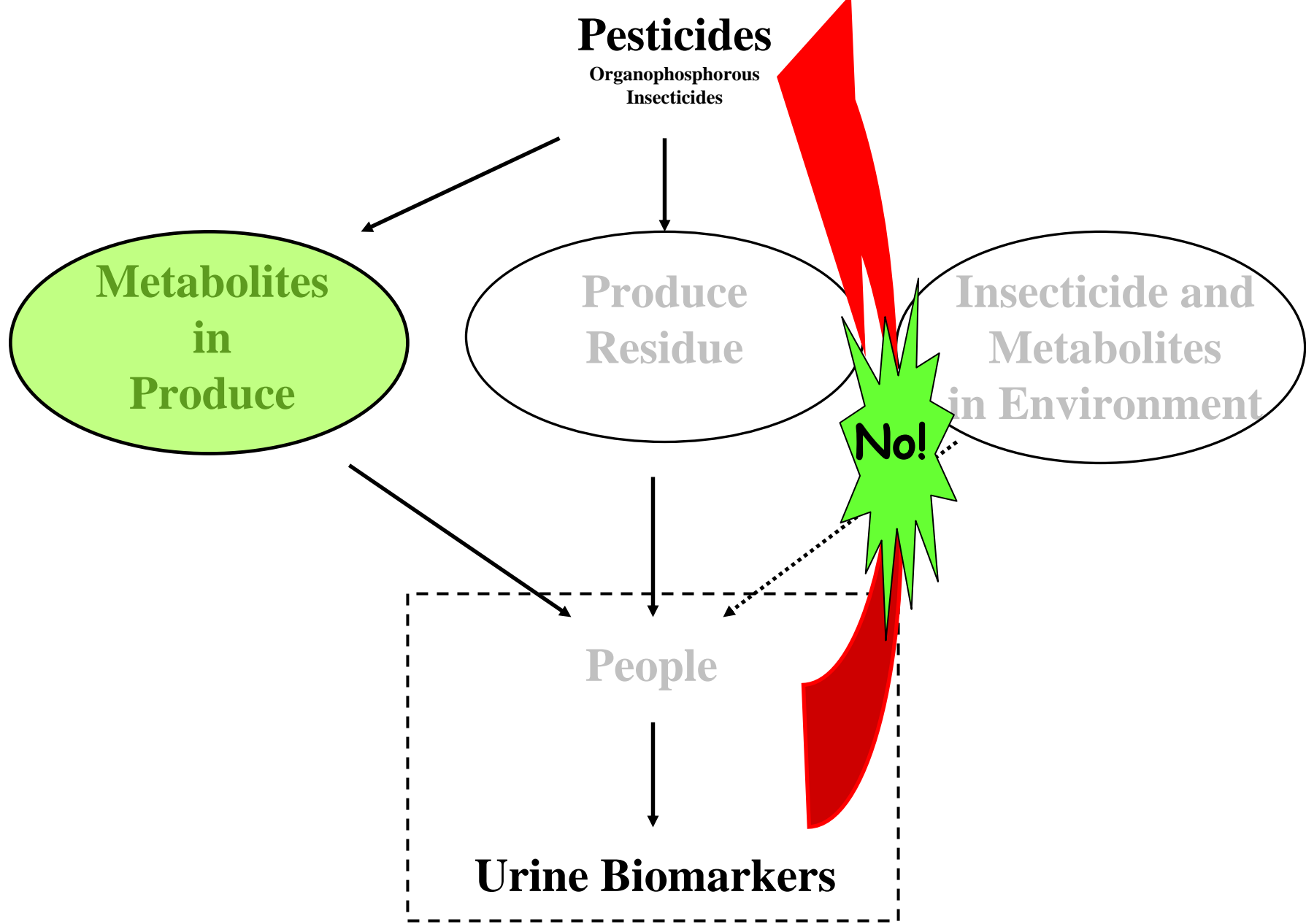


↓ Strawberry leaf samples were not collected at this time.

# Nanomol Ratios of DMPs to Malathion in Berries

	Days after Spray	Malathion	DMPs <sup>a</sup>	nmol ratio of DMPs/Malathion	
				mean ± s.d.	Range
<b>2007</b>					
Nor Cal		0.21 ± 0.05	1.48 ± 0.82	8.5 ± 5.6	3.3 ~ 17.3
Fall River	Day 4	0.28 ± 0.07	1.59 ± 0.66	5.9 ± 2.9	1.8 ~ 11.4
Ghesquiere		0.26 ± 0.10	1.86 ± 1.07	7.0 ± 2.0	4.0 ~ 11.1
Nor Cal		0.04 ± 0.02	4.89 ± 1.99	147.8 ± 96.1	34.8 ~ 338.0
Fall River	Day 22	0.08 ± 0.02	6.47 ± 2.38	85.7 ± 21.5	35.1 ~ 109.0
Ghesquiere		0.06 ± 0.01	3.80 ± 1.26	60.3 ± 18.3	36.7 ~ 103.3
<b>2008</b>					
1 <sup>st</sup> Application	0[A1.D19]	0.33 ± 0.10	1.22 ± 0.29	4.1 ± 1.6	1.9 ~ 6.8
	4[A2.D4]	0.70 ± 0.12	1.43 ± 0.31	2.1 ± 0.4	1.1 ~ 2.5
2 <sup>nd</sup> Application	7[A2.D7]	0.27 ± 0.18	1.36 ± 0.24	5.3 ± 1.5	3.9 ~ 8.4
	20[A2.D20]	0.02 ± 0.01	1.51 ± 0.34	76.0 ± 36.5	37.5 ~ 143.4
	24[A2.D24]	0.02 ± 0.00 <sup>b</sup>	1.42 ± 0.45	93.4 ± 30.0	46.0 ~ 152.3
	28[A2.D28]	0.02 ± 0.00 <sup>b</sup>	0.43 ± 0.23	28.6 ± 15.1	4.9 ~ 55.3
3 <sup>rd</sup> Application	34[A3.D5]	0.18 ± 0.15	1.443 ± 0.48	13.4 ± 8.6	2.8 ~ 27.0
	42[A3.D13]	0.05 ± 0.05	0.66 ± 0.34	22.3 ± 25.7	4.3 ~ 91.3
	49[A3.D20]	0.08 ± 0.05	0.79 ± 0.17	9.7 ± 2.3	7.7 ~ 15.5
	56[A3.D27]	0.02 ± 0.00 <sup>b</sup>	2.21 ± 0.49	145.8 ± 32.7	94.5 ~ 202.8
	63[A3.D34]	0.02 ± 0.00 <sup>b</sup>	1.82 ± 0.56	116.9 ± 41.0	54.6 ~ 179.8
	72[A3.D43]	0.02 ± 0.00 <sup>b</sup>	1.41 ± 0.27	92.9 ± 17.9	102.3 ~ 129.2
	79[A3.D50]	0.02 ± 0.00 <sup>b</sup>	3.16 ± 0.64	208.4 ± 42.2	120.5 ~ 267.4





Urine biomarkers represent metabolites of people and preformed ones in produce.



## *In summary...*

- Pesticide biomarkers are formed in foliage, produce, and people (creates a teachable moment about '*body burden*')
- The occurrence of biomarkers in produce and other foods may confound low level pesticide exposure studies
- Biomarkers are more persistent than parent insecticides in strawberries and likely in other fruits and vegetables