# Wet and Dry Atmospheric Deposition of Pesticides in the San Joaquin Valley, California

Michael Majewski, Celia Zamora, William Foreman*, Charles Kratzer

US Geological Survey, California Science Center, Sacramento, California
*USGS, National Water Quality Laboratory, Methods Research and Development Group, Denver, Colorado

USGS science for a changing world

# Presentation Outline

- 2001 Study (January 2001)
  - Objectives
  - Sampling Sites and Methods
  - Results
    - Patterns, Trends, Detected Pesticides
- 2002-2004 Study (January ‘02-August ‘04)
- Conclusions and Summary
- Issues Associated w/ Pesticides in the Air of the San Joaquin Valley

USGS
science for a changing world

# Presentation Outline

- 2001 Study (January 2001)
- 2002-2004 Study (January ‘02-August ‘04)
  - Objectives
  - Sampling Sites and Methods
  - Results
    - Patterns, Trends, Detected Pesticides
- Conclusions and Summary
- Issues Associated w/ Pesticides in the Air of the San Joaquin Valley

USGS
science for a changing world

# 2001 Study Objectives

- To determine if pesticides used during the dormant orchard spray season were drifting into an urban environment
- To determine the potential contribution of rainfall to the pesticide loads in urban runoff

USGS
science for a changing world

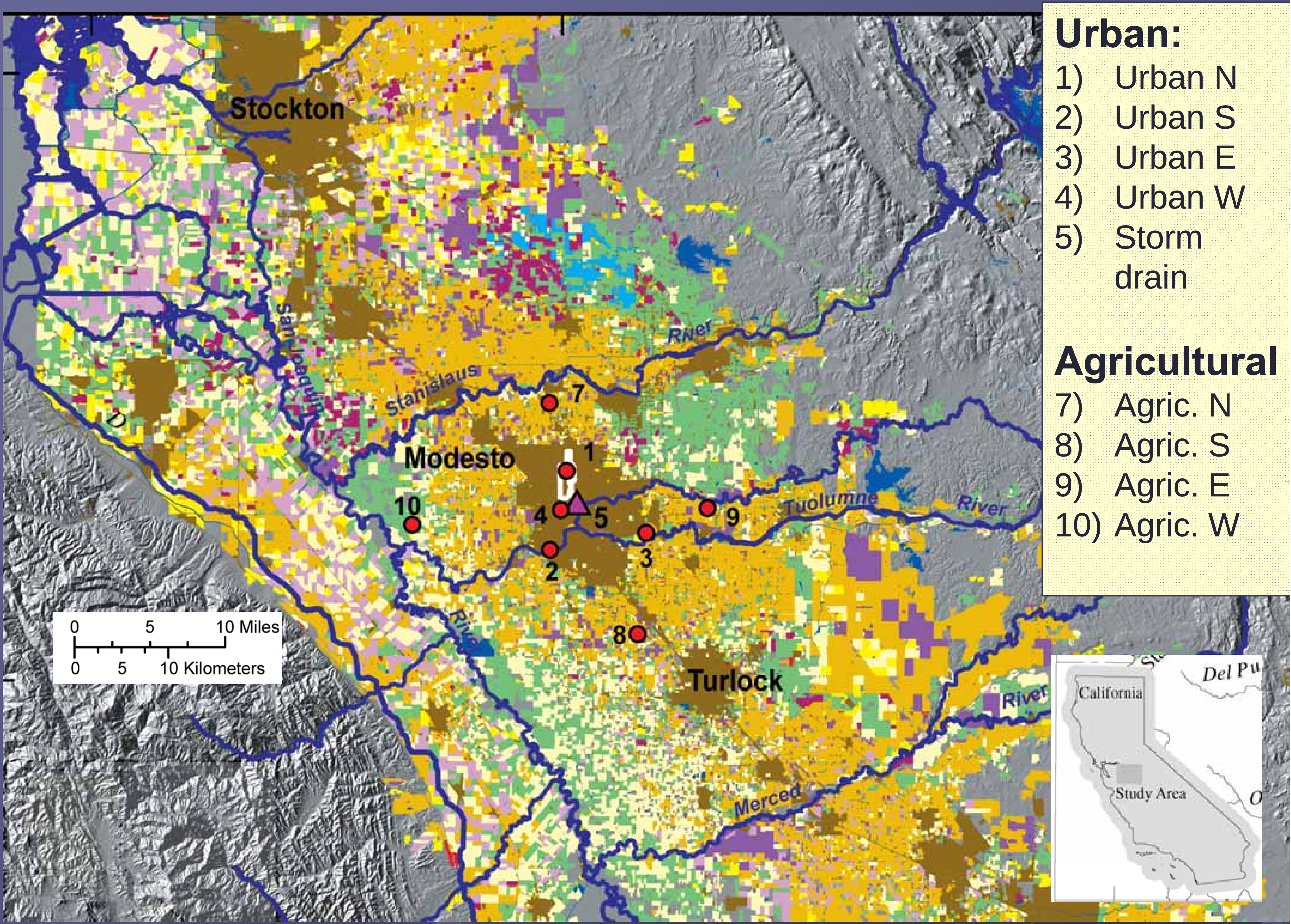
# 2001 Analytes

- GS/MS-SIM Analysis
  - 27 Herbicides
  - 16 Insecticides
  - 4 Transformation Products

# 2001 Sampling Sites

- Four rainfall collectors in agricultural areas surrounding Modesto, CA
- Four rainfall collectors within the Modesto urban area
  - Spatially distributed and provided a good representation of the predominant land uses in study area
- Runoff from a small urban watershed
  - One rainfall collector in upper watershed
  - One rainfall collector just outside lower watershed

USGS
science for a changing world


Stockton
San Joaquin
Stanislaus
River
Modesto
Tuolumne
River
Merced
River
Turlock
1
2
3
4
5
7
8
9
10
0 5 10 Miles
0 5 10 Kilometers
California
Study Area
Urban:
1) Urban N
2) Urban S
3) Urban E
4) Urban W
5) Storm drain
Agricultural
7) Agric. N
8) Agric. S
9) Agric. E
10) Agric. W

# Analytes Detected at All Sites

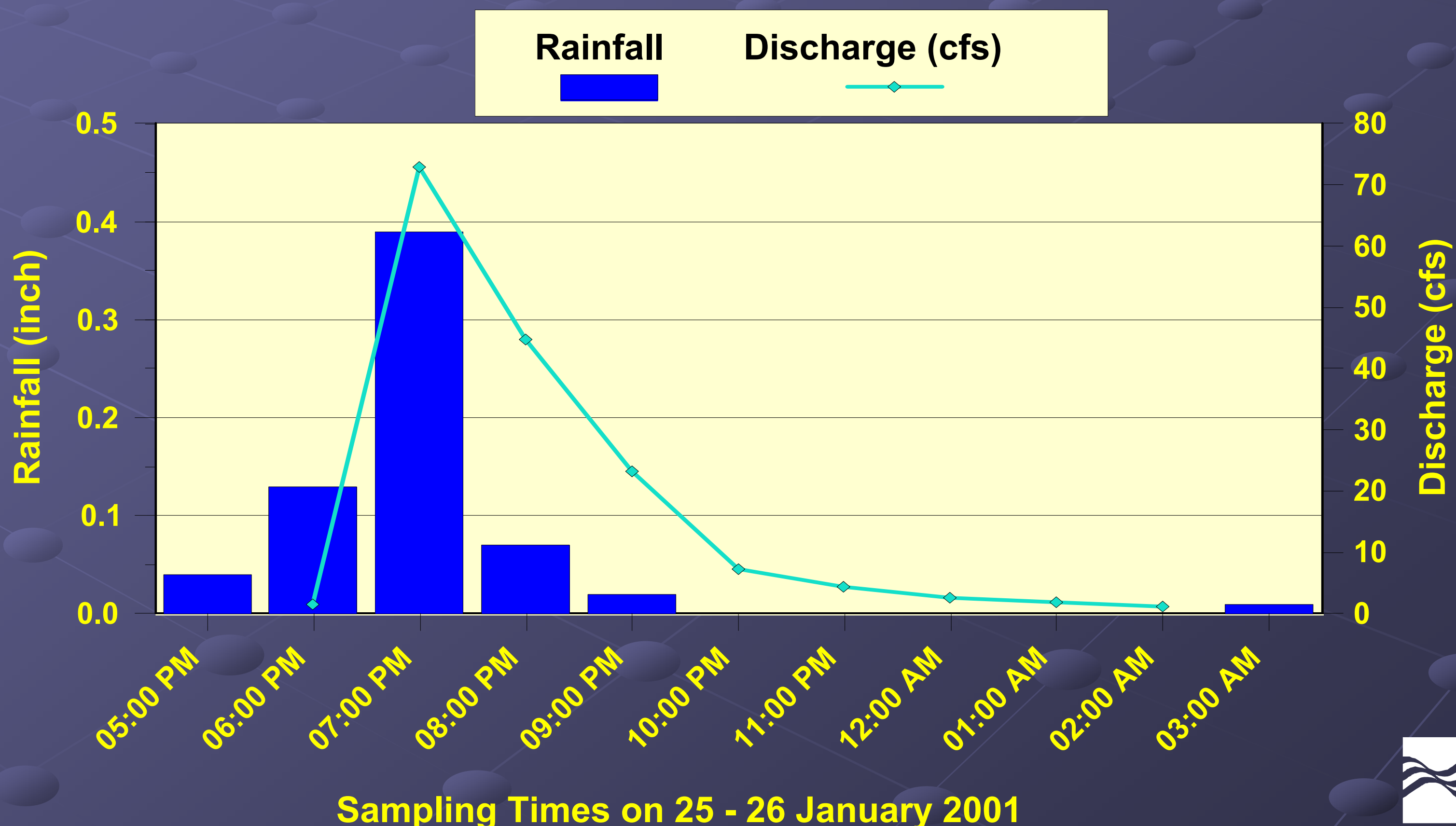
- 6 Herbicides
  - DCPA, Metolachlor, Napropamide, Pendimethalin, Simazine, Trifluralin
- 3 Insecticides
  - Carbaryl, Chlorpyrifos, Diazinon

- Malathion detected at only 1 agric. site, but present in runoff – Urban use indicator?
- Atrazine, Terbacil, and DDE were detected at only 1 ag. site.

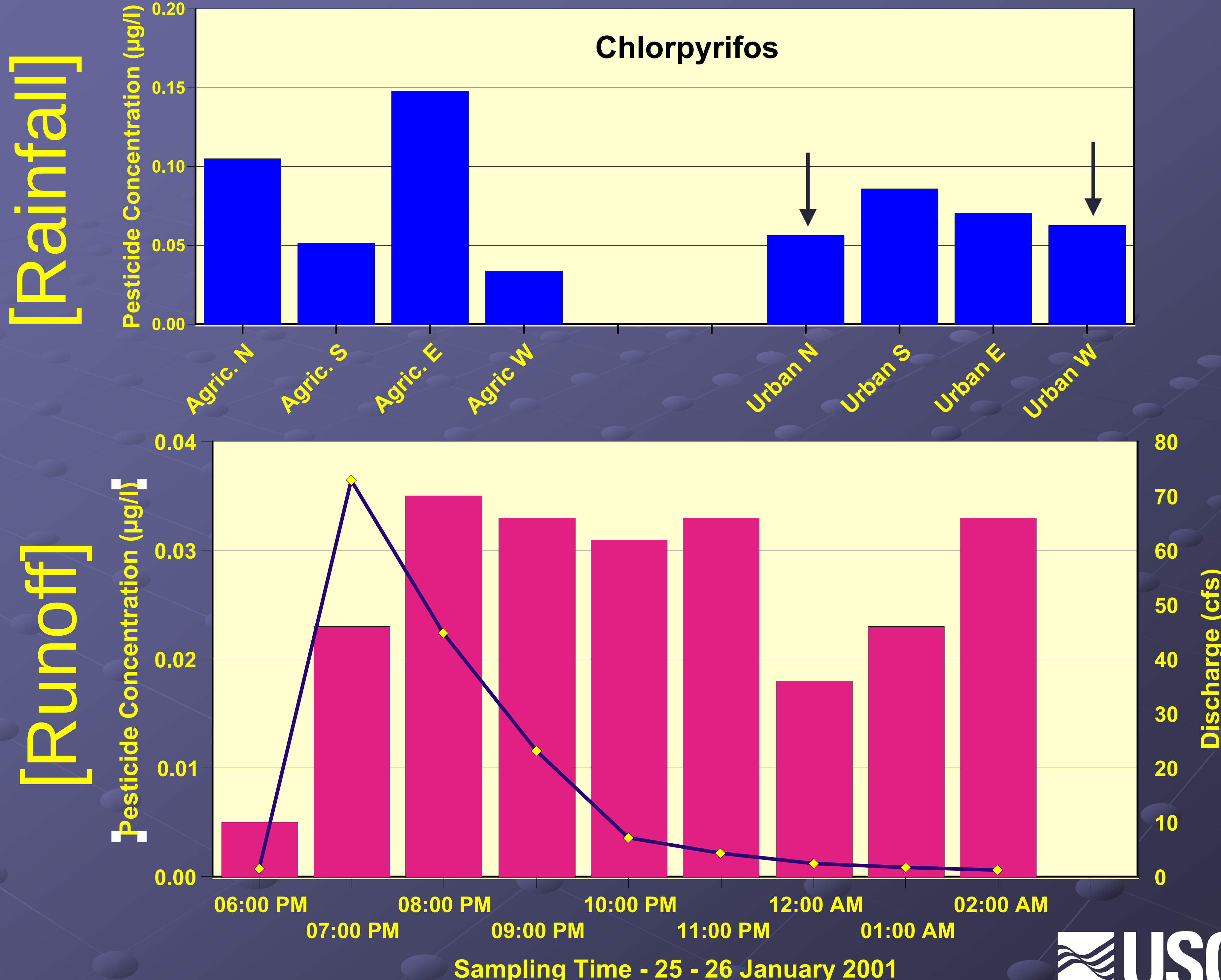
USGS
science for a changing world

# Discharge Concentration Pattern

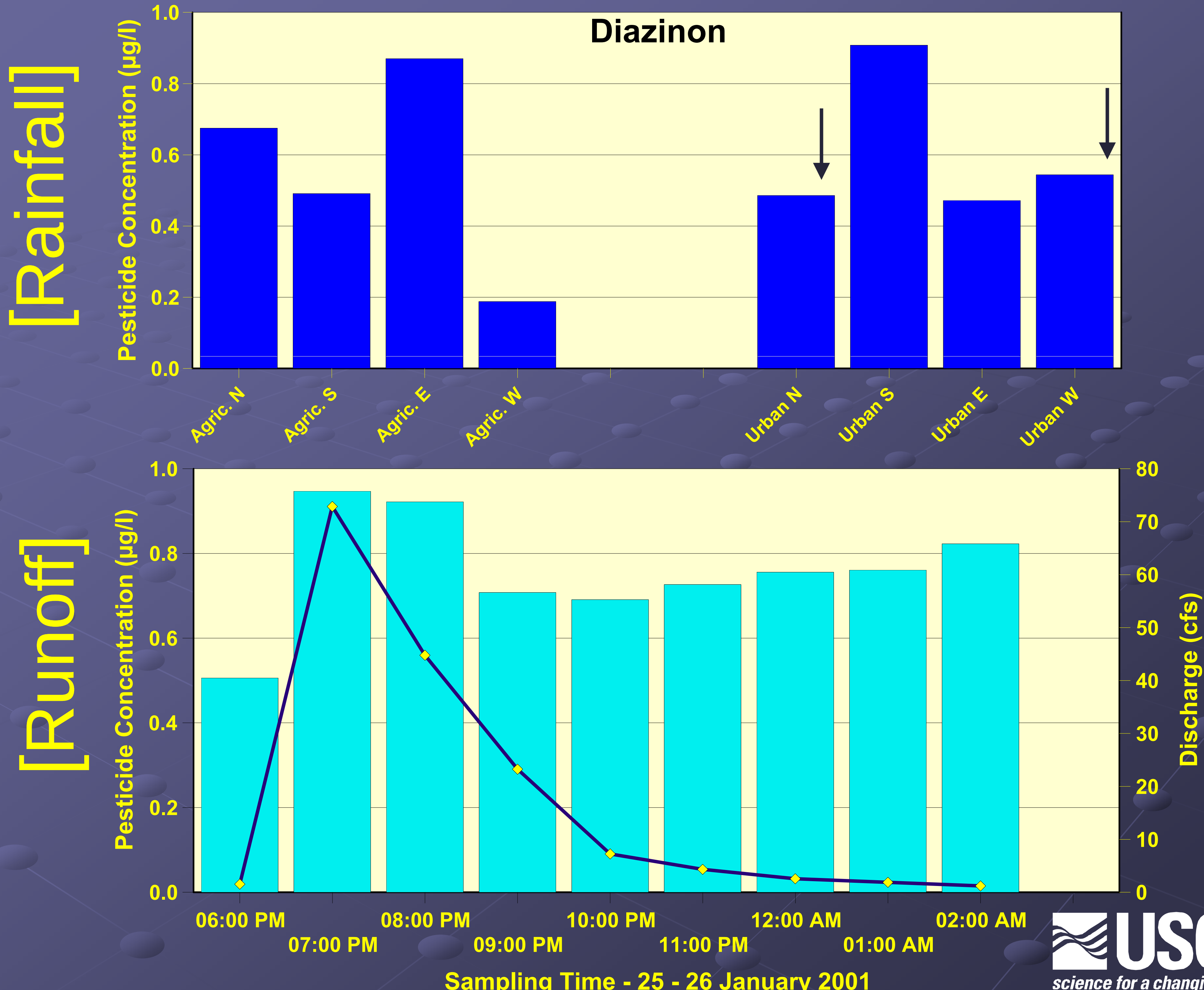
- Two distinct runoff concentration patterns
  - Initial concentration low, but reached a maximum at or slightly after the maximum discharge. Then concentrations slowly declined on falling limb of hydrograph
  - Concentration maximum occurred in first discharge sample and decreased thereafter




USGS
science for a changing world




USGS
science for a changing world

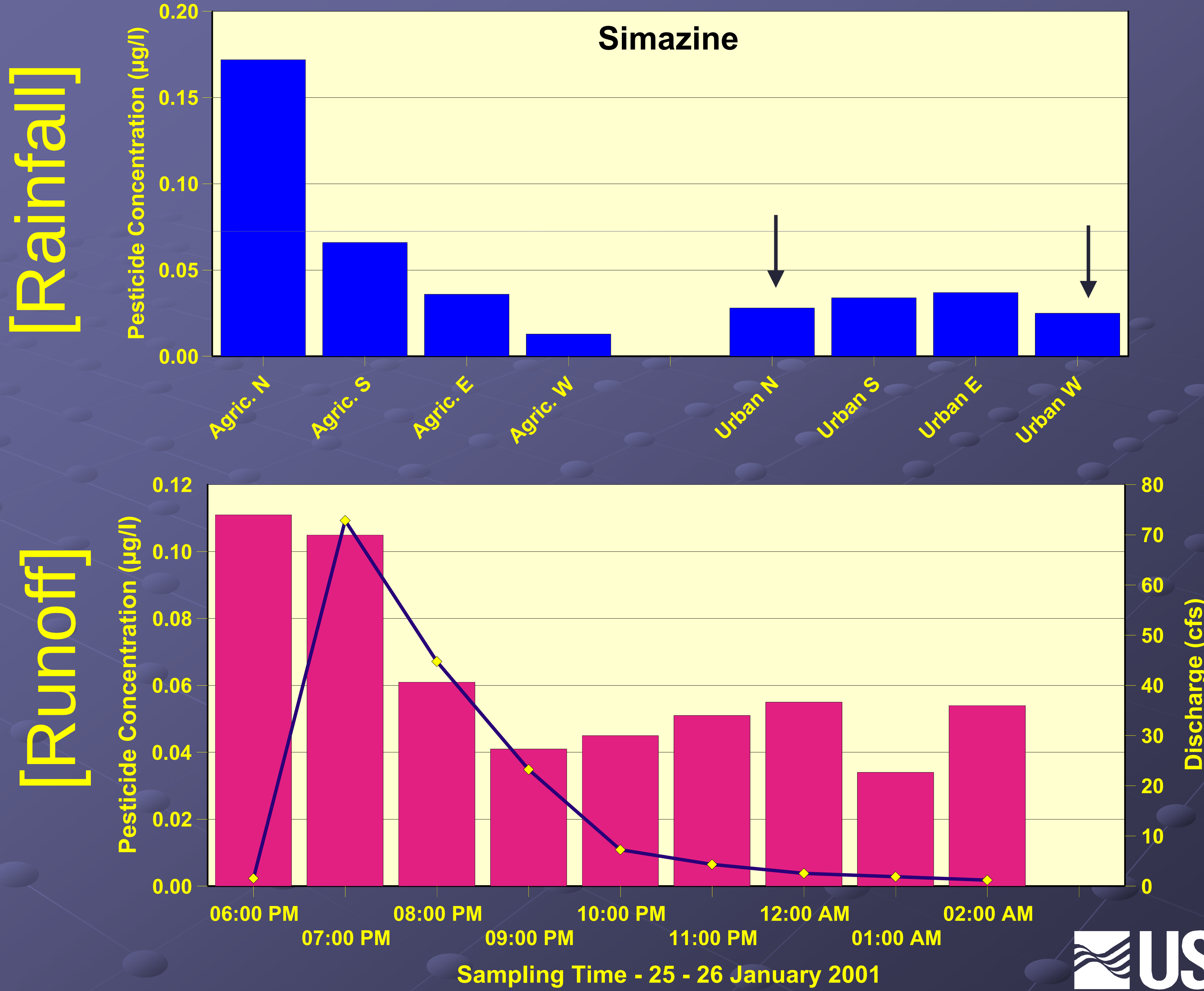



USGS
science for a changing world

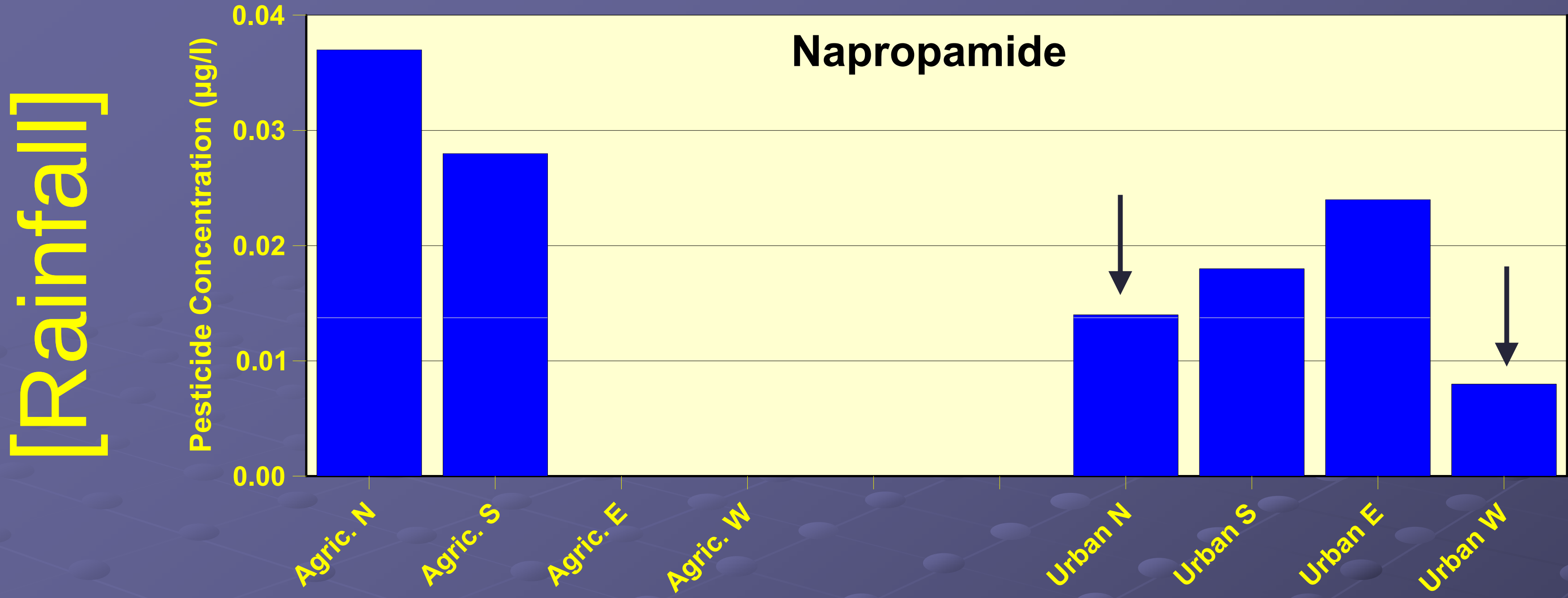
# Discharge Concentration Pattern

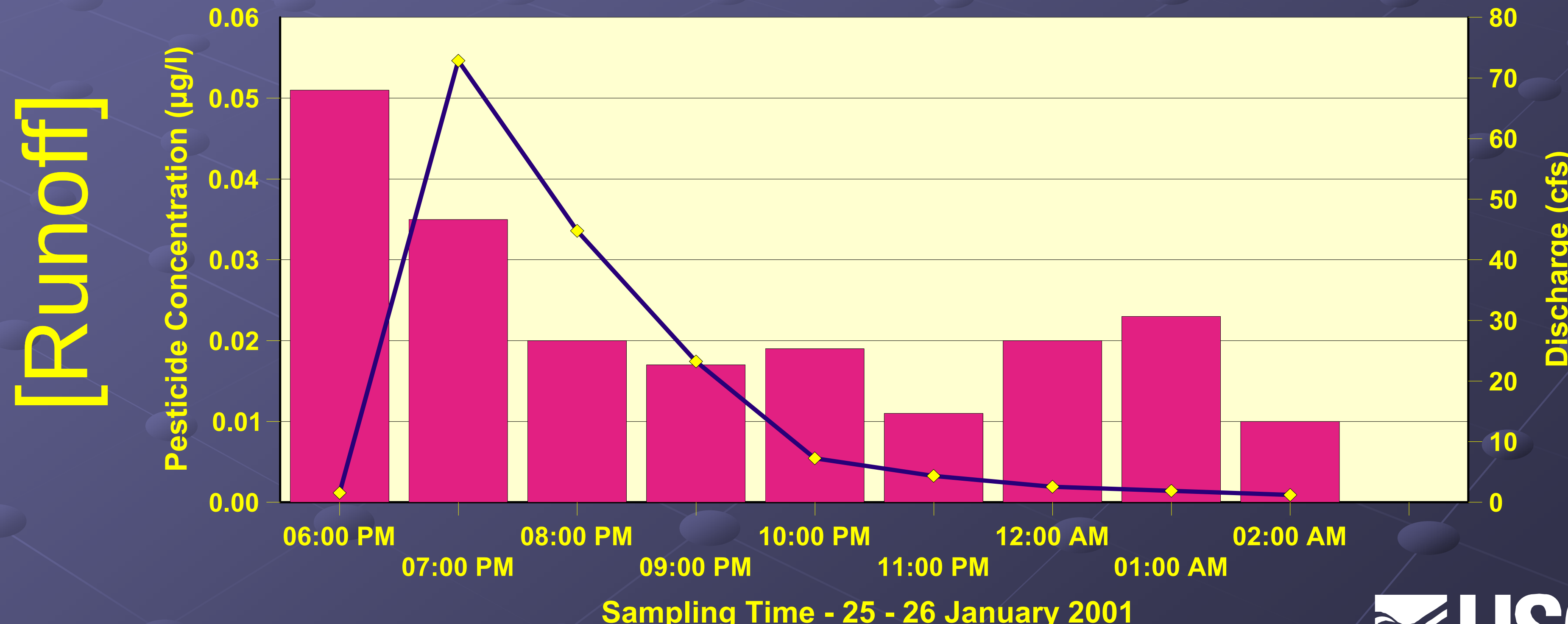
- Two distinct runoff concentration patterns
  - Initial concentration low, but reached a maximum at or slightly after the maximum discharge.  Then concentrations slowly declined  on falling limb of hydrograph
  - Concentration maximum occurred in first discharge sample and decreased thereafter

USGS
science for a changing world




USGS
science for a changing world




USGS
science for a changing world

# 2001 Results

# Mean Concentration (µg/L) of Detected Pesticides

| | RAIN | RUNOFF | S (mole/m$^3$) | log Koc |
|---|---|---|---|---|
| Simazine | 0.051 | 0.062 | 2.52 | 2.14 |
| Metolachlor | 0.004 | 0.009 | 1.87 | 2.29 |
| Napropamide | 0.024 | 0.023 | 0.849 | 2.83 |
| Malathion | 0.007 | 0.049 | 0.264 | 2.61 |
| Carbaryl | 0.082 | 0.176 | 2.53 | 2.31 |
| Pendamethalin | 0.149 | 0.077 | 0.0022 | 2.21 |
| Diazinon | 0.578 | 0.760 | 0.125 | 3.13 |
| DCPA (Dacthal) | 0.011 | 0.005 | 0.0306 | 3.81 |
| Trifluralin | 0.025 | 0.007 | 0.00244 | 3.7 |
| Chlorpyrifos | 0.077 | 0.026 | 0.00125 | 3.95 |
| DDE | 0.003 | 0.002 | 0.00055 | 5.39 |

# Contributions from Rain

## Diazinon

- 64% of concentration in runoff can be attributed directly to rainfall
  - More water soluble
  - Less sorption to organic matter

## Chlorpyrifos

- Concentrations in rain higher than concentrations in storm runoff
  - Less water soluble
  - More sorption to organic matter

USGS
science for a changing world

# 2001 Study Summary

## Wet Deposition

- Can make important contributions to pesticide loading in runoff for some compounds
  - 64% of Diazinon in urban runoff attributed to rainfall
- Dependent on physical/chemical properties of pesticide
  - Water Solubility
  - Soil Sorption Potential

## Two distinct concentration trends in runoff

- Concentrations increasing to hydrograph maximum
  - Less water soluble compounds, higher sorption to organic matter
- Concentrations highest at onset of discharge and decreasing thereafter
  - More water soluble compounds, lower sorption to organic matter
  - Malathion & Simazine indicators of urban use?

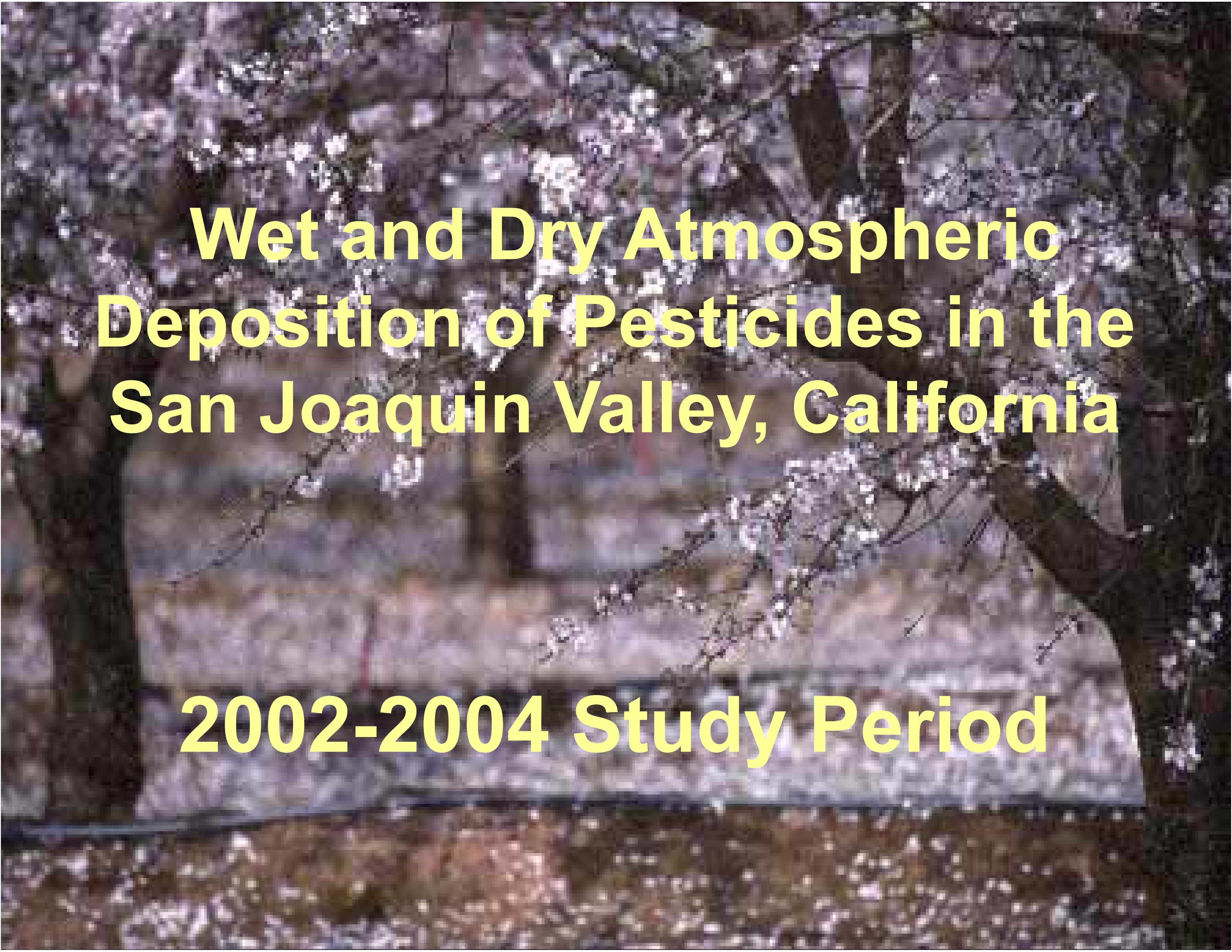
USGS
science for a changing world

# 2001 Study Summary

## Rainfall vs. Runoff Concentrations

- Higher rainfall concentrations
  - Implies sorption to organic matter from dissolved phase
    - This study did not analyze the filtered material
- Higher runoff concentrations
  - Implies accumulation of dry deposition
  - Urban use

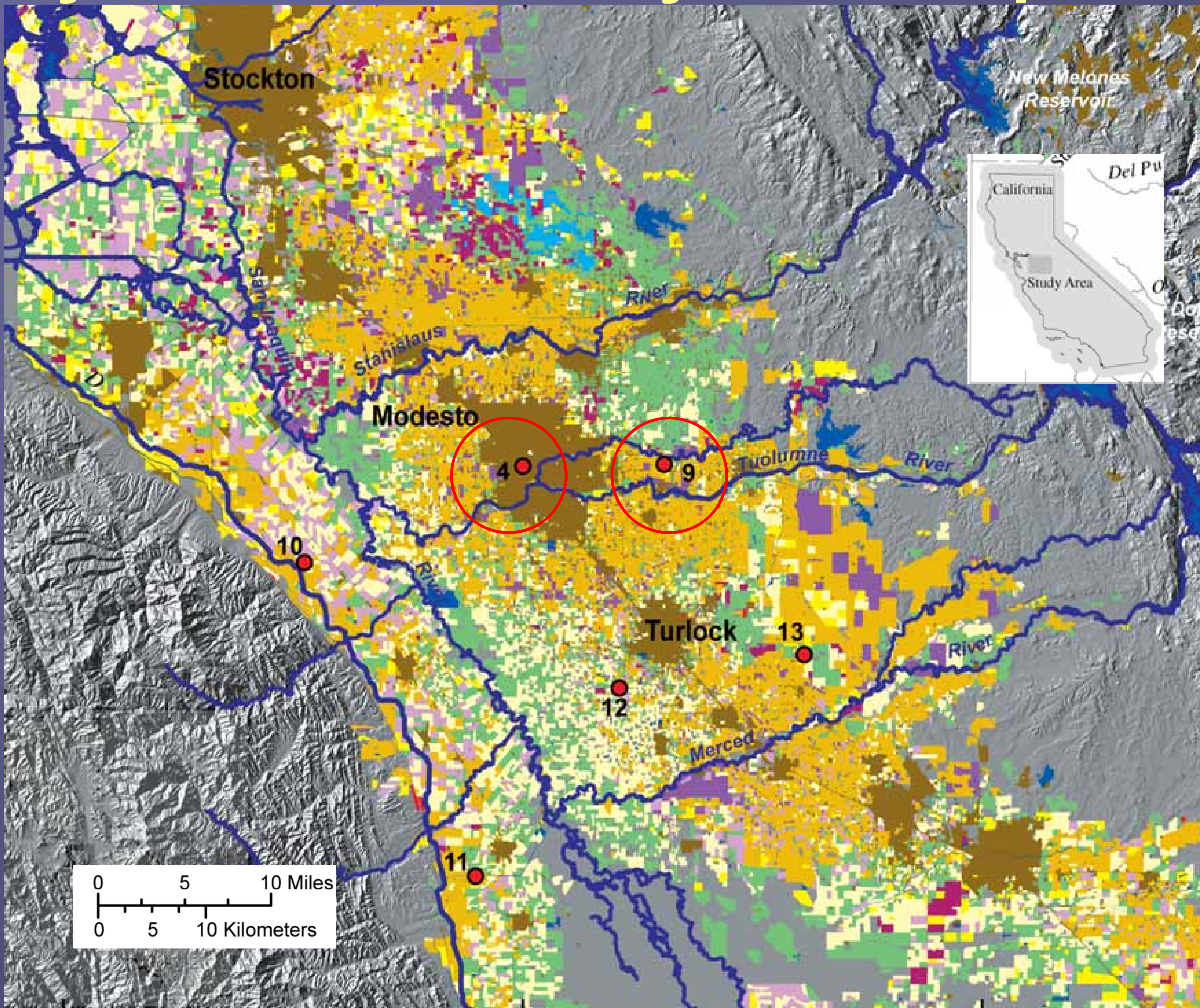
USGS
science for a changing world


Wet and Dry Atmospheric Deposition of Pesticides in the San Joaquin Valley, California
2002-2004 Study Period

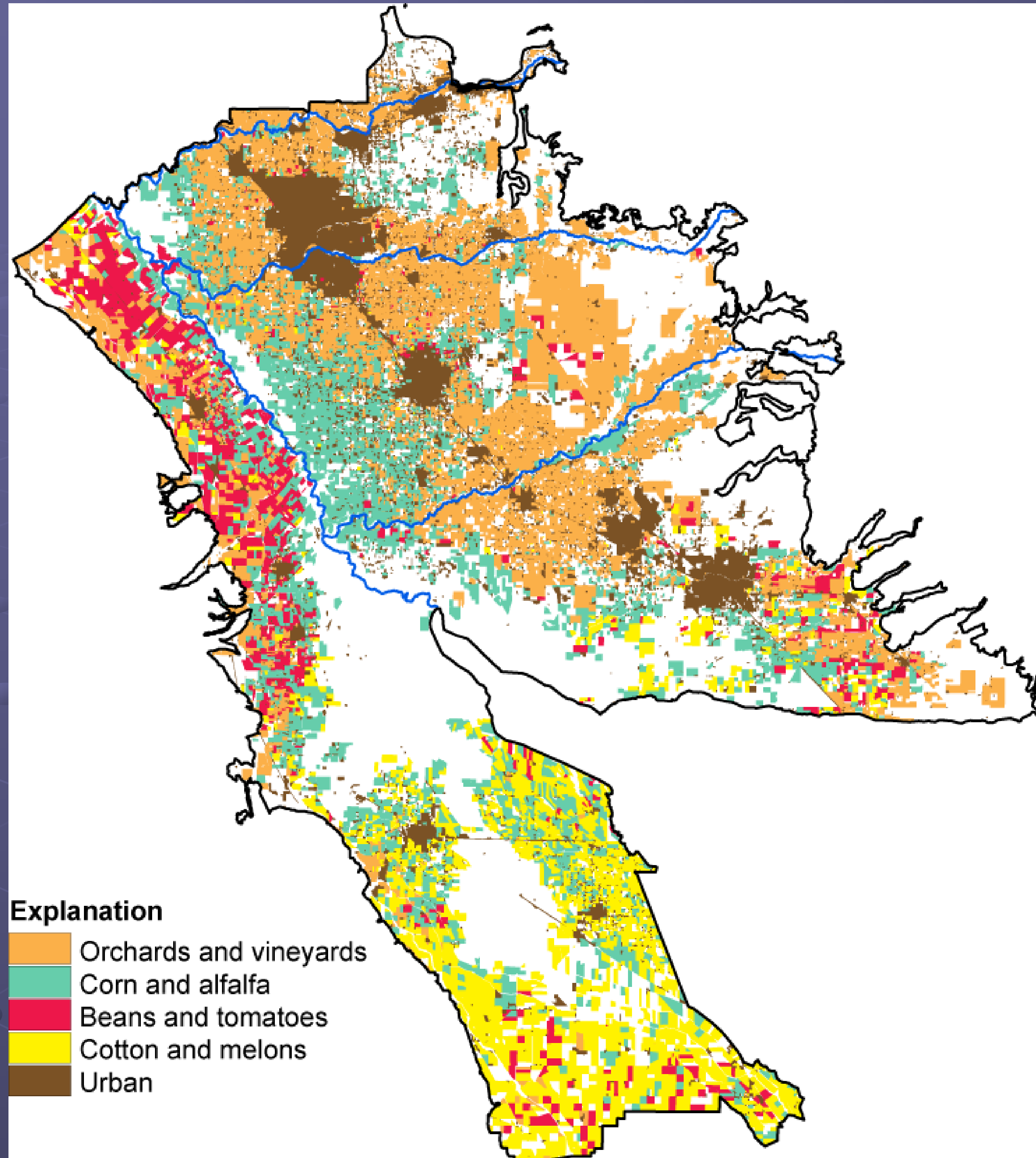
# 2002-2004 Study Objectives

- To quantify the concentration and load of pesticides in wet and dry deposition
- Determine the seasonal variation of pesticides in wet and dry deposition
- Use a soil box to measure atmospheric inputs to and runoff output from a natural surface
- Compare results for an urban and a nearby agricultural (primarily orchards) site
- Determine if the atmosphere is a significant source of pesticides in the San Joaquin Valley, California

# Study #2 Area: January 2002 – April 2004

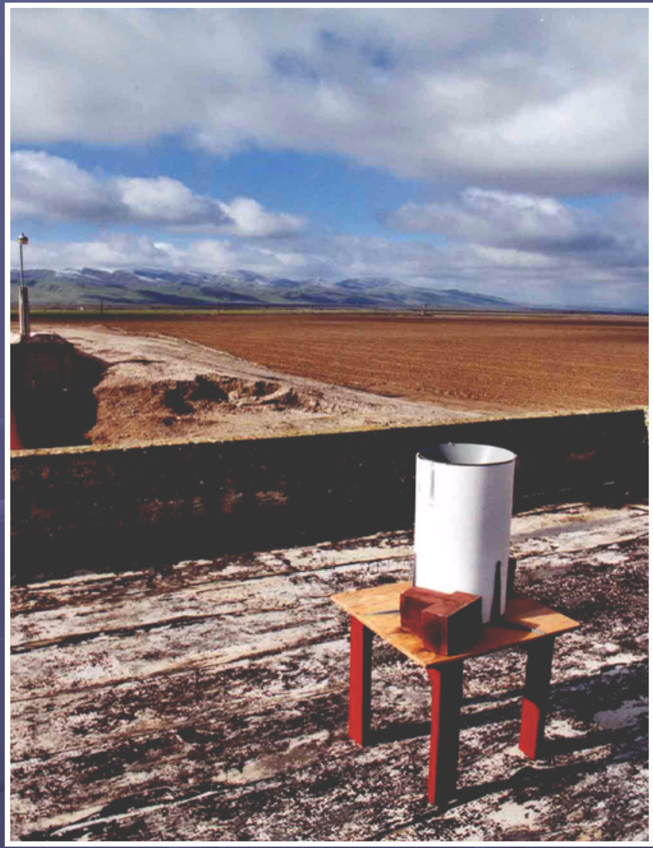


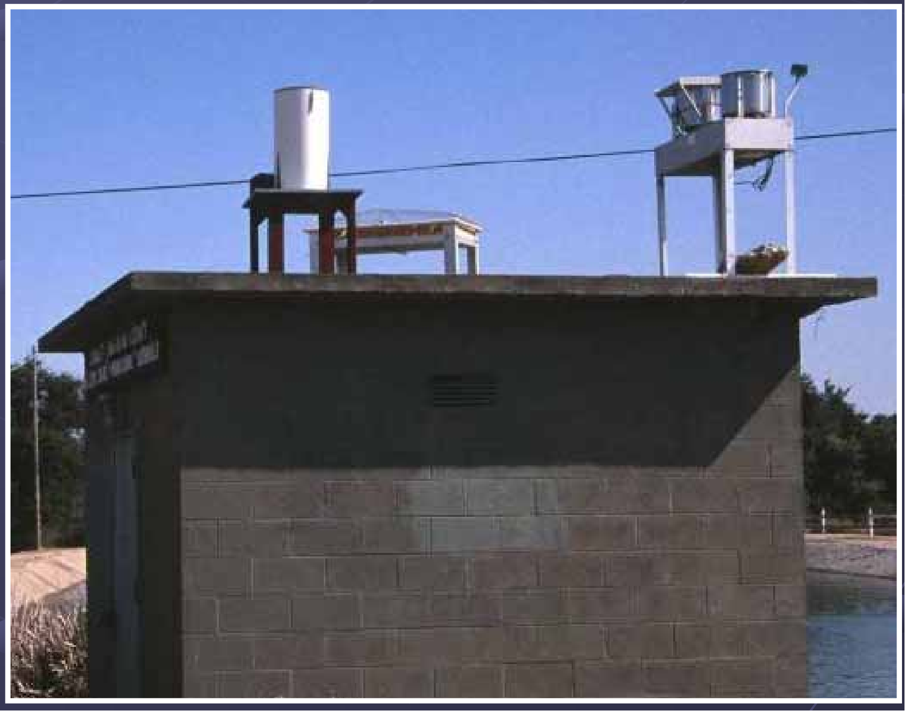
# Location of main crops receiving applications of diazinon, chlorpyrifos, simazine, and metolachlor



# Sampling Methods

- 32 cm, Teflon-lined funnels (6)
- Wet/Dry auto sampler (2)
  - Rainfall event samples
  - Dry deposition composite samples
    - Weeks to months
    - Rinsed with water then solvent
- Fully instrumented weather station at two sites
- Soil Boxes (2)





# Soil Boxes

- Filled ~10cm deep with native soil
- Area~ 1 $m^2$
- Locations- 1 urban, 1 ag. 1 control
  - Collected Dry and Wet Deposition
  - Runoff- dissolved and suspended sediments
  - Collected from one side of box
  - Soil box sloped at 5°
  - Required sufficient rain intensity to produce run
- Sample Types analyzed
  - Filtered water (dissolved phase)
  - Suspended sediments on filters

# Soil Box Samples- surficial soil

- Exposure duration between samples
  - 51, 291, and 352 days
- Samples taken across surface only
  - Composite of 11 subsamples
    - 0.3-cm depth x 2.54-cm diameter
  - Zone of primary sediment mobilization
    - Assumed primary deposition zone

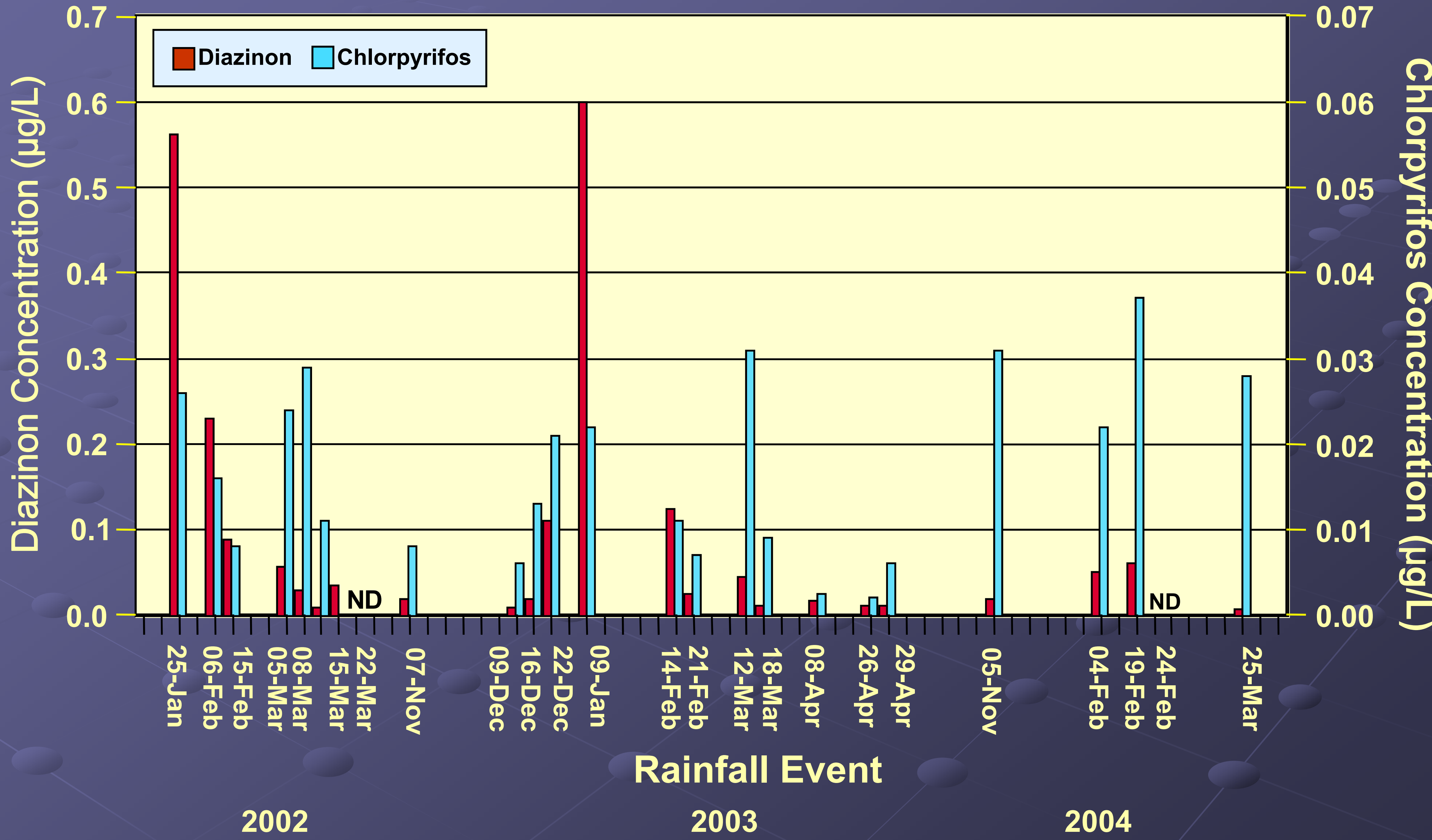
# Analytical Methods (all matrices)

## GCMS-SIM analysis

- 21 Insecticides
- 18 Herbicides
- 3 Fungicides
- 24 Transformation Products

# 2002-2004 Results

# Concentrations of Diazinon and Chlorpyrifos in Rainfall, 1/02 – 4/04 (Turlock Airport site)



# Detected Pesticides (>50% wet, mean)

| Pesticide | Type | Wet Deposition Percent | Wet Deposition (µg/L) | Dry Deposition Percent | Dry Deposition (ng/smpl) |
|---|---|---|---|---|---|
| Dacthal | H | 100 | 0.011 | 89 | 15 |
| Simazine | H | 99 | 0.147 | 68 | 149 |
| Diazinon | I | 93 | 0.170 | 51 | 26 |
| Chlorpyrifos | I | 89 | 0.053 | 78 | 115 |
| Pendimethalin | H | 88 | 0.056 | 32 | 30 |
| Trifluralin | H | 78 | 0.010 | 65 | 30 |
| Carbaryl | I | 68 | 0.048 | 65 | 52 |
| Myclobutanil | F | 65 | 0.087 | 54 | 92 |
| Metolachlor | H | 60 | 0.010 | 70 | 60 |
| Iprodione | F | 53 | 1.91 | 27 | 76 |

# Detected Pesticides (25% - 49% wet, mean)

| Pesticide | Type | Wet Deposition Percent | Wet Deposition (µg/L) | Dry Deposition Percent | Dry Deposition (ng/smpl) |
|---|---|---|---|---|---|
| Malathion | I | 43 | 0.031 | 16 | 20 |
| Prometryn | H | 42 | 0.024 | 0 | NA |
| Diazinon OA | TP | 39 | 0.041 | 18 | 25 |
| Methidathion | I | 39 | 0.043 | 5 | 287 |
| 3,4-Dichloroaniline | TP | 39 | 0.039 | 16 | 7 |
| Chlorpyrifos OA | TP | 35 | 0.026 | 11 | 385 |
| Malathion OA | TP | 34 | 0.050 | 35 | 60 |
| Pronamide | H | 29 | 0.012 | 3 | 6 |
| 1-Naphthol | TP | 26 | 0.014 | 32 | 16 |
| Azinphos-methyl | I | 26 | 0.043 | 51 | 94 |

# Frequently Detected Pesticides

| Pesticide | Deposition Wet | Dry | Runoff | SJ River |
|---|---|---|---|---|
| Diazinon | 93% | 50% | 87% | 70% |
| Chlorpyrifos | 89% | 74% | 81% | 62% |
| Simazine | 99% | 68% | 94% | 94% |
| Metolachlor | 60% | 68% | 94% | 98% |

# Mean Concentrations in Rain, Soil box Runoff, & San Joaquin River

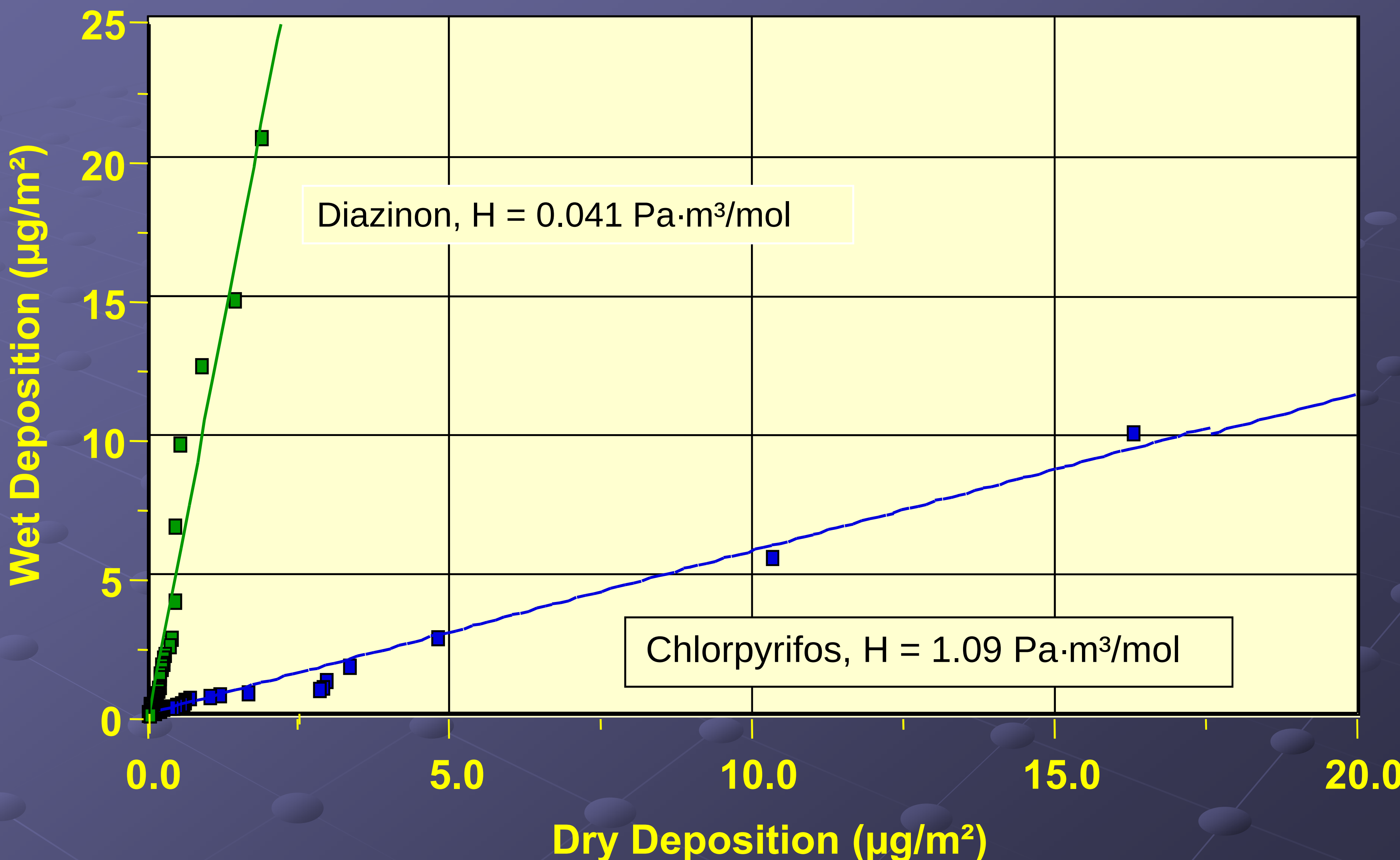
| Pesticide | Main Use Months | Rain (µg/L) | Runoff (µg/L) | SJR (µg/L) |
|---|---|---|---|---|
| Diazinon | Jan | 0.170 | 0.279 | 0.008 |
| Chlorpyrifos | May-Aug, Mar, Jan | 0.053 | 0.074 | 0.006 |
| Simazine | Nov-Apr, May-Jul | 0.147 | 0.360 | 0.066 |
| Metolachlor | Apr-Jun | 0.010 | 0.100 | 0.037 |

# Mean Depositional Mass ($\mu g/m^2$)

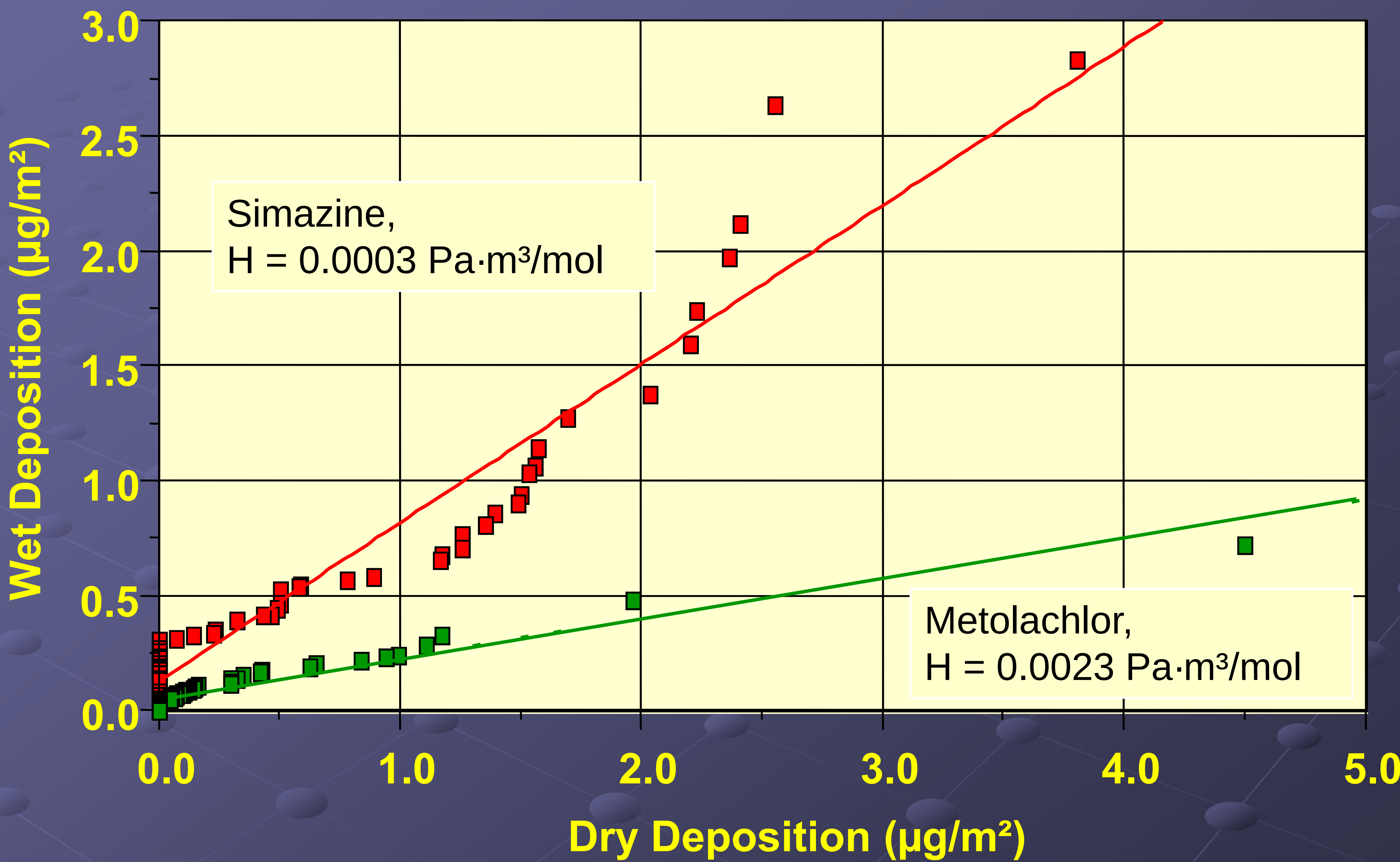
| Pesticide | Henry's law* (H) | Main Use Months | Deposition Wet | Deposition Dry |
|---|---|---|---|---|
| Diazinon | 0.041 | Jan | 2.31 | 0.22 |
| Chlorpyrifos | 1.09 | May-Aug, Mar, Jan | 0.71 | 1.53 |
| Simazine | 0.0003 | Nov-Apr, May-Jul | 2.65 | 1.50 |
| Metolachlor | 0.0023 | Apr-Jun | 0.18 | 0.71 |

*$Pa \cdot m^3/mol$

# Significance of Deposition Mechanism



# Significance of Deposition Mechanism



# Conclusions

- Variety of pesticides in Dry Deposition & Rain
  - Concentrations at Ag sites similar or higher than urban sites
  - Diazinon and Carbaryl somewhat higher at urban site
    - Indicative of urban use
- Similar pesticides detected in native soil used in soil box and in subsequent soil box samples compared to rain/dry deposition
  - High native conc. for some analytes complicated soil box study
  - Diazinon was not detected in any soil box samples

# Conclusions

- Surficial Soil
  - 1-2 orders of magnitude less that wet/dry input of soil residue for Chlorpyrifos
  - Lack of suspended sediment detection for Chlorpyrifos surprising
  - Some Inputs (especially wet) vs. Outputs fairly similar for Simazine , others differ by 2 orders of magnitude
    - But, high simazine in native soil

# Are Pesticides in Air a Significant Source in the San Joaquin Valley, California?

# Are Pesticides in Air A Significant Source in the San Joaquin Valley, California?

- YES!! However, the relative contribution of wet versus dry deposition depends on:
  - physiochemical properties of the pesticide,
  - application timing and method, and
  - other factors such as meteorological conditions
- Wet deposition can be a very significant contributor to pesticide levels in surface waters (diazinon, simazine)
- Dry deposition may be more significant than wet deposition for some pesticides (chlorpyrifos, metolachlor)

# Issues Associated with Pesticides in the Air of the San Joaquin Valley

**TMDL for diazinon and chlorpyrifos**

- contribution to loads in SJR

**Drift from SJV to Sierra-Nevada Mountains**

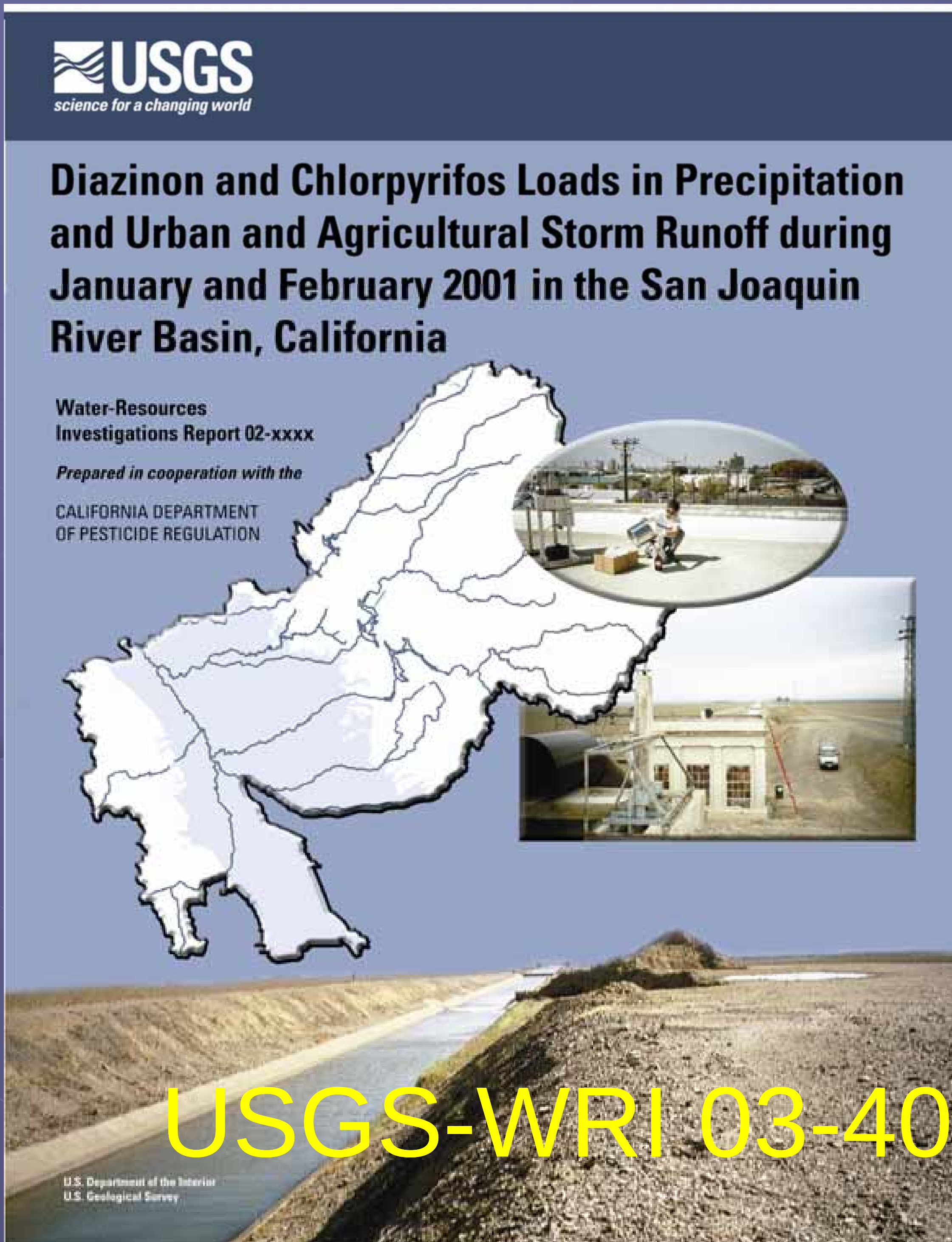
- impact on amphibian populations in Sierras

**Human Health**

- effect of pesticides mixed with other contaminants (photochemical smog, particulates, VOCs, etc.) in some of the Nation’s worst air

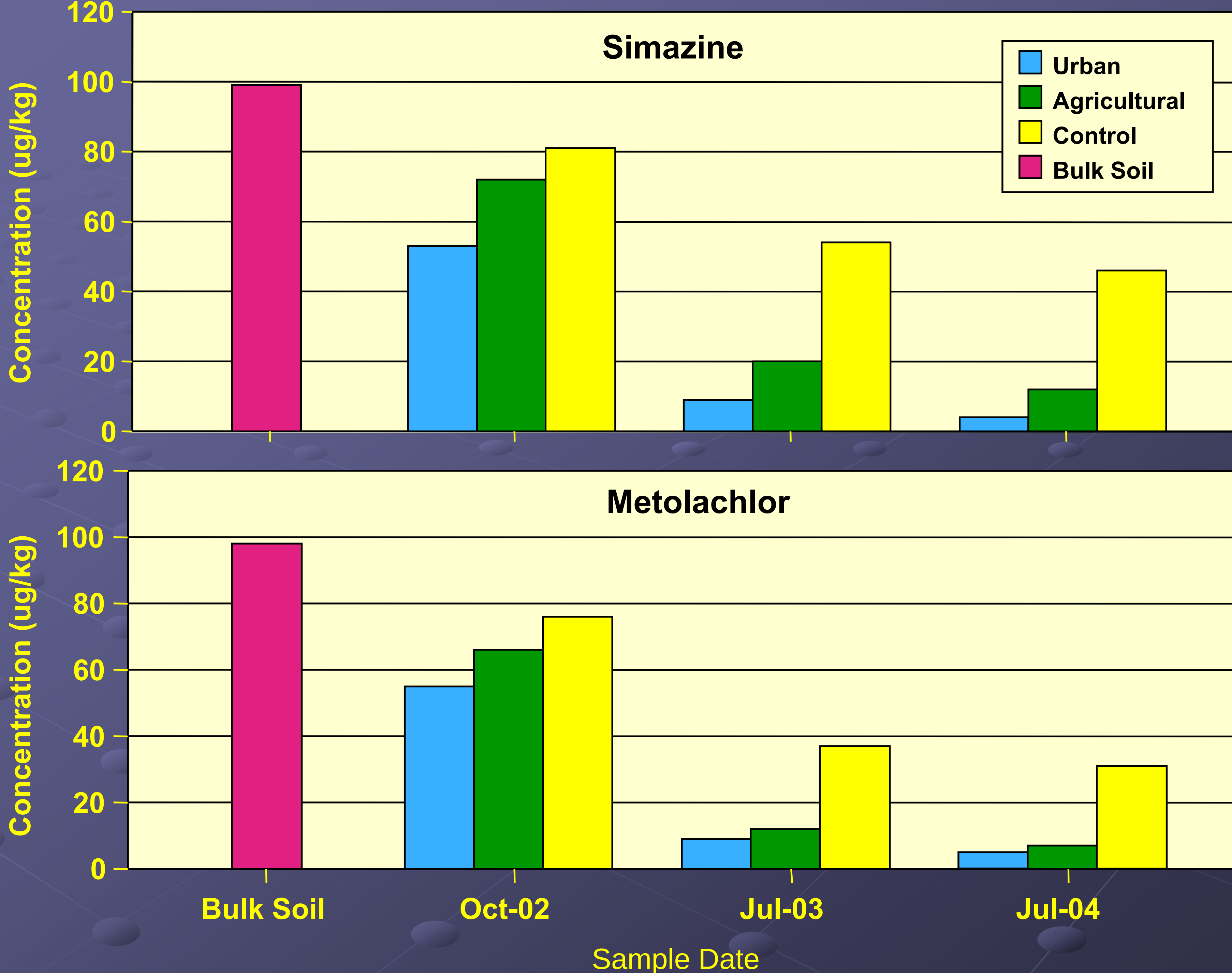
# Issues Associated with Pesticides in the Air of the San Joaquin Valley

**A wide variety of pesticides are being transported and deposited onto non-target areas where their use and presence was never intended**

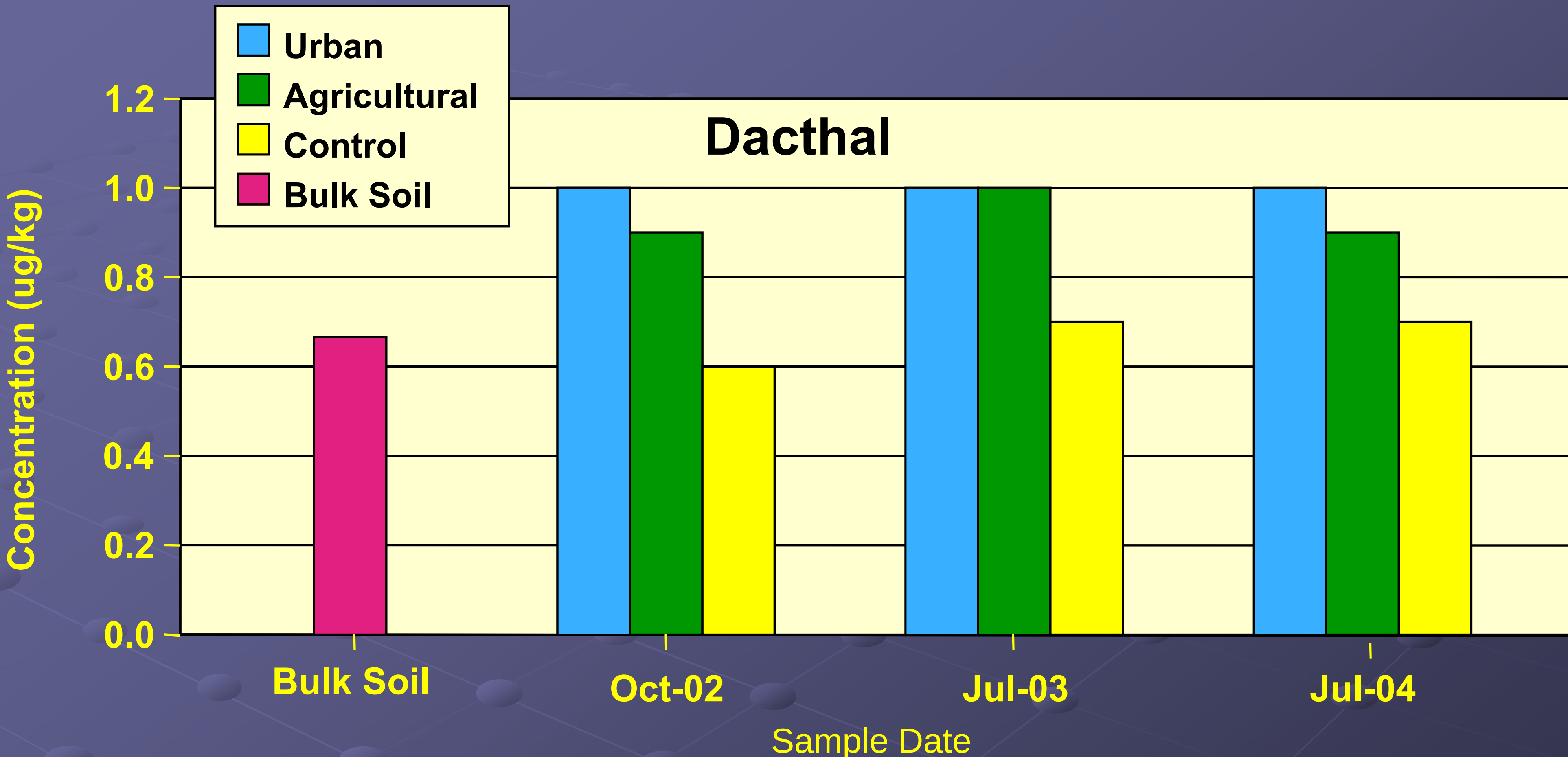



USGS-WRI 03-4091

# Long-Term Soil Trends

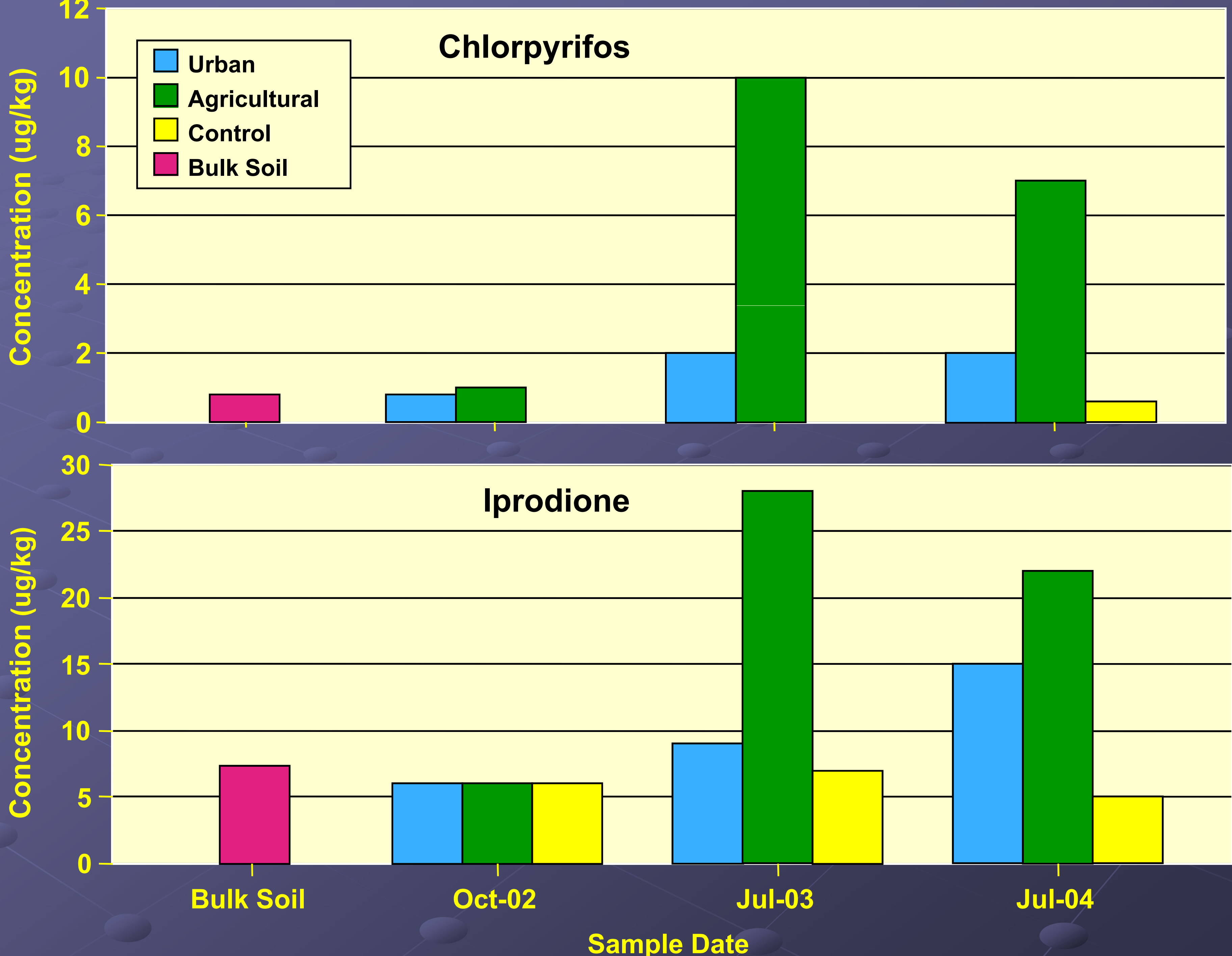


# Long-Term Soil Trends




**NOTE: No Diazinon detected in any soil box samples!**

# Long-Term Soil Trends



# Diazinon, Chlorpyrifos, Simazine, and Metolachlor
## (Main Uses in SJB)

| Pesticide | Main Uses | Main Use Months |
|---|---|---|
| Diazinon | Almonds, non-ag (2002 only), prunes, peaches, melons | Jan |
| Chlorpyrifos | Almonds, walnuts, alfalfa, corn, cotton, non-ag (2002 only) | May-Aug, Mar, Jan |
| Simazine | Almonds, walnuts, non-ag, vineyards | Nov-Apr, May-Jul |
| Metolachlor | Beans, tomatoes, corn, cotton | Apr-Jun |

# Normalizing Data to Compare Events and Sites

| | Concentration (µg/L) | Depositional Amt. (µg/m²) | Annual Load (kg/yr) |
|---|---|---|---|
| Wet Dep. | Measured | Calculated[1] | Calculated[2] |
| Dry Dep. | NA | Measured | Calculated[2] |
| SJ River | Measured | NA | Calculated[3] |

[1] Dep. Amt. (µg/m²) = Conc. (µg/L) x $\frac{\text{(rainfall amount, L)}}{\text{(collector surface area, m}^2\text{)}}$

[2] Annual Load (kg/yr) = Dep. Amt. (µg/m²) x SJB surface area (m²) x kg/$10^9$ µg x Events/yr

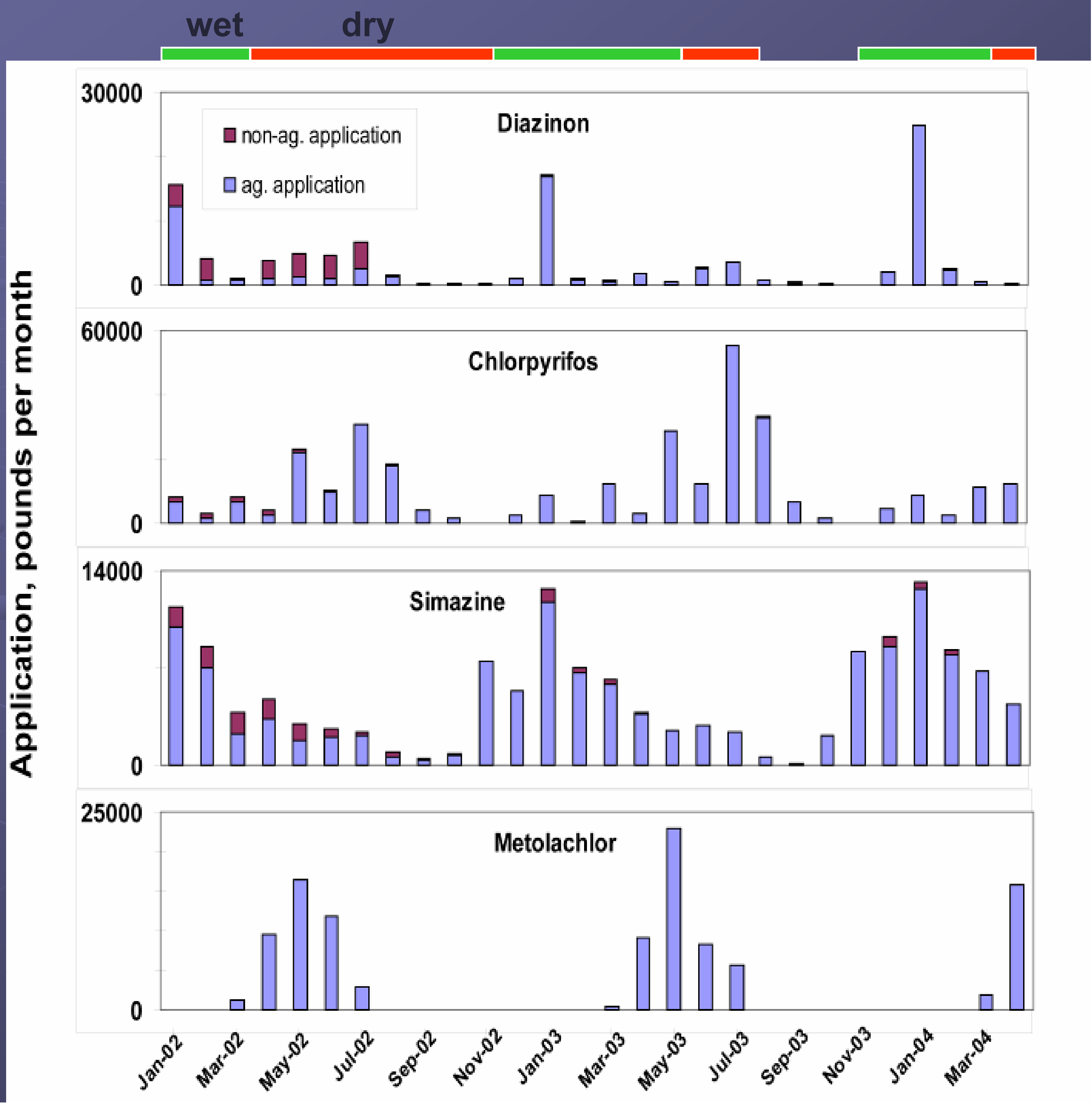
[3] Annual Load (kg/yr) = 0.893 x Mean Annual Conc. (µg/L) x Mean Annual Flow (ft³/s)

# Mean Annual Loads Applied, Wet and Dry Deposition, and SJR (in kg/yr)

| Pesticide | Total Applied | Deposition* Wet | Deposition* Dry | SJ River |
|---|---|---|---|---|
| Diazinon | 17,000 | 442 | 21 | 14 |
| Chlorpyrifos | 64,100 | 136 | 147 | 11 |
| Simazine | 24,800 | 508 | 144 | 116 |
| Metolachlor | 20,100 | 35 | 68 | 65 |

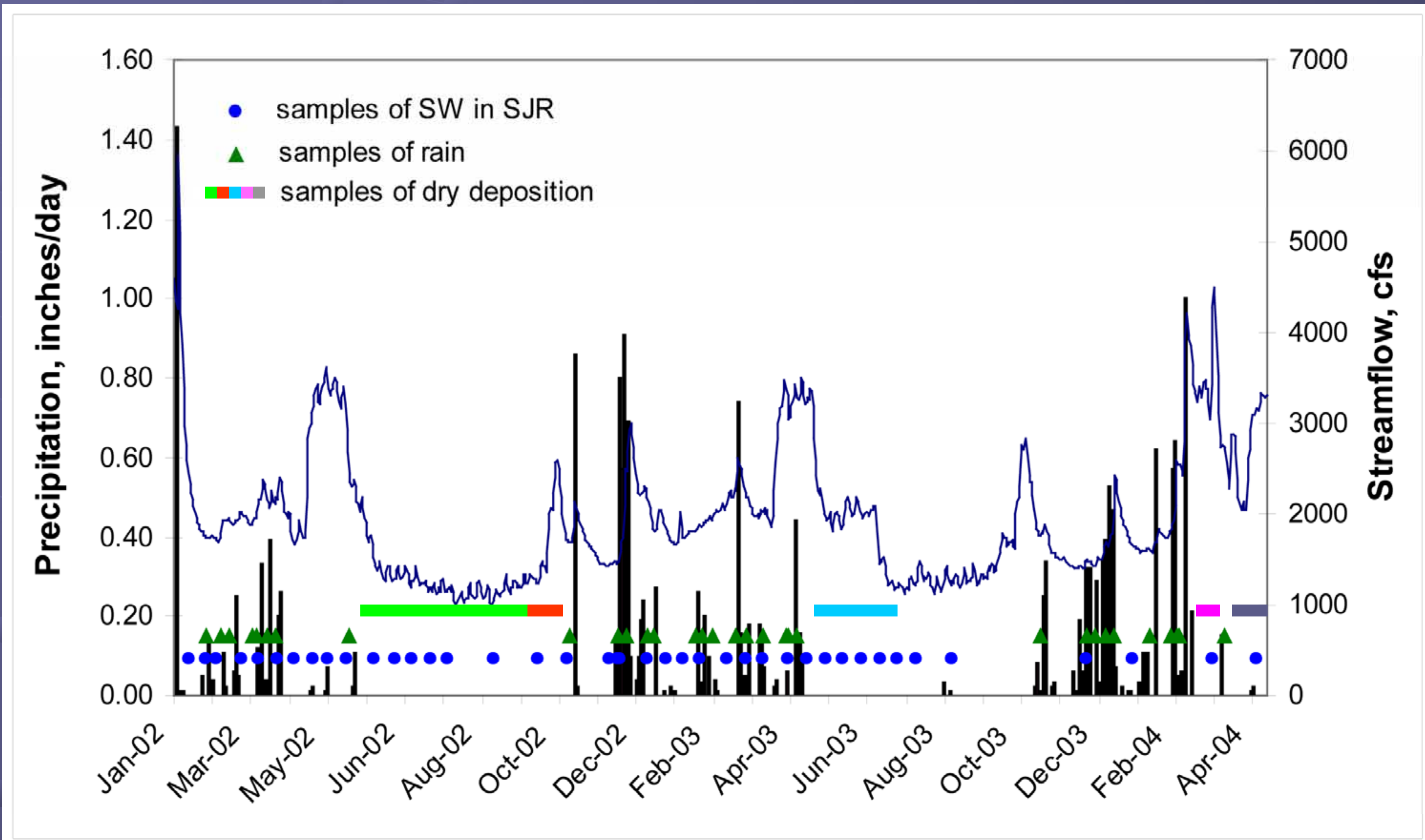
*Assuming 10 wet events/yr and 5 dry events/yr distributed across 19,200 $km^2$ of SJB

# Monthly Pesticide Applications, Jan 2002 through April 2004

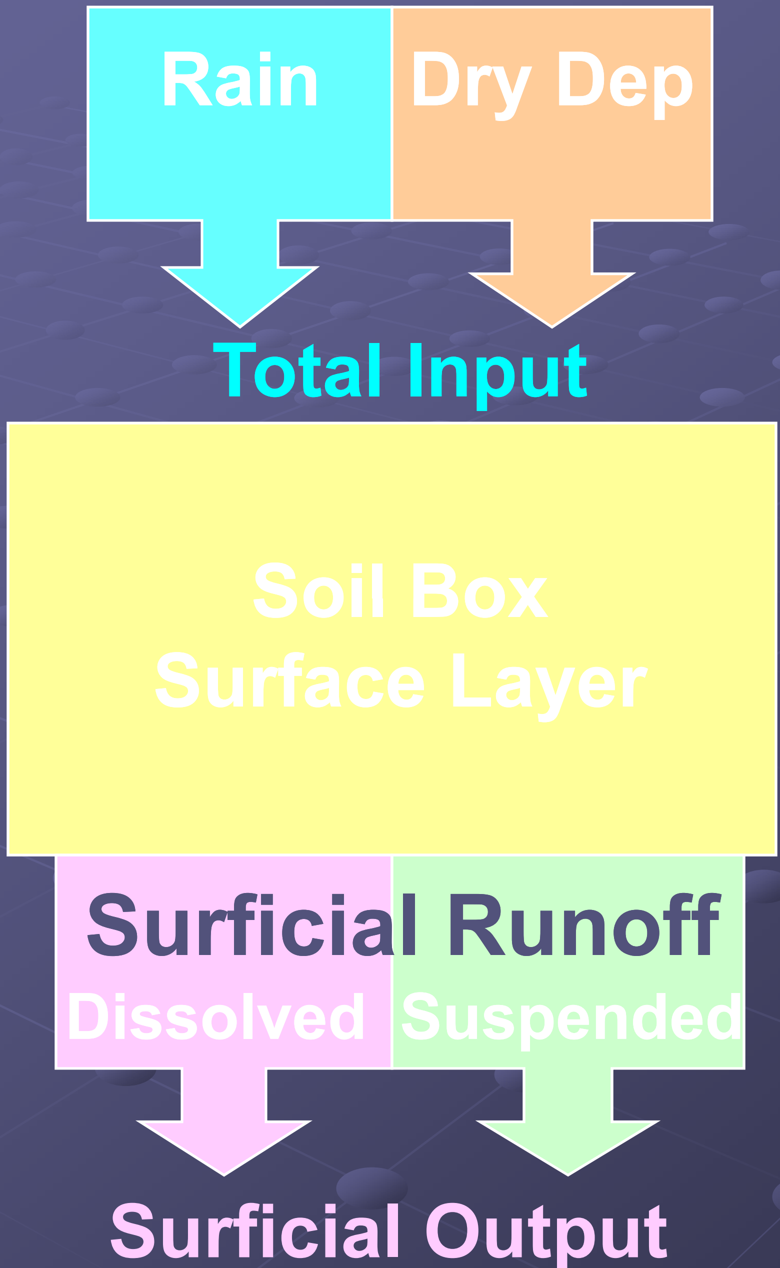


# Sample Collections:

## Rain (n = 151), Dry Deposition (n = 37), SJ River (n = 50)



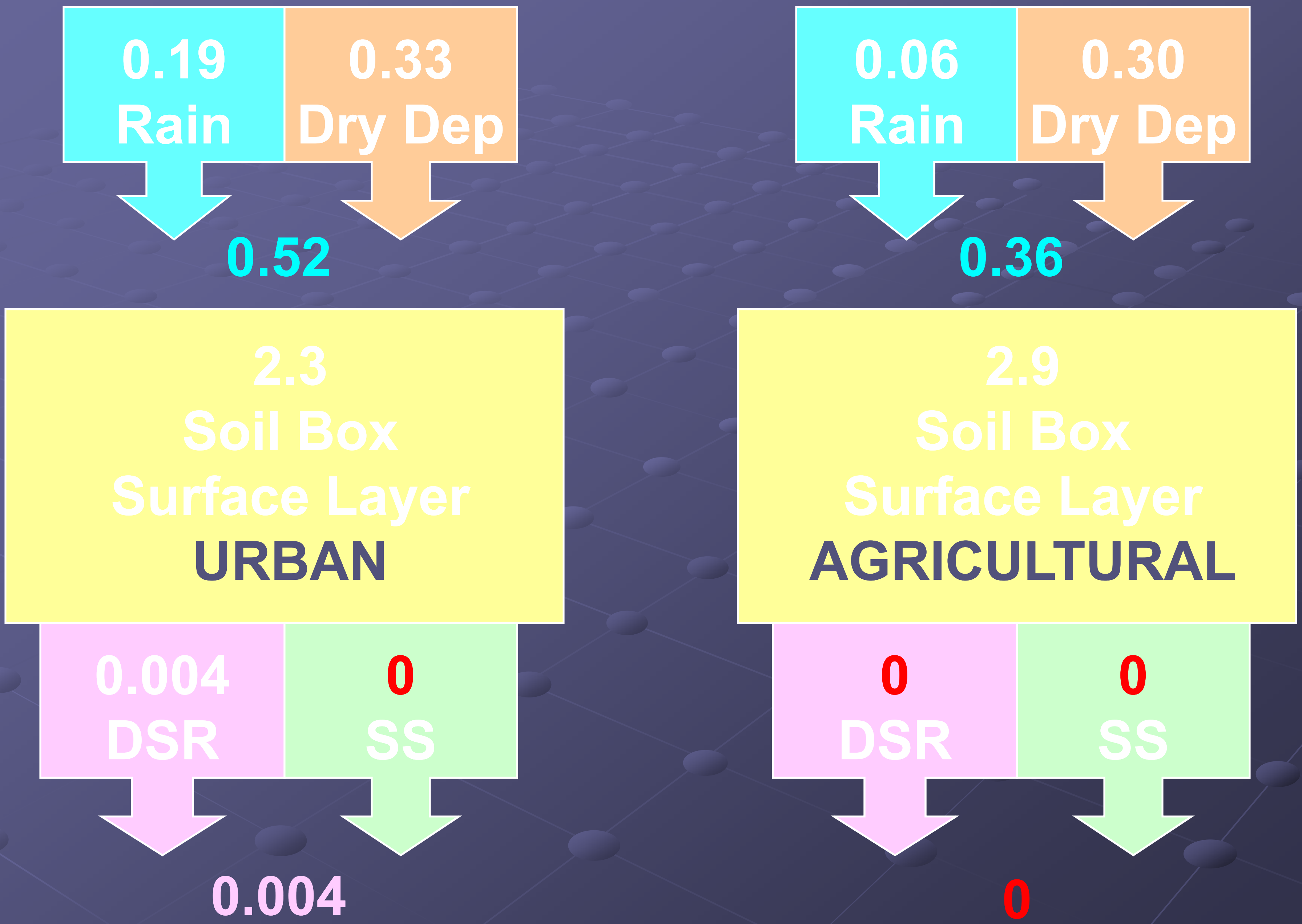
# (Pseudo-) Mass Balance Estimate




Units = micrograms

# 2002 Chlorpyrifos (51 days)

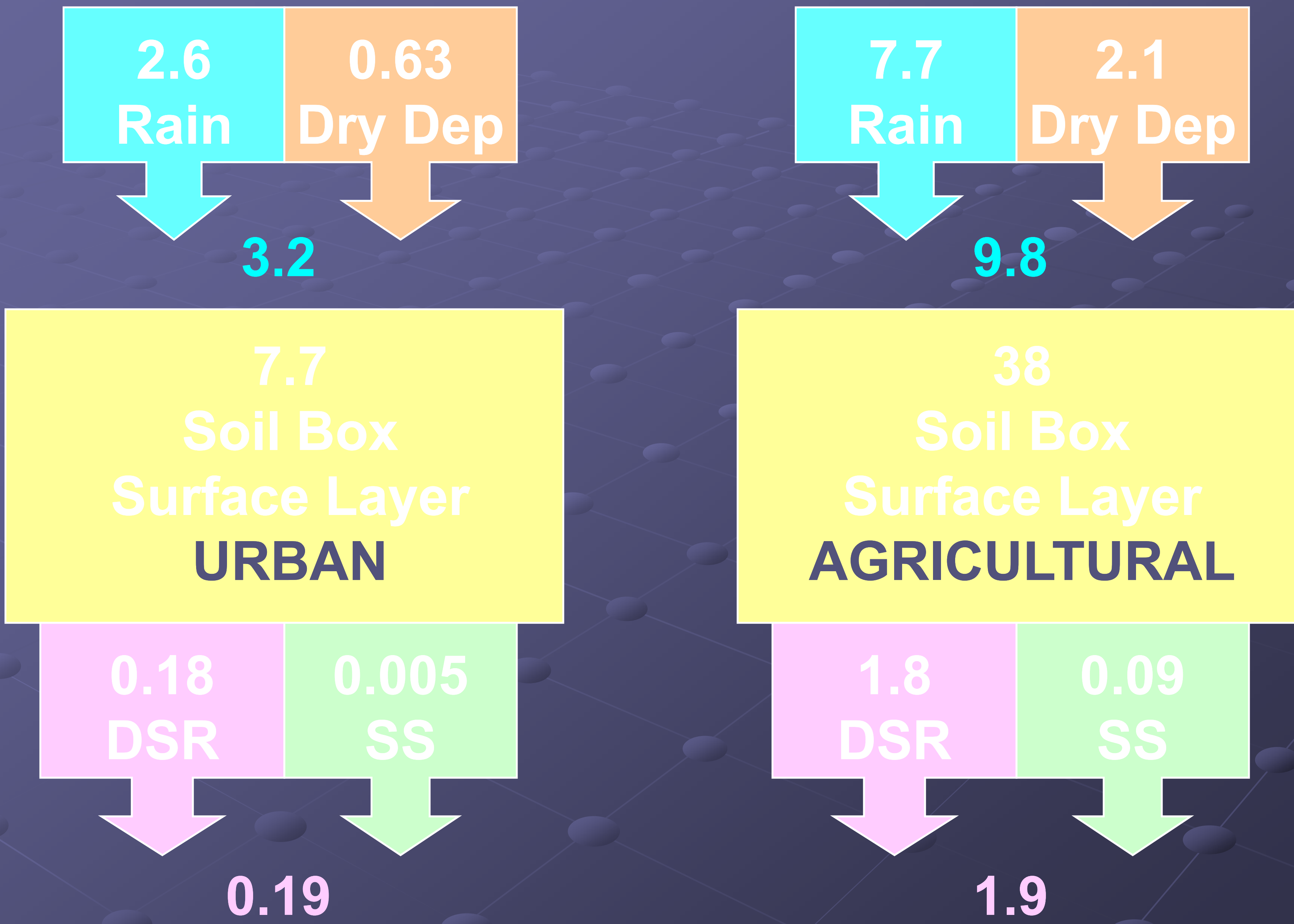
$K_{oc}$ = 6070; Solubility = 0.003 mol/$m^3$, H = 1.1 Pa-$m^3$/mol




Units = micrograms Initial Bulk Soil = 2.5

# 2003 Chlorpyrifos (291 total days )

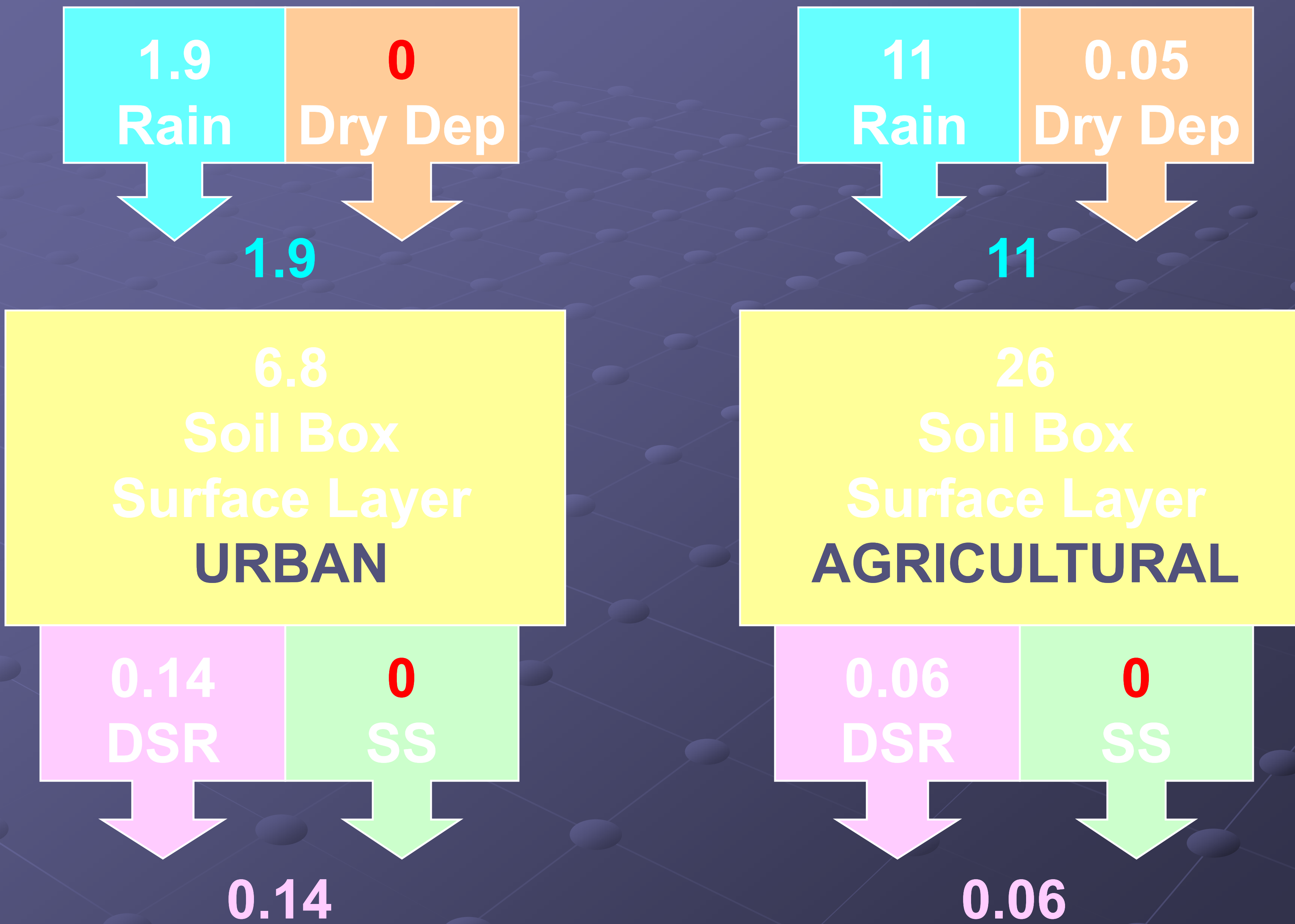
Koc = 6070; Solubility = 0.003 $mol/m^3$, H = 1.1 $Pa\text{-}m^3/mol$




**Units = micrograms** **Initial Bulk Soil = 2.5**

# 2004 Chlorpyrifos (352 total days )

Koc = 6070; Solubility = 0.003 mol/$m^3$, H = 1.1 Pa-$m^3$/mol




**Units = micrograms** **Initial Bulk Soil = 2.5**

# Input vs Output

| | | Urban Soilbox soil surface (ug) | Urban In/Out (Rain vs RO diss) | Urban Total In/Out (rain+DD vs RO) | Urban % Runoff vs Soil+In | Ag Soilbox soil surface (ug) | Ag In/Out (Rain vs RO diss) | Ag Total In/Out (rain+DD vs RO) | Ag % Runoff vs Soil+In | Sol. $mol/m^3$ | Koc mL/g |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Chlorpyrifos | 02 | 2 | 51 | 142 | 0.1 | 3 | NDRO | NR | 0 | 0.0031 | 6070 |
| | 03 | 8 | 14 | 17 | 1.7 | 38 | 4 | 5 | 4.0 | | |
| | 04 | 7 | 14 | 14 | 1.6 | 26 | 188 | 189 | 0.2 | | |
| Simazine | 02 | 153 | 0.9 | 5 | 0.2 | 211 | NDRO | 82 | 0.0 | 2.41 | 130 |
| | 03 | 35 | 2 | 2 | 3.4 | 75 | 0.6 | 2 | 8.0 | | |
| | 04 | 14 | 26 | 28 | 0.9 | 45 | 8 | 8 | 4.2 | | |
| Metolachlor | 02 | 159 | 1 | 1 | 0.1 | 193 | NDRO | 5 | 0.0 | 1.8 | 200 |
| | 03 | 35 | 2 | 2 | 1.7 | 45 | 0.1 | 0.2 | 3.9 | | |
| | 04 | 17 | 5 | 6 | 0.5 | 26 | 1 | 1 | 0.7 | | |
| DCPA | 02 | 3 | 33 | 47 | 0.2 | 3 | NDRO | 31 | 0.1 | 0.029 | 5600 |
| | 03 | 4 | 22 | 23 | 1.0 | 4 | 3 | 4 | 3.9 | | |
| | 04 | 3 | 9 | 9 | 1.6 | 3 | 4 | 4 | 4.0 | | |

# Soil Box "Control" Samples

- Covered box with board
  - 3/4" air gap
  - Omited direct sunlight, rain, & large particle deposition
  - Exposed control soil to some environmental conditions (ambient temperature, humidity)
    - Passive gaseous pesticide uptake likely
    - Fine particle deposition possible

# Soil Box Samples

- Exposure duration between samples
  - 51, 291, and 352 days
- Samples taken across surface only
  - Composite of 11 subsamples
    - 0.3-cm depth x 2.54-cm diameter
  - Zone of primary sediment mobilization
    - Assumed primary deposition zone