Making Jacob Rubin's Vision a Reality:

New Contributions to Ground-Water Science from the National Water-Quality Assessment Program

Jack Barbash

National Water-Quality Assessment Program (NAWQA)

Pesticide National Synthesis Project

U.S.Geological Survey

GSA National Meeting (October 2008, Houston TX)

New Contributions to Ground-Water Science from the NAWQA Program

- **Nationwide summaries of existing information**
- **Nationwide study design → Occurrence → Prediction**
- **Investigation of previously un(der)examined contaminants**
- **Nationwide investigation of trends**
- **Effects of environmental factors (e.g., reduction-oxidation, or redox conditions) on water quality**
- **Use of solute transport-and-fate models to predict ground-water quality in multiple settings around the Nation**

[redacted]

Nationwide Summaries of Existing Information

[redacted]

Nationwide Summaries of Existing Information

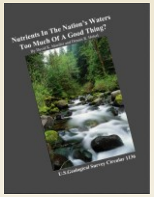
Sources, transport, occurrence, fate, and effects of major contaminant groups — Examples

[redacted]

<u>Nationwide Summaries of Existing Information</u>

Sources, transport, occurrence, fate, and effects of major contaminant groups — Examples

- Nutrients in the Nation’s Waters – Too Much of a Good Thing?

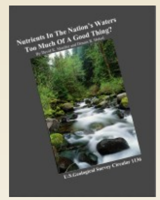


[redacted]

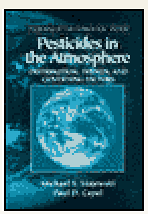
Nationwide Summaries of Existing Information

Sources, transport, occurrence, fate, and effects of major contaminant groups — Examples

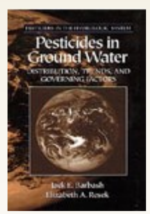
- Nutrients in the Nation's Waters – Too Much of a Good Thing?



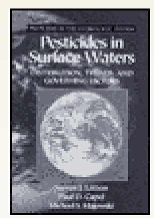
- Pesticides in the Hydrologic System series



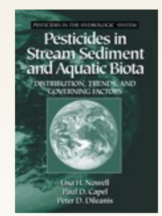
Atmosphere



Ground water



Surface water



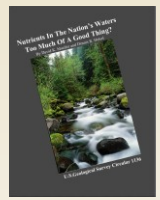
Aquatic biota & sediments

[redacted]

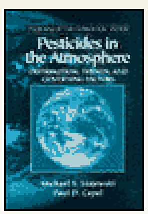
Nationwide Summaries of Existing Information

Sources, transport, occurrence, fate, and effects of major contaminant groups — Examples

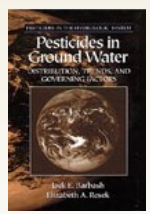
- Nutrients in the Nation's Waters – Too Much of a Good Thing?



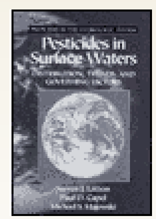
- Pesticides in the Hydrologic System series



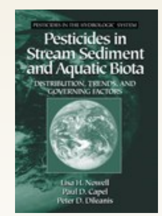
Atmosphere



Ground water



Surface water

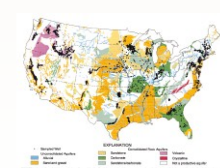


Aquatic biota & sediments

- VOCs

[redacted]

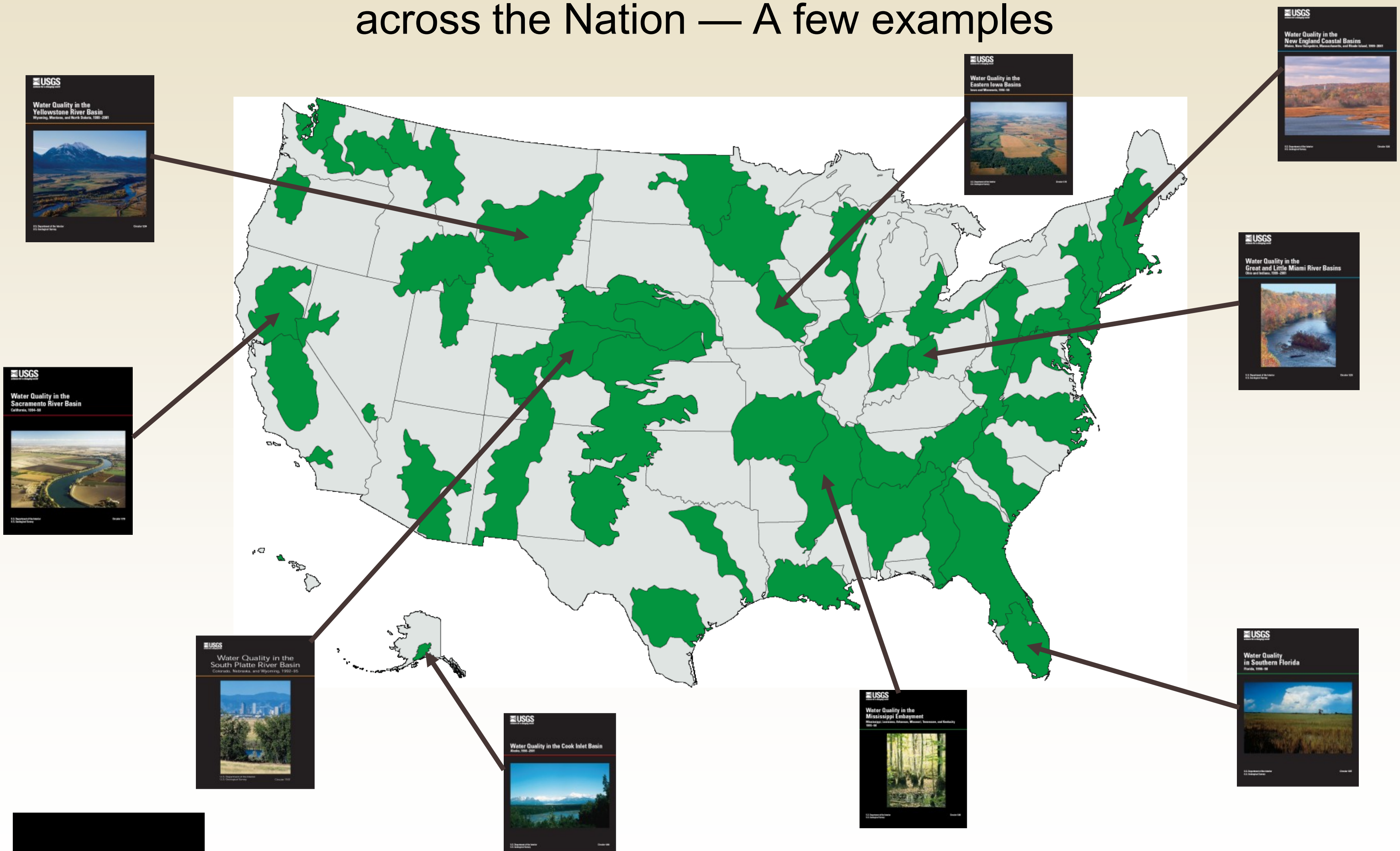
Environmental chemistry



Occurrence in ground water

Nationwide Summaries of Existing Information

Summaries of environmental characteristics, ground-water quality and contaminant sources in 52 major hydrologic basins (Study Units) across the Nation — A few examples



[redacted]

Nationwide Summaries of Existing Information

Ancillary data to support data interpretation - Examples

- Topography and watershed boundaries
- Geology
- Climate
- Soil properties
- Hydrology (e.g., runoff, recharge, streamflow, base-flow, etc.)
- Ecoregions
- Geochemistry
- Population
- Land use
- Water use
- Contaminant releases (e.g., pesticides, nutrients, MTBE, etc.)

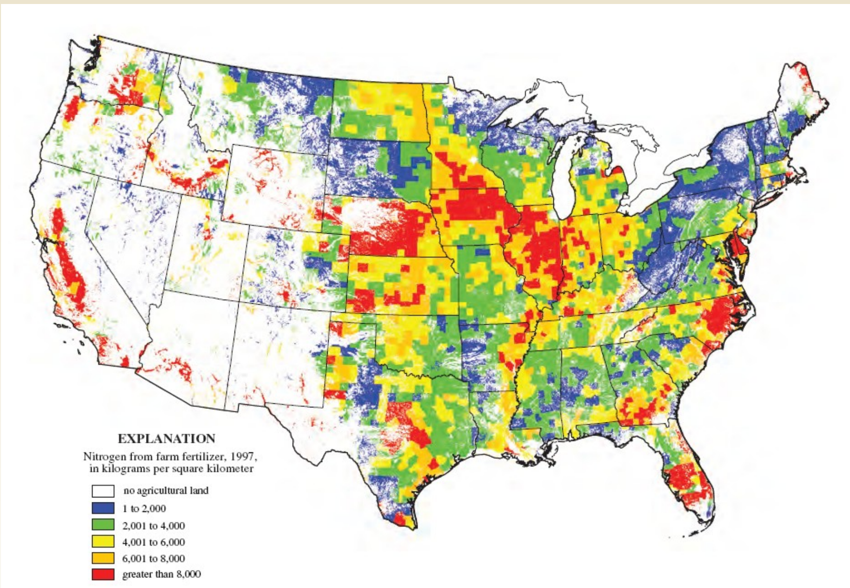
(http://water.usgs.gov/nawqa-only/gis/gis_data.html)

[redacted]

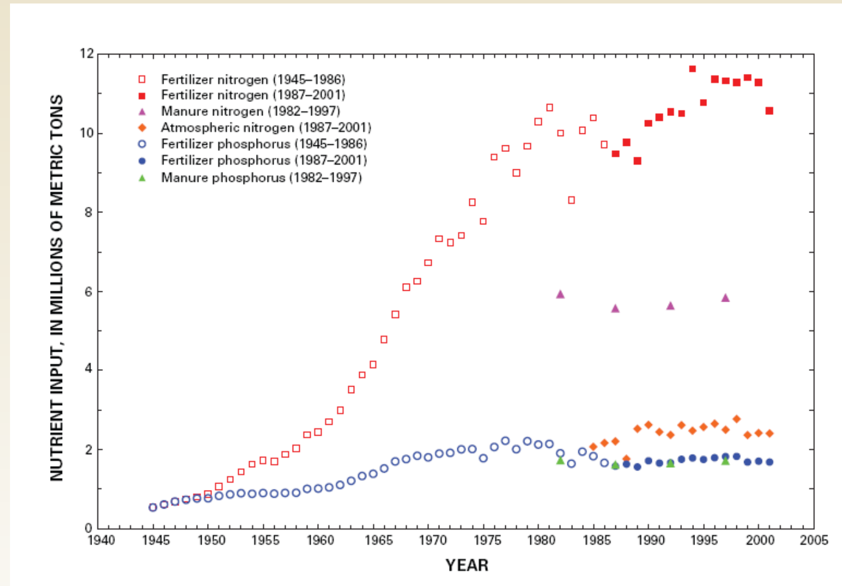
Nationwide Summaries of Existing Information

Chemical inputs – Nutrients

(Ruddy and others, 2006)



Nitrogen inputs from farms (1997)

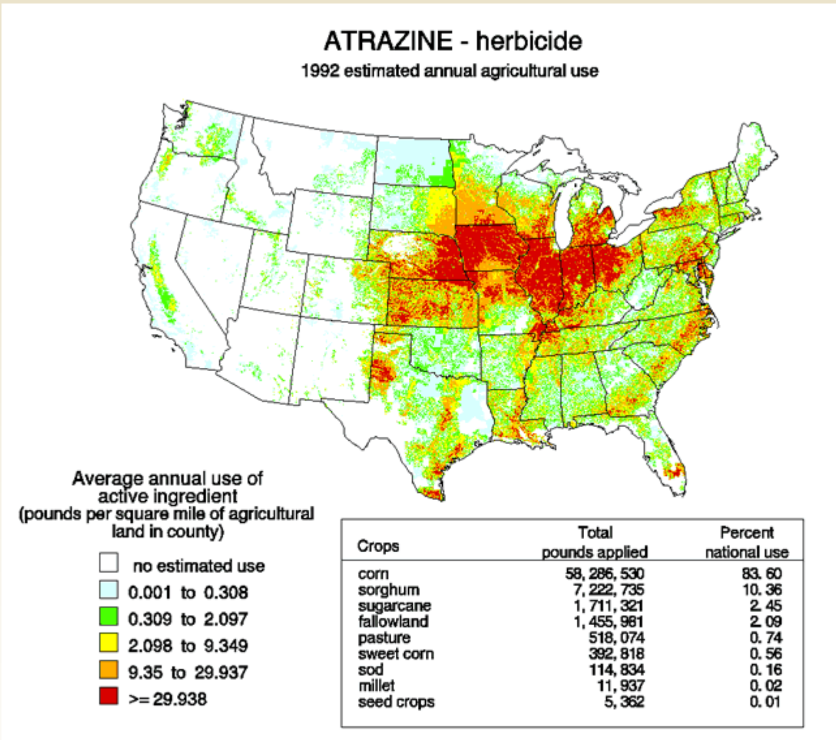


Annual inputs across the United States (1945-2001)

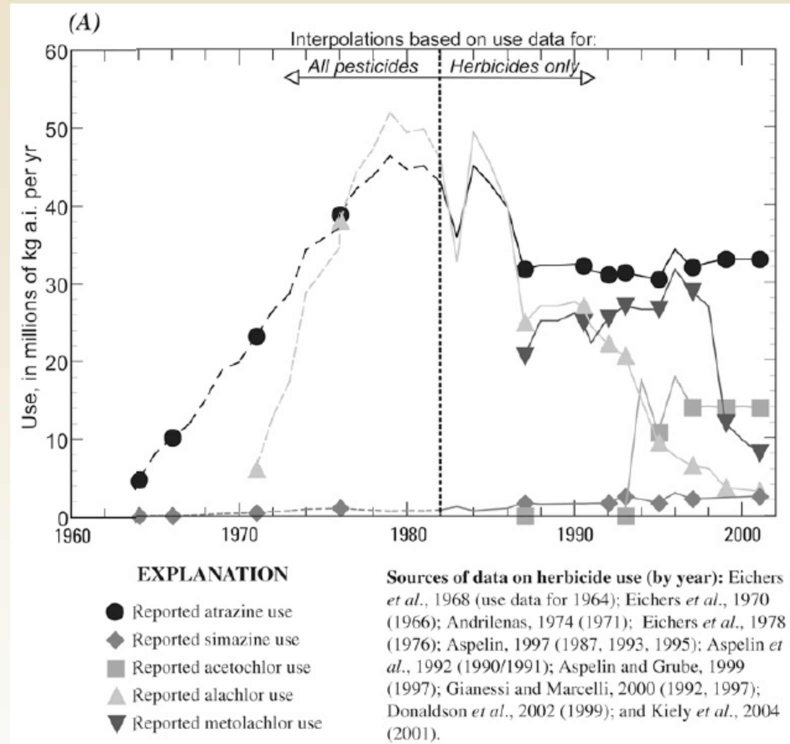
[redacted]

Nationwide Summaries of Existing Information

Chemical inputs – Pesticides



Atrazine use in agricultural settings, 1992
(http://water.usgs.gov/nawqa/pnsp/usage/maps/)

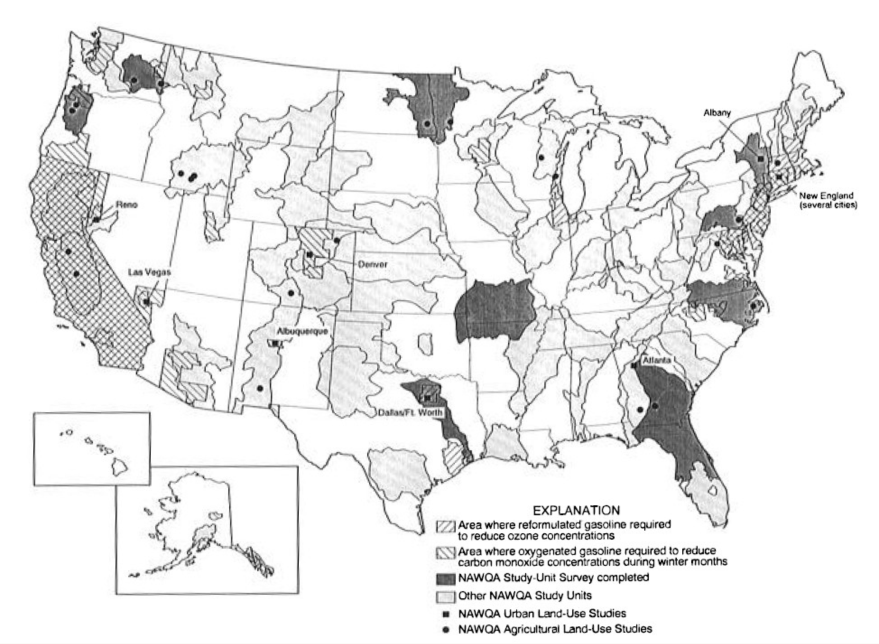


Herbicide inputs across the United States, 1964-2002
(Steele and others, 2008)

[redacted]

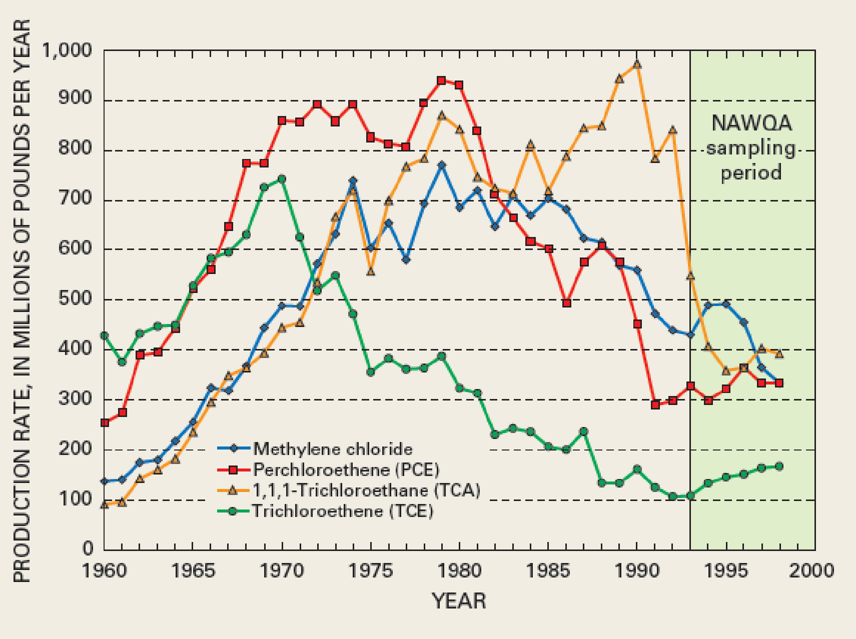
Nationwide Summaries of Existing Information

Chemical inputs – VOCs



Areas where use of oxygenated or reformulated gasoline is required (cross-hatched) relative to locations of NAWQA Study Units

(Squillace and others, 1996)

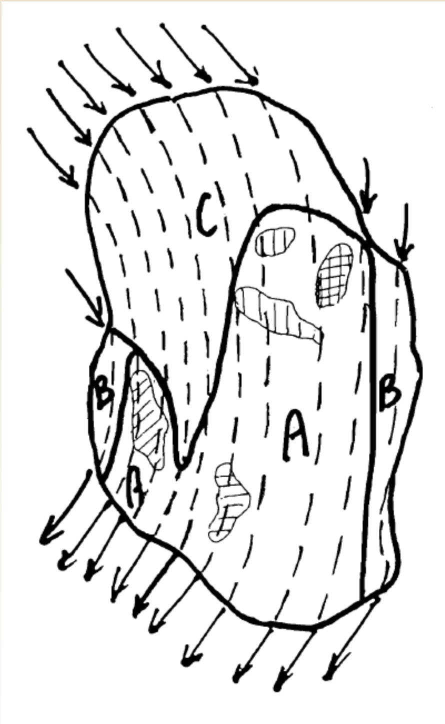


Production of solvents in the United States, 1960-1998

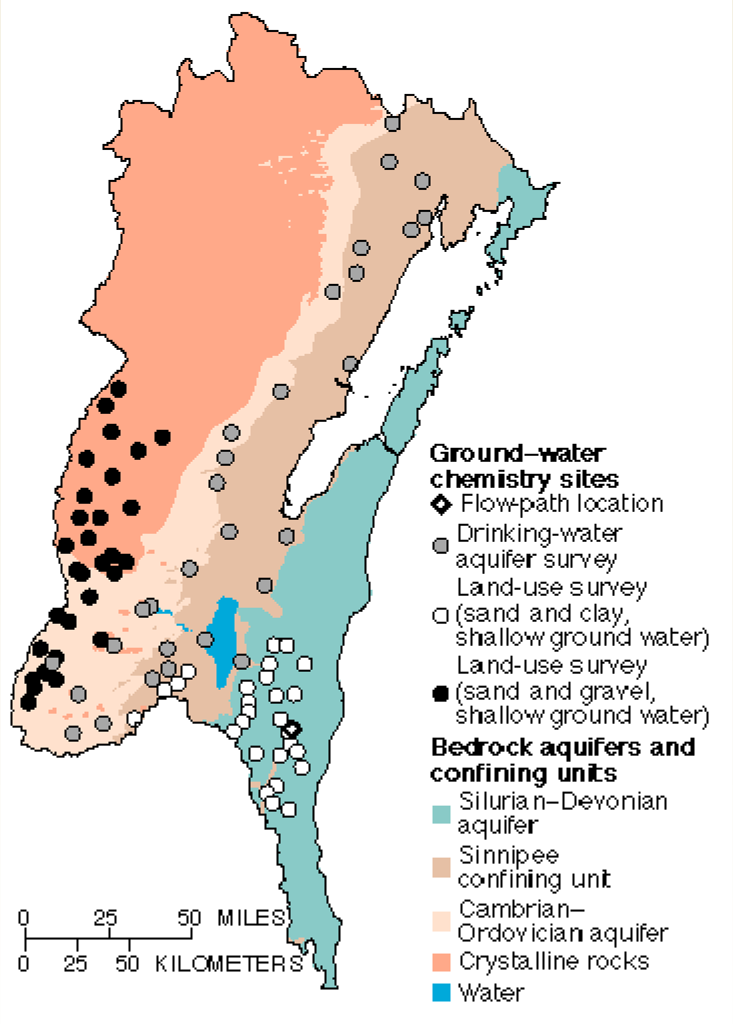
(Zogorski and others, 2006)

[redacted]

Nationwide, multi-scale, nested study design

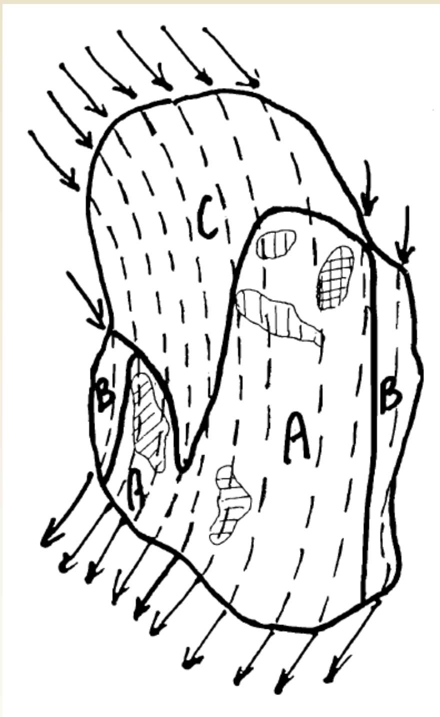


Rubin's "Creeping Survey" for a single basin (Rubin, 1993)

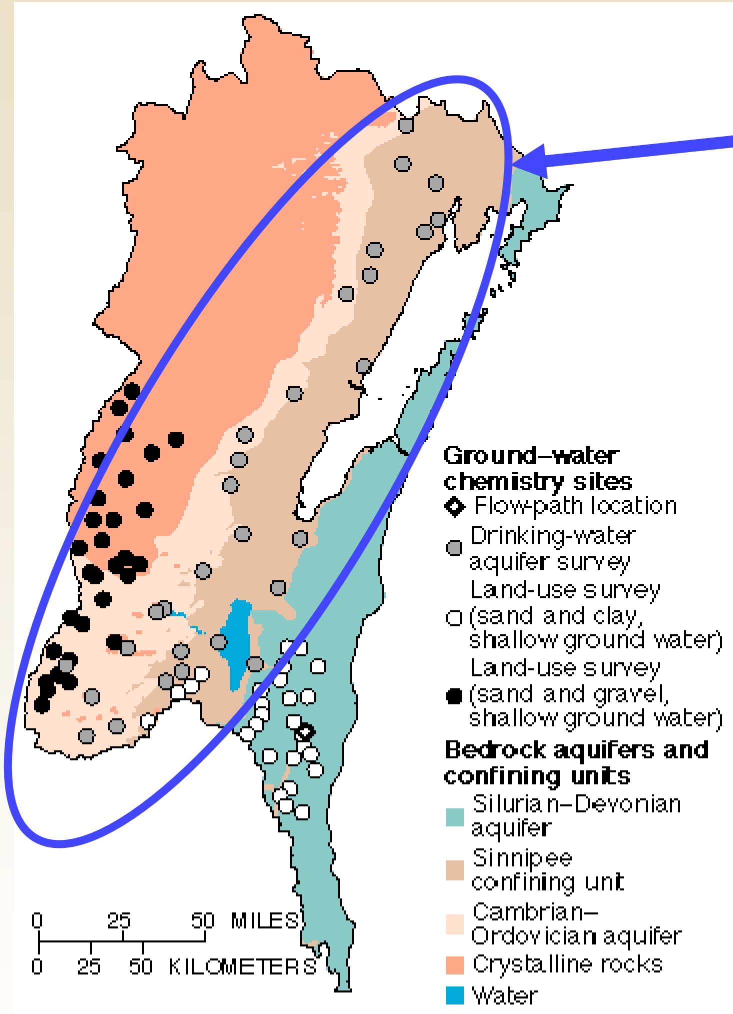


NAWQA study design for a single basin or "Study Unit" (Peters and others, 1998)

Nationwide, multi-scale, nested study design



Rubin's "Creeping Survey"
for a single basin
(Rubin, 1993)

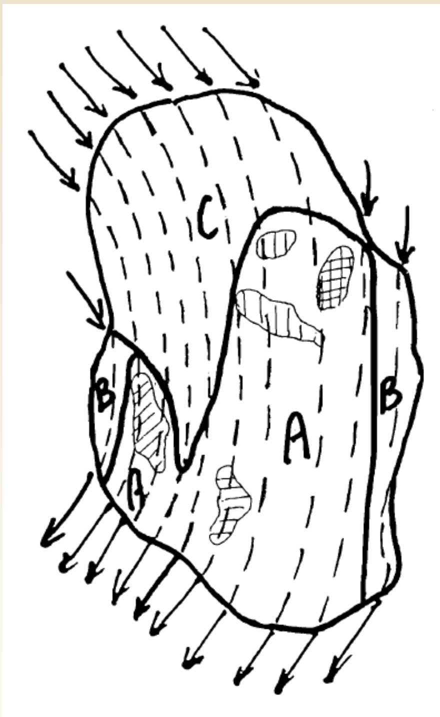


Aquifer survey

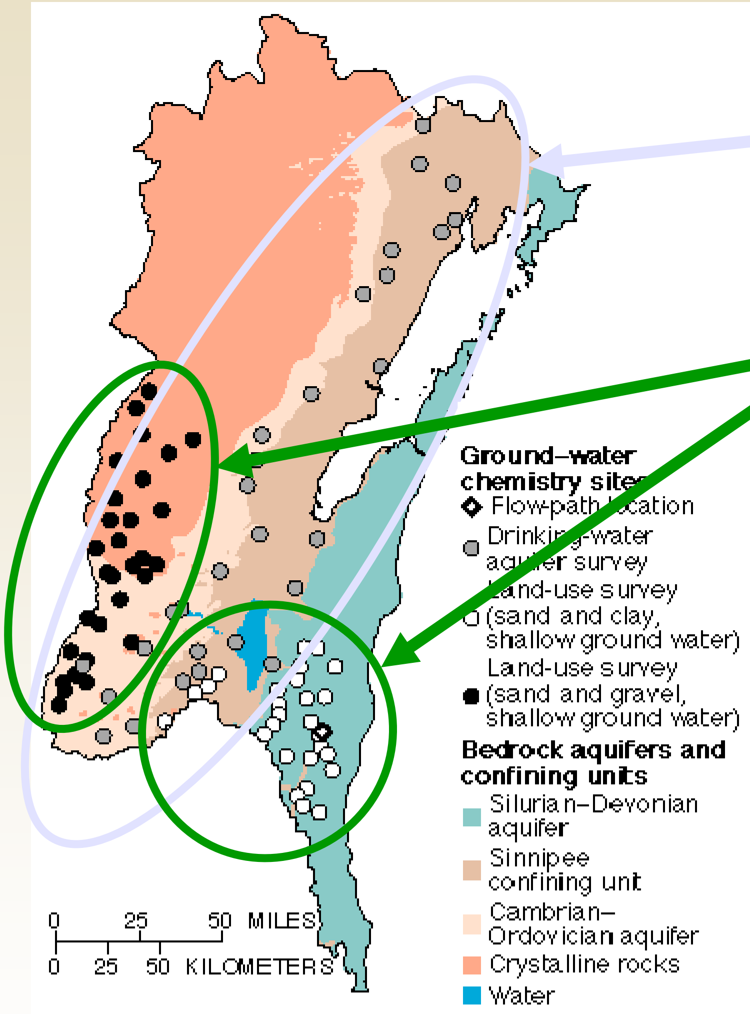
NAWQA study design
for a single basin or "Study Unit"
(Peters and others, 1998)

science for a changing world

Nationwide, multi-scale, nested study design



Rubin's "Creeping Survey"
for a single basin
(Rubin, 1993)



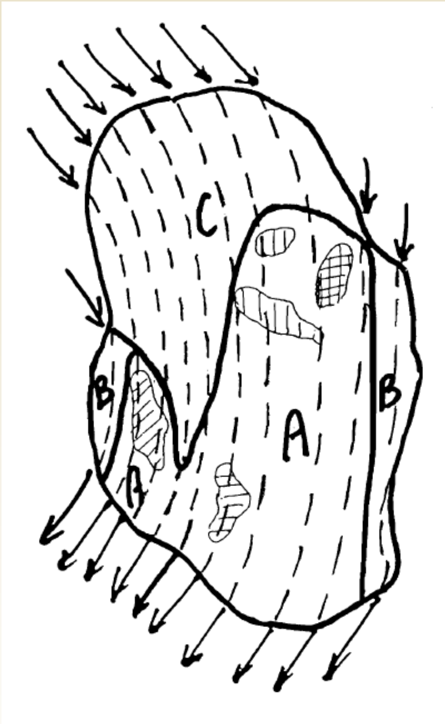
Aquifer survey

Land-use studies

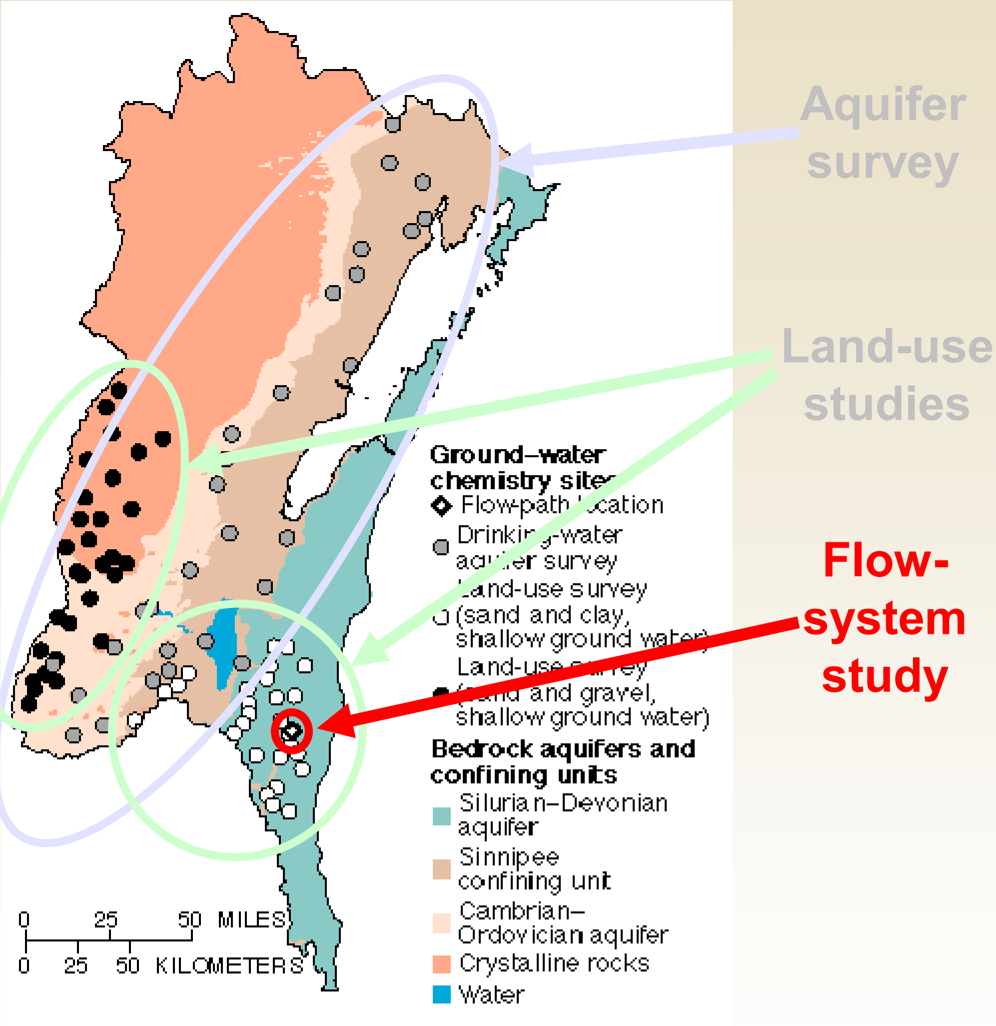
NAWQA study design
for a single basin or "Study Unit"
(Peters and others, 1998)

USGS
science for a changing world

Nationwide, multi-scale, nested study design



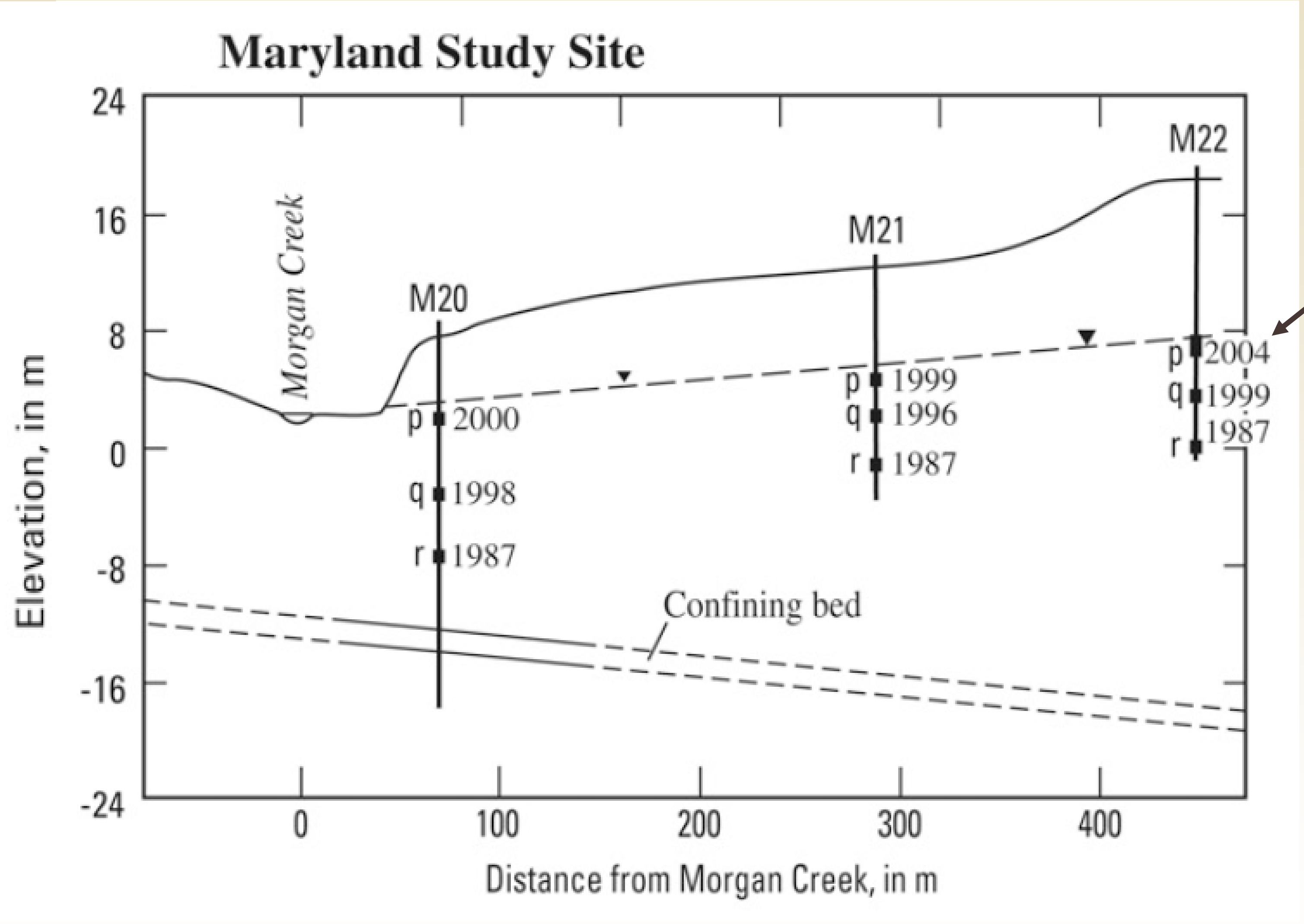
Rubin's "Creeping Survey"
for a single basin
(Rubin, 1993)



NAWQA study design
for a single basin or "Study Unit"
(Peters and others, 1998)

USGS
science for a changing world

Flow-System Studies

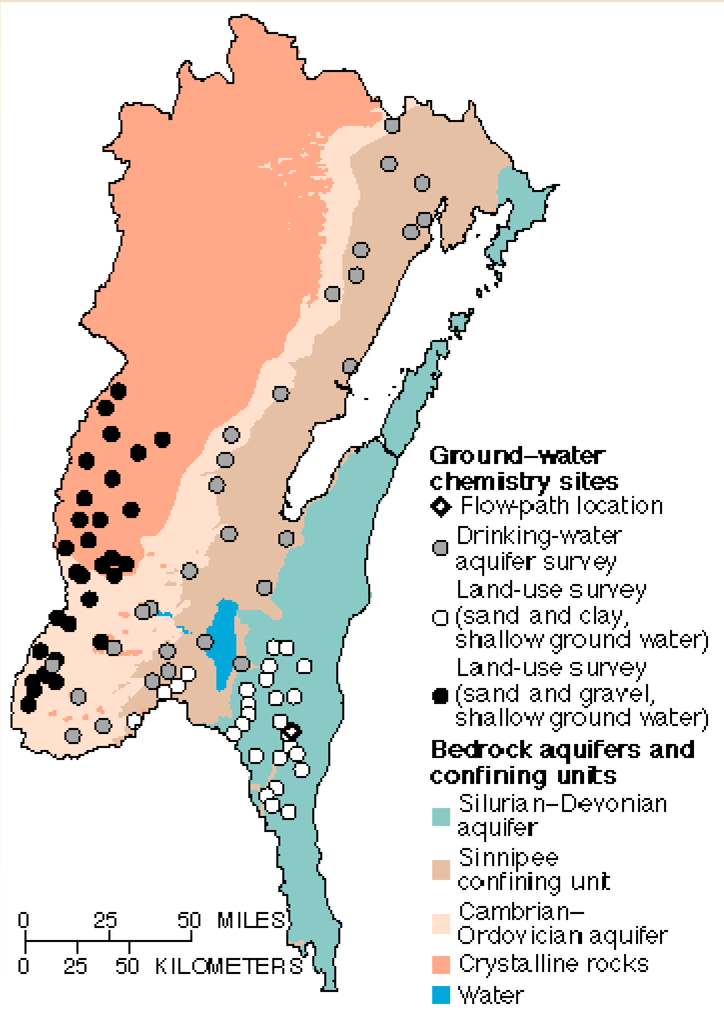


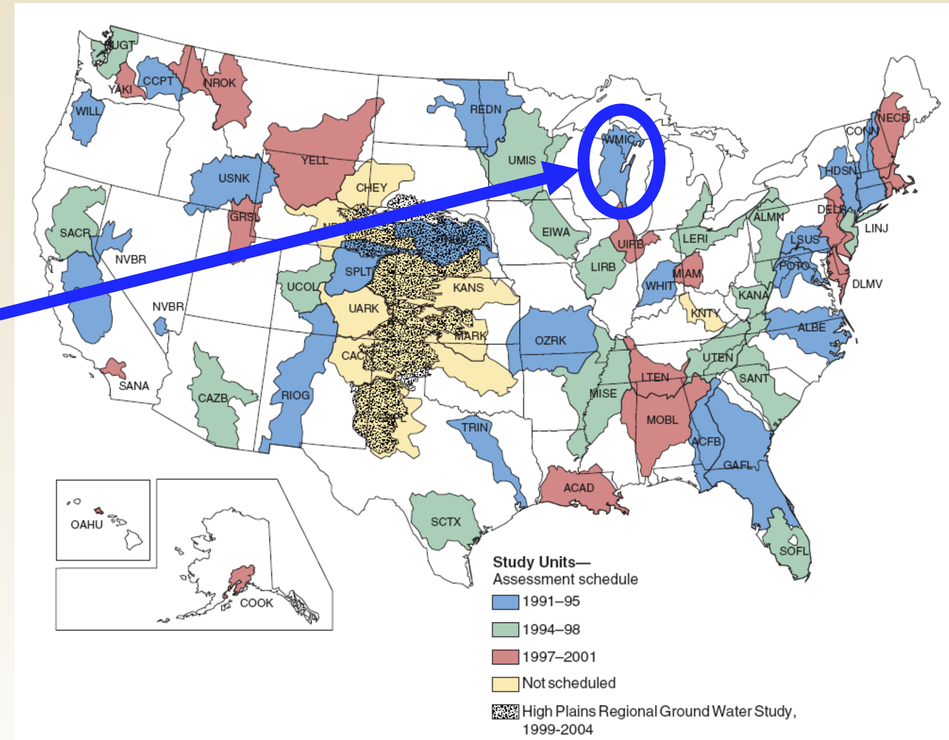
Estimated year of recharge

USGS science for a changing world

(Steele and others, 2008)

Nationwide, multi-scale, nested study design





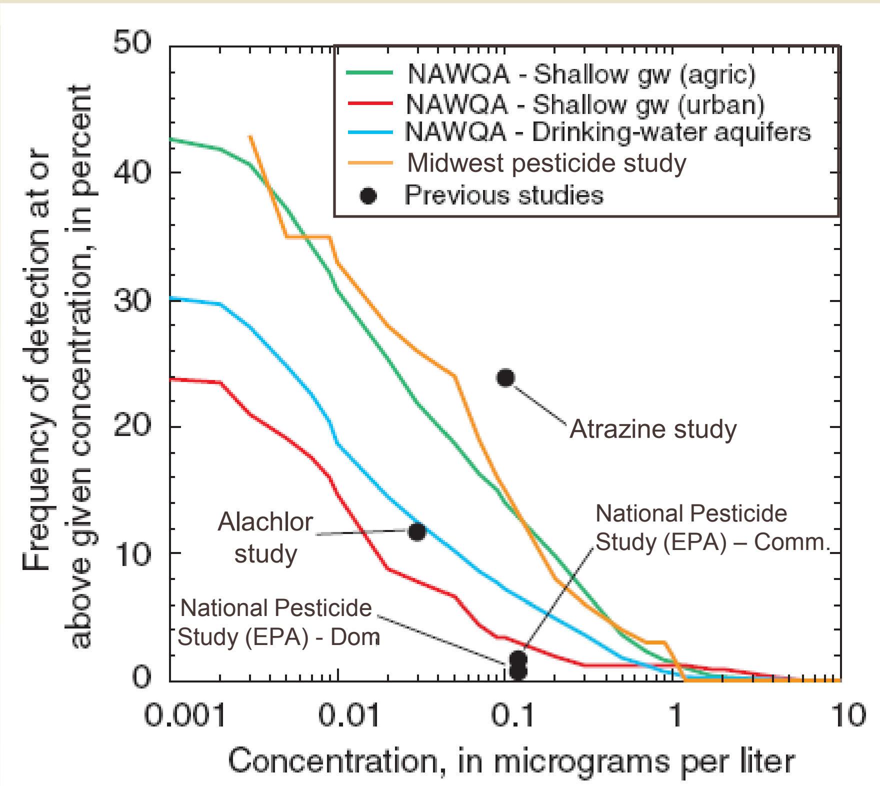
NAWQA Study Units
(Cycle 1)

USGS
science for a changing world

How representative are the NAWQA results?

How representative are the NAWQA results?

Atrazine

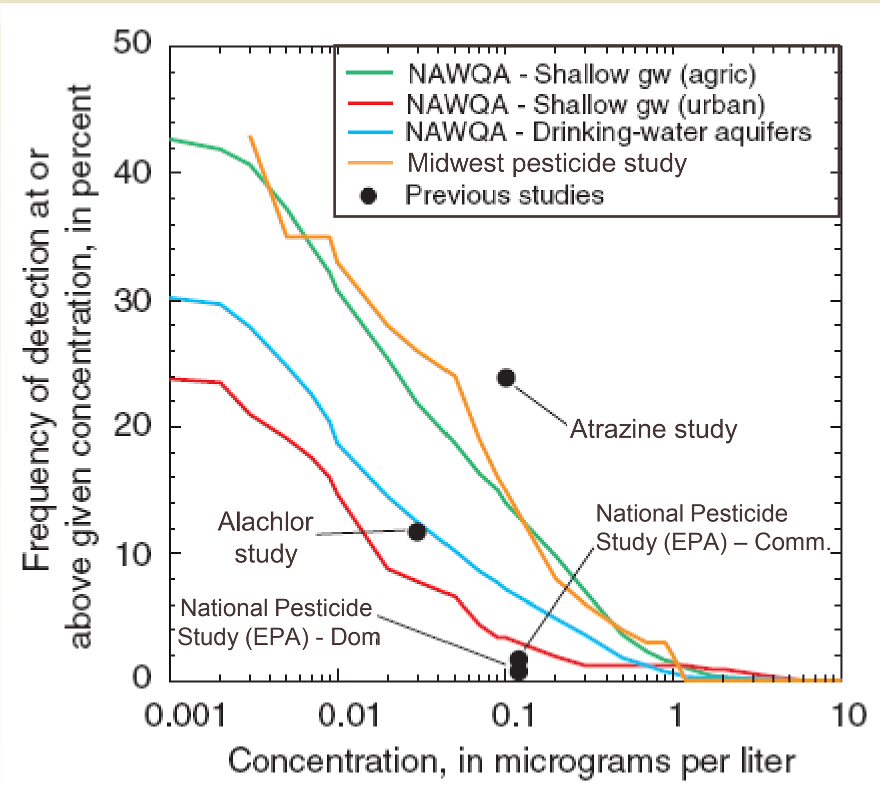


[redacted]

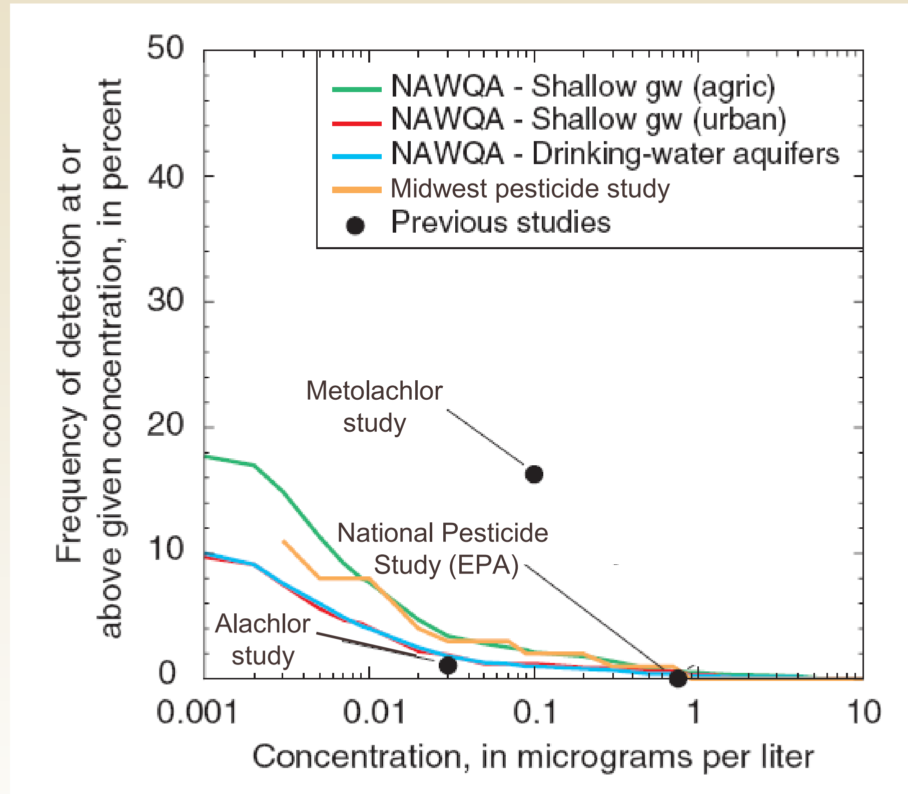
(Barbash and others, 1999)

How representative are the NAWQA results?

Atrazine



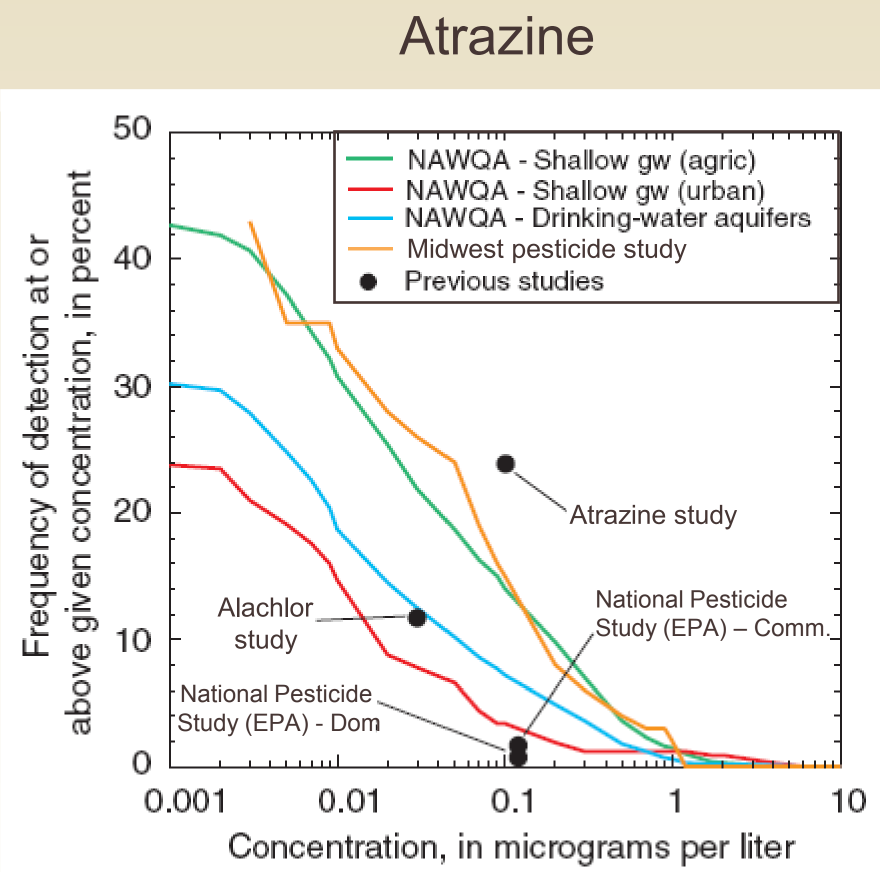
Metolachlor

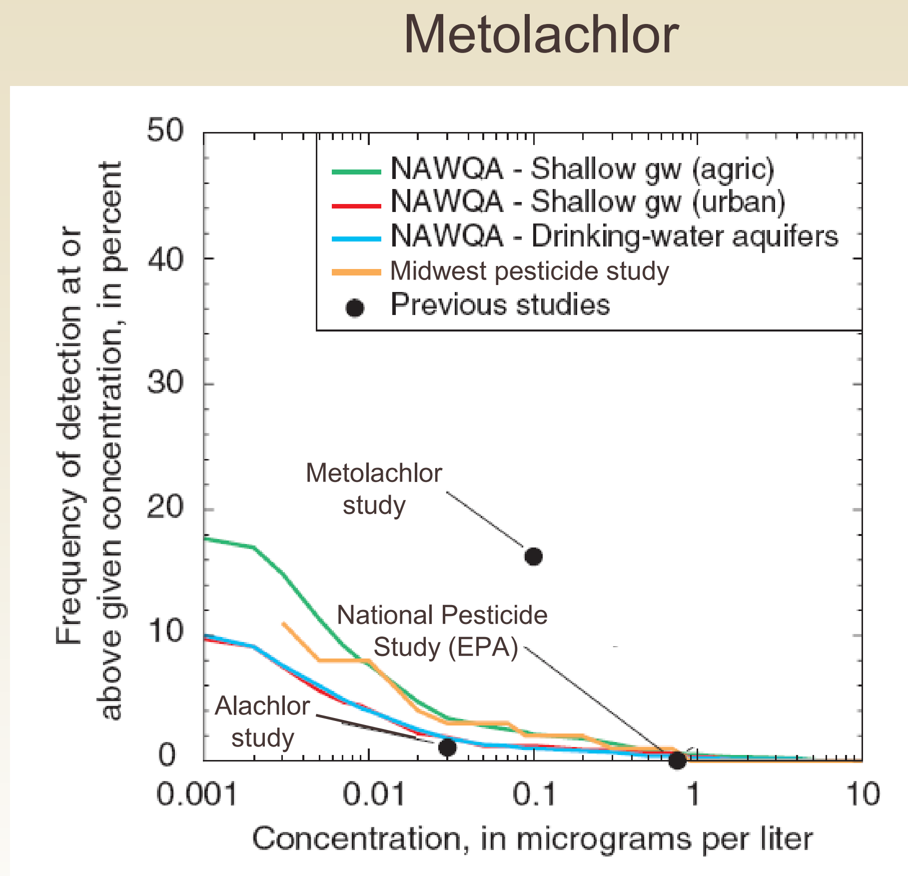


[redacted]

(Barbash and others, 1999)

How representative are the NAWQA results?





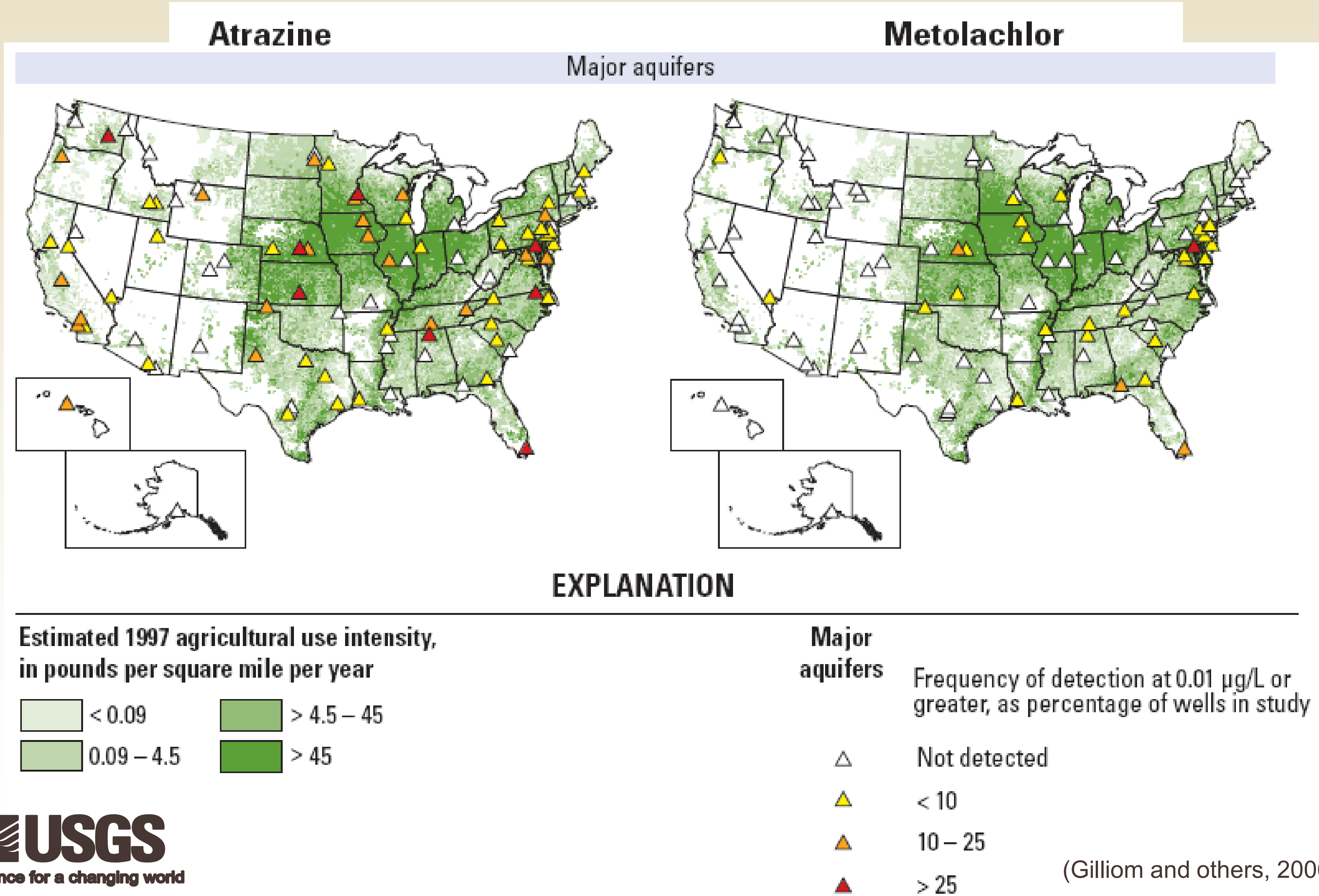
Detection frequencies (for pesticides) found to be generally consistent with those from previous studies

[redacted]

(Barbash and others, 1999)

National Assessments of Contaminant Occurrence

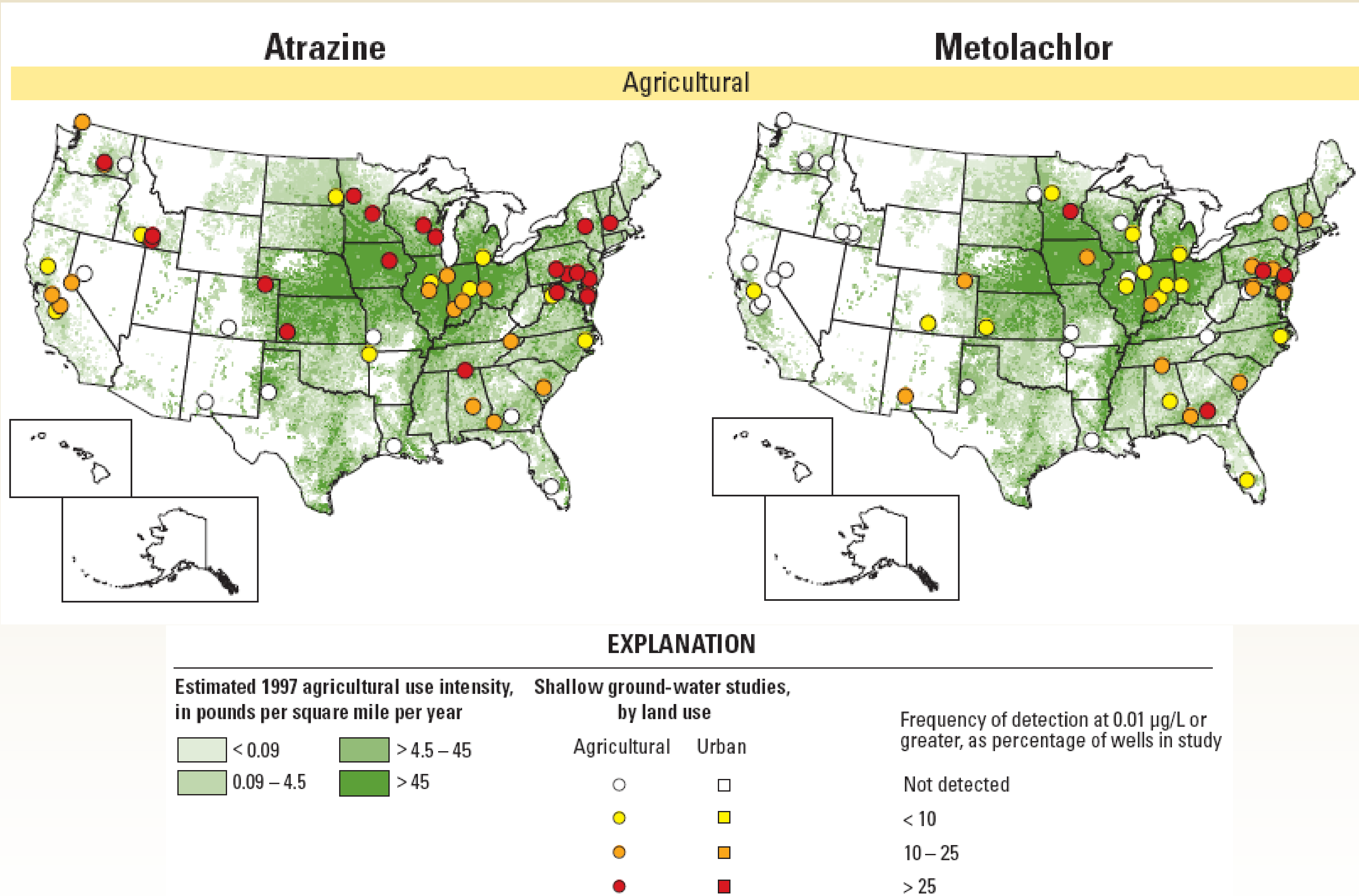
Pesticides (Major aquifers)



(Gilliom and others, 2006)

National Assessments of Contaminant Occurrence

Pesticides (Agricultural areas)

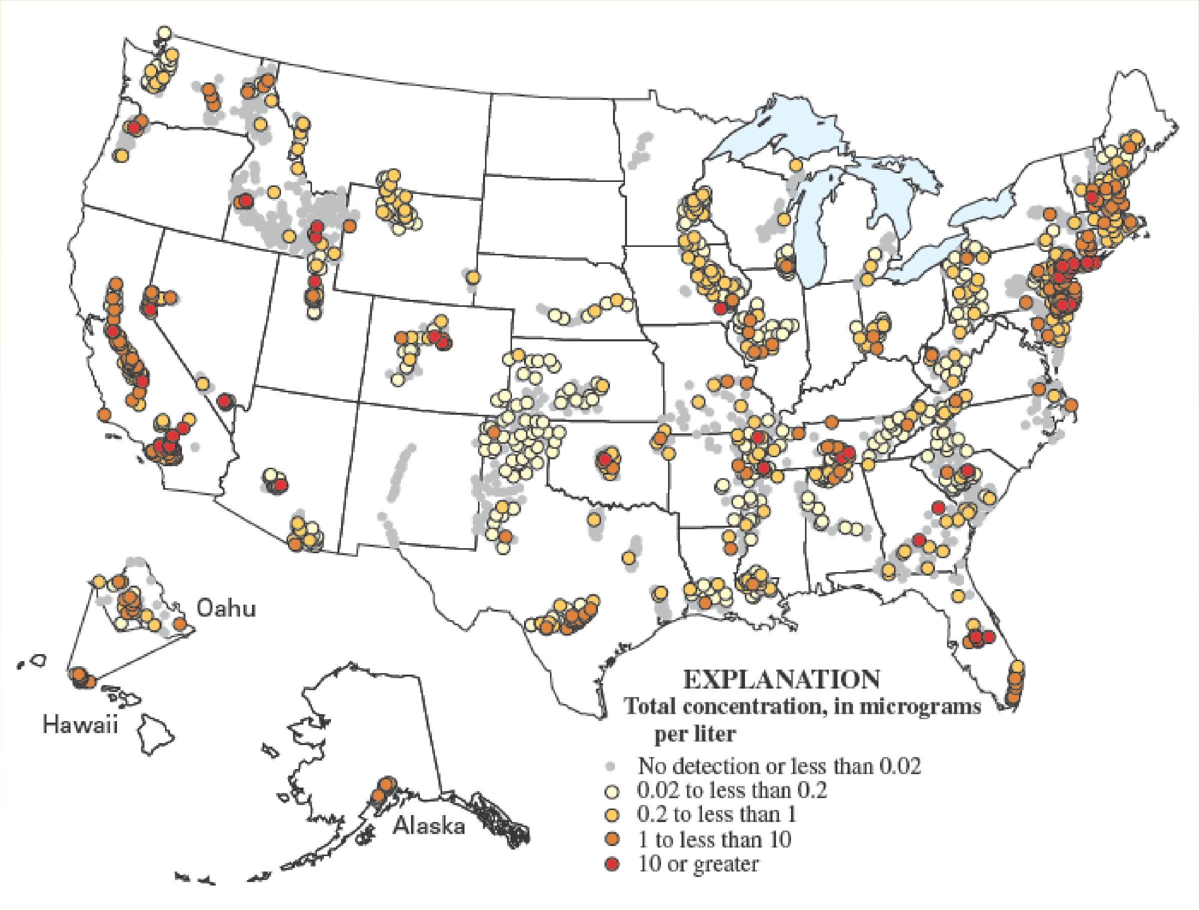


[redacted]

(Gilliom and others, 2006)

National Assessments of Contaminant Occurrence

VOCs

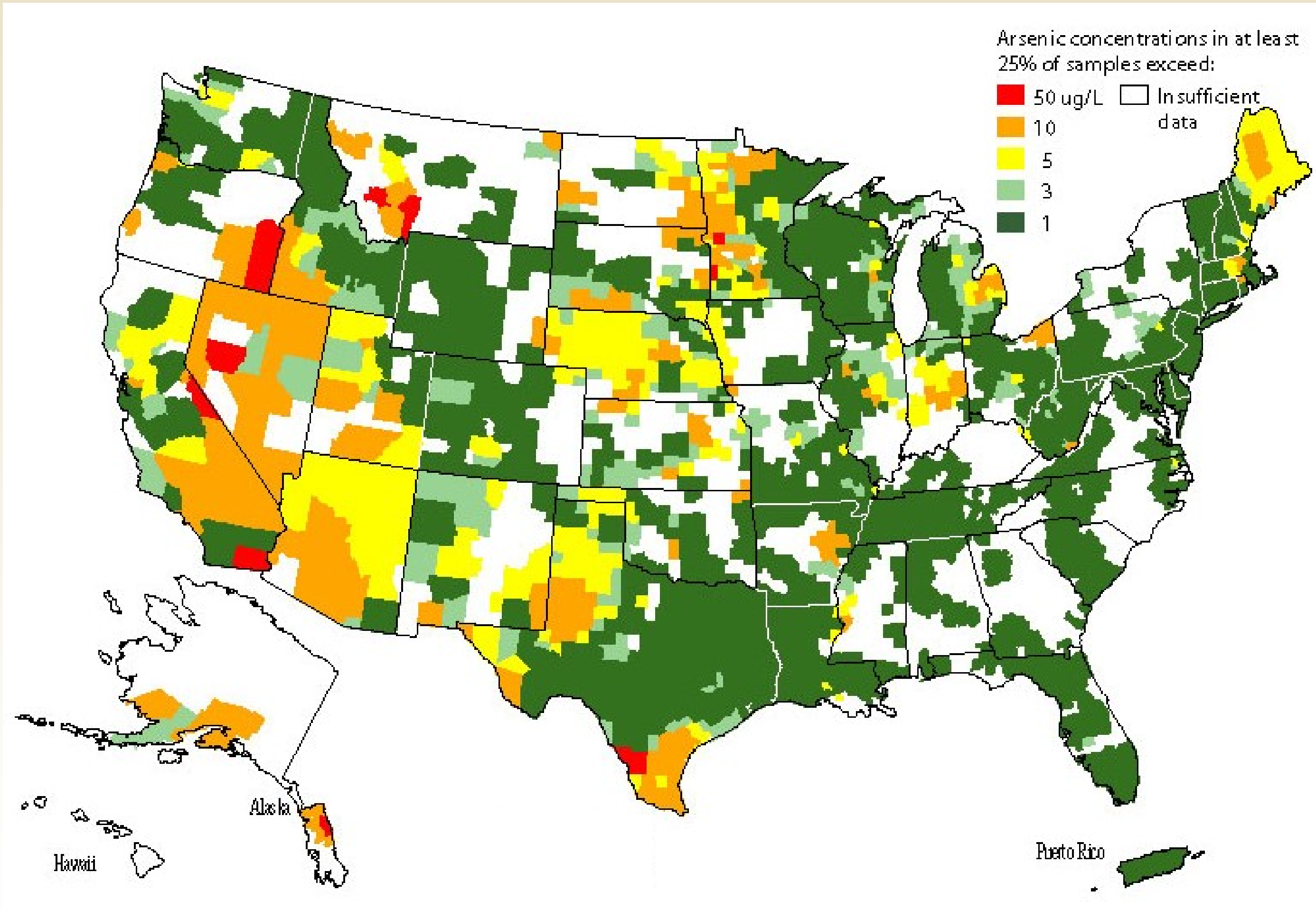


[redacted]

(Zogorski and others, 2006)

National Assessments of Contaminant Occurrence

Arsenic



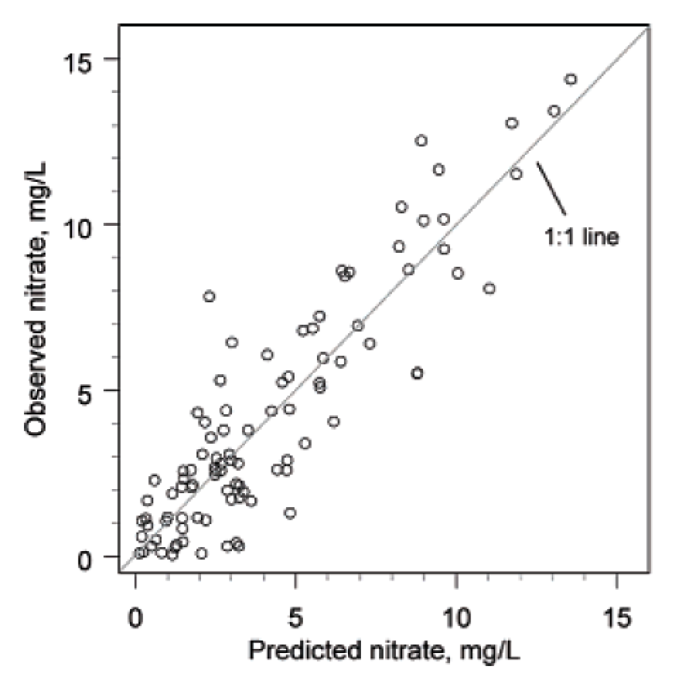
[redacted]

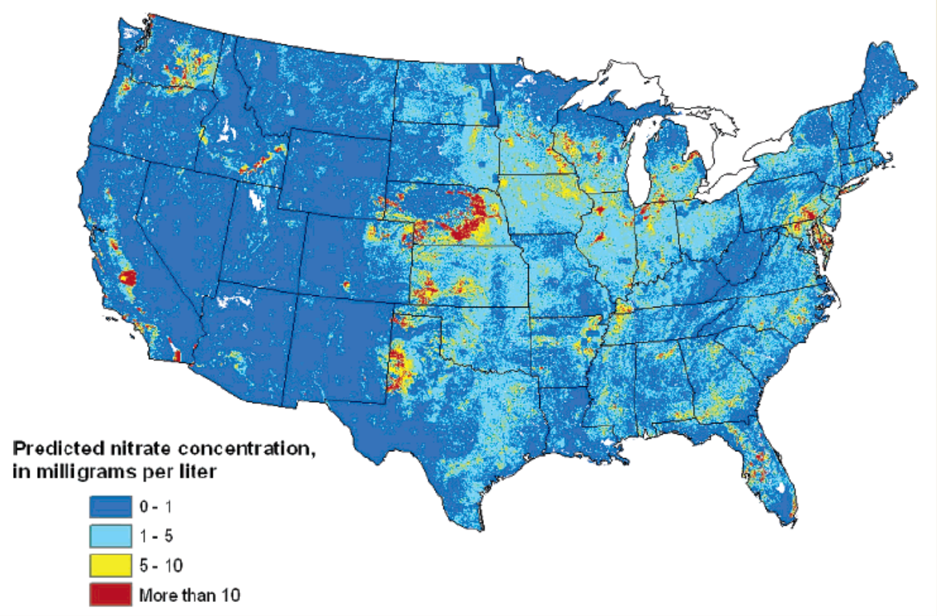
(Ryker, 2001)

Nationwide Predictions of Contaminant Occurrence

(Statistical approaches)

Nitrate Concentrations Predicted in Shallow Ground Water Using a Nonlinear Regression Model





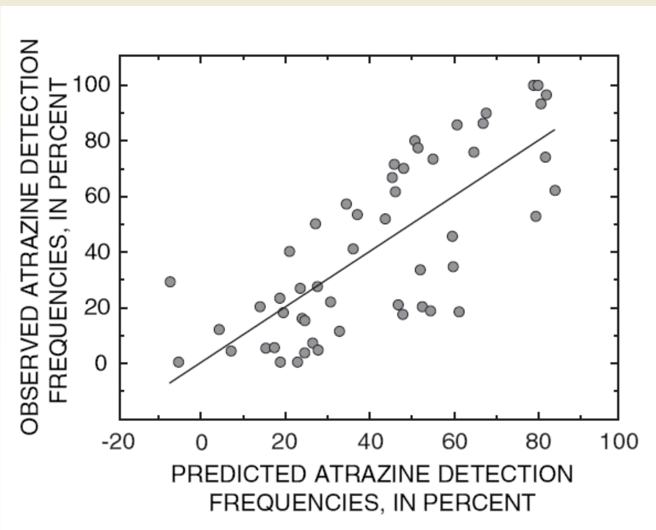
[redacted]

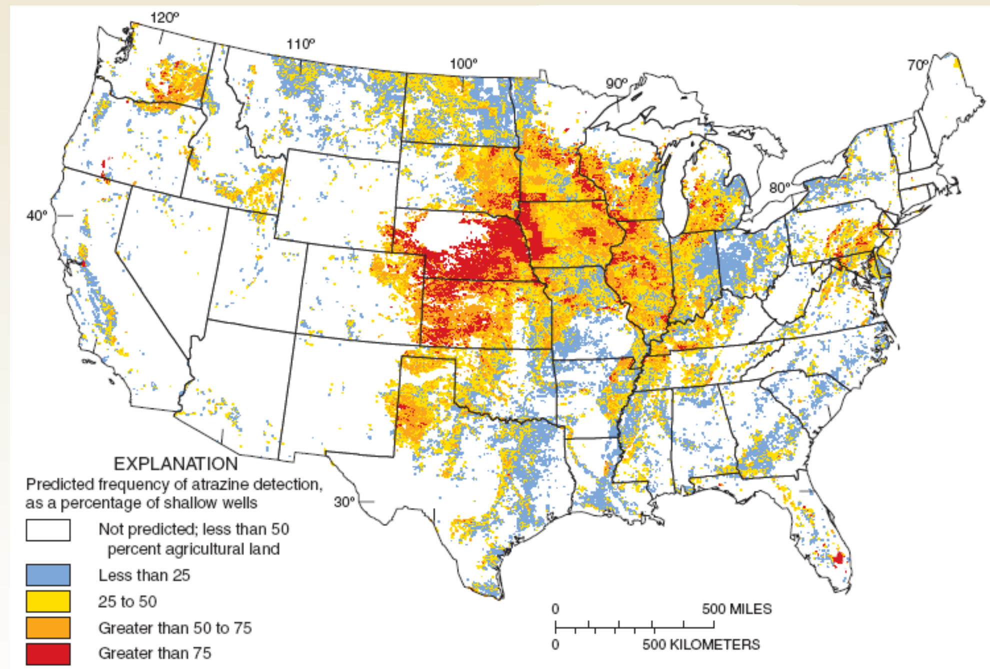
(Nolan and Hitt, 2006)

Nationwide Predictions of Contaminant Occurrence

(Statistical approaches)

Frequencies of Atrazine Detection in Shallow Ground Water Predicted Using a Nonlinear Regression Model





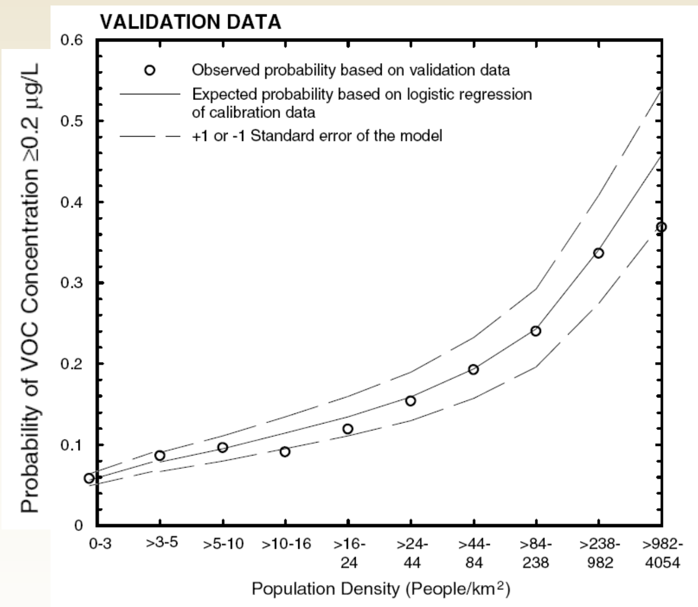
[redacted]

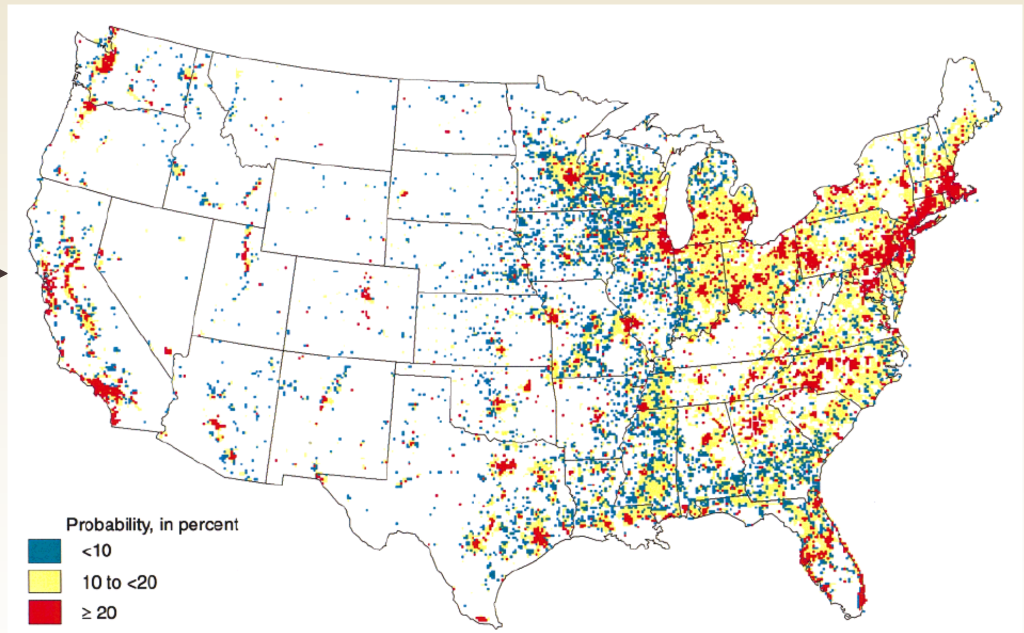
(Stackelberg and others, 2005)

Nationwide Predictions of Contaminant Occurrence

(Statistical approaches)

Probability of Detecting a VOC in Untreated Ground Water (where 5 or more people per sq. km. use ground water)





[redacted]

(Squillace and others, 1999)

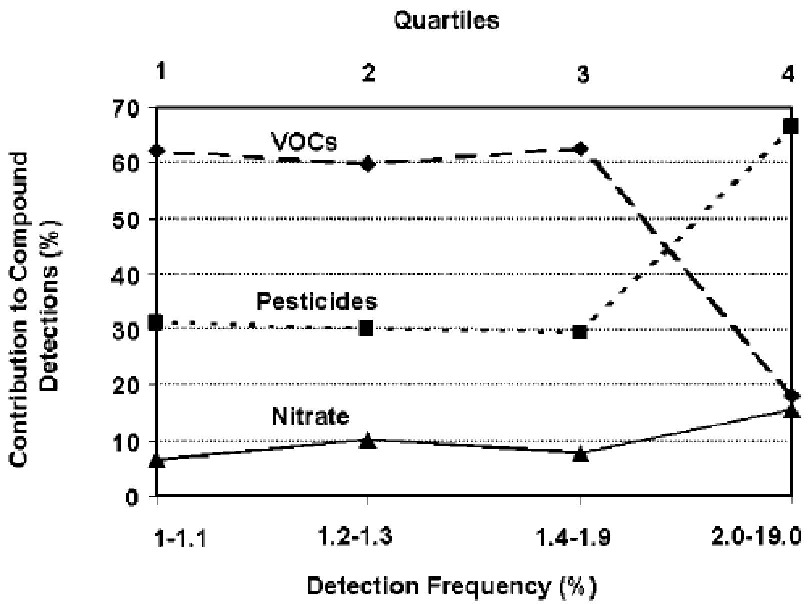
Unprecedented Analytical and Spatial Scope Allows Analysis of Broad Issues

- Co-occurrence among contaminant groups
- Investigation of previously un(der)examined compounds
    - Study of newly introduced compounds
    - Comparisons of detection patterns between degradates and parent compounds
- Examination of factors affecting occurrence and persistence

[redacted]

Co-occurrence Among Contaminant Groups

Nitrate, pesticides and VOCs in 1255 domestic wells and 242 public water supplies across the Nation



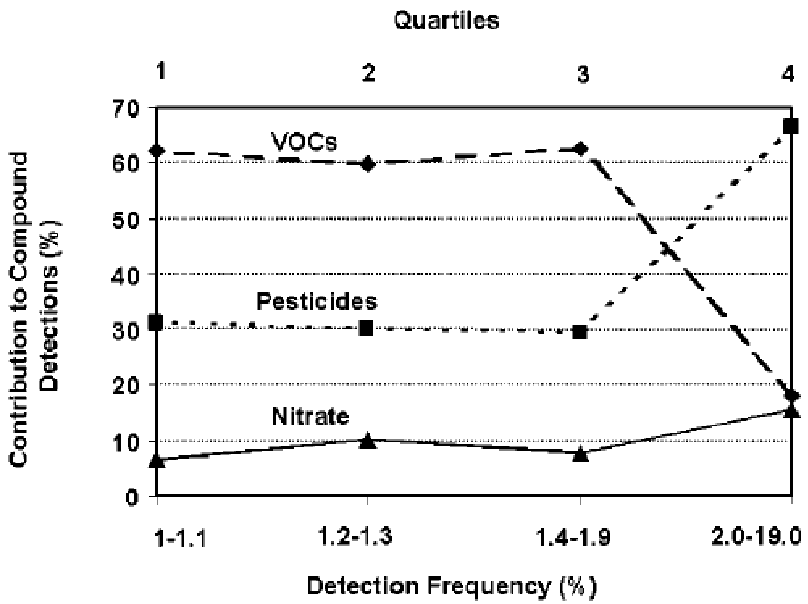
Pesticides predominate over VOCs and nitrate in the most common mixtures

[redacted]

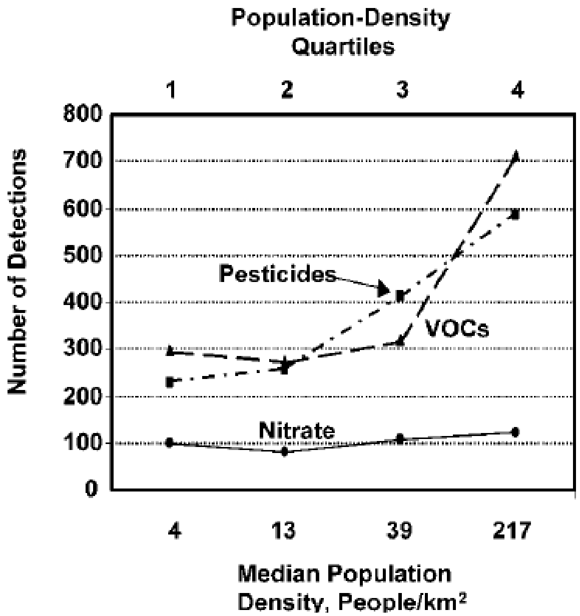
(Squillace and others, 2002)

Co-occurrence Among Contaminant Groups

Nitrate, pesticides and VOCs in 1255 domestic wells
and 242 public water supplies across the Nation



Pesticides predominate over VOCs and nitrate in the most common mixtures



Detections are more frequent with increasing population density for pesticides and VOCs, but much less so for nitrate

[redacted]

(Squillace and others, 2002)

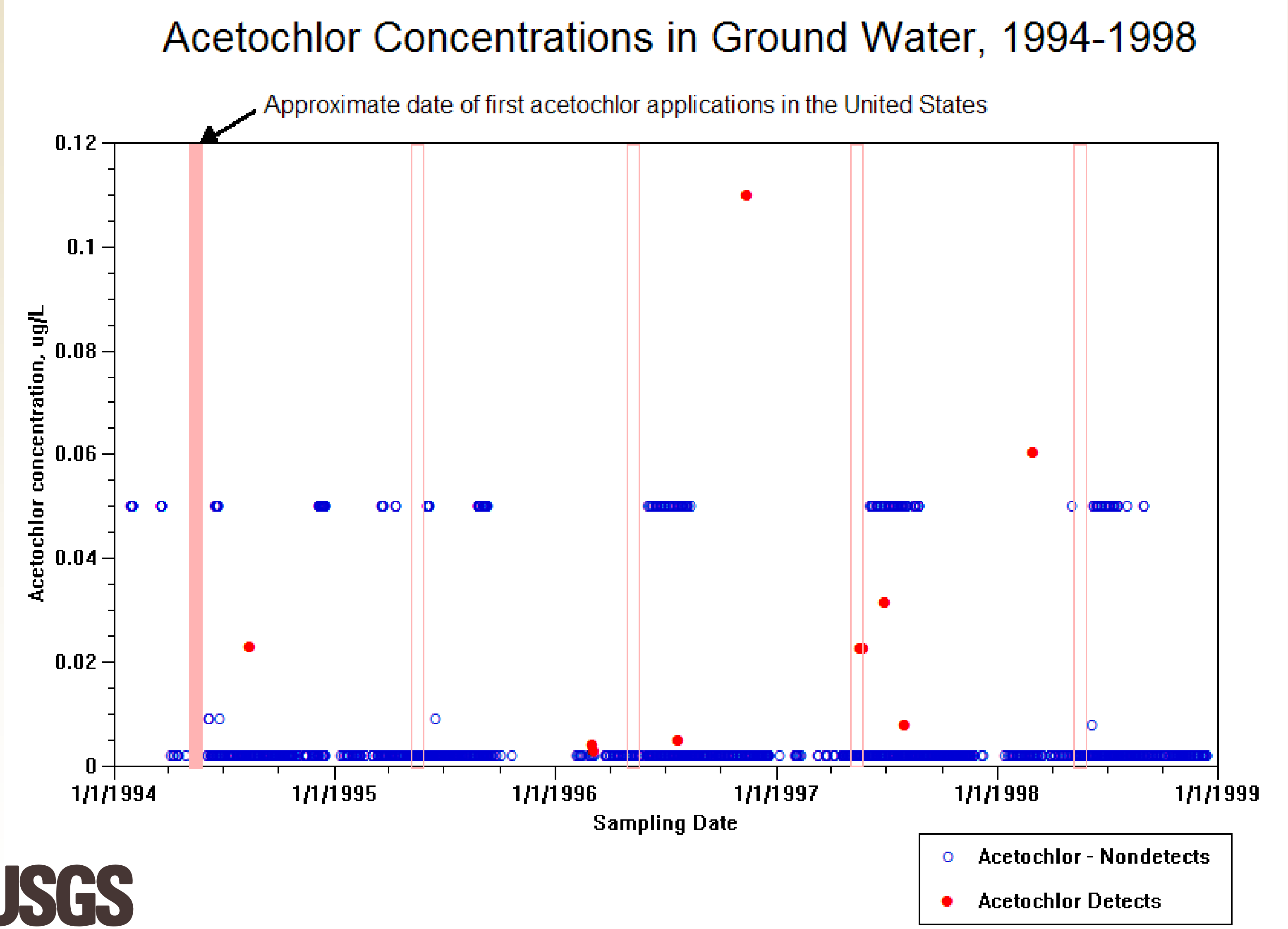
Large-Scale Assessments of Previously Un(der)examined Contaminants

- Methyl *tert*-butyl ether (MTBE)
- Acetochlor
- Glyphosate *(Round-Up)*
- Prometon
- Several pesticide degradates (e.g., from acetochlor, alachlor, metolachlor, cyanazine, fipronil)
- Wastewater compounds *(on the horizon)*

[redacted]

Large-Scale Assessments of New Contaminants

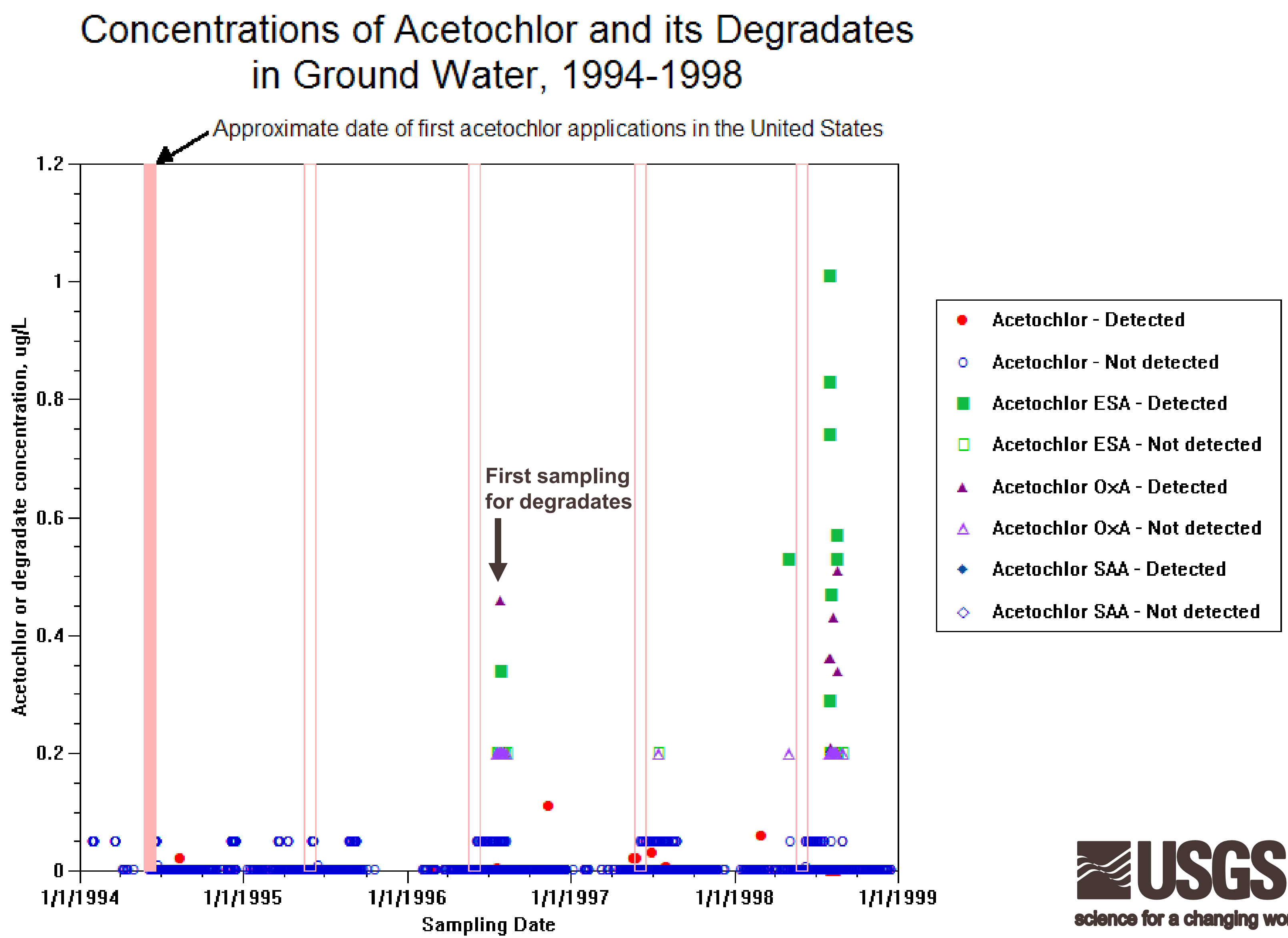
The world's first continent-wide solute transport experiment!



USGS
science for a changing world

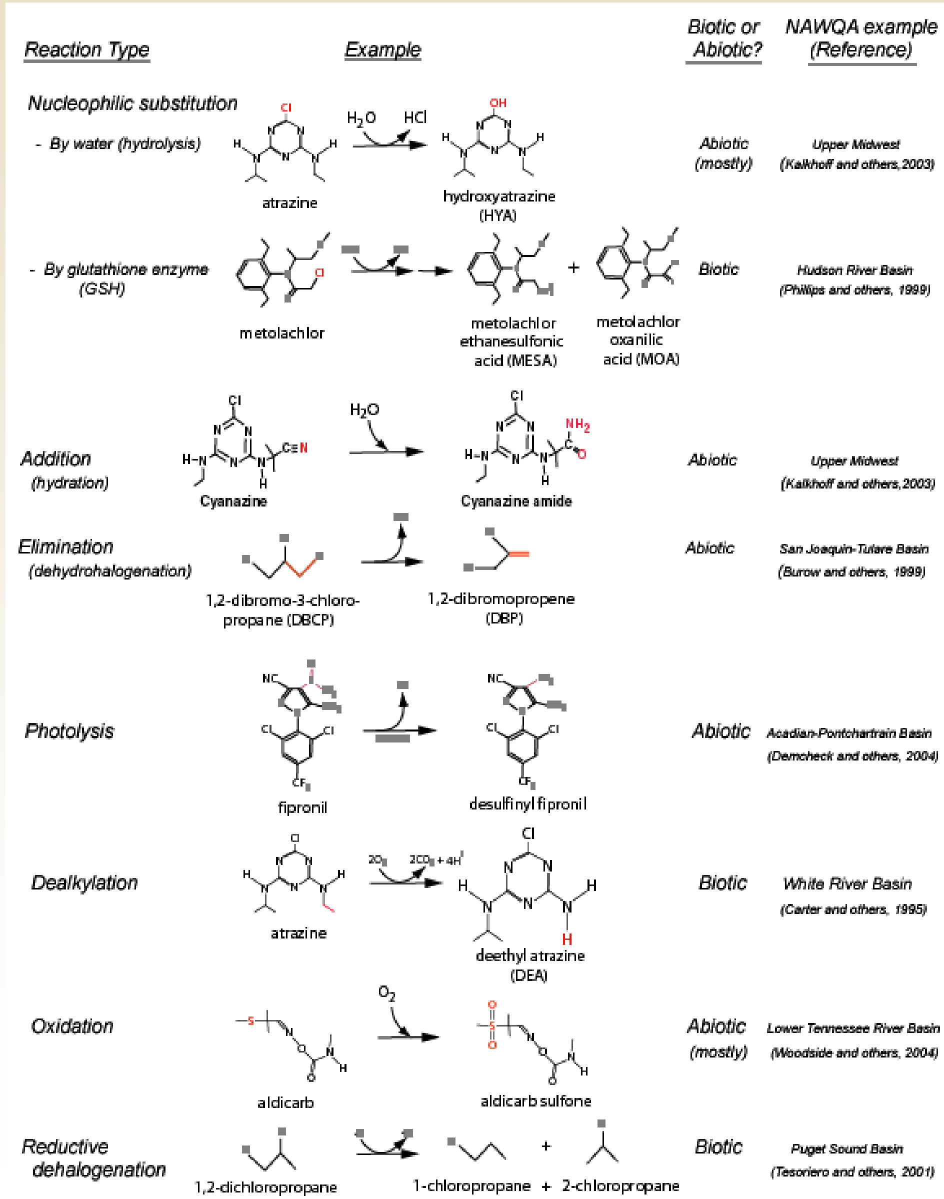
Large-Scale Assessments of New Contaminants

The world's first continent-wide solute transport experiment!



USGS
science for a changing world

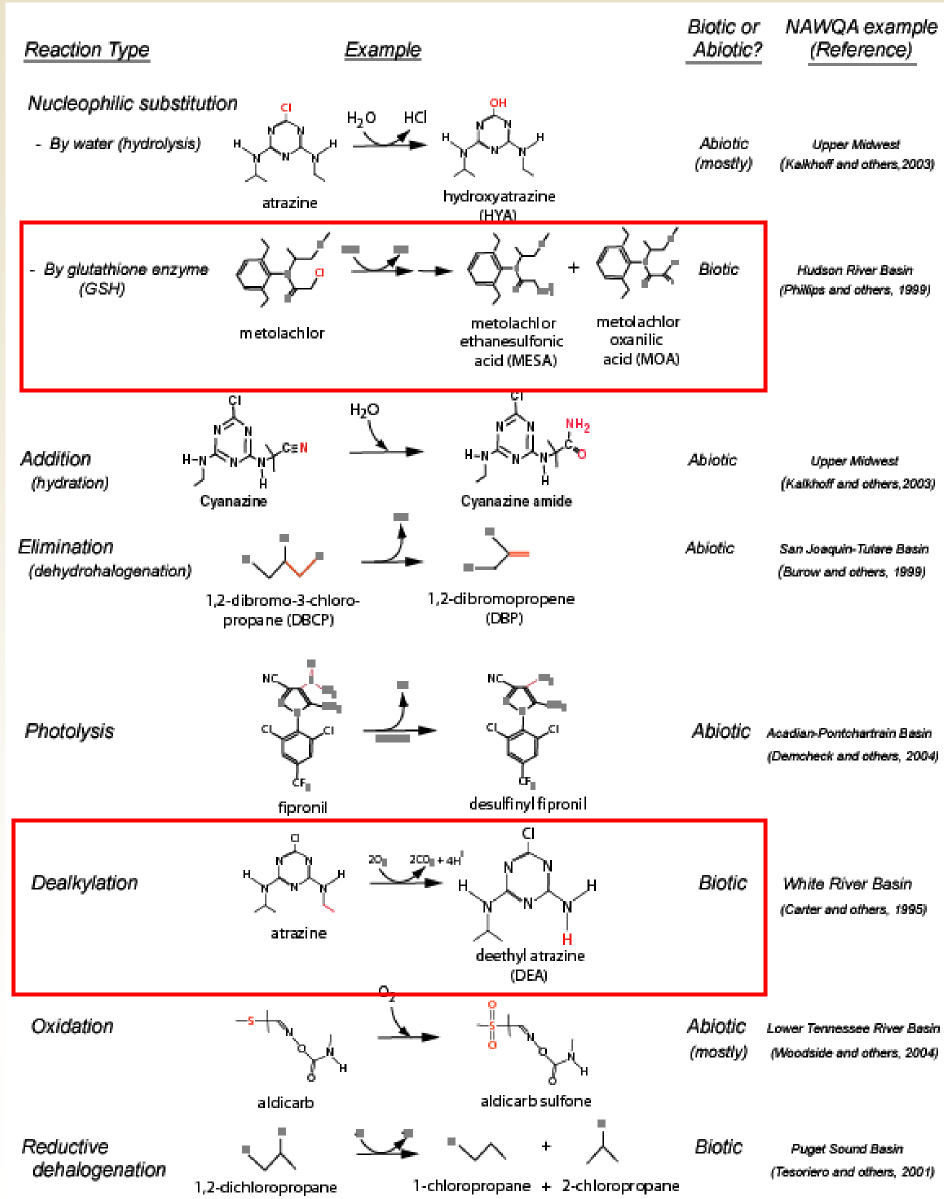
Broad scope of degradates included most of the principal reactions involved in pesticide transformation



[redacted]

Broad scope of degradates included most of the principal reactions involved in pesticide transformation

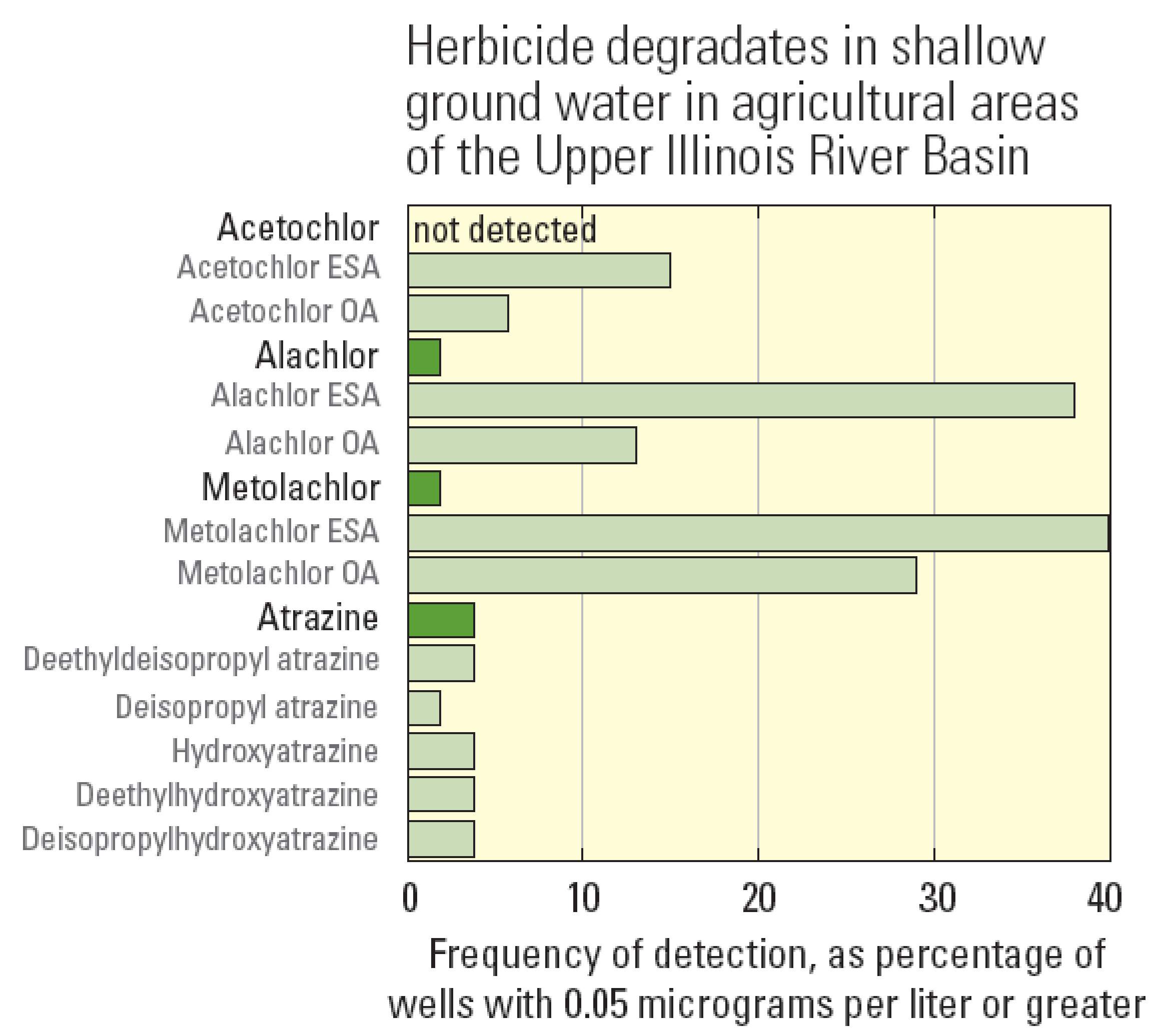
metolachlor → MESA + MOxA



atrazine → DEA

[redacted]

Many degradates detected more often than their parent compounds

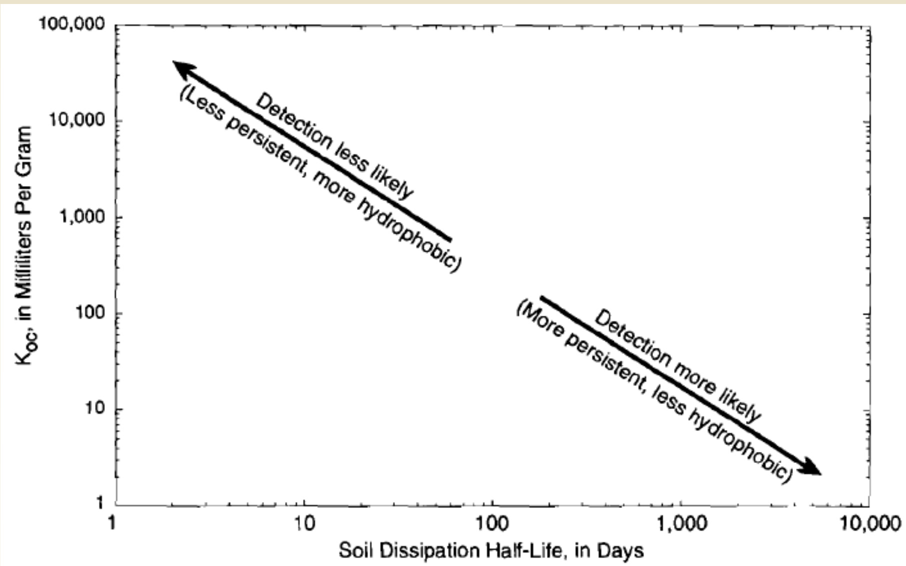


[redacted]

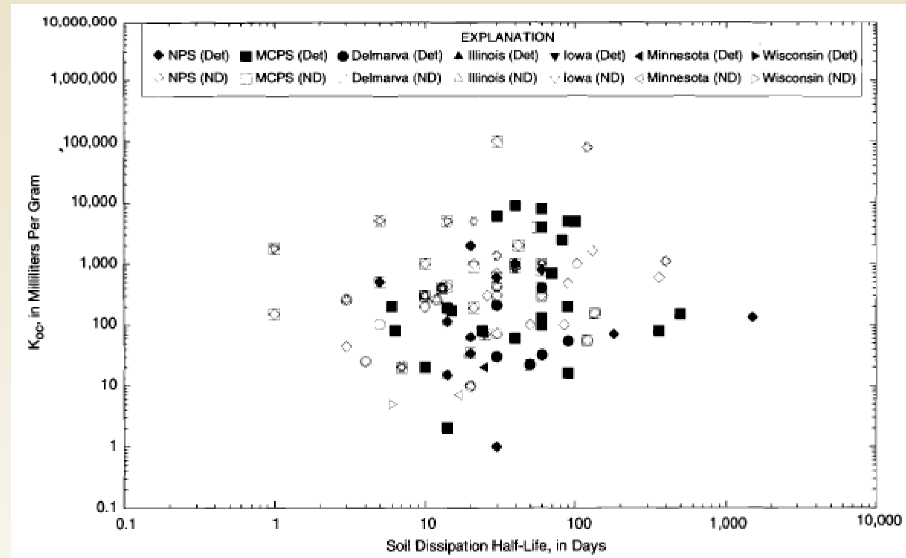
(Groschen and others, 2004)

Factors Associated with Contaminant Detections

Previous studies suggested that chemical properties
are poor predictors of pesticide detections



Expected pattern



Observations from seven earlier
multi-state studies

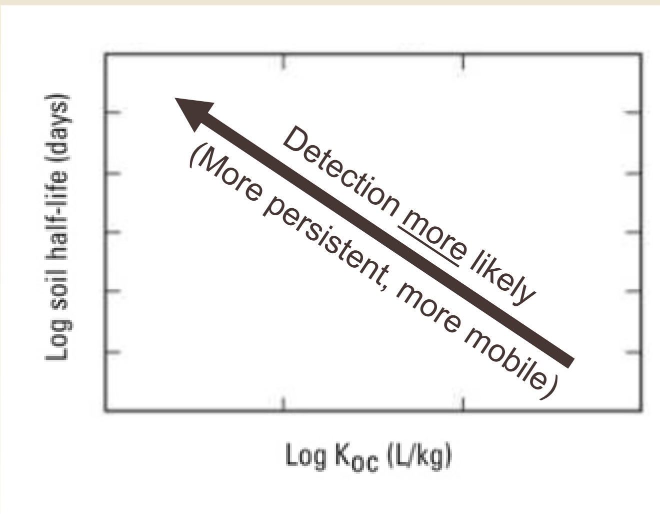
Solid symbols – Compound detected
Open symbols – Compound not detected

[redacted]

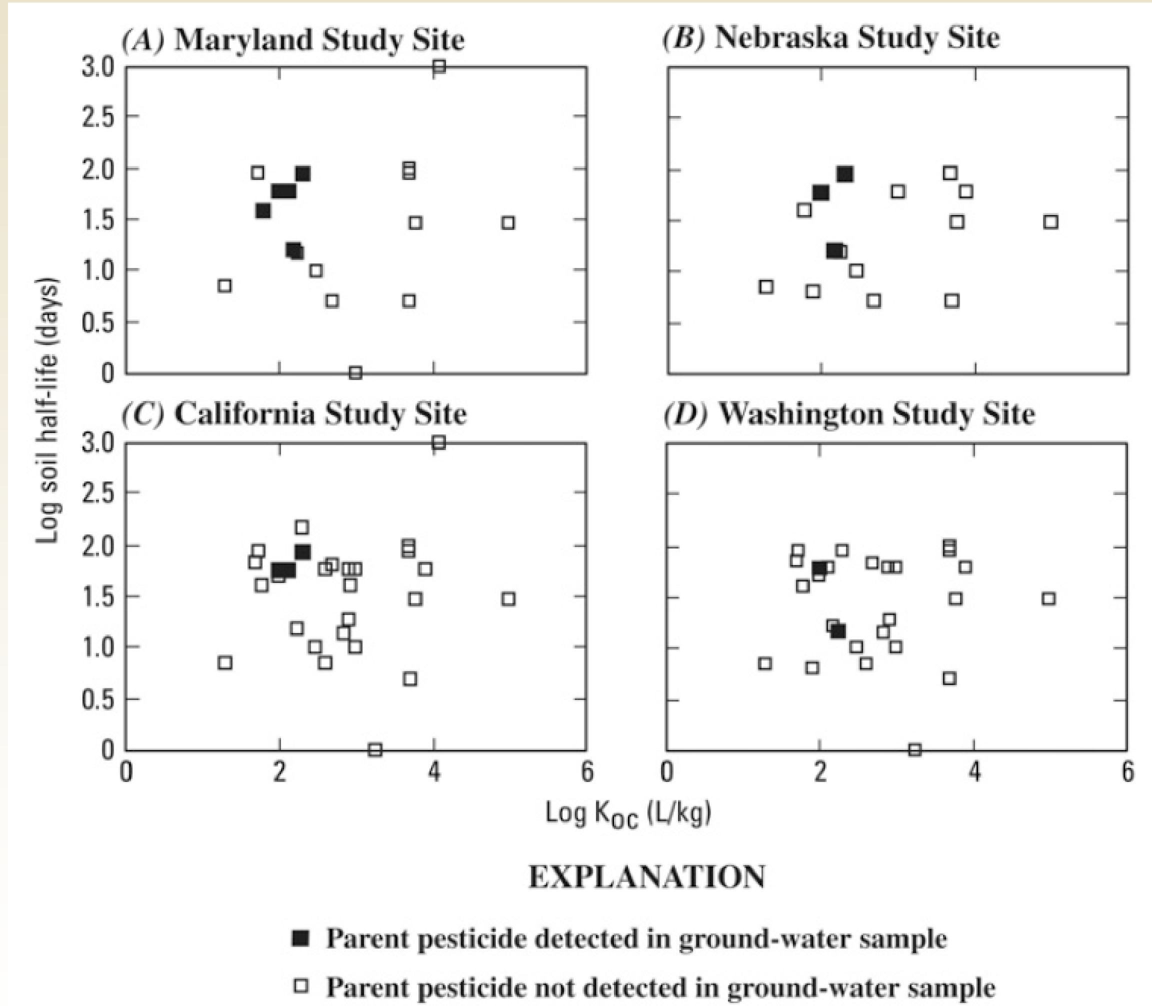
(Barbash and Resek, 1996)

Factors Associated with Contaminant Detections

During the NAWQA program, physical and chemical properties were again found to be only moderately reliable predictors of occurrence



Expected pattern



Four ag areas examined for the ACT studies (Steele and others, 2008)

[redacted]

Factors Associated with Contaminant Detections

Pesticide detection frequencies found to be related to use and persistence

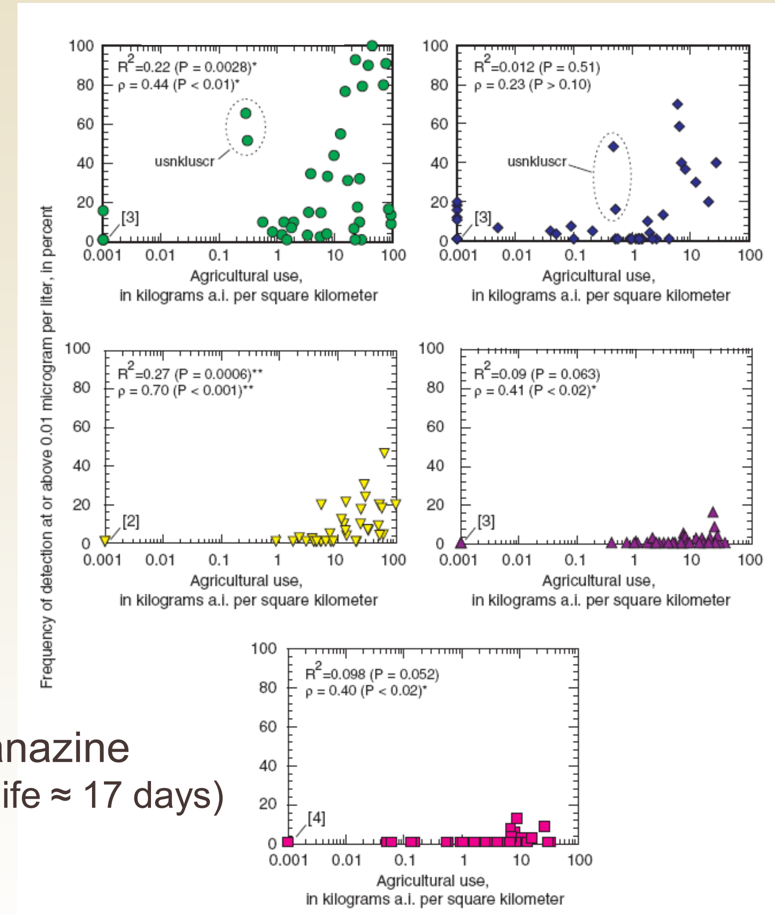
Atrazine
(Soil half-life ≈ 146 days)

Simazine
(Soil half-life ≈ 91 days)

Metolachlor
(Soil half-life ≈ 26 days)

Alachlor
(Soil half-life ≈ 21 days)

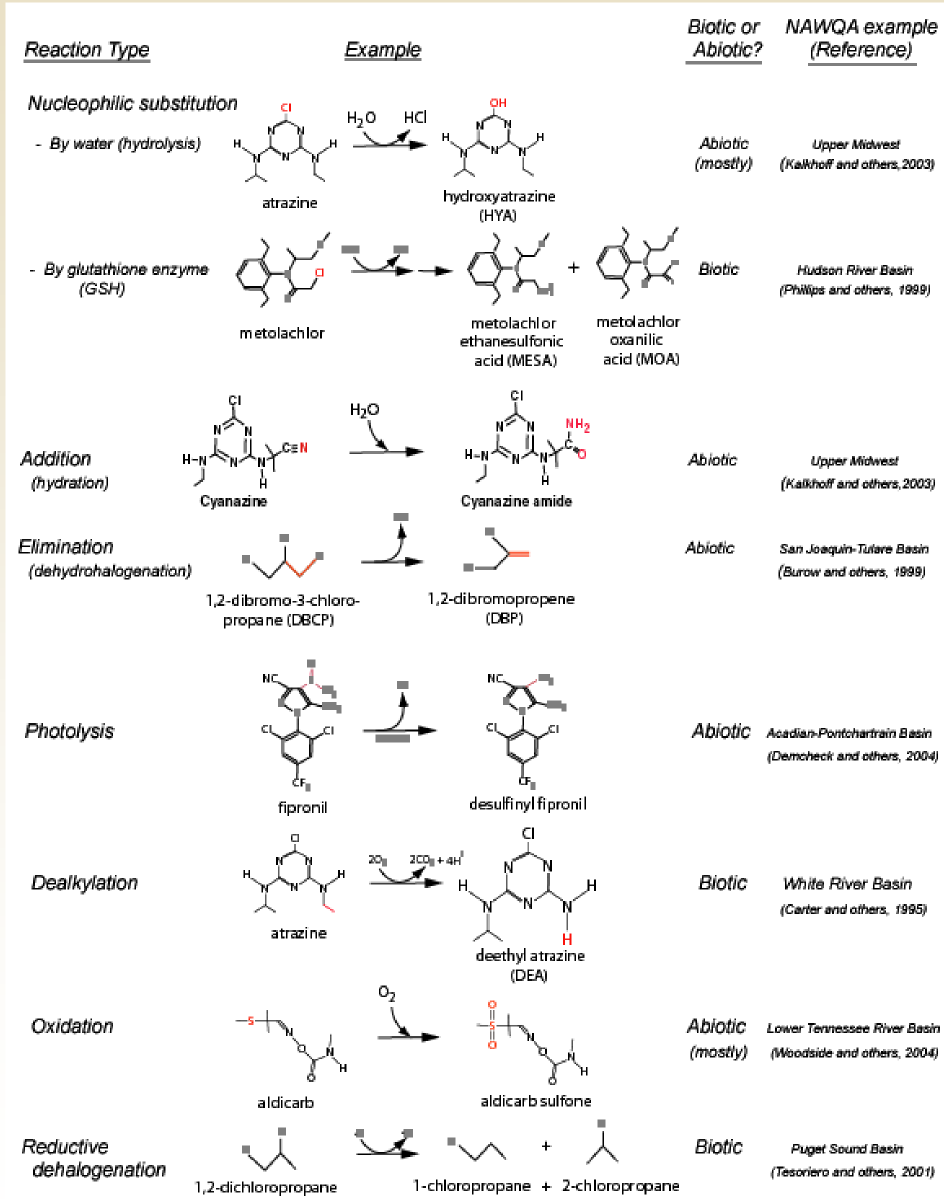
Cyanazine
(Soil half-life ≈ 17 days)



Herbicide detection frequencies
versus agricultural use
(Barbash and others, 1999)

[redacted]

Factors Controlling Persistence

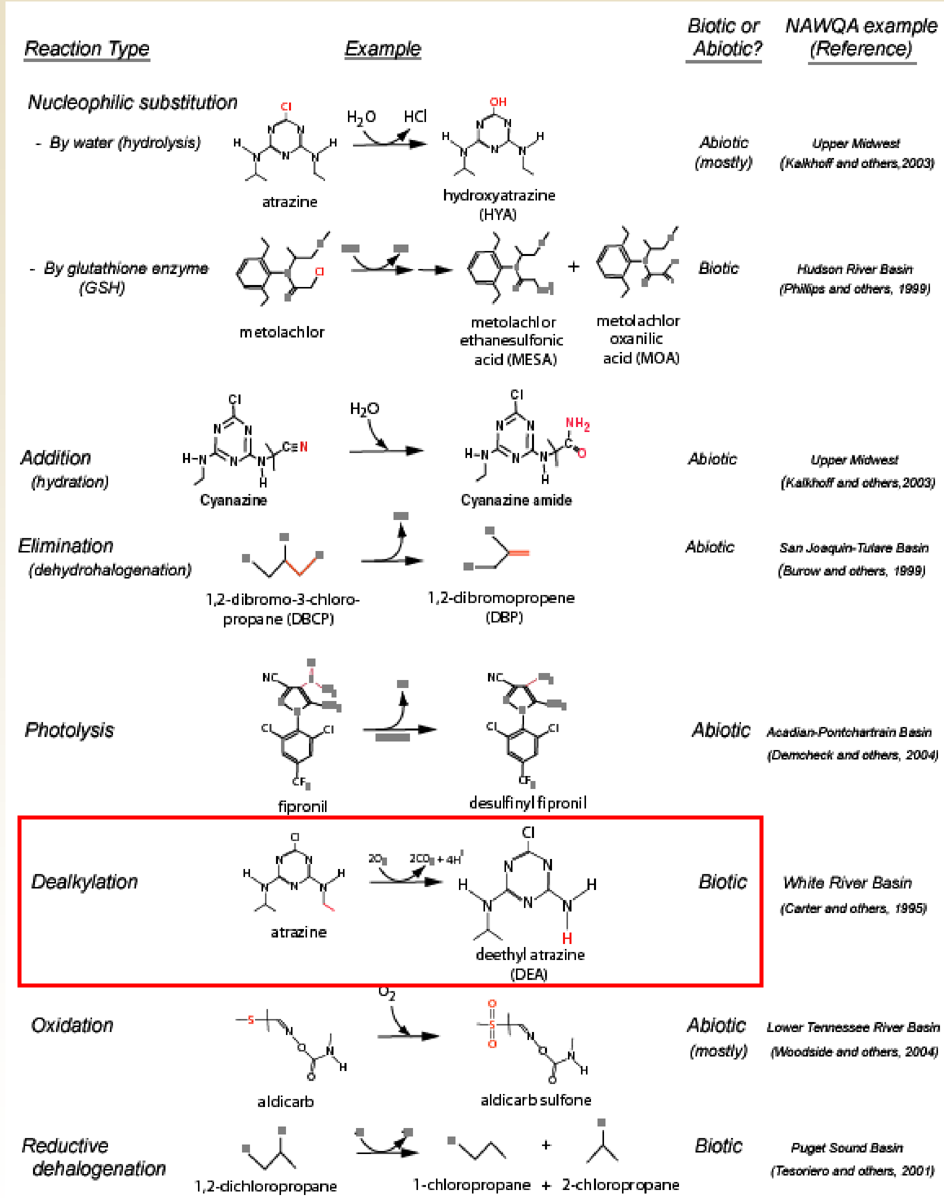


Reaction Type	Example	Biotic or Abiotic?	NAWQA example (Reference)
Nucleophilic substitution - By water (hydrolysis)	atrazine → hydroxyatrazine (HYA) (H_2O, HCl)	Abiotic (mostly)	Upper Midwest (Kalkhoff and others, 2003)
- By glutathione enzyme (GSH)	metolachlor → metolachlor ethanesulfonic acid (MESA) + metolachlor oxanilic acid (MOA)	Biotic	Hudson River Basin (Phillips and others, 1999)
Addition (hydration)	Cyanazine → Cyanazine amide (H_2O)	Abiotic	Upper Midwest (Kalkhoff and others, 2003)
Elimination (dehydrohalogenation)	1,2-dibromo-3-chloro-propane (DBCP) → 1,2-dibromopropene (DBP)	Abiotic	San Joaquin-Tulare Basin (Burow and others, 1999)
Photolysis	fipronil → desulfinyl fipronil	Abiotic	Acadian-Pontchartrain Basin (Demcheck and others, 2004)
Dealkylation	atrazine → deethyl atrazine (DEA)	Biotic	White River Basin (Carter and others, 1995)
Oxidation	aldicarb → aldicarb sulfone (O_2)	Abiotic (mostly)	Lower Tennessee River Basin (Woodside and others, 2004)
Reductive dehalogenation	1,2-dichloropropane → 1-chloropropane + 2-chloropropane	Biotic	Puget Sound Basin (Tesoriero and others, 2001)

[redacted]

Factors Controlling Persistence

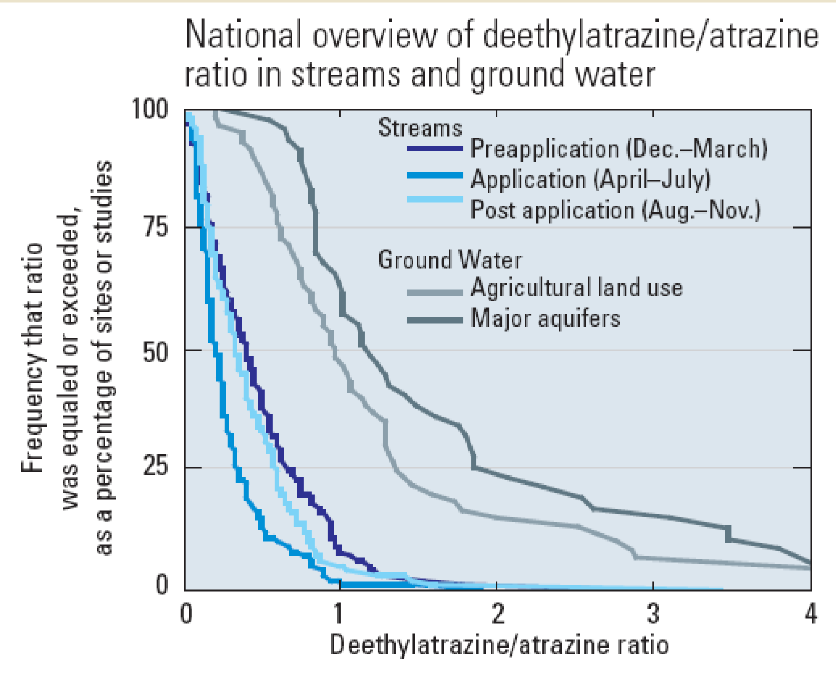
atrazine → DEA

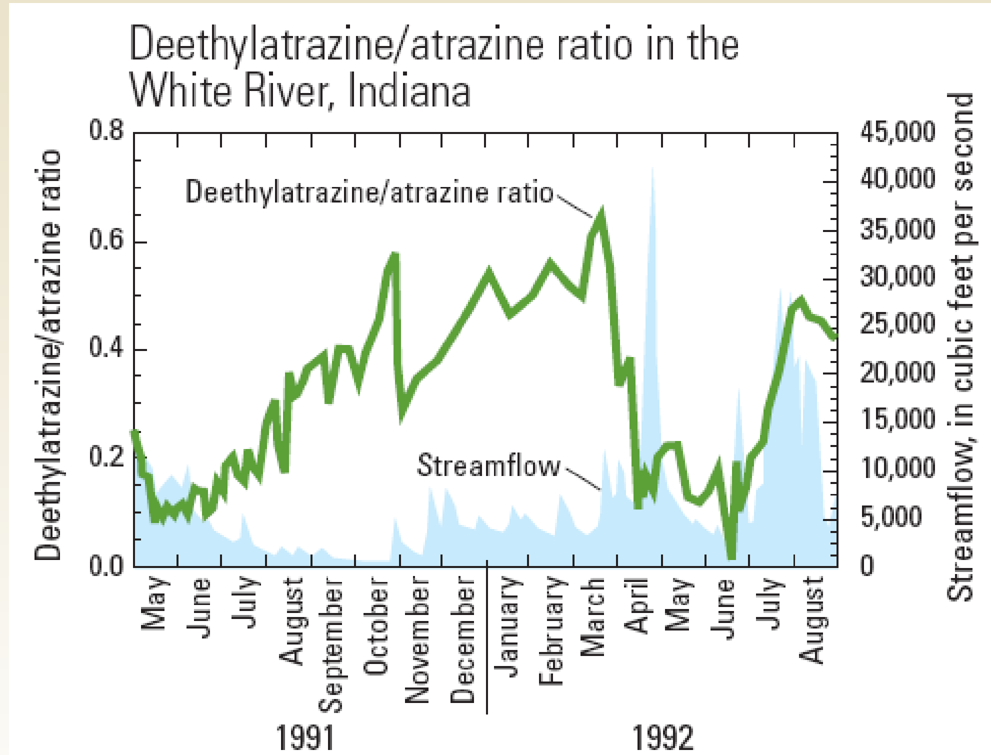


[redacted]

Factors Controlling Persistence

Ratio of DEA to atrazine concentrations (extent of reaction) increases with increasing soil contact time



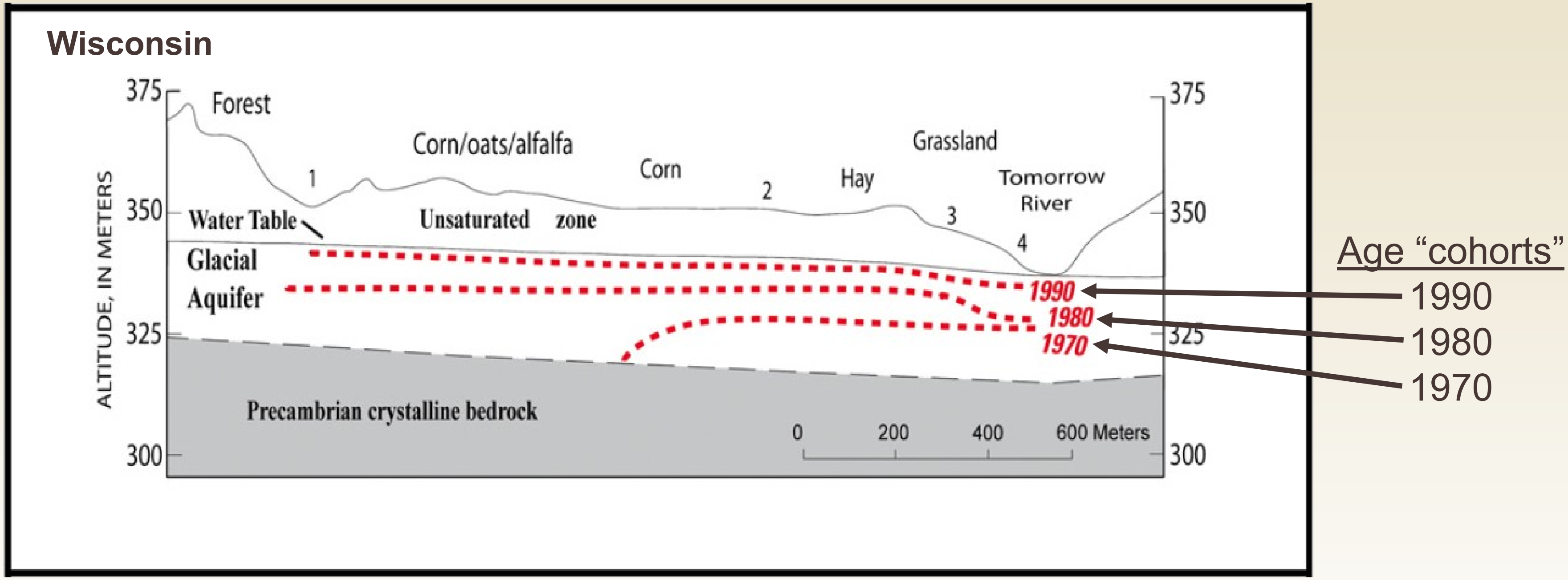


⇒ Transformation of atrazine to DEA appears to occur primarily in soils

[redacted]

(Gilliom and others, 2006)

Use of Subsurface Residence Times to Understand Changes in Ground-Water Quality



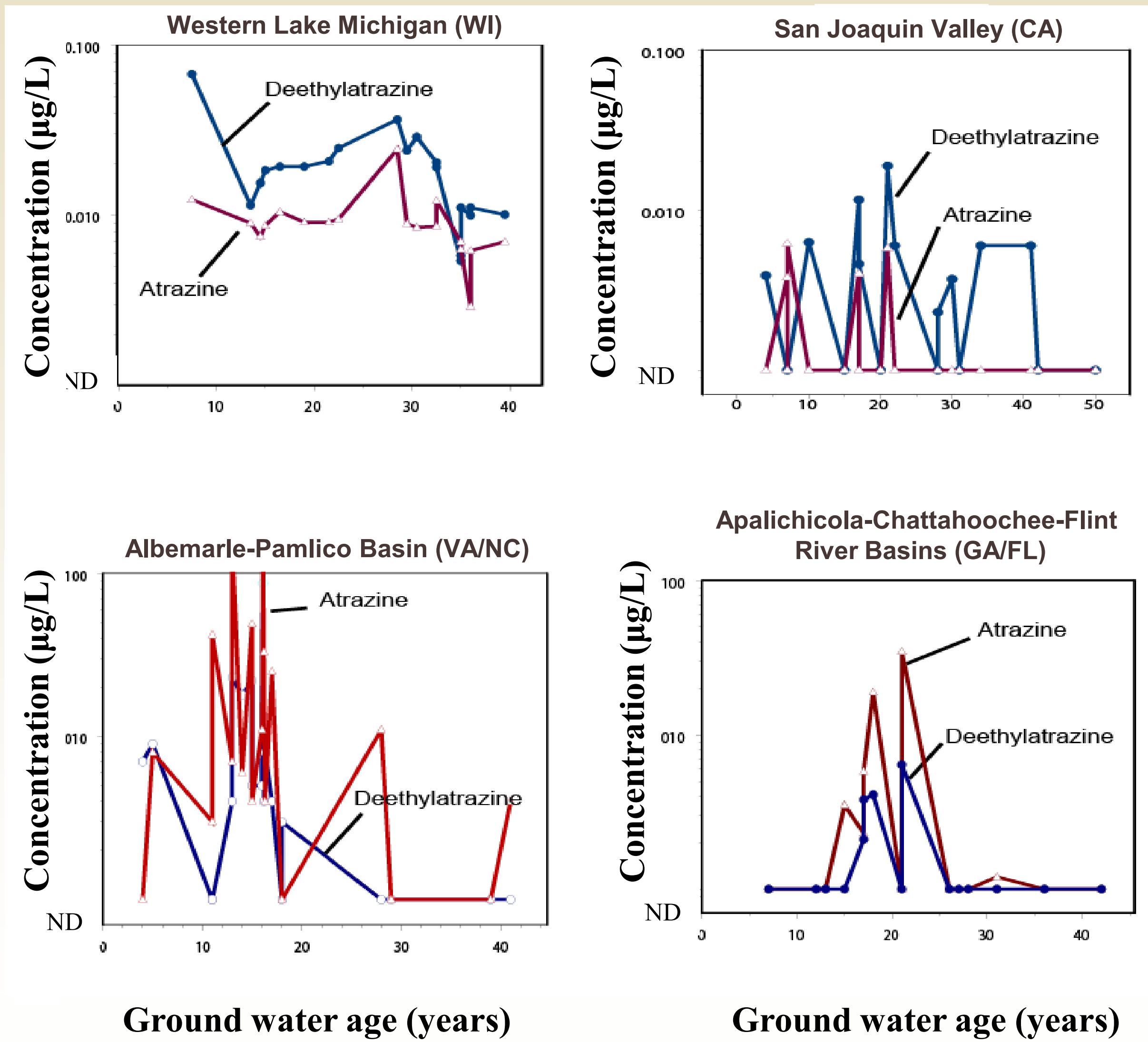
(Tesoriero and others, 2007)

Use of Ground-Water Residence Times to Study Geochemical Processes

Formation of DEA favored in areas with thicker unsaturated zones

Thick Unsaturated Zone (>10 m)

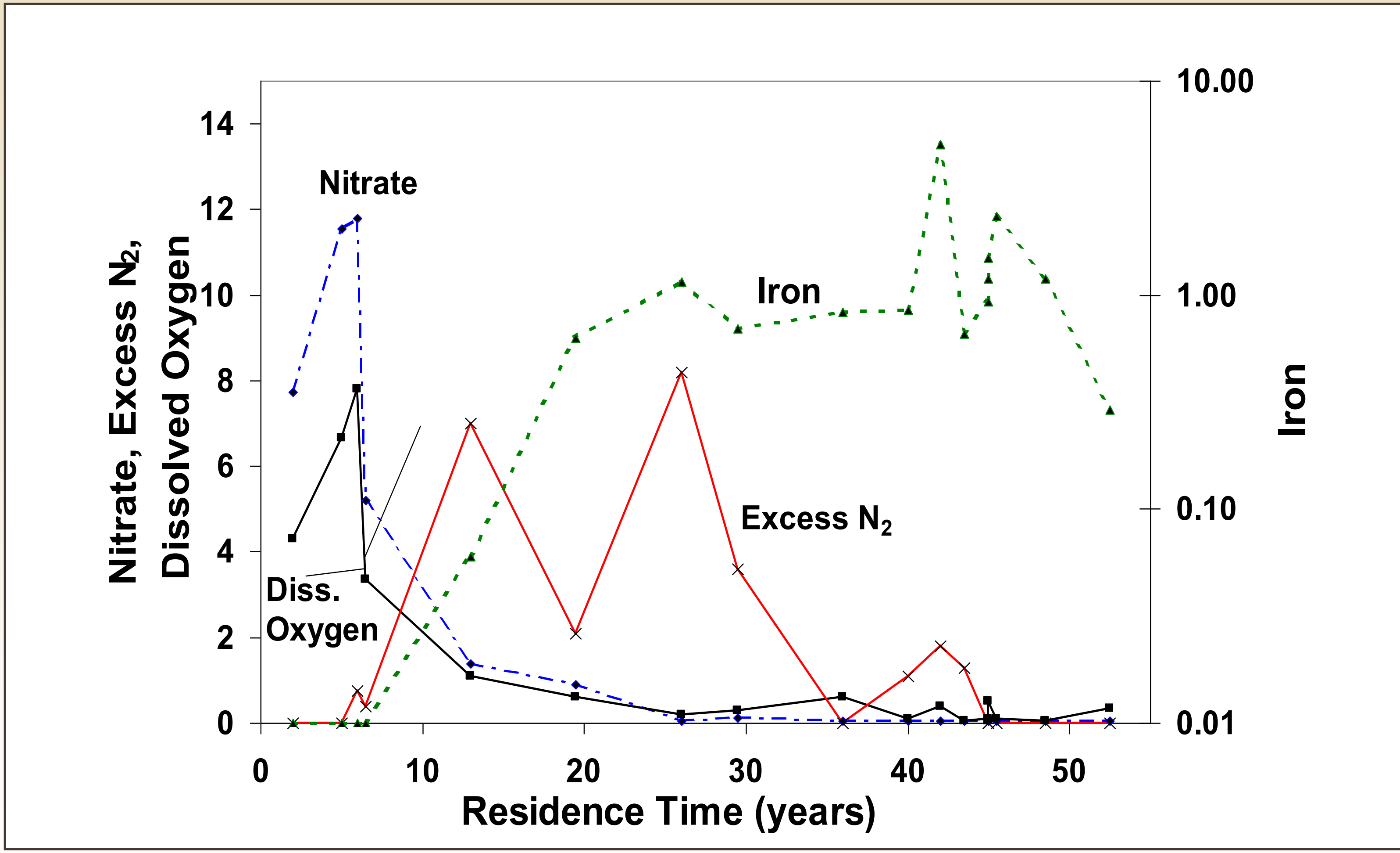
Thin Unsaturated Zone (<2m)



[redacted]

(Tesoriero and others, 2007)

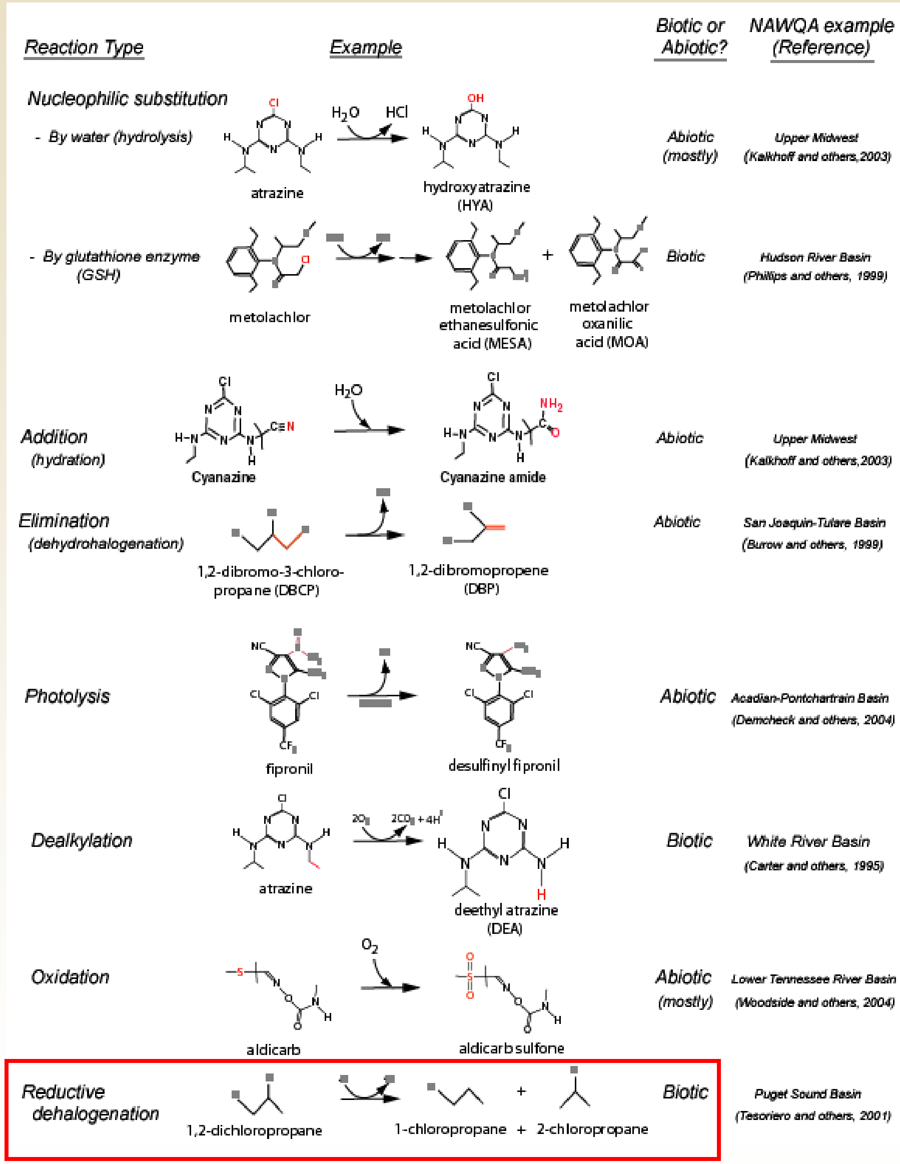
Evolution of Redox Conditions in Ground Water



[redacted]

(Tesoriero, personal communication, 7/29/05)

Effects of Redox Conditions on Persistence



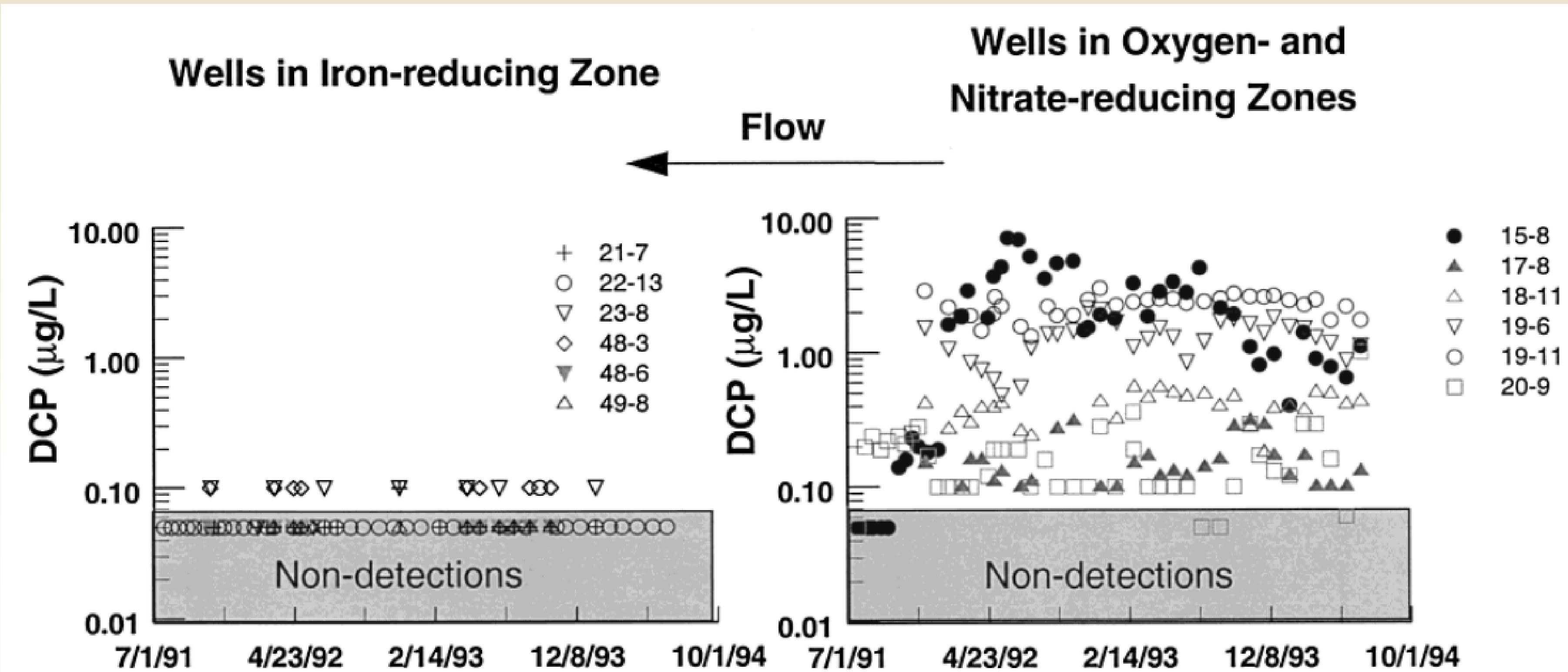
[redacted]

1,2-dichloropropane (DCP [fumigant]) → 1-chloropropane (1-CP) + 2-chloropropane (2-CP)

Scaling up from the Laboratory to the Field

Dechlorination of DCP to CP Requires Iron-Reducing Conditions

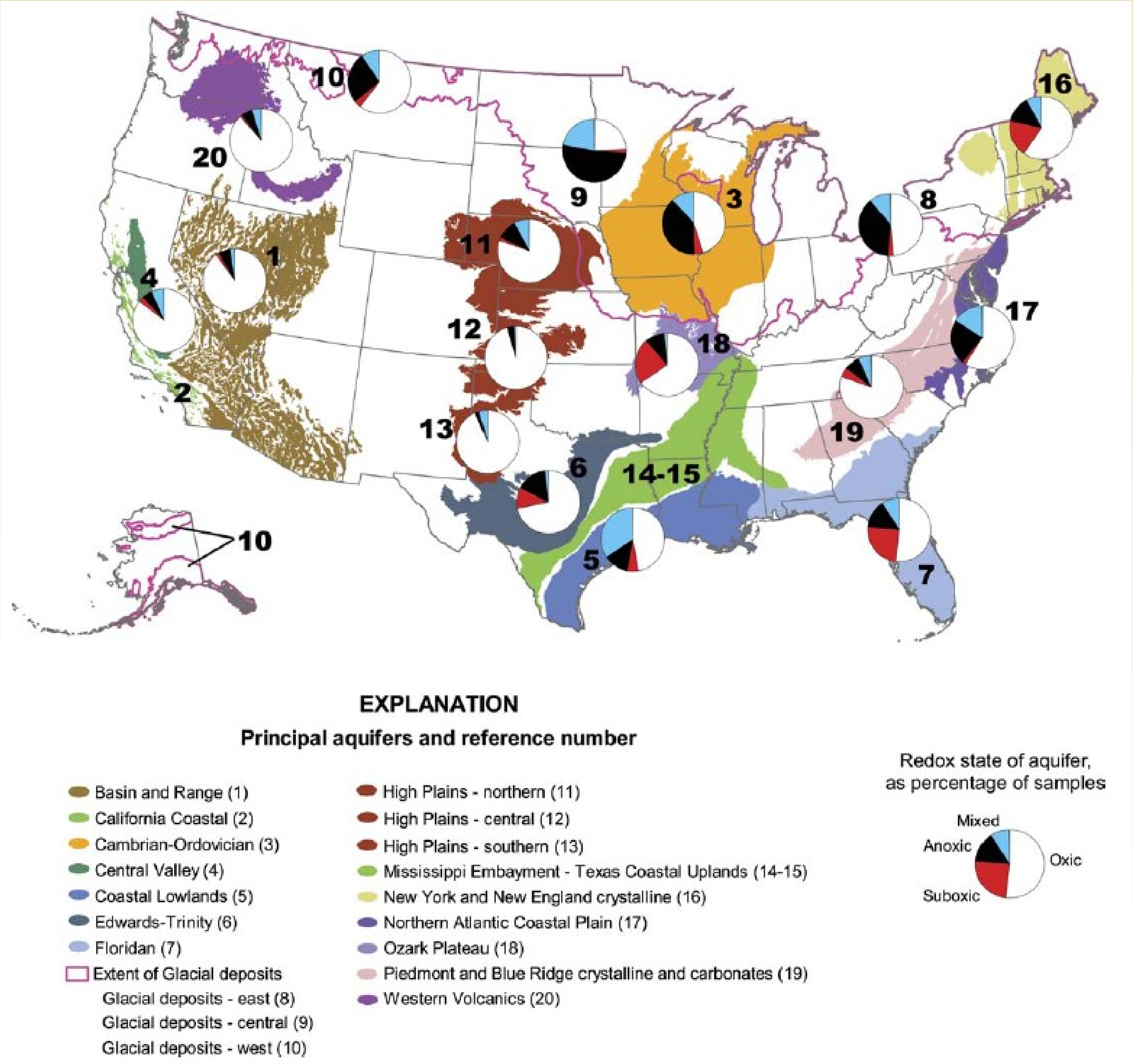
(Flow-system study in northwestern Washington)



[redacted]

(Tesoriero and others, 2001)

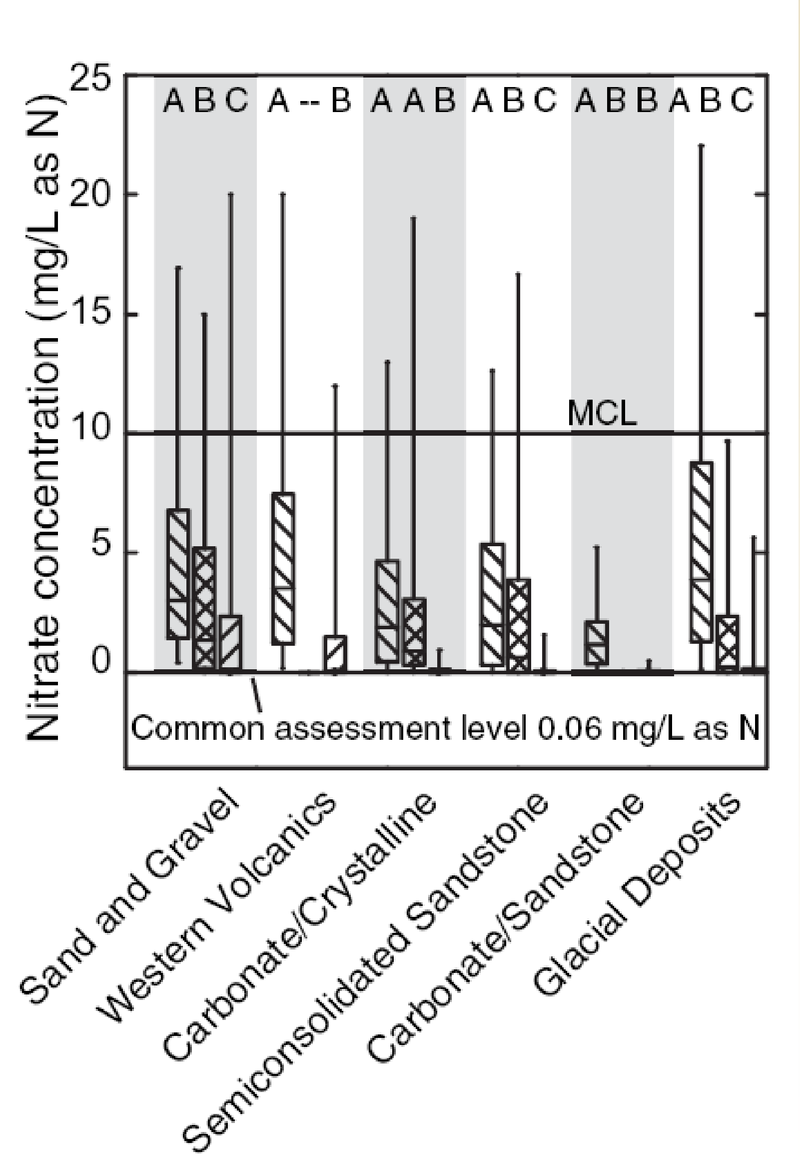
First National Map of Redox Conditions

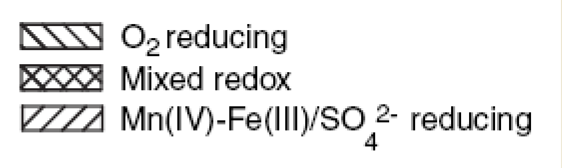


[redacted]

(McMahon and Chapelle, 2007)

Consistent with previous studies, nitrate concentrations were lower under more reducing conditions

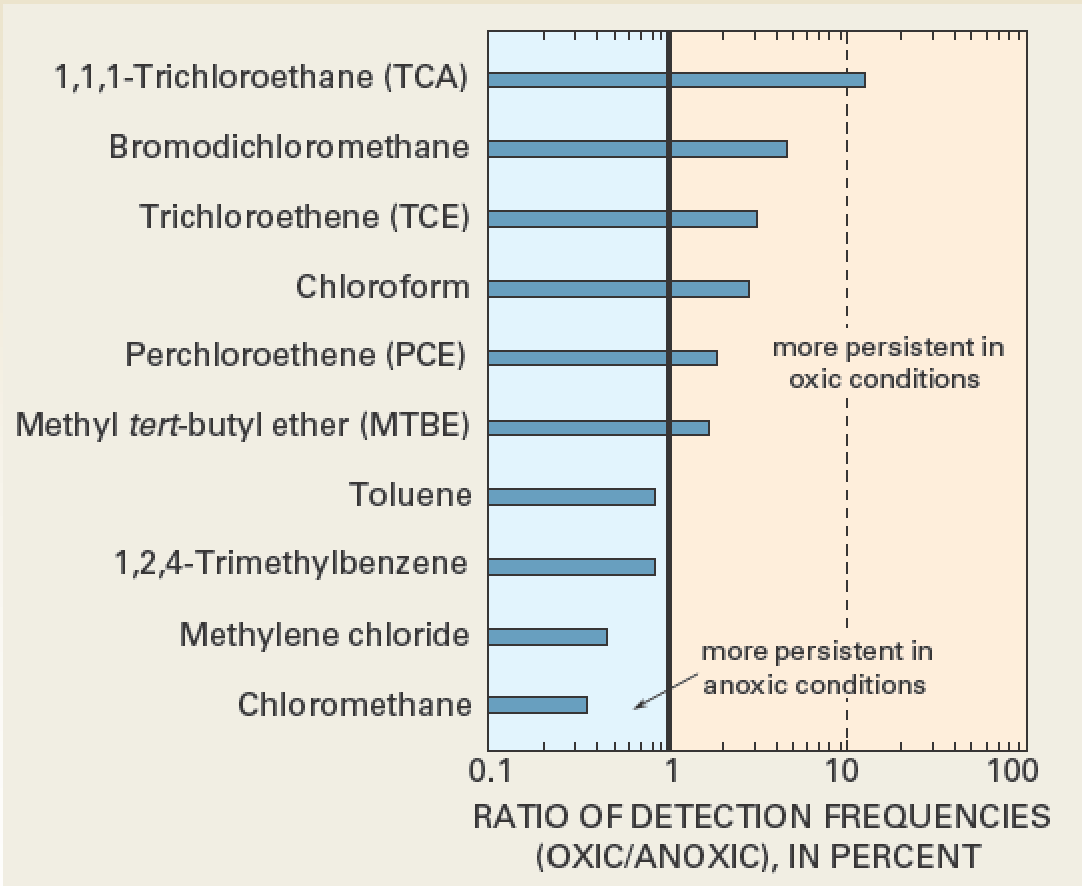




[redacted]

(McMahon and Chapelle, 2007)

Consistent with laboratory studies, the more heavily chlorinated (oxidized) VOCs were detected more frequently in oxic than in anoxic ground waters

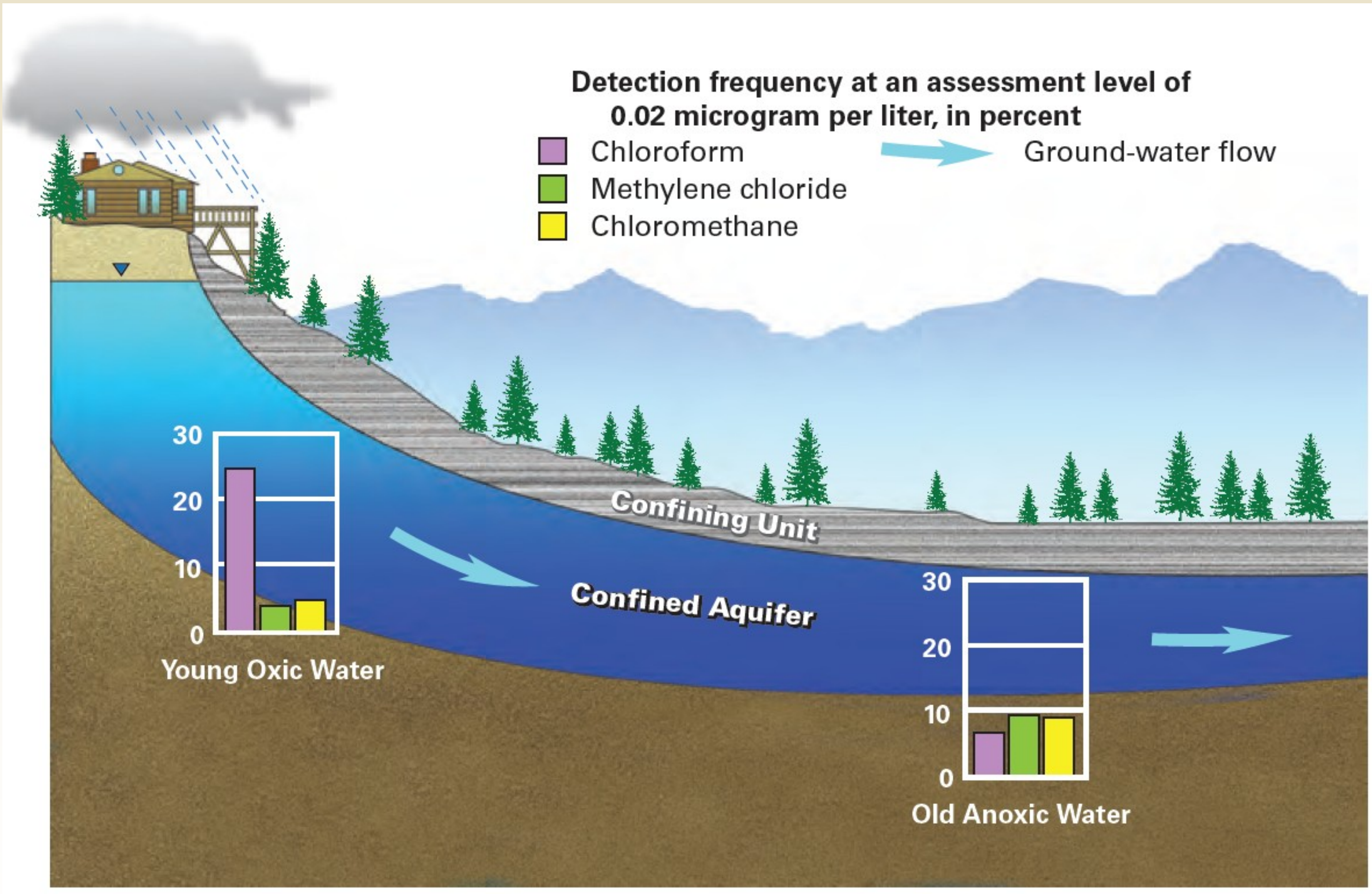


[redacted]

(Zogorski and others, 2006)

Scaling up from the Laboratory to the Field

Dechlorination of Chloroform With Onset of Anoxic Conditions



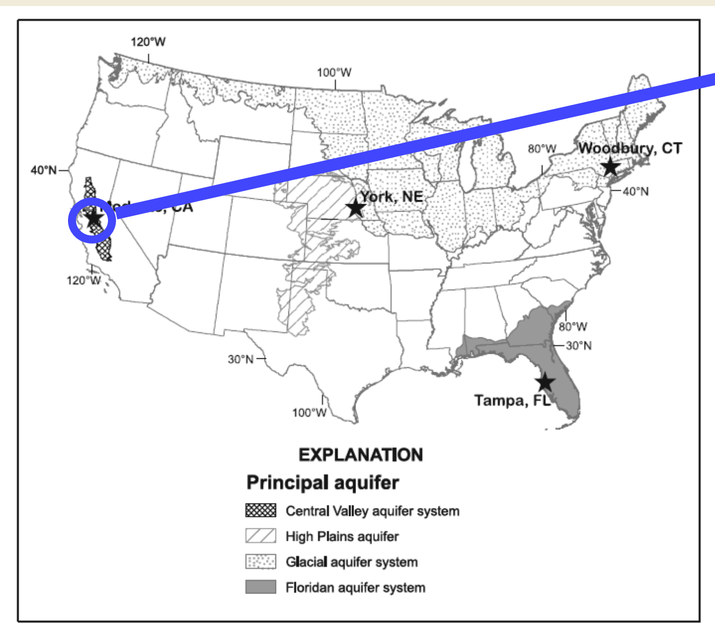
[redacted]

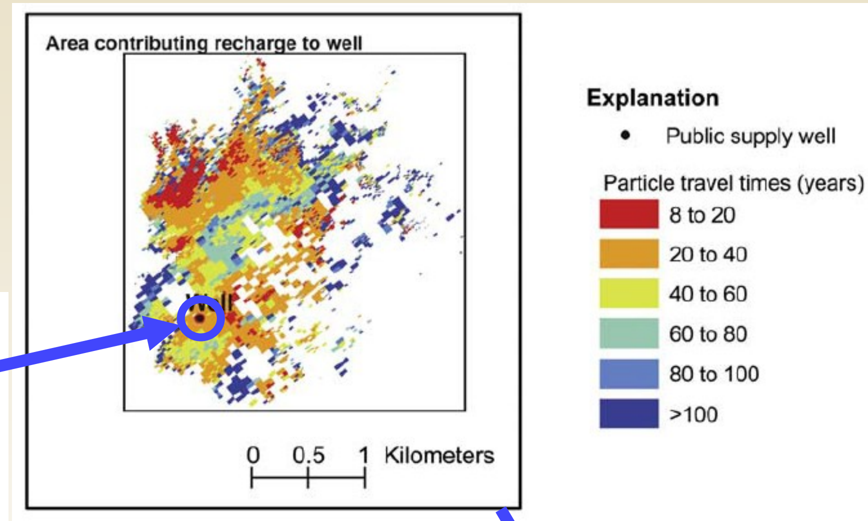
(Zogorski and others, 2006)

Prediction of Contaminant Occurrence in Ground Water

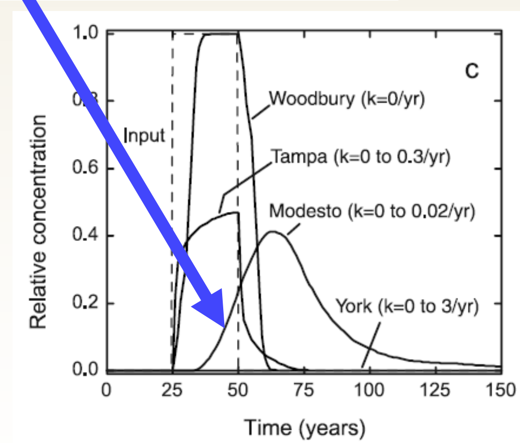
Solute Transport-and-Fate Simulations

(Burow and others, 2008; McMahon and others, 2008)





Modeled Age Distribution

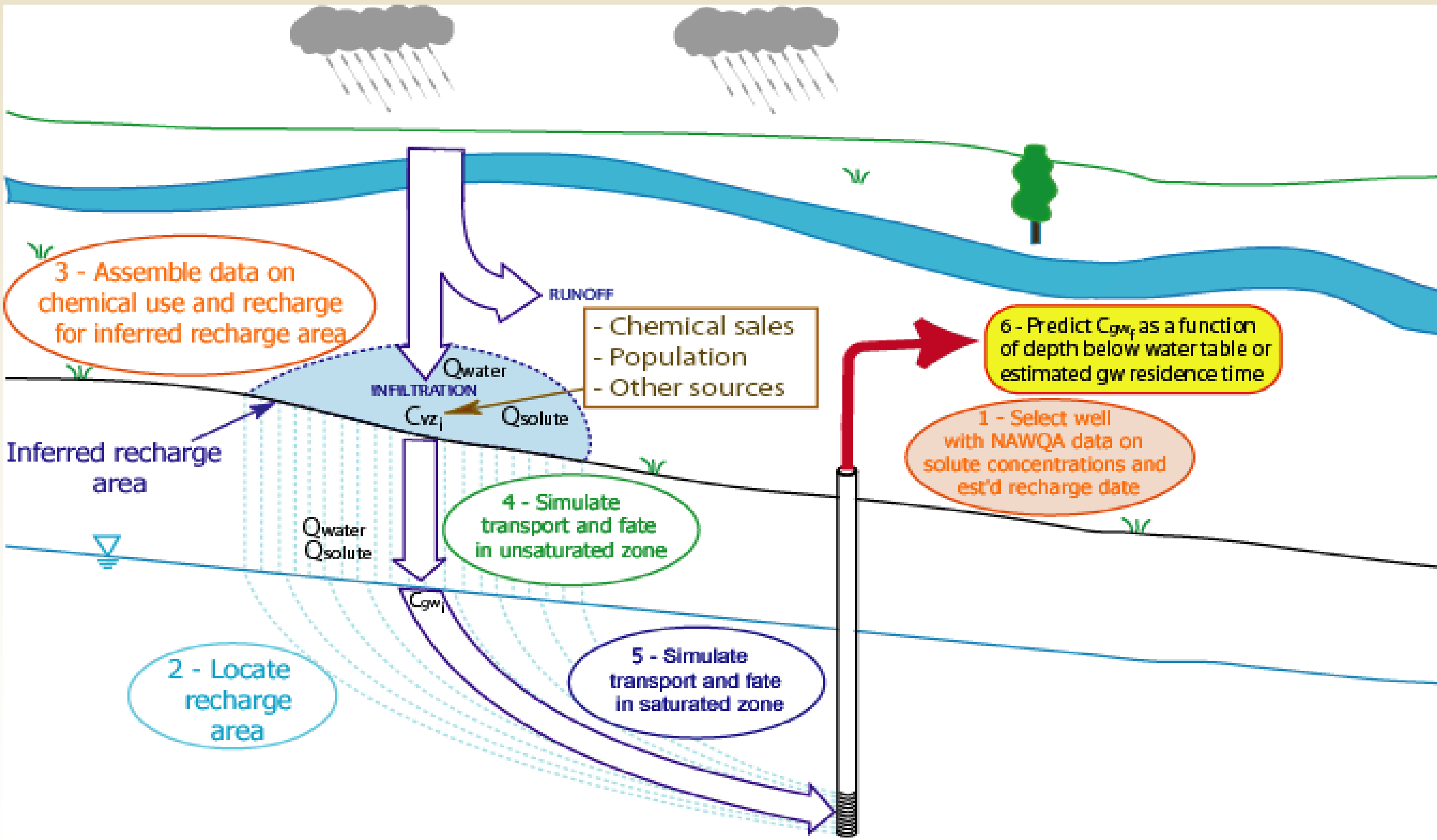


Predicted nitrate concentrations over time

[redacted]

Putting It All Together

Proposed System for Predicting Ground-Water Vulnerability to Surface-Derived Contamination Across the United States

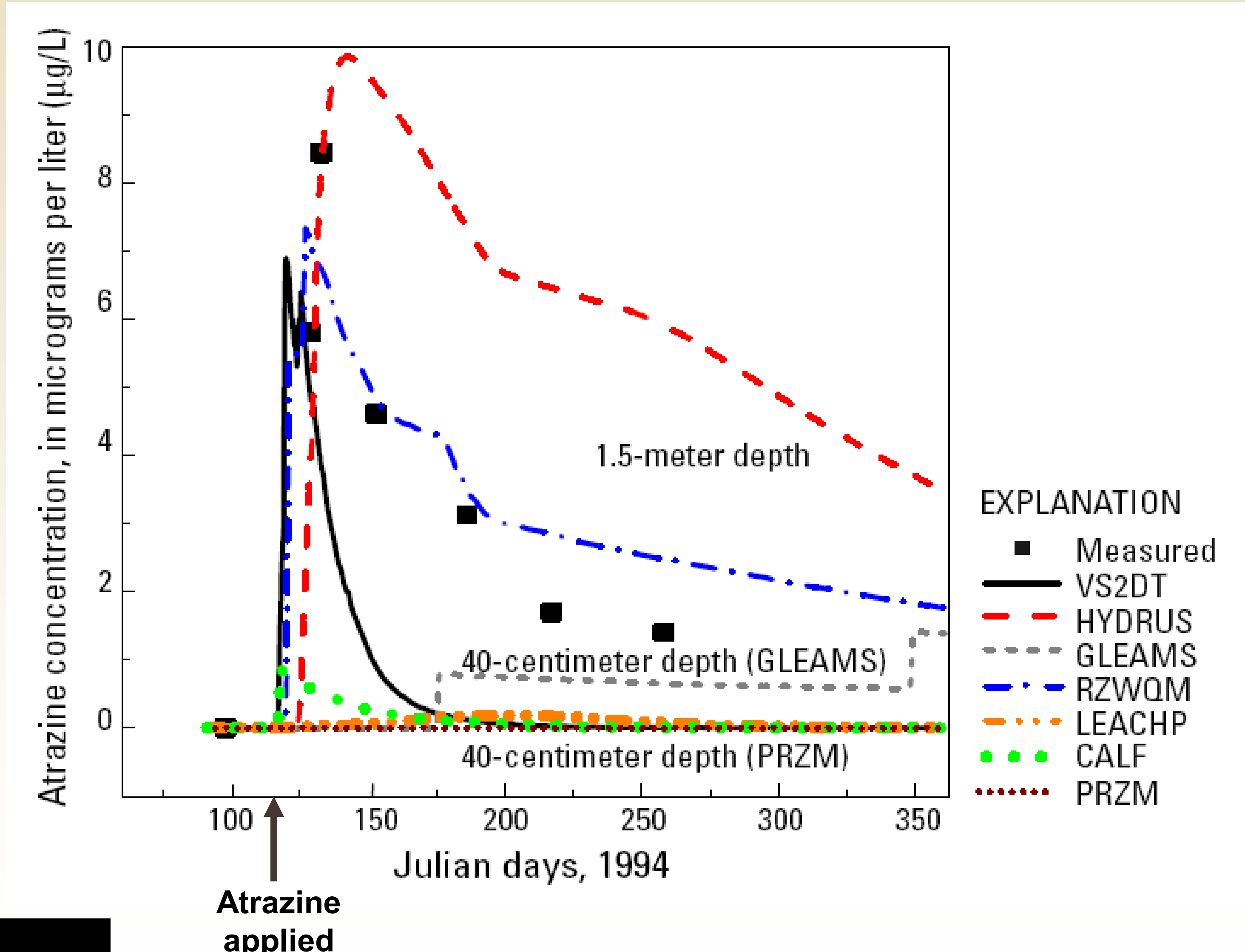


[redacted]

(Barbash, 2006)

Comparisons of Vadose-Zone Model Predictions Against Field Observations

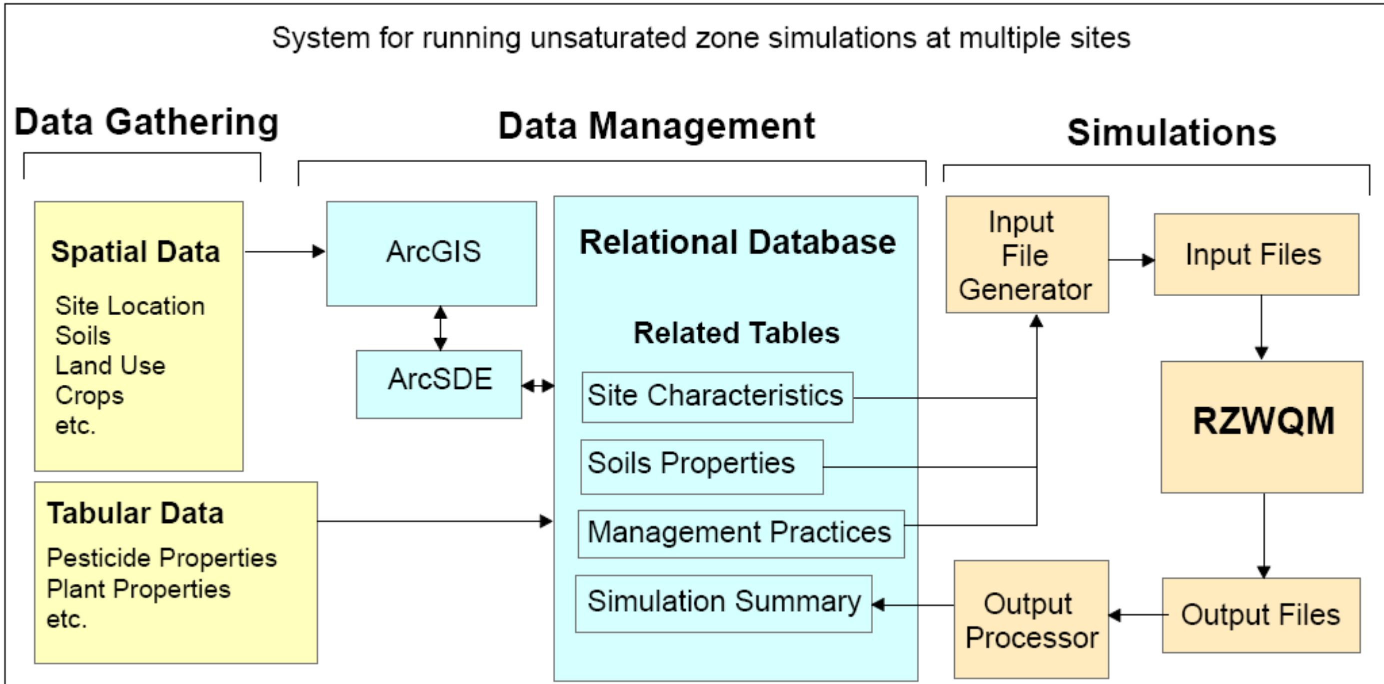
(White River Basin, Indiana – Uncalibrated simulations)



[redacted]

(Nolan and others, 2005)

Use of GIS-Linked Modeling to Predict Ground-Water Vulnerability to Surface-Derived Contamination Across the United States



National Scale datasets collected

Spatial data imported into a GIS (ArcGIS)

Tabular data imported into tables in relational database (SQL Server)

Spatial data stored in ArcGIS geodatabases

Spatial data processed using Tools in Arc Toolbox

Data transferred between ArcGIS and relational database using ArcSDE software

Microsoft's SQL Server 2005 selected for relational database

SQL statements used to manage data and generate model input data

Combination of SQL statements and C#.NET programs used to create input files for model and to summarize simulation results

Root Zone Water Quality Model (RZWQM) used to simulate pesticide leaching through the unsaturated zone at a site

Contact information:
Frank Voss, US Geological Survey, 934 Broadway, Suite 300, Tacoma, WA 98402, phone (253) 552-1689 email fdvoss@usgs.gov
Jack Barbash, US Geological Survey, 934 Broadway, Suite 300, Tacoma, WA 98402, phone (253) 552-1610 email jbarbash@usgs.gov

[redacted]

New Contributions to Ground-Water Science from the NAWQA Program

- **Nationwide summaries of existing information**
- **Nationwide study design → Occurrence → Prediction**
- **Investigation of previously un(der)examined contaminants**
- **Nationwide investigation of trends**
- **Nationwide study of factors and processes controlling sources, transport and fate of contaminants (e.g., redox conditions)**
- **Use of solute transport-and-fate models to predict ground-water quality in multiple settings around the Nation**

[redacted]

Vat's Next?

- **Continued investigation of trends in ground-water quality**
- **Increased emphasis on the use of solute transport-and-fate models to:**
  - **Predict ground-water trends**
  - **Predict ground-water vulnerability to contamination**
- **Examination of other previously un(der)examined sources, such as:**
  - **Confined animal feeding operations (CAFOs)**
  - **Road salt**
  - **Septic systems**
- **Examination of other previously un(der)examined contaminants, such as:**
  - **Pharmaceuticals**
  - **Personal care products**
  - **Additional pesticides and degradates**
  - **Pesticide adjuvants ("inert" ingredients)**

[redacted]