Chlorpyrifos 2016 Refined Drinking Water Assessment

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Outline

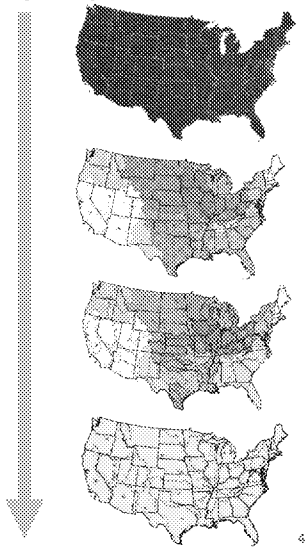
- Background
  - Drinking Water Assessment Framework
  - Conceptual Exposure Model
  - Assessment Tools

- Chlorpyrifos Drinking Water Assessment
  - **One of, if not the most highly refined drinking water assessment completed for surface water**

Background

Drinking Water Assessment Framework

- Tiered approach is used to prioritize resources
  - Low tiers are easy to use, simple input and output
  - High tiers require more input, more complex and detailed output
- Upper bound estimate of exposure
  - If level of concern is not exceeded using screening exposure estimate, high confidence of low risk
  - If level of concern is exceeded, there could be risk, or it may be the result of overestimating exposure – refinements considered



Assessment Tools

Monitoring Data

- Direct **measure**
- **Actual** pesticide use for specific site
- Often limited in time
- Often available for many sites with varying vulnerabilities
- Tends to underestimate frequency of occurrence and peak exposure

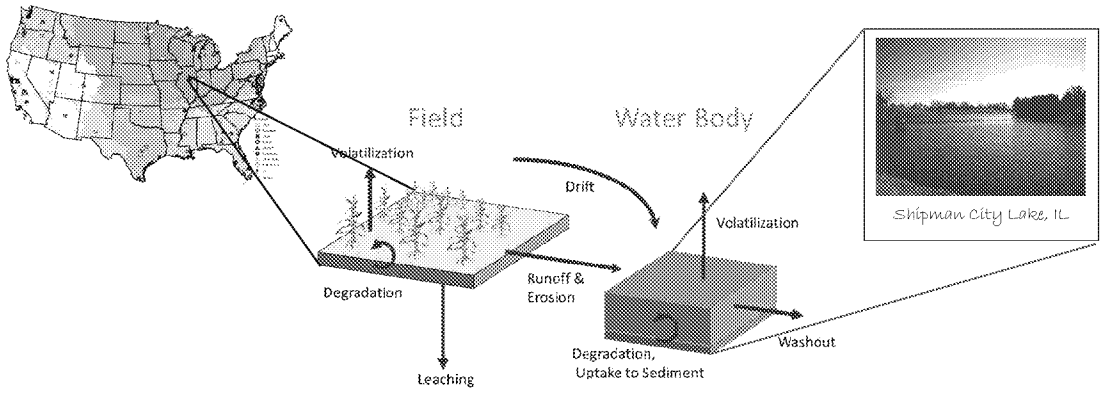
Modeling Data

- Direct **estimate**
- **Maximum** or **typical** pesticide use
- Simulations over long time
- Based on a few standard vulnerable sites
- Daily concentrations and inputs can be adjusted to be more or less conservative

Monitoring Data

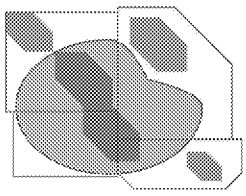
- Data sources include federal, state, academic, and other sources
- Monitoring data can elucidate what is happening under **current use** practices (not necessarily maximum label rates) and under **specific** conditions (may not be predictive of concentrations in other areas)
- All known monitoring data are considered in drinking water exposure assessments
  - Data are analyzed and characterized based on contextual information (*i.e.,* ancillary data) and the quality of the data varies tremendously
    - explain why some sites have greater exposures than others
    - year to year variability
    - extrapolate to sites where there are no data
- Generally monitoring data are NOT used quantitatively in risk assessments due to the challenges with interpreting the data from limited sampling (time and space); however, often it is used for characterization and to ground truth modeling estimates

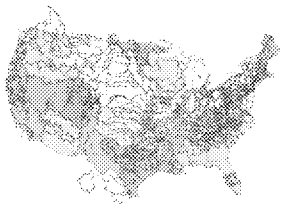
Drinking Water Conceptual Model for Pesticide Fate and Transport to Source Surface Water

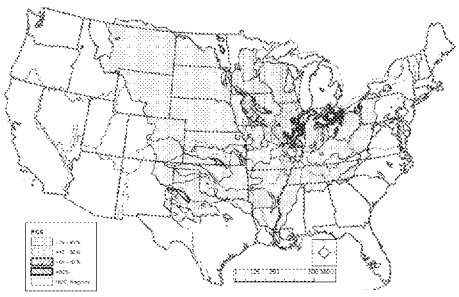


Drinking Water Intake Watersheds and Associated Community Water Systems Vulnerable to Pesticide Contamination

- Percent Cropped Area (PCA) is used in drinking water assessments to account for the fact that a watershed is not likely to be devoted entirely to agriculture
  - Derived from cropland data (NLCD) overlay with acres harvest data (NASS) and drinking water intake watersheds
  - Available for major crops (*e.g.*, corn, wheat, cotton) and crop groups (*e.g.*, orchards and vegetables)
  - **EXAMPLE:** 0.5 (PCA) x 6.66 µg/L (model concentration) = 3.33 µg/L (source water concentration)







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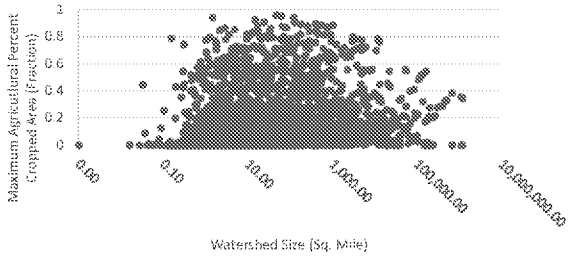
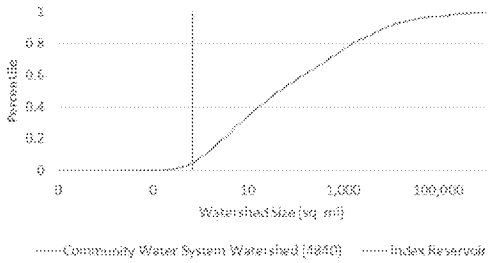
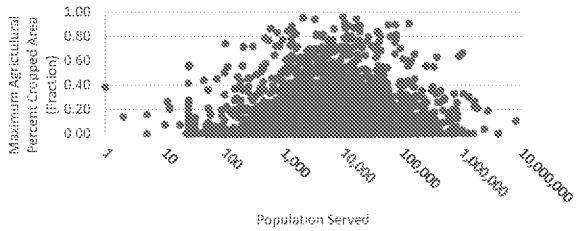
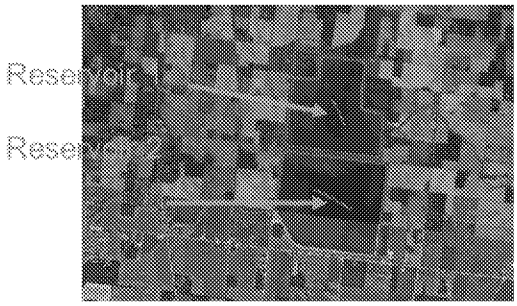




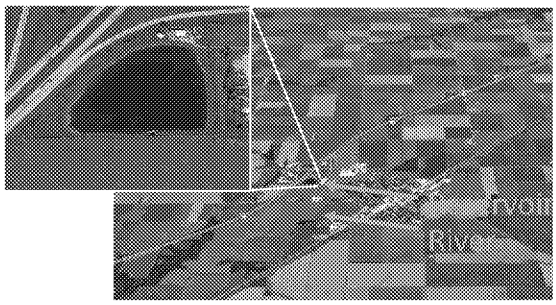


Drinking Water Intake Watersheds and Associated Community Water Systems Vulnerable to Pesticide Contamination

Example 1: "Large" system serving 74,750

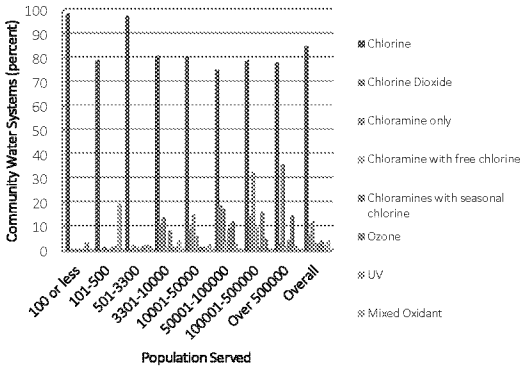


Example 2: "Small" system serving 462



Drinking Water Treatment

- Drinking water assessments consider treatment; however, there are challenges:
  - We do not typically get drinking water treatment data
  - Generally, drinking water treatment does not remove/transform pesticides – exceptions are organophosphates and carbamates which have been shown to covert to the corresponding oxon
- Treatment methods vary across the country and even within facilities.
  - Coagulation-flocculation, filtration and disinfection (chlorine) are the most prevalent treatment processes
  - Advanced treatment methods such as activated carbon are more common for systems serving larger populations



Statute and Implementation

- **FFDCA § 408(b)(2)(A)(ii)** requires EPA to assess "aggregate exposure to the pesticide chemical residue, including all anticipated dietary exposures and all other exposures for which there is reliable information"
  - Dietary exposures include exposures in food and in drinking water
- EPA developed the concept of "risk cup" to facilitate risk refinement when considering aggregate human health risk to a pesticide
  - **Drinking Water Level of Comparison (DWLoC)** approach is used to calculate the amount of exposure which could occur without exceeding the risk level of concern (*i.e.*, the available space in the total aggregate risk cup for exposures to residues in drinking water after accounting for exposures from residues in food and from residential uses)

Chlorpyrifos

Drinking Water Assessment

Summary of Refinements

- Highly refined assessment (tier III+)

  - ✓ Labeled use clarification
  - ✓ Evaluated volatility and spray drift
  - ✓ Summarized the effects of drinking water treatment
  - ✓ Used community drinking water intake watershed percent cropped area adjustment factors for 18 HUC-02 regions

  - ✓ Simulated additional chlorpyrifos use scenarios to evaluate typical use practices
  - ✓ Completed model input sensitivity analysis
  - ✓ Used representative and spatially relevant scenarios

  - ✓ Expanded aquatic modeling approach to encompass use of spatial relevant model (*i.e.*, WARP)
  - ✓ Analyzed all available monitoring data for chlorpyrifos and chlorpyrifos-oxon, developed sampling bias factors (SEAWAVE-QEX)
  - ✓ Compared aquatic modeling and monitoring data (site-specific analysis)

  Many additional analysis have been completed that are not specifically illustrated in the 2016 drinking water assessment but the data are included

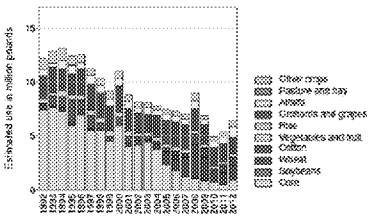
History

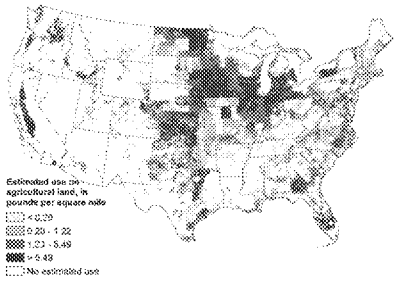
- Previous drinking water assessments
  - Preliminary Drinking Water Assessment (June 30, 2011) – National (**Tier 2**)
  - Updated Drinking Water Assessment (December 23, 2014) – Regional Community Water System Assessment (**Tier 2-3**)
  - Chlorpyrifos Refined Drinking Water Assessment for Registration Review (April 14, 2016) – Highly Refined Assessment (**Tier 2-3+**)
    - ➢ **One of, if not the most highly refined drinking water assessment completed for surface water**

Use and Usage

- Master use summary (label clarification)
  - Single max rates ≤ 4 lb a.i./A except for 6 lb a.i./A is permitted on citrus (limited California counties)
  - Aerial application rates ≤ 2.3 lb a.i./A (Asian citrus psyllid) others ≤ 2.3 lb a.i./A
  - maximum annual rate ≤ 14.5 lb a.i./A/yr (tart cherries)

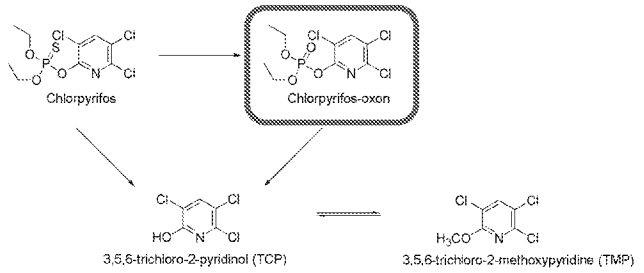
- Agricultural (7.2 million lb/yr) and non-agricultural use sites (no usage data)
  - Highest amount (yearly total) of chlorpyrifos applied to corn and soybean (1.5 million each per year)
  - Large fraction (>40%) of apples, asparagus, broccoli, onions, and walnuts
  - Typical use: single applications at maximum rate likely to occur; however, the number of applications over the course of a year are generally less than what is allowed on the label.





Fate and Transport

- Chlorpyrifos is persistent for several months in the environment and considered slightly mobile
  - aerobic soil and aerobic aquatic metabolism are the primary routes of transformation; volatilization can be significant under some conditions
  - spray drift and runoff (generally by soil erosion rather than dissolution in runoff water of parent chlorpyrifos; drinking water treatment transformation to oxon
- Chlorpyrifos is readily converted to the oxon in the presence of free chlorine but not chloramines



Treatment Method	[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]		[illegible]
	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 12
Permit Restriction	90.3	85.7	8.7	9.2	34.3	27.5	15.3	5.2	14.5	1.9	7.6	3.1	60.9	30.3	100.0
System Population Capacity	Percentage of Plants Performing Each Treatment Practice for Surface Water[1]														
100 or less	98.4		0		0		1.6		3.1		-	-	0		0
101-500	79		1.2		0		9.2		1.7		-	-	1.4		2.5
501-3,300	97.4		2.2		0		7.8		2.2		-	-	1.5		3.4
3,301-10,000	80.8		13.7		11		24.7		1.4		-	-	1.4		19.2
10,001-50,000	80.5		14.8		8.7		32.9		1.3		-	-	1.2		16.9
50,001-100,000	75.1		17.1		18.5		26.8		2.6		-	-	11.8		5.2
100,001-500,000	78.9		32.4		14		26.3		4.7		-	-	15.8		11.8
Over 500,000	78.0		35.6		2.5		21.2		1.7		-	-	14.4		21.2

1. Experience at time was representative of typical drinking water treatment conditions
2. Chamberlain E, Bai R, Huang Y, Wu Y, Palmer A, Adams C / Amer. Chem. Chem. 2012 50, 354-363
3. U.S. EPA Office of Water 2006 Community Water System Survey May 2006 Survey Data

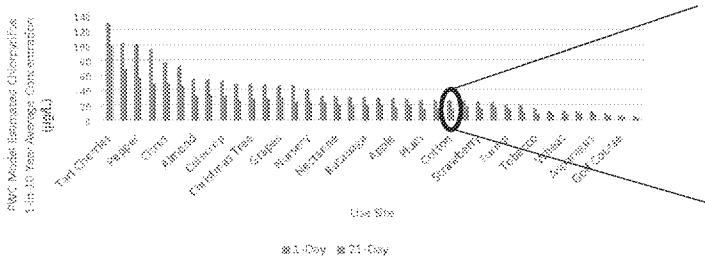
Chlorine (Cl2): chlorine dioxide (ClO2); chloramines (NH4); lime/soda ash softener (treatment feeds, mainly to hydrolyze of pH 12); bioactive C (pH 12); Potassium permanganate (KMnO4)

Drinking Water Exposure Summary

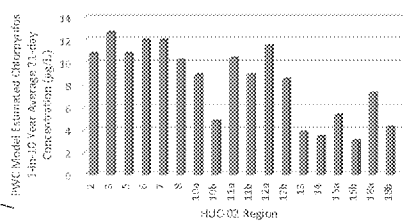
- Acetyl cholinesterase (AChE) inhibition reaches steady state at or around 2-3 weeks of exposure; therefore, the critical exposure duration for risk assessment is 21-days
- Current label (master use summary) and typical rates
  - Current label rates (agricultural): 6.2 – 129 µg/L (1-day), 3.1 – 83.8 µg/L (21-day)
- Estimates for some urban uses are higher (uses were not combined)
- Model input (*e.g.*, fate and dates) and output (*i.e.*, PCA, exceedance counts) sensitivity analysis
- Extensive monitoring data analysis

Drinking Water Exposure Summary

Current label rates (agricultural)
6.2 – 129 µg/L (1-day), 3.1 – 83.8 µg/L (21-day)

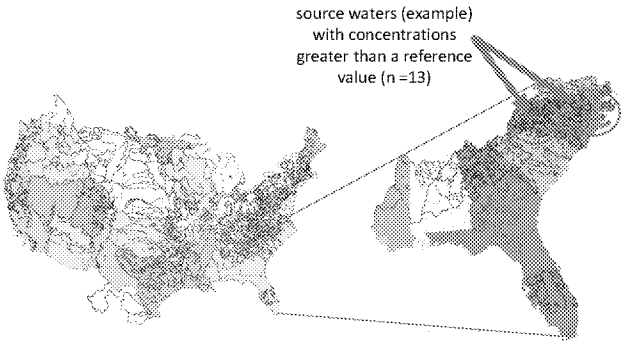


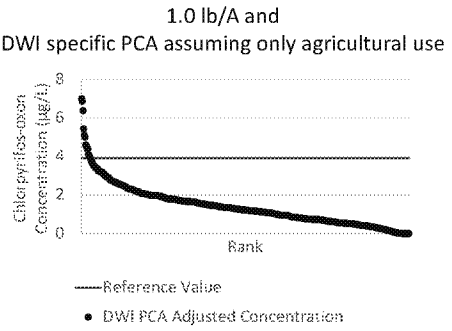
Typical label rates (1.0 lb/A) and
regional PCAs assuming only agricultural use



time series data provided to HED for direct use in dietary risk assessment

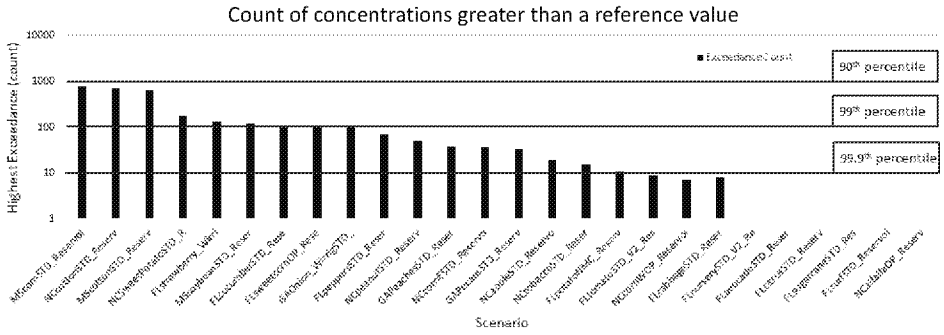
Drinking Water Exposure Characterization





Example from December 23, 2014 DWA; data in 2016 DWA permits the same spatial resolution

Drinking Water Exposure Characterization



Example from December 23, 2014 DWA; times series data in 2016 DWA permits same analysis

Monitoring Data Analysis

Comprehensive/refined monitoring data analysis

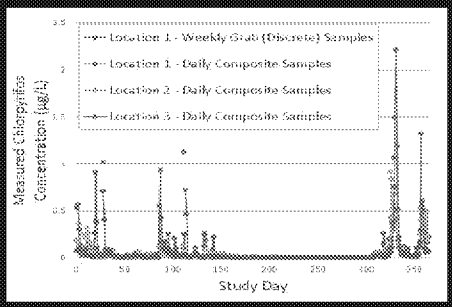
- 16 programs/databases spanning 1992-2016
- 14.7 µg/L (unfiltered water), 5.61 µg/L (dissolved/filtered water)

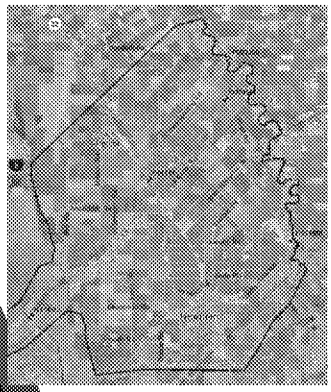
Sampling bias factors (addresses uncertainty with non-daily sample frequency – 10x for 21-day average for 7-28 day sampling intervals)

- 30 sites; USGS stream quality index, registrant monitoring program (flowing systems)

Site-Specific Monitoring Analysis

- Model simulations parametrized to reflect use result in estimated concentration (1.1-2.7 µg/L) comparable to measured concentrations (0.9-2.2 µg/L)





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Represented Location	Represented Crop Use	Estimated Drinking Water Concentration µg/L (PCA adjusted concentration)			Maximum Detected Chlorpyrifos Concentration (associated use)
		1-in-10 Year Peak	1-in-10 Year Annual Average	30 Year Average	
1	Walnut	13.4 (2.68)	2.35 (0.47)	1.73 (0.35)	1.32 µg/L (walnut, spray drift) April 22, 1997 (day 357)
2	Alfalfa	5.66-12.9 (1.13-2.58)	0.69-1.56 (0.14-0.31)	0.61-1.39 (0.12-0.28)	0.92 µg/L (alfalfa, spray drift) March 22, 1997 (day 325)
3					2.22 µg/L (alfalfa, flood irrigation) March 28, 1997 (day 331)

Drinking Water Assessment Conclusions

The concentrations of chlorpyrifos and chlorpyrifos-oxon in drinking water are expected to vary (in time and space) across the country with the highest potential for exposure in high use areas in vulnerable (*i.e.*, runoff prone) watersheds, and is highly dependent on drinking water treatment processes.

Use of sampling bias factor adjusted measured concentrations of chlorpyrifos (and chlorpyrifos-oxon) or the use of model estimated concentrations of chlorpyrifos and chlorpyrifos-oxon as an estimated upper bound exposure is expected to result in similar dietary risk assessment conclusions.

Summary of Refinements

- Highly refined assessment (tier III+)

  - ✓ Labeled use clarification
  - ✓ Evaluated volatility and spray drift
  - ✓ Summarized the effects of drinking water treatment
  - ✓ Used community drinking water intake watershed percent cropped area adjustment factors for 18 HUC-02 regions

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Extra Slides

Drinking Water Exposure Summary

Treatment Method[1]	FC		MCA		ClO_2		MnO_4^-		UV		H_2O_2		O_3		Softening
	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 6.6	pH 8.6	pH 12
Percent Reduction[2]	90.3	85.7	8.7	9.2	34.3	27.5	15.3	5.2	14.5	1.9	7.6	3.1	60.9	30.3	100.0
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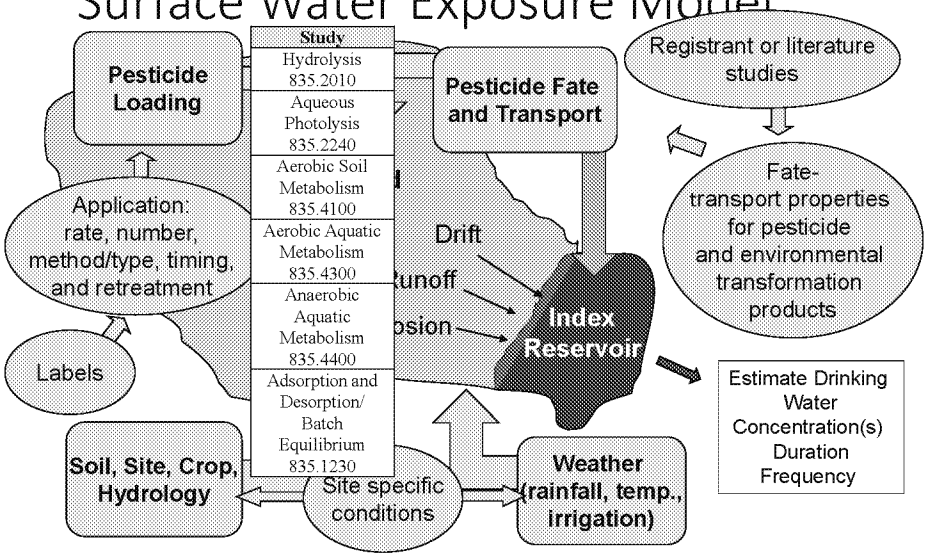
3. U.S. EPA Office of Water 2006 Community Water System Survey, May 2009 (survey data)

Chlorine (FC); Chlorine dioxide (ClO_2); Chloramines (MCA); Lime/soda ash softener (assumed to be similar to hydrolysis at pH 12); Ultraviolet light (UV); Ozone (O_3); Potassium permanganate (MnO_4^-)

Surface Water Exposure Model



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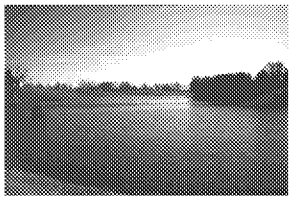
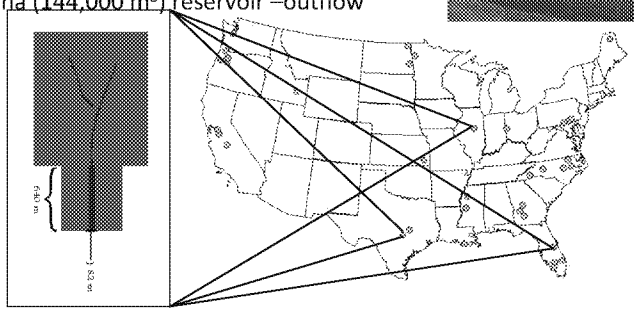
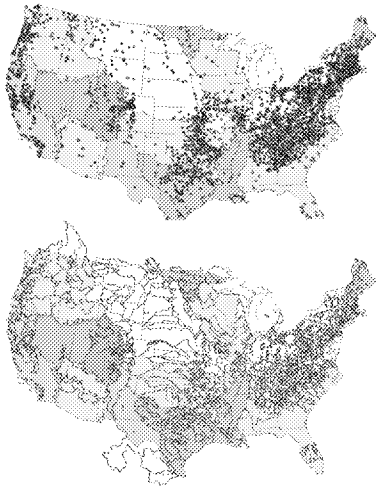
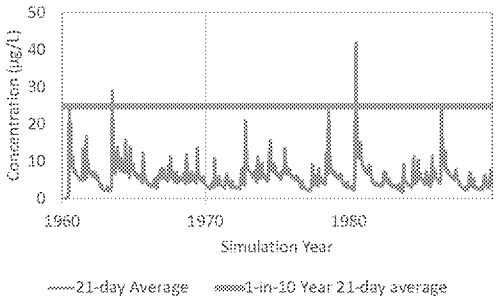
Index Reservoir and Scenarios

- Based on small mid-western reservoir (Shipman City Lake, IL) with an agricultural watershed
  - 172.8 ha (427 a) watershed;
  - 5.3 ha (144,000 m^3) reservoir –outflow







Example of 21-day Time Series Concentrations Used for Pesticide Drinking Water Assessments

- recurrence interval, set by USEPA policy, of 10, meaning once every 10 years
- highest 1-in-10-year 21-day average is compared to the DWLoC; time series data input in PBPK by HED)