Assessment of Trends in Concentrations and Loads of Pesticides in Urban Streams of the Western United States

By

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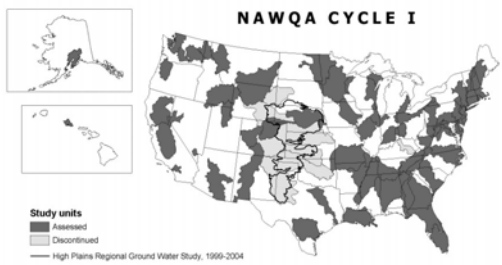
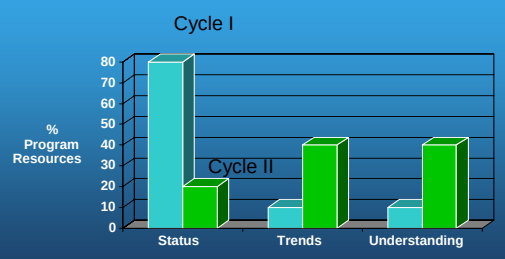
Data Collected by NAWQA

- USGS National Water Quality Assessment (NAWQA) Program started data collection in early to mid-90's
- Initially water quality data were collected during routine and storm event conditions
- Arcade Creek became a long-term trends site after 2000
- No systematic study of trends at these sites until recently



Changes in Resource Allocation -- Initial Implementation Plans



Study Units for Cycle II

Trend Themes (10% ➡ 40%)

- **Trends and changes in status --** What are the trends and changes in the status of water quality since the NAWQA cycle I status assessment and before?
- **Effects of urbanization --** What are the effects of urbanization on the quality of streams and ground water?
- **Response to agricultural management practices** -- How has water quality changed in response to changes in agricultural practices, such as tillage methods, chemical use, and crop patterns?

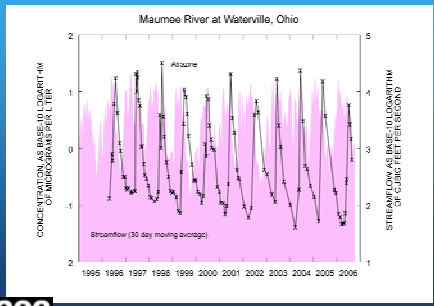
Major River Pesticides Project

- NAWQA is funding studies at the regional scale
  - This is called the Major River Basins Assessment

Funding was provided to assess trends in California, Washington, Oregon, and Idaho using existing data (1991-2005)

Sites include agricultural, urban, and integrator (large river basin)

Example, Atrazine at Maumee River, Ohio



Approaches to trend assessment

- Non-parametric methods are limited because of the high proportion of censored (non-detects) data
- Parametric models work well for nutrients, major ions, dissolved organic carbon, but may be problematic for compounds with seasonal inputs
- A parametric regression model was developed by the NAWQA Pesticide Synthesis Group to address the seasonality in use patterns

Model development, continued

- NAWQA Pesticide Synthesis Group tested the model (Wave Model) with three herbicides and two insecticides at three streams, including Arcade Creek
- Currently, this model is being used to assess trends in concentrations and loads at Arcade Creek and other urban streams in California, Oregon, and Washington, as well as agricultural and integrator (large river) sites.

The Wave Model

Depends on:

- Application Date
- Application Rate
- Half-life of Degradation

Model Equation

$$\frac{d}{d}W(t) = \lambda(t) - \phi W(t)$$

$$\lambda(t) = \sum_{k-1}^{12} \omega_k I\left(\frac{k-1}{12} \le t < \frac{k}{12}\right)$$

$$[-0.5 \le t \le 0.5]$$

Where;

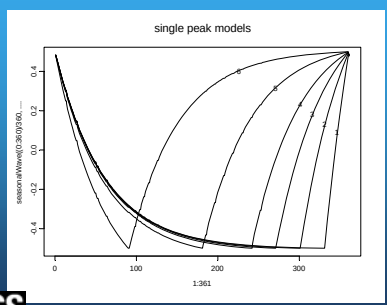
- W(t) = the total amount (kilograms) of a particular pesticide in the basin at time *t*
- $\lambda(t)$ = is an instantaneous input function,
- ω_k = is the instantaneous input rate (kilograms per year) for the approximately one-month interval beginning at time *(k-1)/12*
- ϕ = is the half-life (1-4) which controls the rate at which the pesticide is removed.
- I(.) = is the indicator function with I(.)=1 if t lies in the given interval and I(.)=0 otherwise.

Model Coefficient Choices

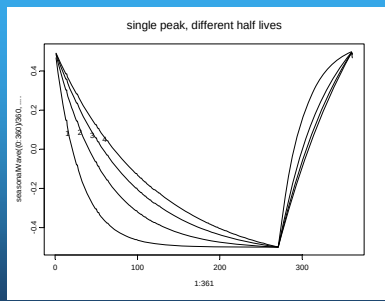
Model	ϕ half-life	ω	ω2	ω3	ω4	ω5	ω6	ω7	ω8	ω9	ω10	ω11	ω12
1	1,2,3,4	0	0	0	0	0	**1**	0	0	0	0	0	0
2	1,2,3,4	0	0	0	0	0	**1**	**1**	0	0	0	0	0
3	1,2,3,4	0	0	0	0	0	**1**	**1**	**1**	0	0	0	0
4	1,2,3,4	0	0	0	0	0	**1**	**1**	**1**	**1**	0	0	0
5	1,2,3,4	0	0	0	0	**1**	**1**	**1**	**1**	**1**	0	0	0
6	1,2,3,4	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	**1**	0	0	0
7*	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	**1**	0	0	0
8	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	0	**1**	0	0
9	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	0	0	**1**	0
10	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	0	0	0	**1**
11	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0.75**	**0.75**	0	0	0
12	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	**0.75**	**0.75**	0	0
13	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	0	**0.75**	**0.75**	0
14	1,2,3,4	0	0	**1**	**1**	**1**	0	0	0	0	0	**0.75**	**0.75**

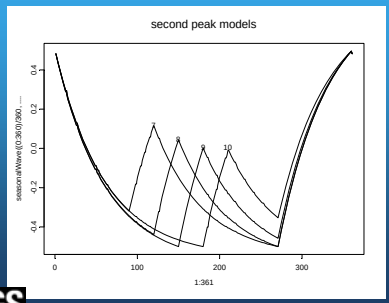
*In the 2 peak Wave model the primary peak application rate is always 3 months
** The secondary peak application rate is lower (0.75) but last for a longer time period (2 months)

Single Peak Models

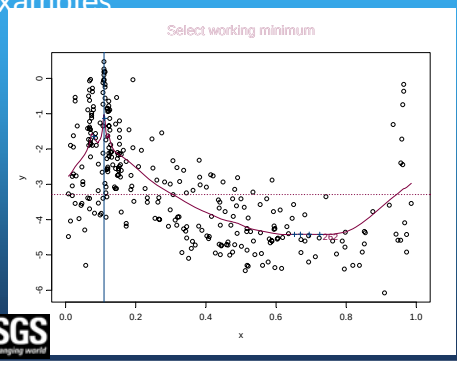


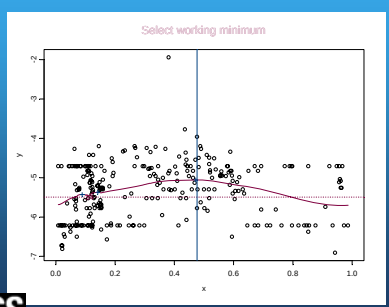
single peak, different half lives




second peak models
seasonalWave(0:360/360, ...
1:361

Examples


Select working minimum
y
x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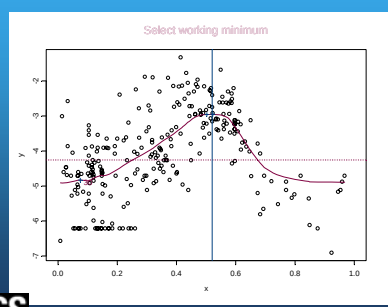
Select working minimum
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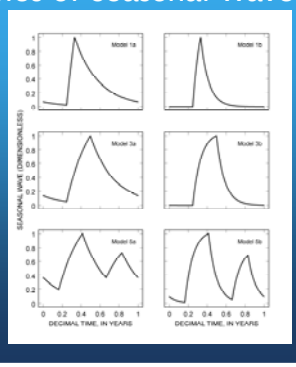
Examples of Seasonal Waves



Model Output

Loads

- Information provided in a Report including statistics (P-value) that can be used to evaluated model performs
- Residual plots
- Monthly load tables, including the monthly load as well as information to calculate Standard Error of Prediction (SEP%) to help evaluate how well did the model estimate loads for a pesticide

  SEP% < 30% model did a good job, 30% SEP%<50% questionable, and SEP%> 50% loads are not well estimated

Trends

- Expressed in the Dectime coefficient with a p-value and a signal, the trend slope will be calculated

Regression model for describing seasonality and possible long-term trends in pesticide concentrations

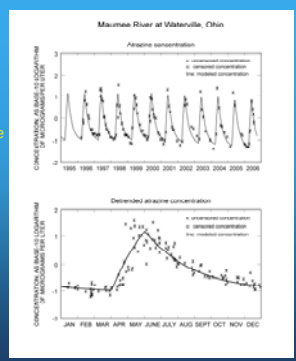
- $\text{Log}\{C(t)\} = \beta_0 + \beta_1[W(t)-0.5] + \beta_2\tau(t) + \varepsilon(t)$

$$\tau(t)=(t-t^*)\{I(t^*\le t\le t^*+D)\}+D\{I(t>t^*+D)\}$$

Data sets analyzed so far show that log-transformed concentrations are approximately linearly related to *W(t)—i.e. other processes have to be considered.*

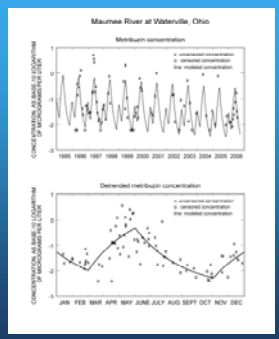
Example

Model describes 81% of the variability in concentration.



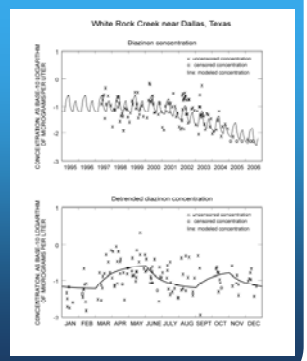
Example 2

- 59% of variability explained

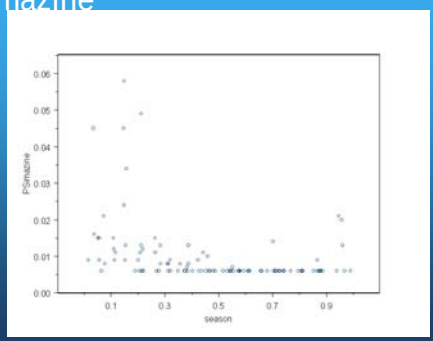


Example 3

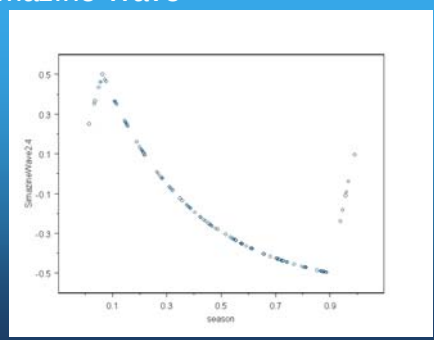
51% of variability in concentration explained. Note the double wave, suggesting two application "seasons".



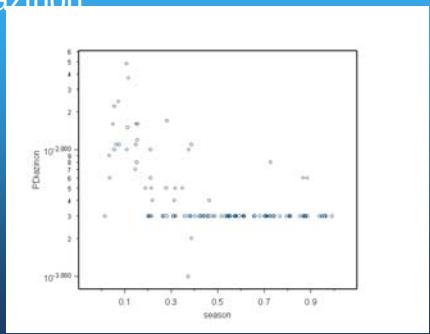
Sacramento River at Freeport, Simazine



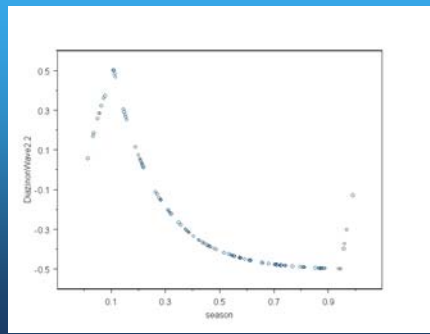
Sacramento River at Freeport, Simazine Wave



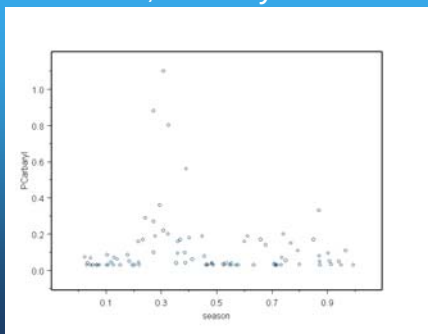
Sacramento River at Freeport, Diazinon



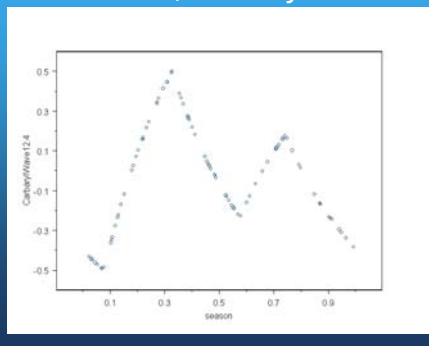
Sacramento River at Freeport, Diazinon Wave



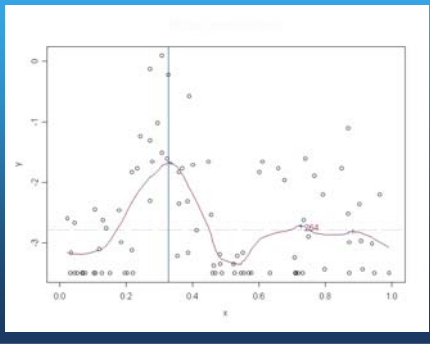
Arcade Creek, Carbaryl



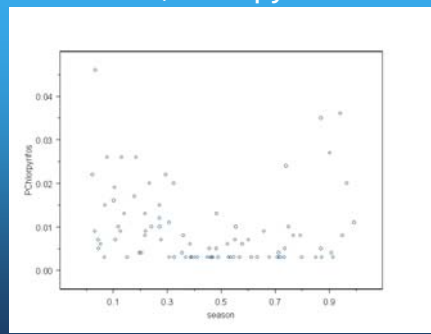
Arcade Creek, Carbaryl Wave



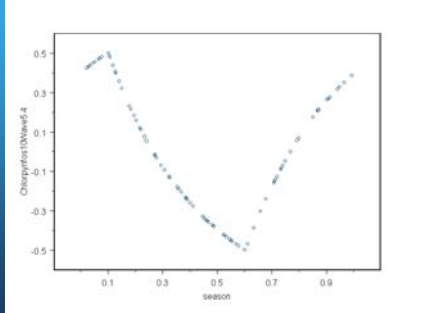
Arcade Creek, Carbaryl confirm plot



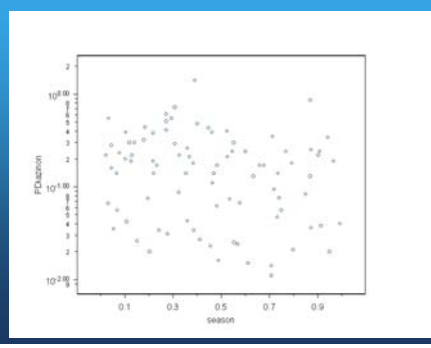
Arcade Creek, Chlorpyrifos



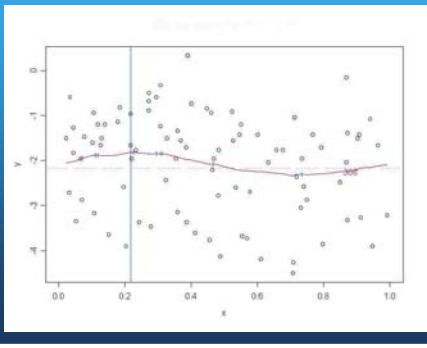
Chlorpyrifos Wave, Arcade Creek



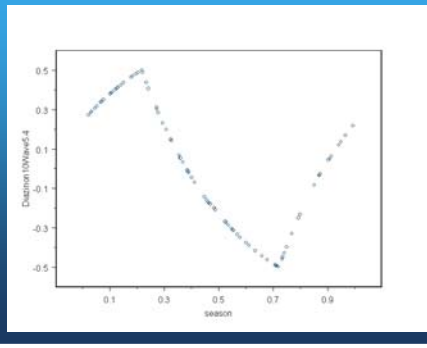
Arcade Creek, Diazinon



Arcade Creek Diazinon Confirm Plot



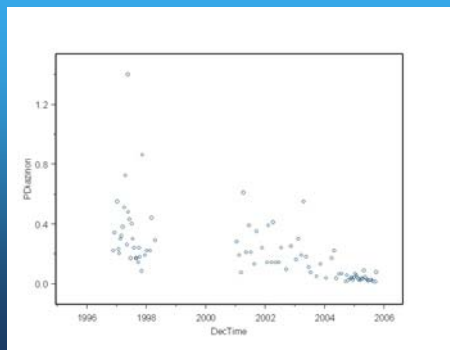
Arcade Creek Diazinon Wave

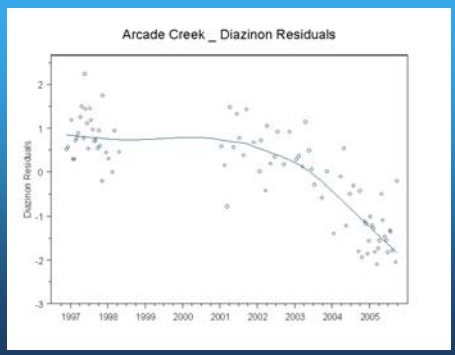


Arcade Creek

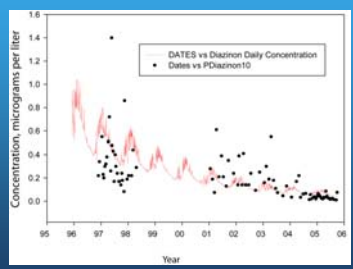
Pesticide Name	Time Period	nobs	ncens	df	t	start date	end date	central time	dectime coeff	Upper bound dectime coeff	Lower bound dectime coeff	dectime squared coeff	dectime std dev	dectime pvalue	midpoint date	FA Trend in concentration (mean % change/yr)
Chlorpyrifos	**1993-2005**	**88**	**38**	**14**	**1.993**	**11/26/96**	**09/28/05**	**2001.180**	**-0.117**	**-0.045**	**-0.188**		**0.036**	**0.00025**	**0.159**	**-11.001**
	1993-2005	30	8	3	2.052	11/26/96	04/23/98	1997.570	-0.098	0.852	-1.048		0.463	0.74070	0.052	-9.344
	2000-2005	58	30	8	2.009	01/17/01	09/28/05	2003.480	0.037	0.209	-0.136		0.086	0.61571	-0.070	3.732
Diazinon	**1993-2005**	**88**	**0**	**14**	**1.993**	**11/26/96**	**09/28/05**	**2001.180**	**-0.254**	**-0.203**	**-0.306**		**0.026**	**0.00000**	**0.159**	**-22.465**
	1993-2005	30	0	3	2.052	11/26/96	04/23/98	1997.570	-0.289	0.241	-0.820		0.259	0.19076	0.052	-25.114
	2000-2005	58	27	0	2.002	01/17/01	09/28/05	2003.480	-0.557	-0.432	-0.681		0.062	0.00000	-0.070	-42.696
Simazine	**1993-2005**	**88**	**26**	**14**	**1.993**	**11/26/96**	**09/28/05**	**2001.180**	**-0.023**	**0.060**	**-0.106**		**0.042**	**0.52580**	**0.159**	**-2.264**
	1993-2005	30	8	3	2.052	11/26/96	04/23/98	1997.570	-0.594	0.861	-2.049		0.709	0.32342	0.052	-44.801
	2000-2005	58	18	8	2.009	01/17/01	09/28/05	2003.480	0.133	0.306	-0.040		0.086	0.07814	-0.070	14.212

Arcade Creek: Diazinon Concentrations

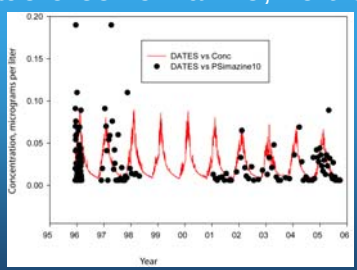




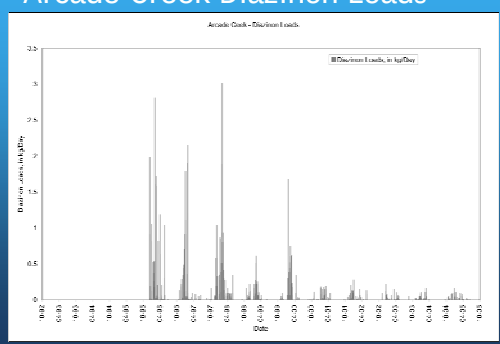
Diazinon Simulated concentrations



Arcade Creek Simazine, no trend



Arcade Creek Diazinon Loads



Summary

- Wave model simulates seasonal pulses of pesticides
- Model is simple to implement
- Works well with censored data sets
- Especially useful for modeling seasonal inputs

- Description of Wave model to be published in a forthcoming issue of AWRA (Vecchia, Martin, and Gilliom)