Trend Analysis on Chlorpyrifos Concentration in Surface Water of Central Valley, California

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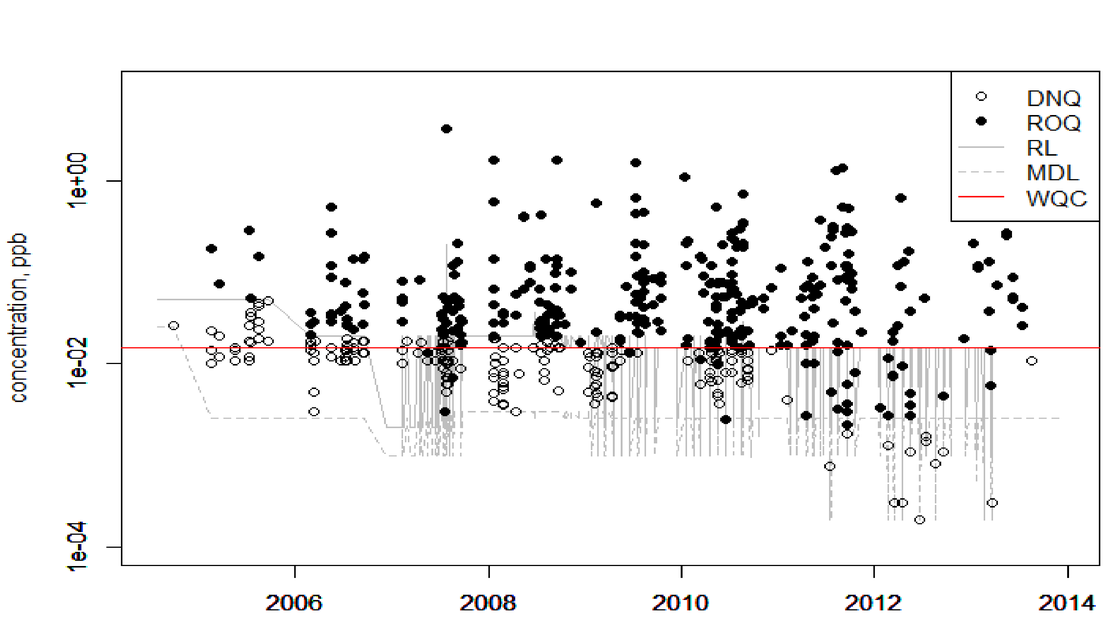
Abstract

The California Department of Pesticide Regulation placed agricultural use of chlorpyrifos in reevaluation in 2004 because monitoring data revealed that chlorpyrifos concentrations in Central Valley water bodies frequently exceeded water quality criteria. In support of the reevaluation, this study evaluated chlorpyrifos concentrations in surface water samples that were collected by Central Valley water quality coalitions from 2004-2013. The use of conventional trend analysis methods is not ideal for this dataset since concentrations of a large portion of the samples are below the analytical method's detection limit or reporting limit (i.e., censored data). The Nondetects And Data Analysis for environmental data (NADA) package designed specifically for censored data was used in this study. Our analysis identified a downward trend for this pesticide's annual application rate since 2005 and for its exceedance rate since 2008. We also observed a continuous downward trend in this pesticide's concentration level from 2010-2013. In addition, this study revealed that concentration levels and exceedance rates of chlorpyrifos appear to be influenced by application rates and winter storm events.

Challenges

- Changing detection limit (MDL) and reporting limit (RL) over time.
- 84% of samples have concentration less than their MDL, chlorpyrifos was not detected (ND); 6% of samples have concentration between their MDL and RL, chlorpyrifos was detected but not reliably quantifiable (DNQ); only 10% samples have concentration above their RL, chlorpyrifos was reliably quantified (ROQ). Conventional trend analysis methods can only include samples in ROQ or maybe DNQ, information contained in ND samples is unused.
- If MDL or RL is larger than the water quality criterion (WQC), one cannot tell whether an ND or DNQ sample indeed exceeds the WQC.

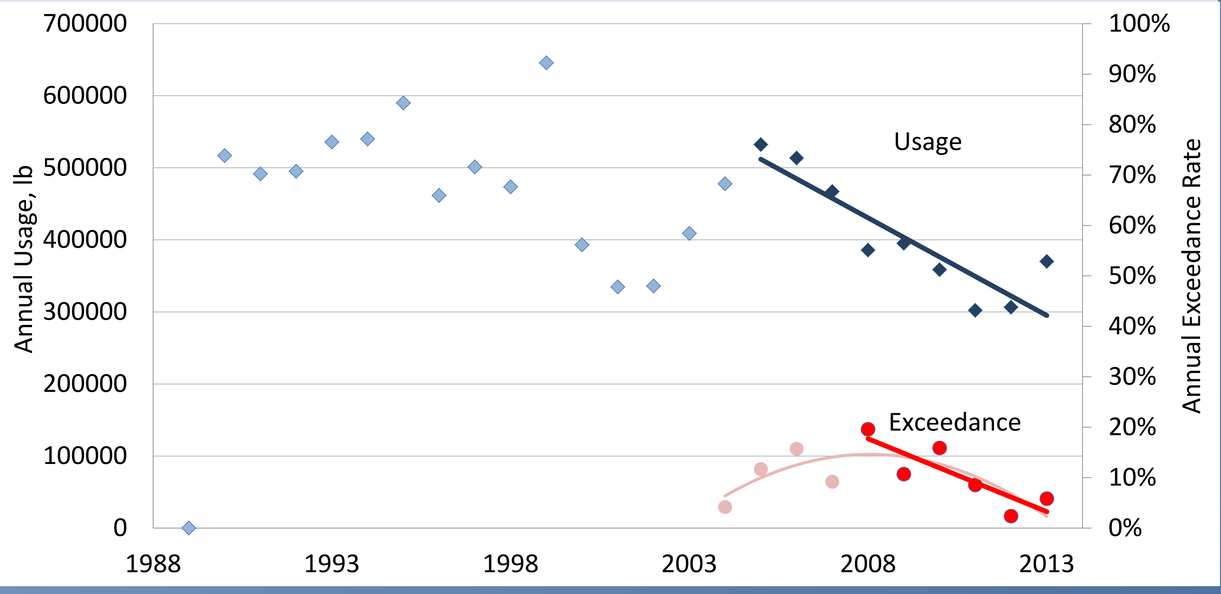


Methodology

- Calculate the exceedance rate with respect to WQC of 0.015 ppb: count both DNQ and ROQ samples; exclude 2004 data because their MDL>WQC.
- Use NADA package to "guess" the concentrations of the samples under censorship and then include all samples in data visualization and regression analysis iteratively.
- Evaluate seasonal patterns in chlorpyrifos concentration level: compare monthly exceedance rate to monthly use rate and storm season.

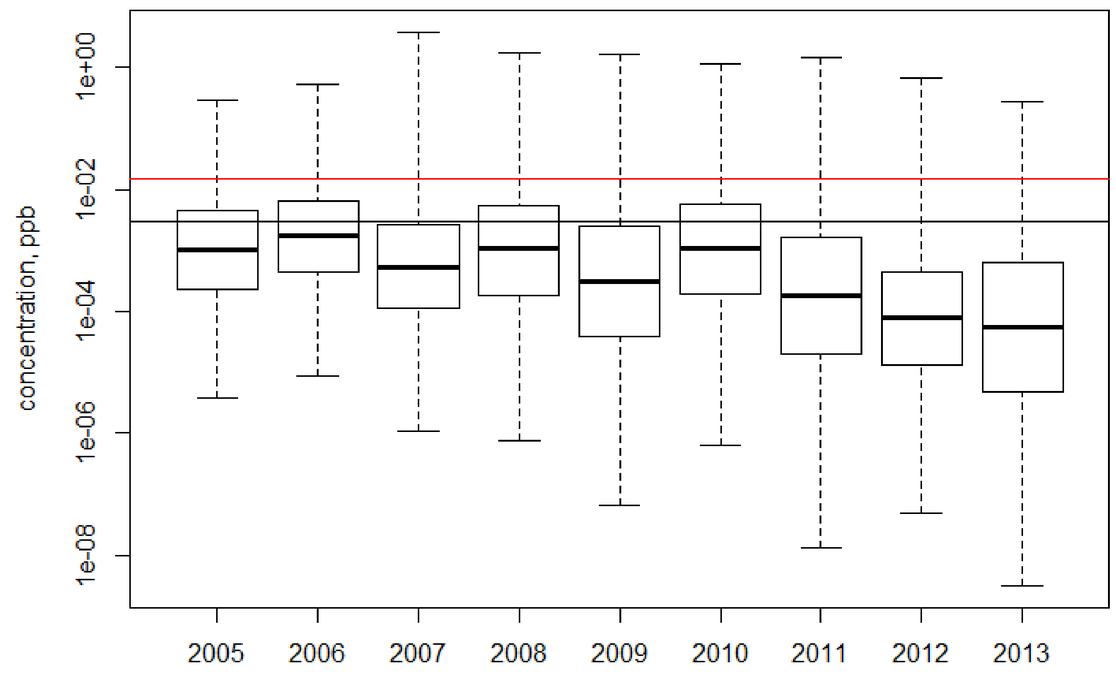
Results: Annual Chlorpyrifos Use and Exceedance

The annual exceedance rate has been decreasing since 2008, three years after the pesticide's use rate started to decrease in 2005.



Results: Long-term Trend in Chlorpyrifos Concentration

NADA visualization showed continuous decreasing trend in concentration level in 2010-2013. NADA regression showed decreasing trend that is more prominent in later years (steeper slope) but not enough data to show a statistically significant trend in 2010-2013.

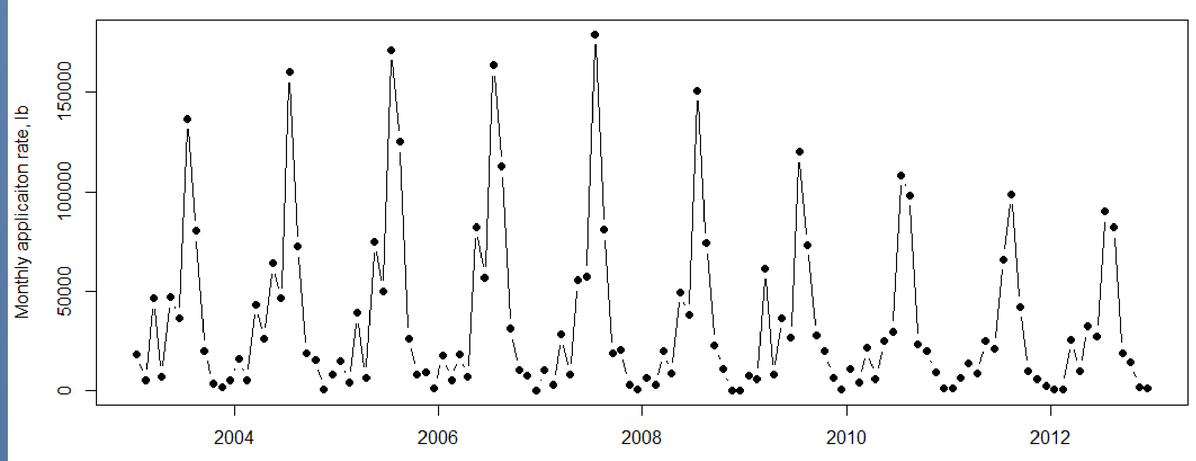


Data in ND range censored	Mann-Kendall trend test log-transformed		MLE Regression lognormal distribution	
	ATS line slope[5]	p-value	Slope[5]	p-value
All data (2005-2013, n=3505)	**-1.34×10^{-3}**	<< 0.05	**-8.41×10^{-4}**	<< 0.05
Exceedance rate decreased since 2008 (2008-2013, n=2615)	**-2.77×10^{-3}**	<< 0.05	**-2.28×10^{-3}**	<< 0.05
NADA visualizes continuous decreasing trend (2010-2013, n=1887)	-2.87×10^{-3}	0.210	-1.79×10^{-3}	0.052

Results: Seasonality

Highest exceedance rate in Jul.-Sep. corresponding to spike in use rate in Jul.-Aug.; second highest exceedance rate in May corresponding to second spike in use rate in May; high exceedance rate in Jan. may be corresponding to storm season.

Month	**1**	2	3	4	**5**	6	***7***	***8***	***9***	10	11	12
Number of samples	217	343	294	312	406	399	436	407	303	130	107	142
% > WQC (ROQ and DNQ range)	**9.7**	5.2	6.1	6.4	**9.9**	4.8	***19.7***	***13.5***	***19.1***	8.5	4.7	2.1



References

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3. Vecchia, A.V., Martin, J.D. and Gilliom. R.J. 2008. Modeling variability and trends in pesticide concentrations in streams. J Am. Water Resour. As., 44 (5): 1308-1324.