

# **A linear mixed model for assessing long-term trend in atrazine occurrence in raw water of U.S. Community Water Systems**

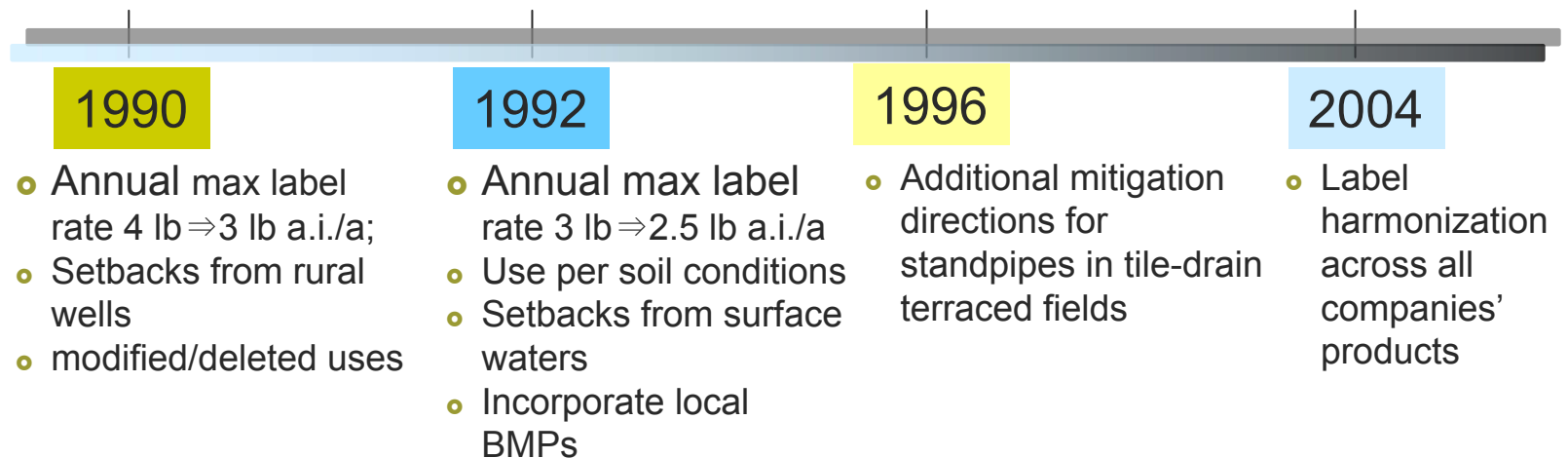
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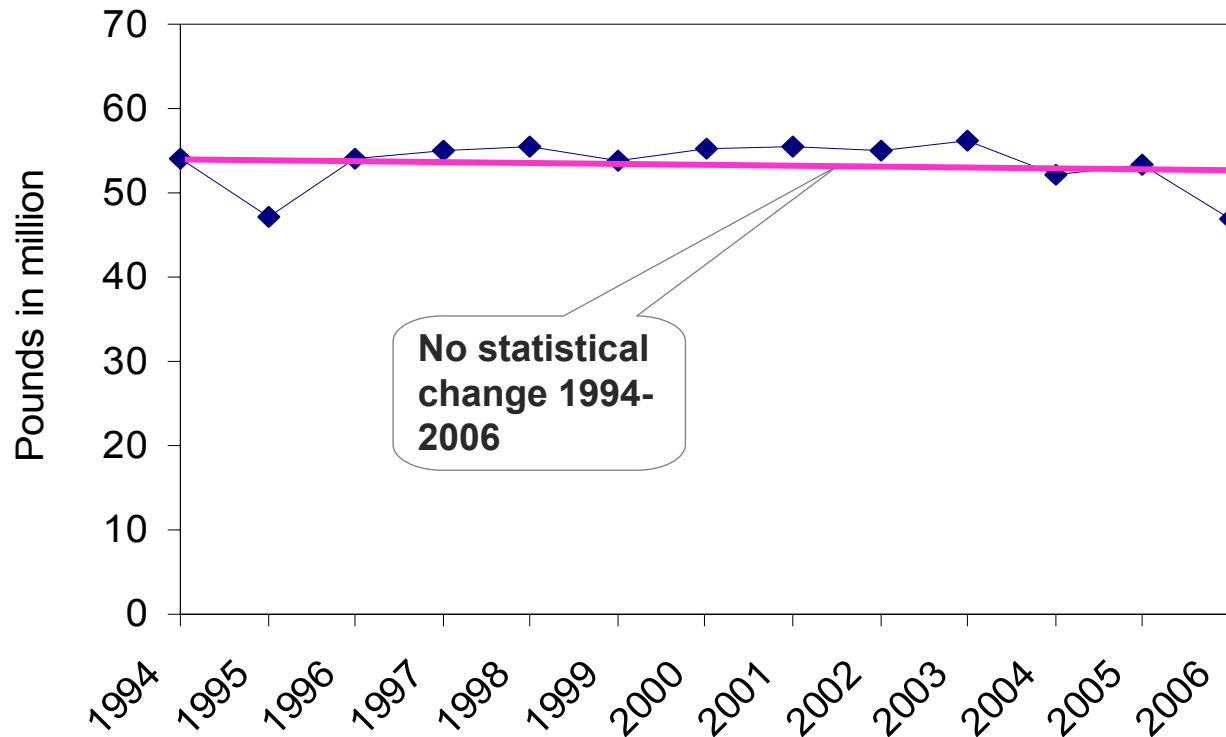
# [ Background ]

- Popular product, long use history (~50 years), and comprehensive monitoring data
- Over 130 atrazine-containing products sold by 40 companies
- Label uses changed over time



# [ Background ]

- Total atrazine use in 9 Midwest Cornbelt states + TX, LA, & PA. 1994 – 2006 (Doane Data)



# [ Objective ]

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- Provide a statistical assessment of the long term trend in atrazine occurrence in raw water samples from surface water Community Water Systems (CWS) from 1994 to 2006.

# [ Method ]

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- Linear mixed effect model
  - Fixed and random effects
  - Suitable for temporal/longitudinal repeated measurements such as CWS monitoring data
  - Allows for analysis of unbalanced data structure
  - Robust for estimating error covariance and autocorrelation

# [ Mixed effects ]

- Mono-phasic

Conc. at CWS  $i$  in year  $j$  of group  $k$

year

Residual error

$$y_{ijk} = \alpha_k + \beta_k X_{ijk} + \delta_{ik} + \varepsilon_{ijk}$$

- Bi-phasic

Group  $k$  intercept

Group  $k$  slope

Random Var. intercept

$$y_{ijk} = \alpha_k (1 + \beta_{3k} Z_j) + (\beta_{1k} + \beta_{2k} Z_j) X_{ijk} + \delta_{ik} + \varepsilon_{ijk}$$

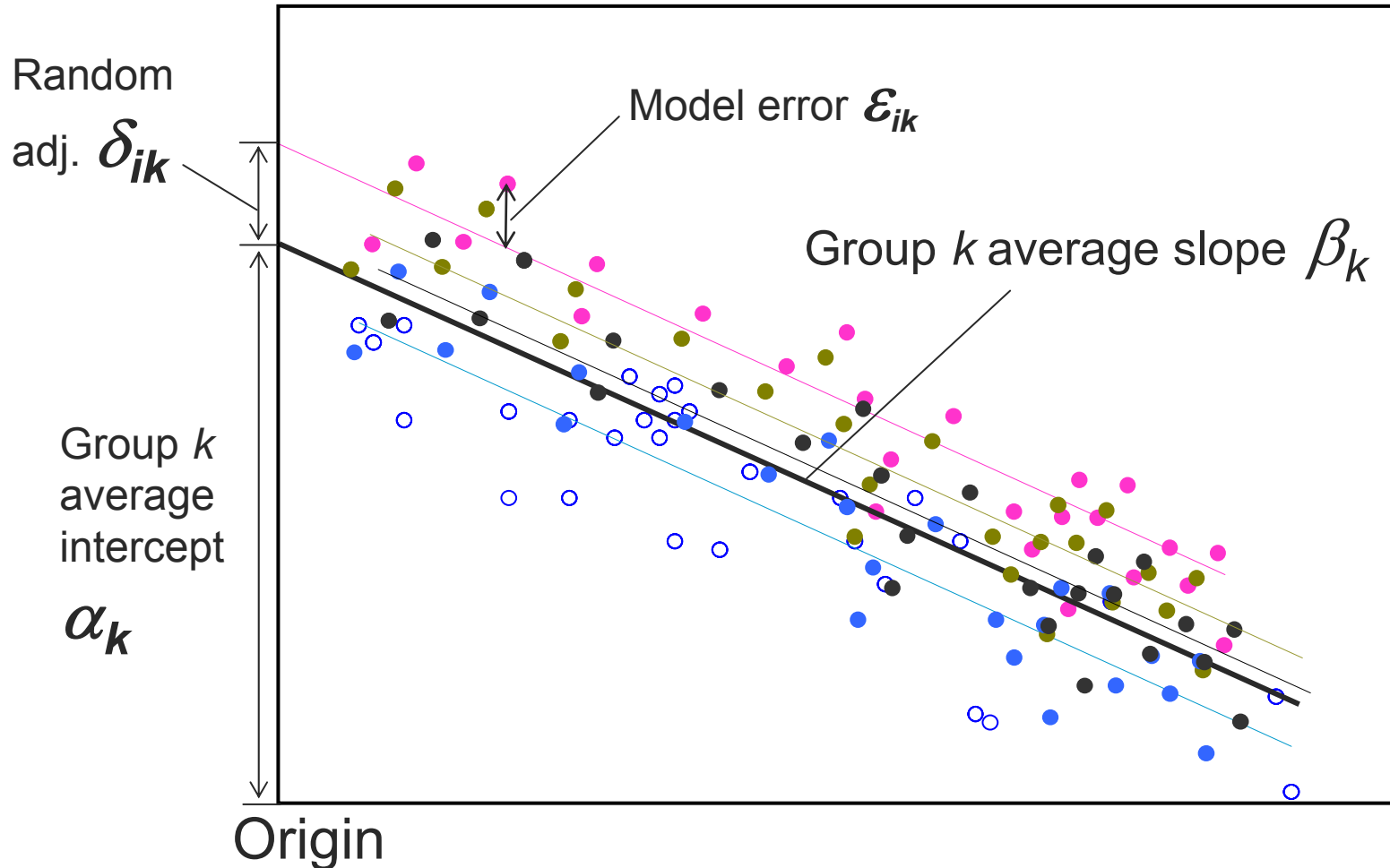
Intercept adj. for period 2

Dummy var., 0 for period-1, 1 for period-2

Slope adj. for period 2

# Hypothetical example

$$y_{ijk} = \alpha_k + \beta_k X_{ijk} + \delta_{ik} + \varepsilon_{ijk}$$



# Data from raw water samples

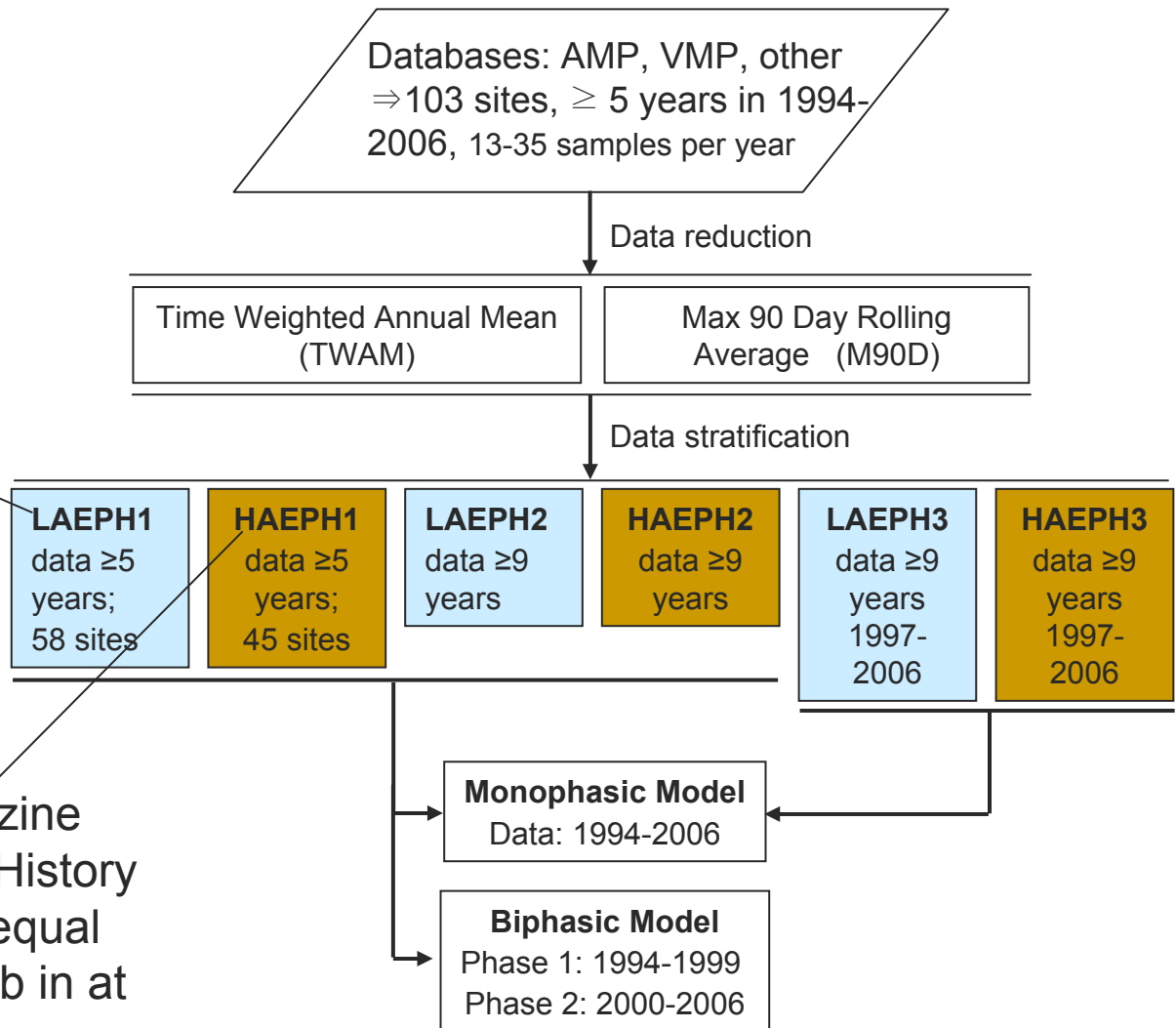
- Three databases (raw water samples from CWS, 9 Midwest Cornbelt states + TX, LA, & PA)
- Syngenta Voluntary Monitoring Program (VMP)
  - 1993-2001
  - Sampling frequency targeted at weekly from April to July and every other week in the rest of the year
  - In 2002, some systems every other week all year
- Syngenta Atrazine Monitoring Program (AMP)
  - 2003-2006
  - Sampling frequency targeted at weekly from April to July and every other week in the rest of the year (~32-35 samples year per site)
- Other atrazine data sets
  - 1995-2001
  - 13-14 samples per year – biweekly mid Mar to Aug, 2 samples from Sep to Feb



# Data stratification

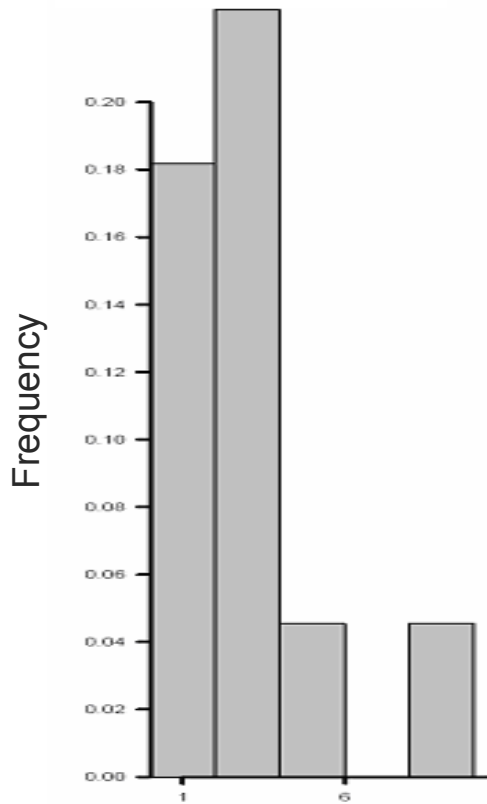
LAEPH = Low Atrazine Exposure Potential History – raw water TWAM did not exceed 3 ppb in any year

HAEPH = High Atrazine Exposure Potential History - raw water TWAM equal to or exceeded 3 ppb in at least one year



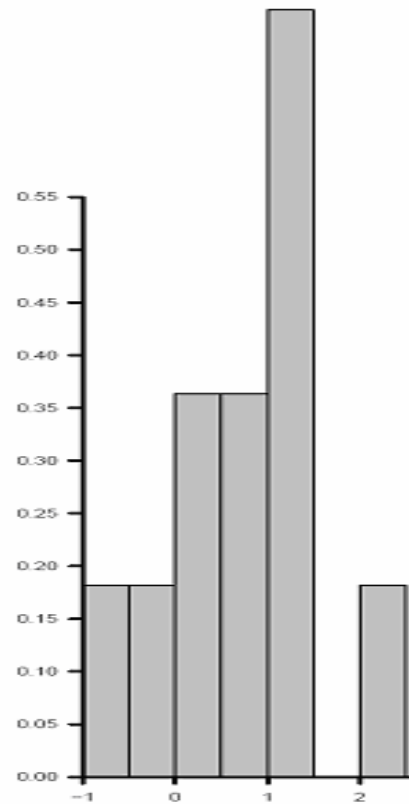
# Data transformation

Raw data from a single site



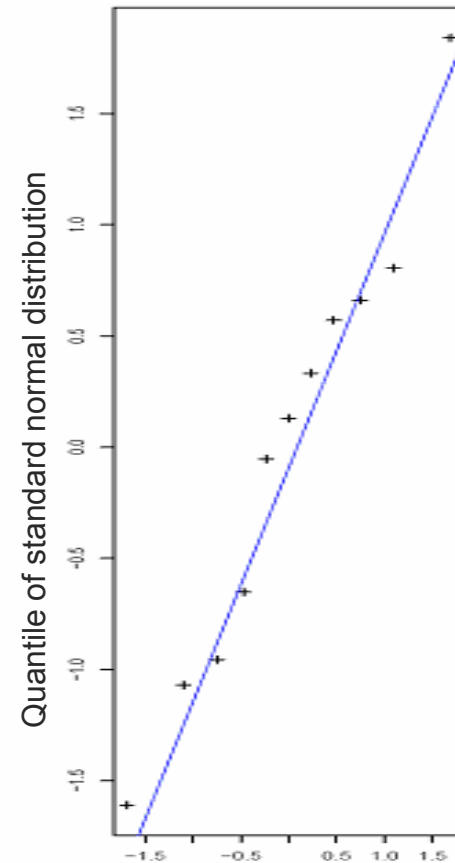
TWAM in raw water (ppb)

Natural log



LN(TWAM\_ppb)

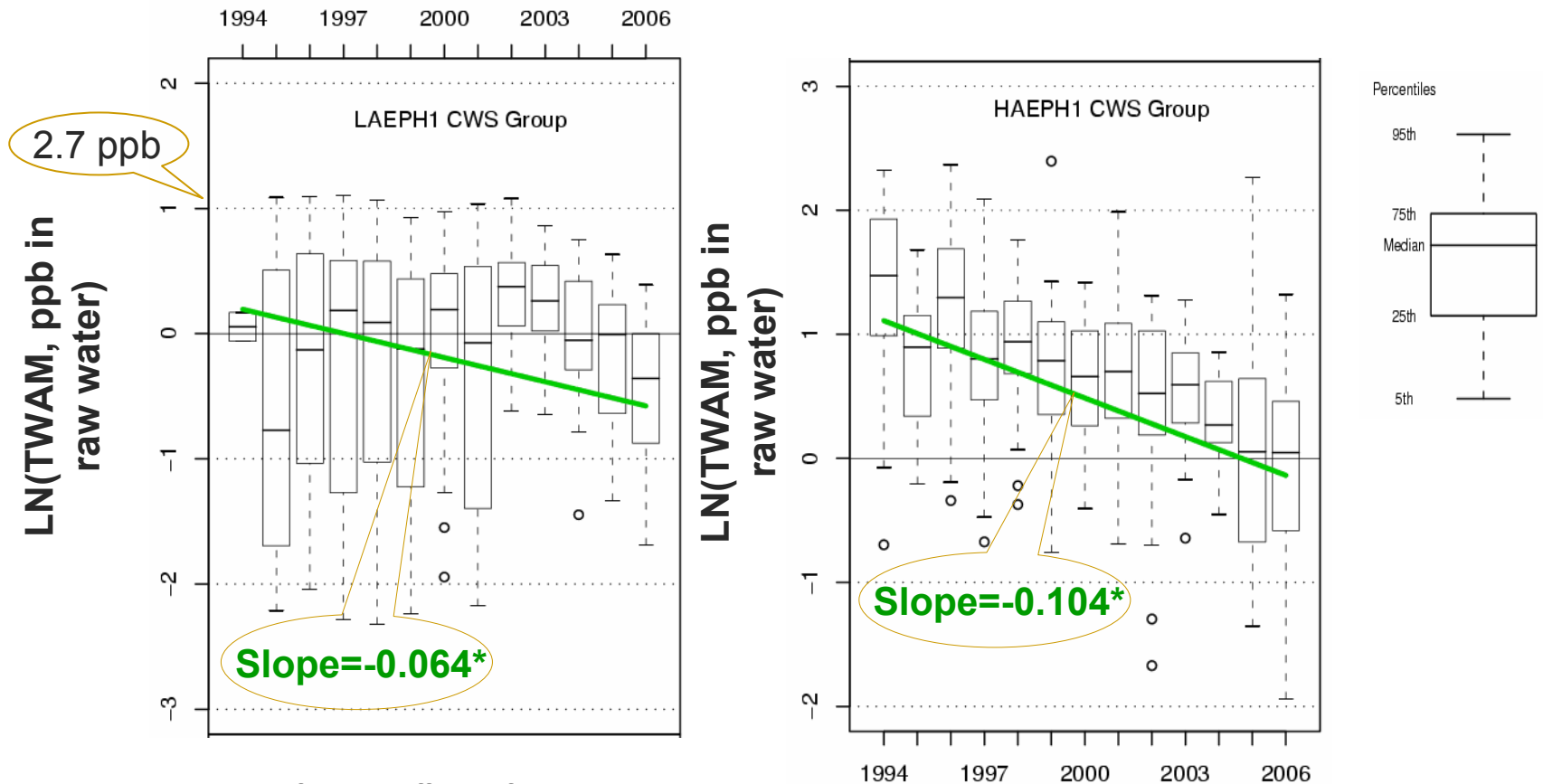
QQ plot



Quantile of LN(TWAM\_ppb)

# Results - mono-phasic model

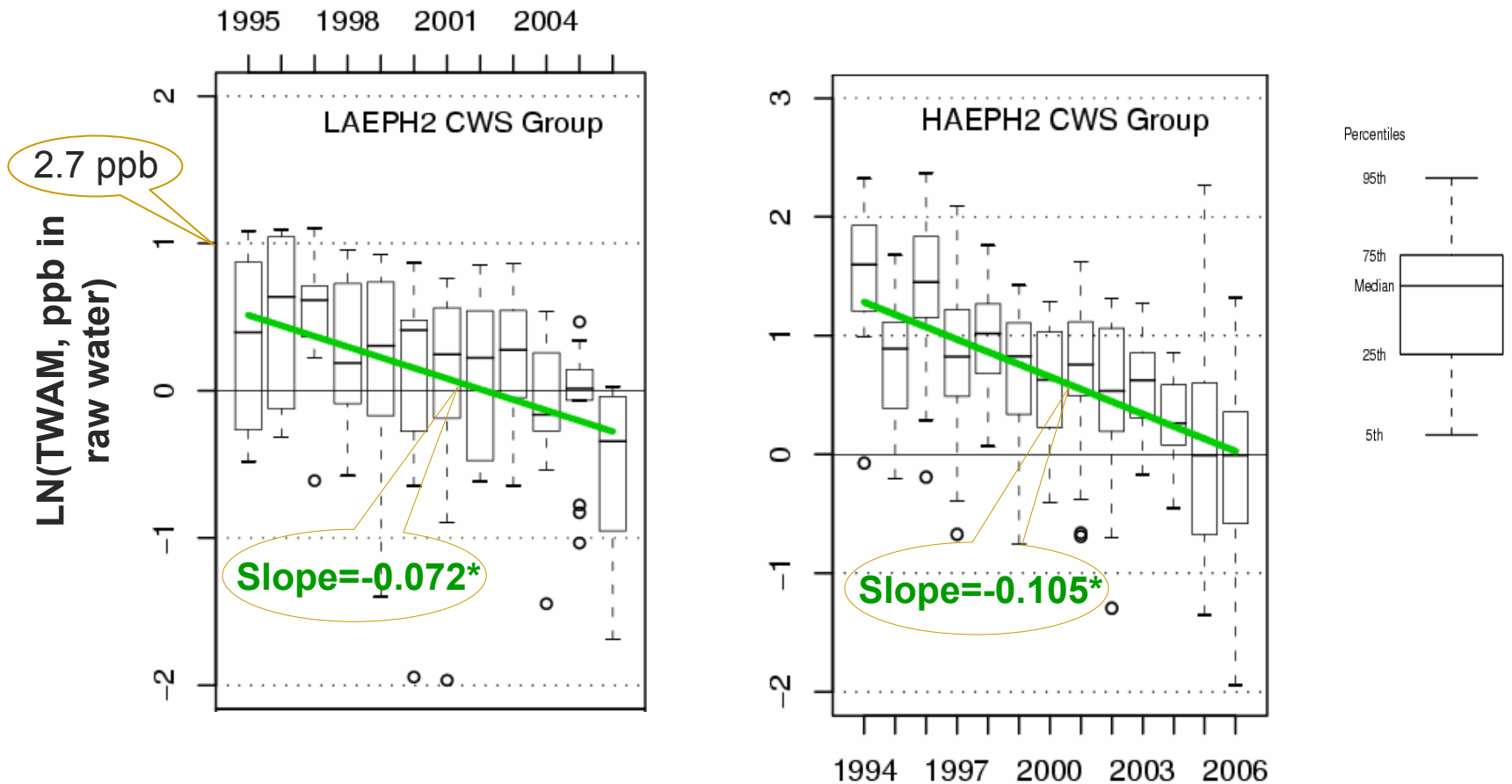
LN(TWAM) dataset: data  $\geq 5$  years, 1994-2006



\* Parameter estimate significantly different from zero ( $p < 0.05$ )

# Results - mono-phasic model

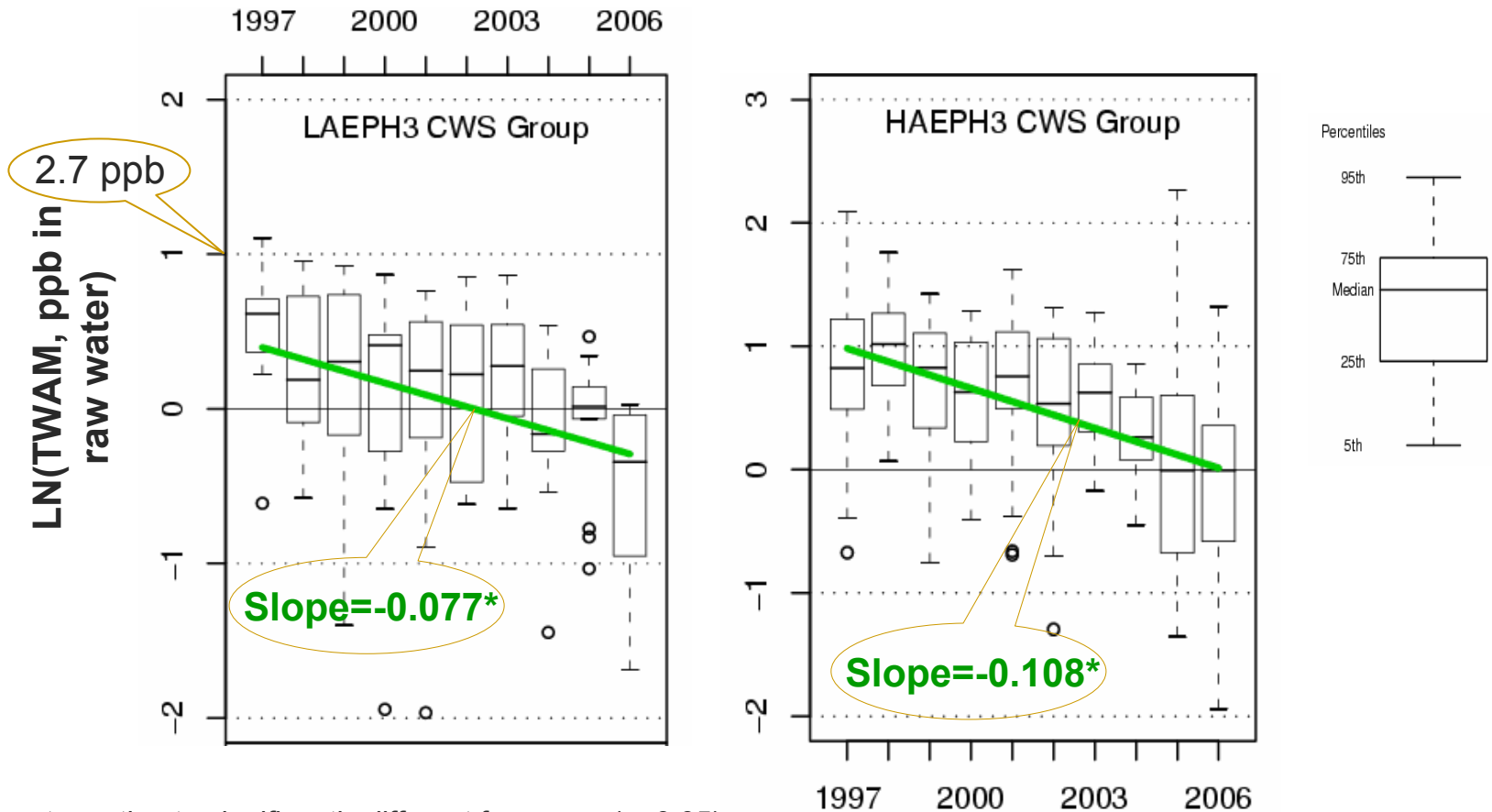
LN(TWAM) dataset: data  $\geq 9$  years, 1994-2006



\* Parameter estimate significantly different from zero ( $p < 0.05$ )

# Results - mono-phasic model

LN(TWAM) dataset: data  $\geq 9$  years, 1997-2006



\* Parameter estimate significantly different from zero ( $p < 0.05$ )

# Result Summary 1

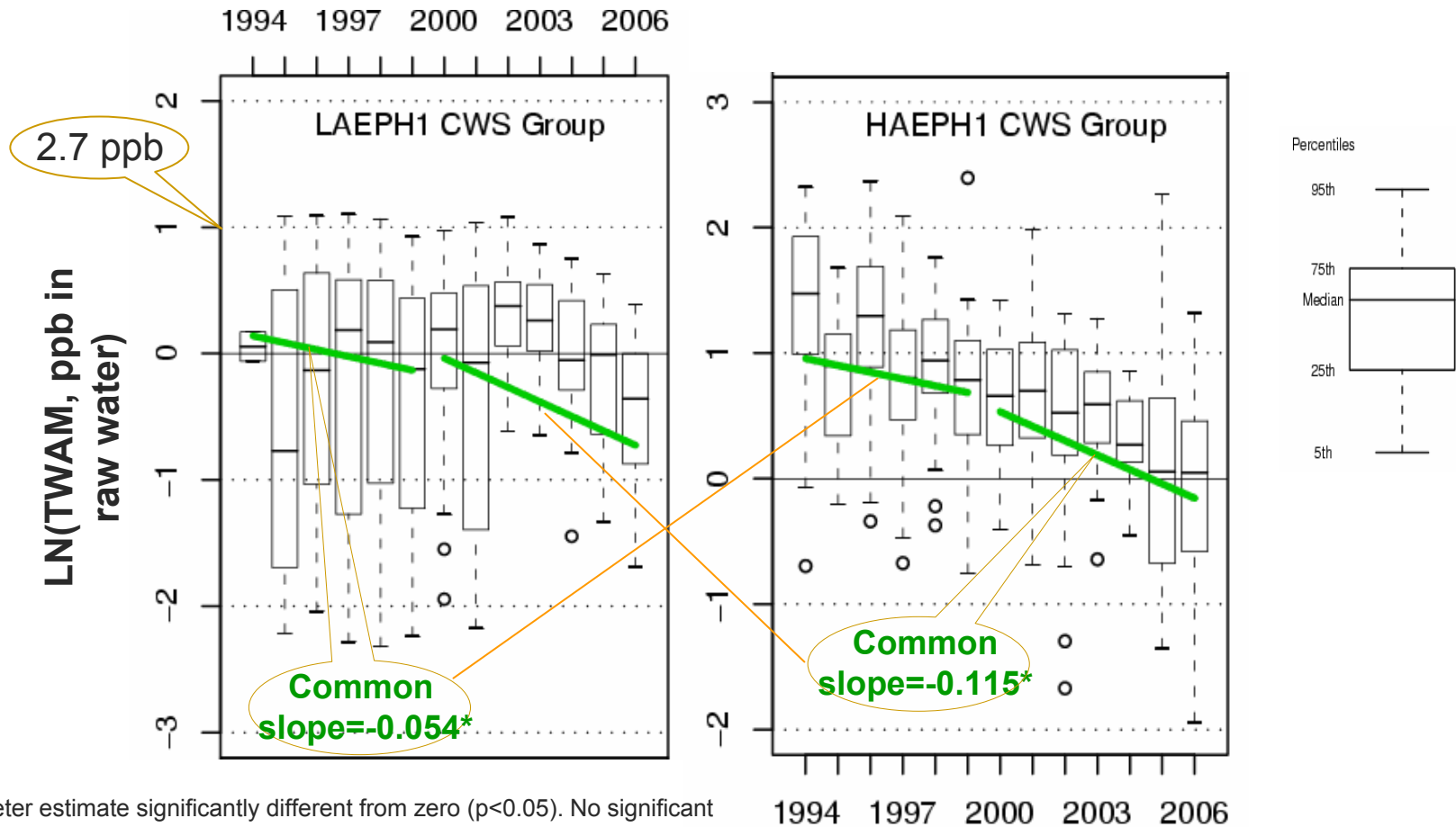
## Mono-phasic model

| Stratum             | Estimated Parameter Value (95% C.I.) |                          |
|---------------------|--------------------------------------|--------------------------|
|                     | M90D (LN ppb)                        | TWAM (LN ppb)            |
| LAEPH1 <i>slope</i> | -0.062 (-0.084, -0.040)*             | -0.064 (-0.083, -0.046)* |
| HAEPH1 <i>slope</i> | -0.103 (-0.120, -0.085)*             | -0.104 (-0.119, -0.089)* |
| LAEPH2 <i>slope</i> | -0.075 (-0.106, -0.044)*             | -0.072 (-0.098, -0.045)* |
| HAEPH2 <i>slope</i> | -0.103 (-0.122, -0.084)*             | -0.105 (-0.121, -0.088)* |
| LAEPH3 <i>slope</i> | -0.074 (-0.111, -0.038)*             | -0.077 (-0.108, -0.045)* |
| HAEPH3 <i>slope</i> | -0.100 (-0.124, -0.077)*             | -0.108 (-0.128, -0.087)* |

\* Estimates statistically significant different from zero (p<0.05).

# Results - bi-phasic model

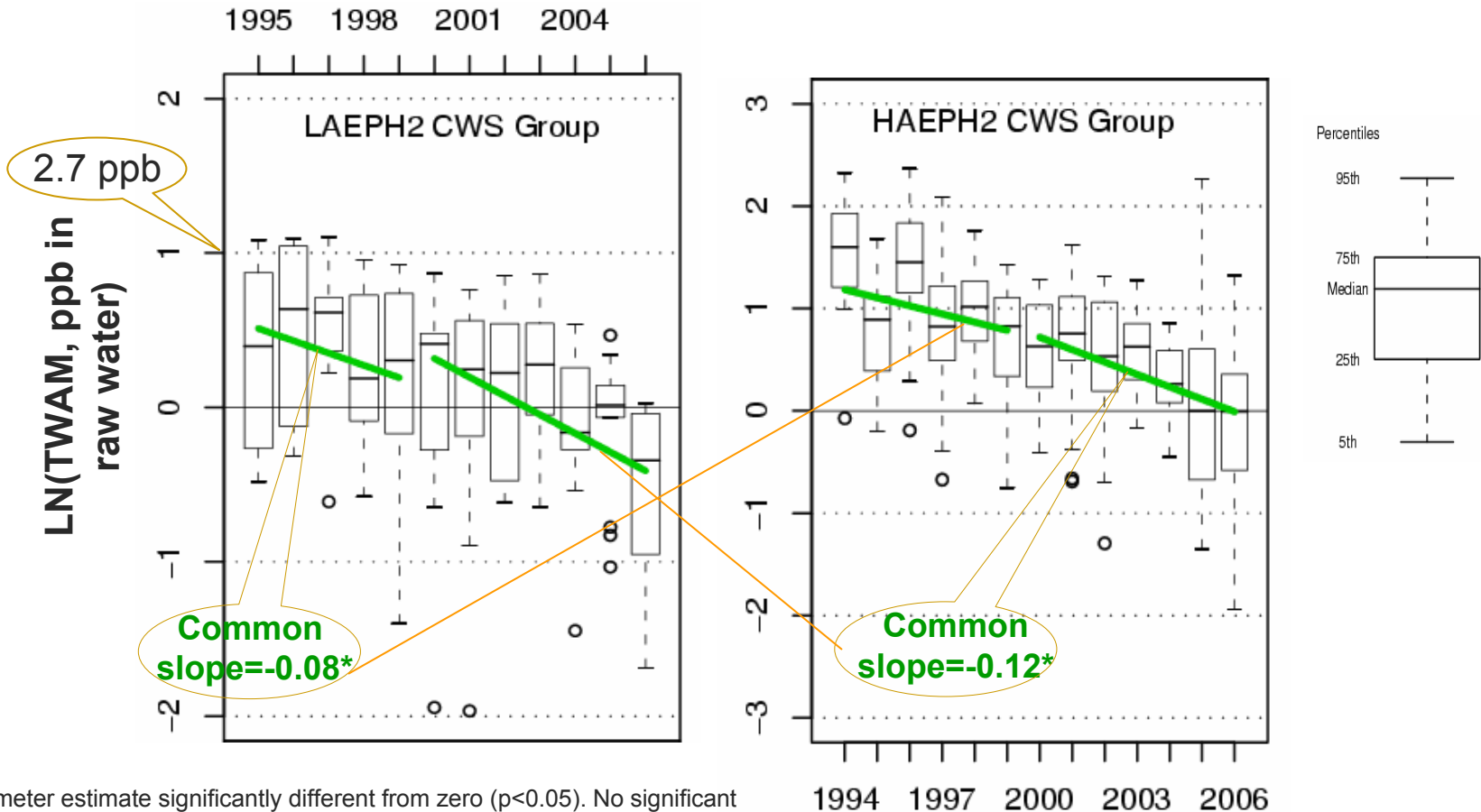
LN(TWAM) dataset: data  $\geq 5$  years, 1994-2006



\* Parameter estimate significantly different from zero ( $p < 0.05$ ). No significant difference between strata HAEPH1 and LAEPH1 slopes.

# Results - bi-phasic model

LN(TWAM) dataset: data  $\geq 9$  years, 1994-2006



\* Parameter estimate significantly different from zero ( $p < 0.05$ ). No significant difference between strata HAEPH2 and LAEPH2 slopes.



# [ Result Summary 2 ]

## Bi-phasic model

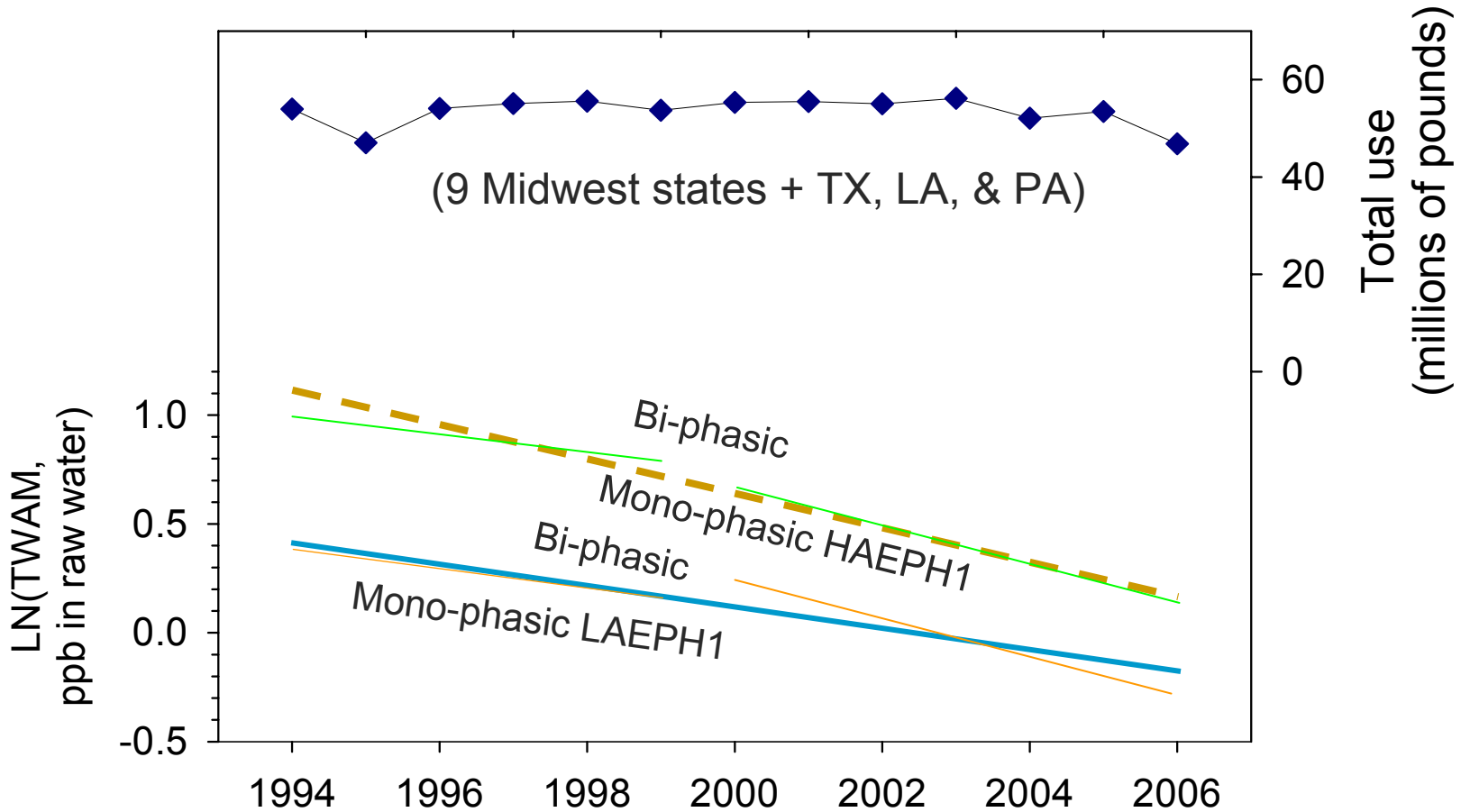
| Stratum            | Parameters             | Estimated Parameter (95% C.I.) |                            |
|--------------------|------------------------|--------------------------------|----------------------------|
|                    |                        | M90D                           | TWAM                       |
| LAEPH1 and HAEPH1† | 1994-1999 <i>slope</i> | -0.060 (-0.103, -0.017)*       | -0.054 (-0.090, -0.019)* § |
| LAEPH1 and HAEPH1† | 2000-2006 <i>slope</i> | -0.100 (-0.128, -0.072)*       | -0.115 (-0.138, -0.092)* § |
| LAEPH2 and HAEPH2† | 1994-1999 <i>slope</i> | -0.094 (-0.153, -0.034)*       | -0.080 (-0.130, -0.029)*   |
| LAEPH2 and HAEPH2† | 2000-2006 <i>slope</i> | -0.108 (-0.143, -0.073)*       | -0.121 (-0.151, -0.091)*   |

† Stratum common slope: Not statistically significant difference between strata HAEPH and LAEPH slopes during this period ( $p < 0.05$ )

\* Estimates statistically significant different from zero ( $p < 0.05$ )

§ Statistically significant different between the two time periods slopes, 1994-1999 vs. 2000-2006 ( $p < 0.05$ )

# Discussion



# [ Conclusion ]

- Atrazine concentrations in raw water declined significantly with a monotonic trend over the 13 years of monitoring in the studied CWS
- All strata, regardless data length or time period, had significant negative trends in both TWAM and M90D.
- For all mono-phasic models, the HAEPH strata had larger negative slope estimates when compared to the respective LAEPH strata.

# [ Conclusion ]

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- All bi-phasic models shown that decline trends were statistically significant in each of the two time periods 1994-99 and 2000-06.

**[ Slides end**

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**Thanks**