

# USGS Water Quality Data

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and  
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Advisor: Dr. Stewart Rounds, USGS



Can we use information  
from the time series to tell  
us anything about the  
discrete sample?

# About the Data

# Time Series

- Samples taken every 30 minutes
- Sampling is automatic
- Relies on sensors
- 15 “vital statistics”
- 144,577 observations

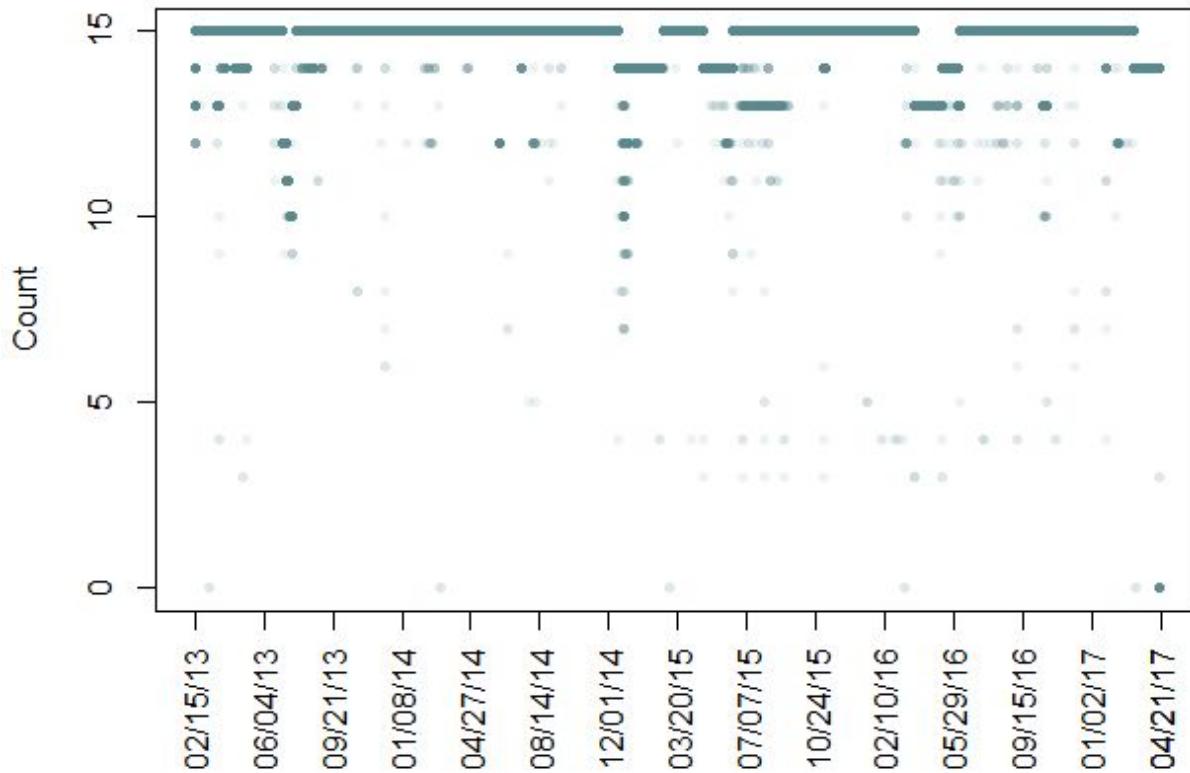
# Discrete

- Samples taken every 1, 2, or maybe even 3 weeks
  - Sampling by hand, analyzed in the lab
  - 969 elements in full set
  - 480 observations
-

# Exploratory Analysis

# Time Series

### Number of Factors Collected by Observation (Date and Time)



## Time Series Data Clean-up

- Collection began for Phycocyanin, fDOM, and Nitrate began 2/15/2013
- 73,219 samples
- 89% or more of data available for each covariate

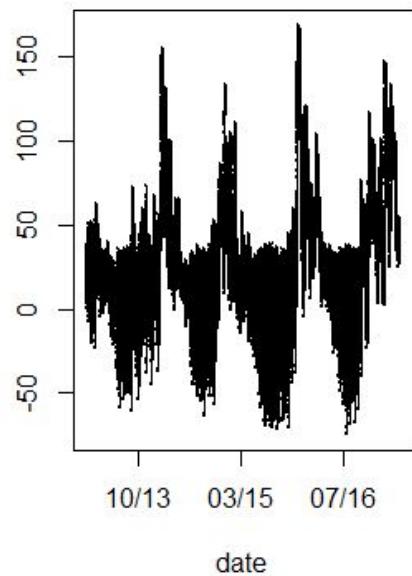
Table 1: Descriptive Statistics

	Min	Q1	Median	Mean	Q3	Max	NAs	Percent_Avail
Discharge (kcfs)	-74.06	16.17	23.80	33.0400	44.07	168.71	503	100
Stream Velocity (feet/sec)	-1.93	0.41	0.61	0.8113	1.11	3.90	503	99
Gage Height (feet)	-0.40	3.50	5.12	5.5390	7.04	17.32	39	99
Sensor Depth (feet)	2.28	7.50	9.22	9.6280	11.12	22.08	8162	100
Water Temperature (deg. C)	1.55	8.54	12.26	13.6700	19.14	26.88	103	89
Dissolved Oxygen (mg/L)	1.53	9.47	11.15	11.0500	12.74	14.72	1100	100
Oxygen % Saturation (% sat.)	17.50	101.10	104.30	104.1000	108.20	140.30	1107	98
pH (std.unit)	6.80	7.23	7.35	7.3320	7.43	8.84	1109	98
Specific Conductance (uS/cm)	51.00	70.00	77.00	77.5000	85.00	134.00	721	98
Turbidity (FNU)	0.30	2.20	3.60	8.0180	8.70	120.00	335	99
Estimated Secchi Depth (feet)	0.53	2.80	4.92	4.9350	6.73	23.95	335	100
Total Chlorophyll (ug/L)	-0.60	0.80	1.40	2.1260	2.50	41.00	718	100
Phycocyanin (ug/L)	-0.80	0.10	0.10	0.1897	0.30	1.50	877	99
fDOM (370/460) (ppb QSE)	-0.20	2.20	5.20	6.4510	9.40	26.00	3195	99
Nitrate (mg/L)	0.00	0.36	0.49	0.5920	0.80	2.26	4440	96

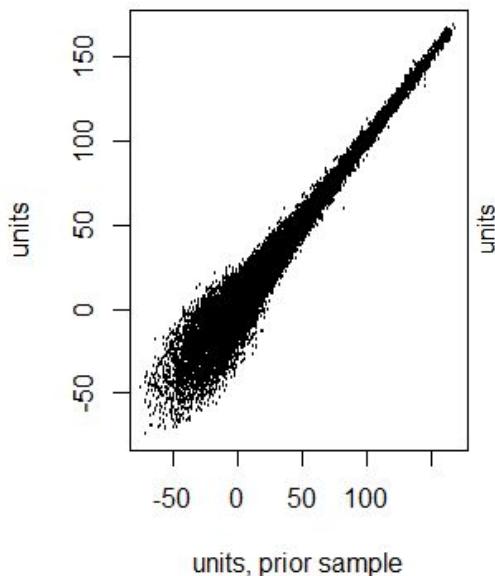
# Univariate Exploratory Graphing

Discharge (kcfs)

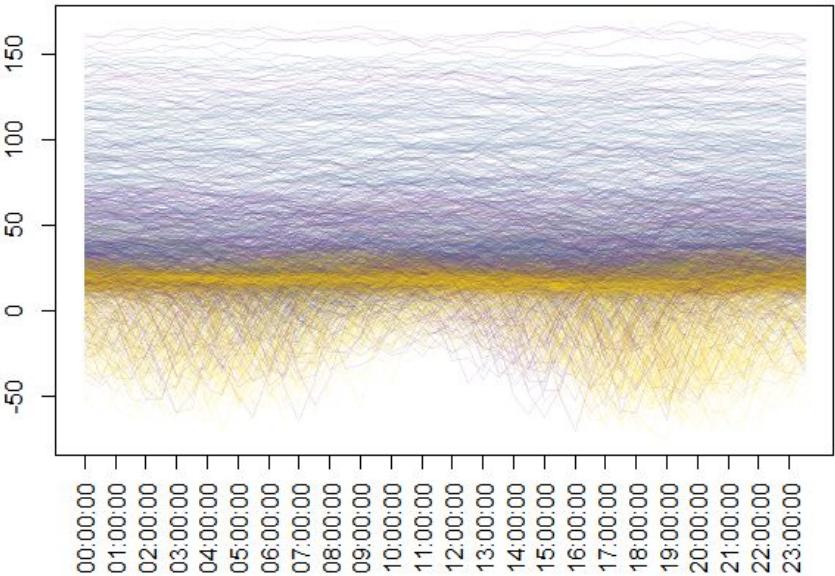
Time Series



Scatterplot



Discharge (kcfs) by Day



Left: measurements over time

Right: current sample vs. prior sample

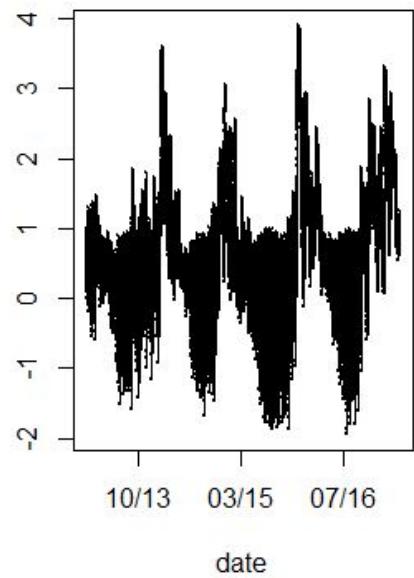
Measurements plotted by time of day.

Q1: Blue, Q2: Brown, Q3: Gold, Q4: Purple

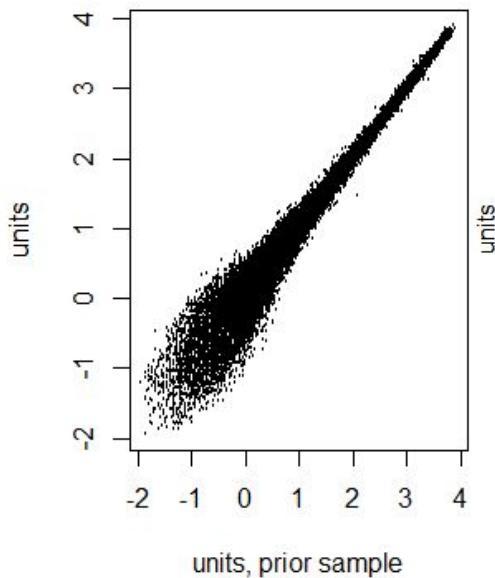
# Univariate Exploratory Graphing

Stream Velocity (feet/sec)

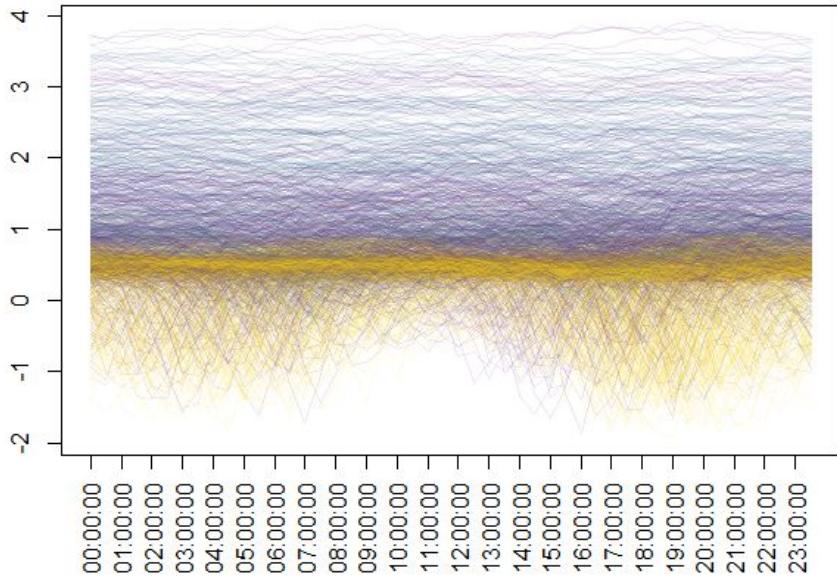
Time Series



Scatterplot



Stream Velocity (feet/sec) by Day



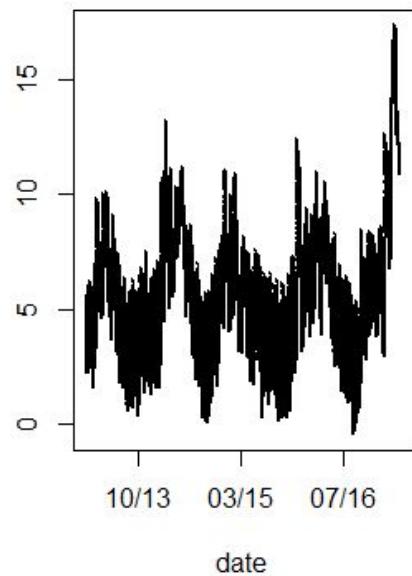
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Measurements plotted by time of day.  
Q1: Blue, Q2: Brown, Q3: Gold, Q4: Purple

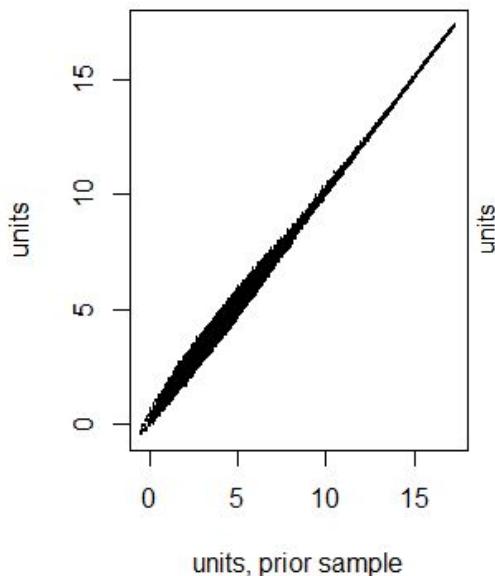
# Univariate Exploratory Graphing

Gage Height (feet)

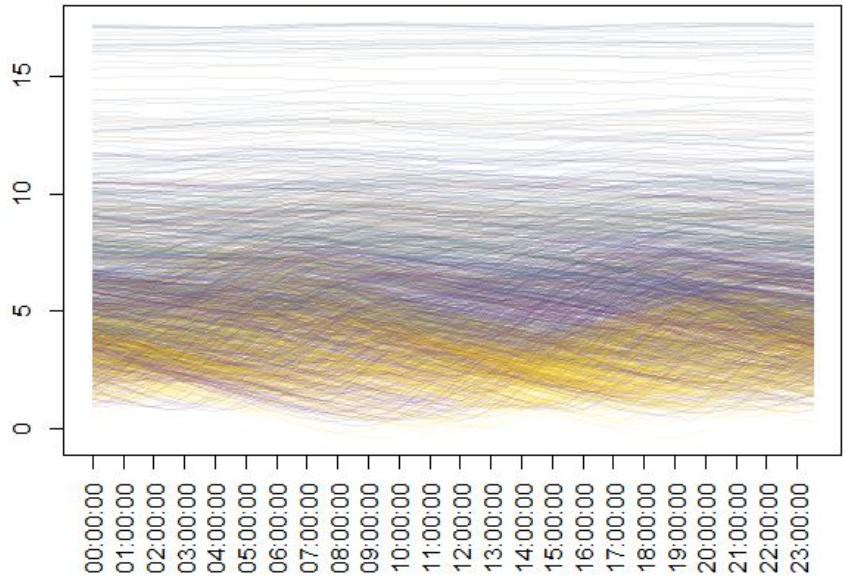
Time Series



Scatterplot



Gage Height (feet) by Day



Left: measurements over time

Right: current sample vs. prior sample

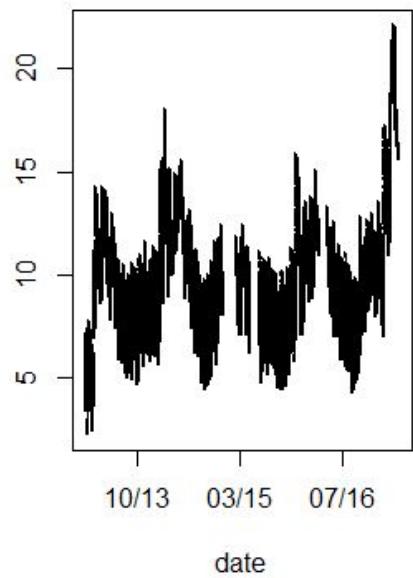
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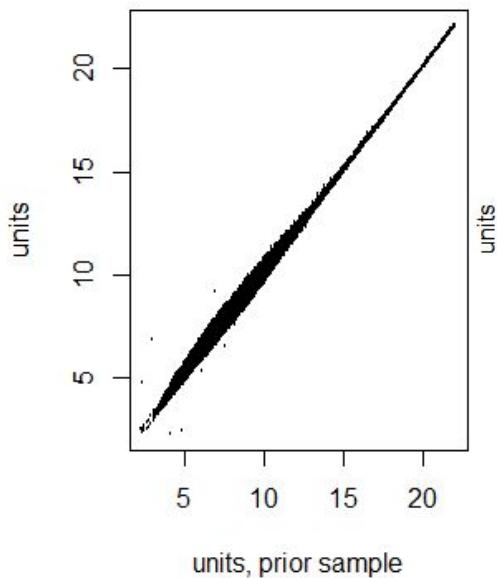
# Univariate Exploratory Graphing

Sensor Depth (feet)

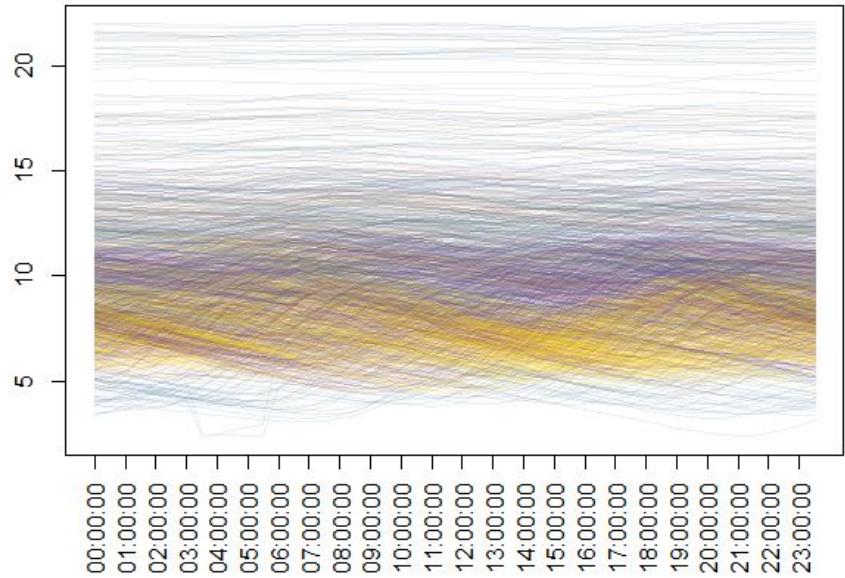
Time Series



Scatterplot



Sensor Depth (feet) by Day



Left: measurements over time

Right: current sample vs. prior sample

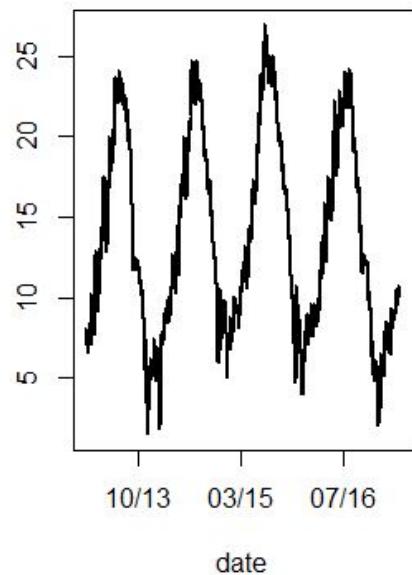
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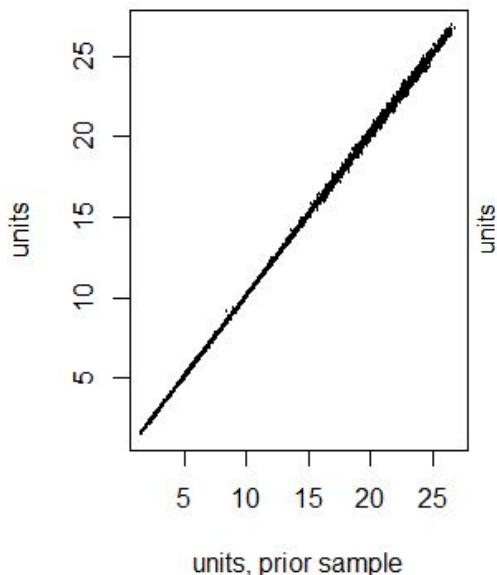
# Univariate Exploratory Graphing

Water Temperature (deg. C)

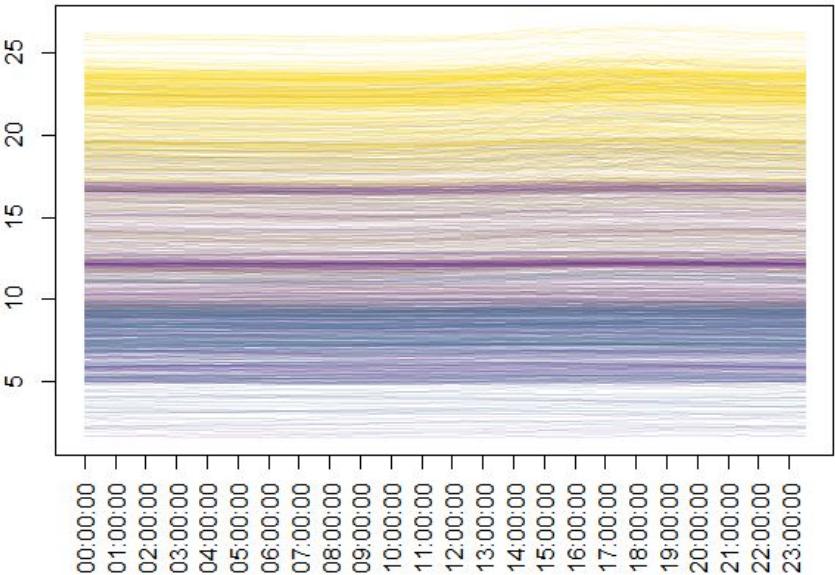
Time Series



Scatterplot



Water Temperature (deg. C) by Day



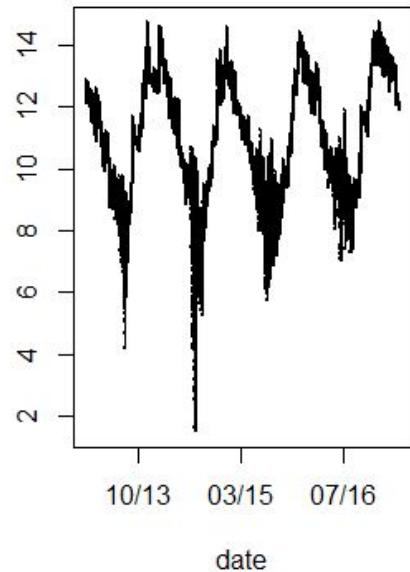
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Measurements plotted by time of day.  
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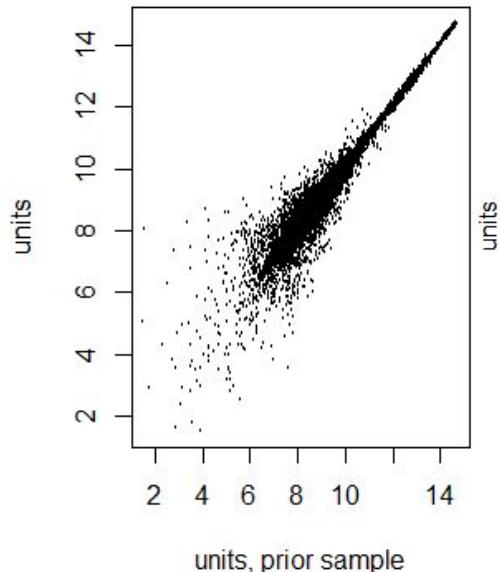
# Univariate Exploratory Graphing

Dissolved Oxygen (mg/L)

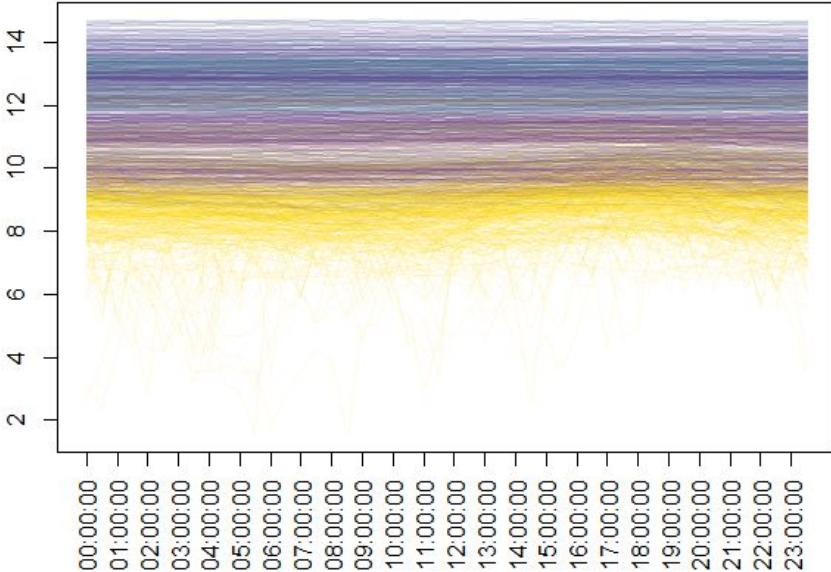
Time Series



Scatterplot



Dissolved Oxygen (mg/L) by Day



Left: measurements over time

Right: current sample vs. prior sample

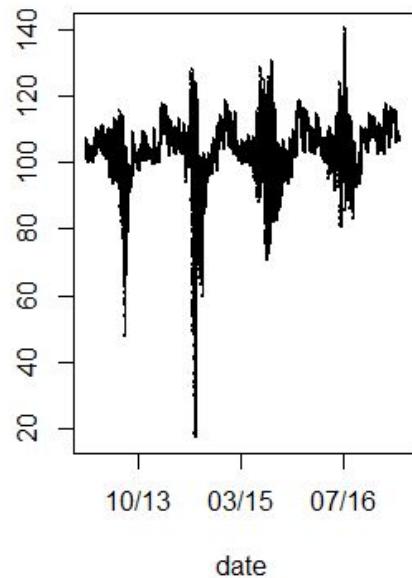
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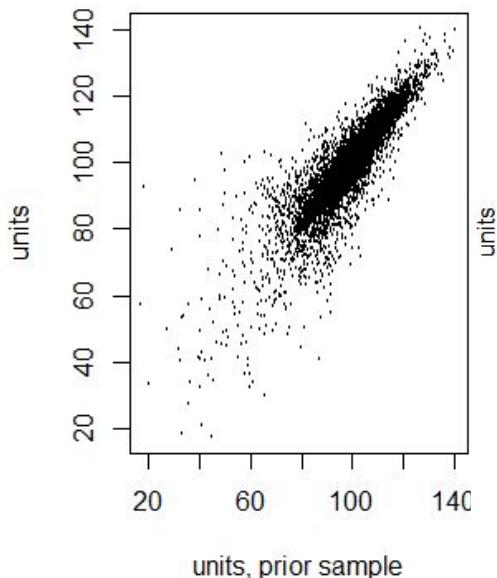
# Univariate Exploratory Graphing

Oxygen % Saturation (% sat.)

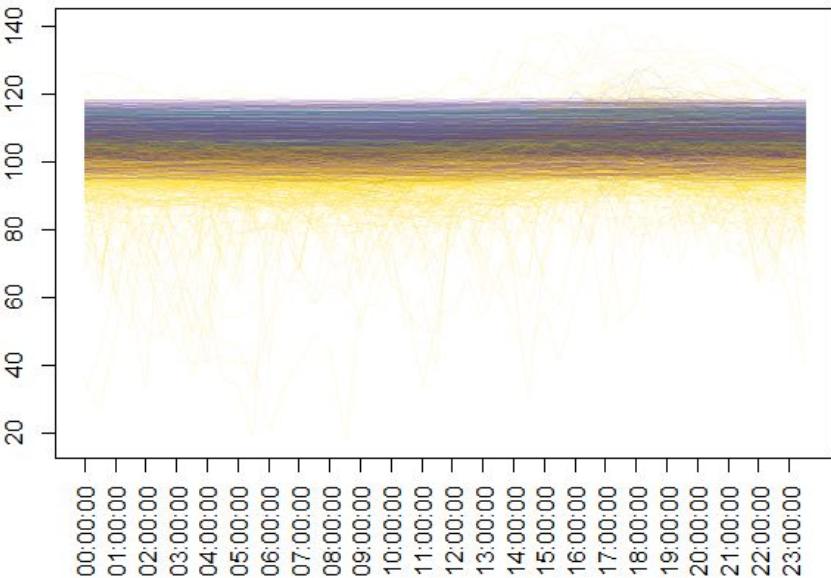
Time Series



Scatterplot



Oxygen % Saturation (% sat.) by Day



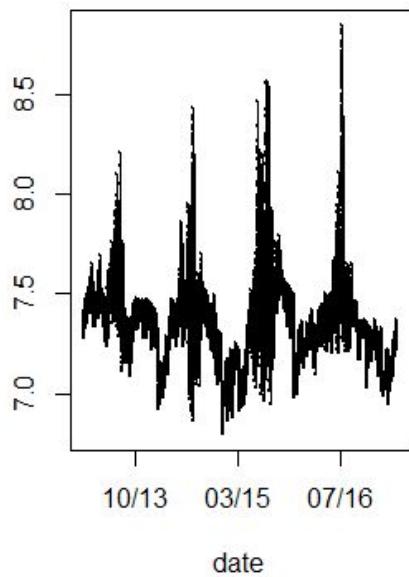
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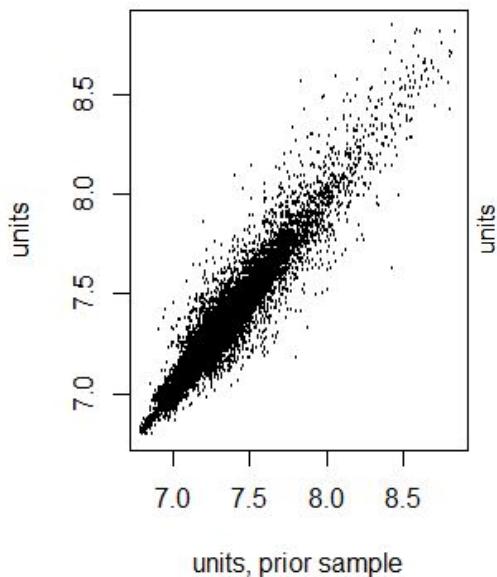
# Univariate Exploratory Graphing

pH (std.unit)

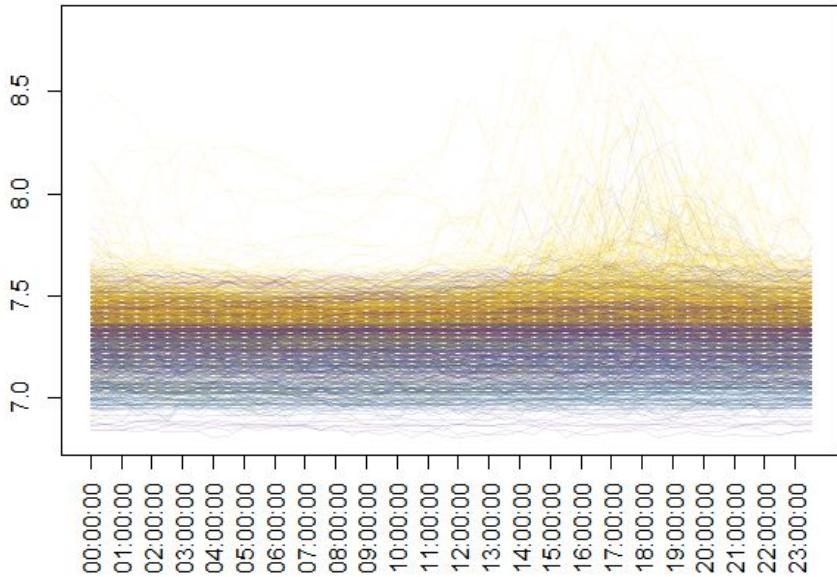
Time Series



Scatterplot



pH (std.unit) by Day



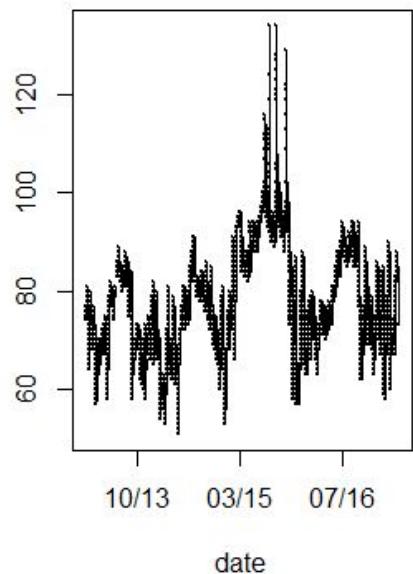
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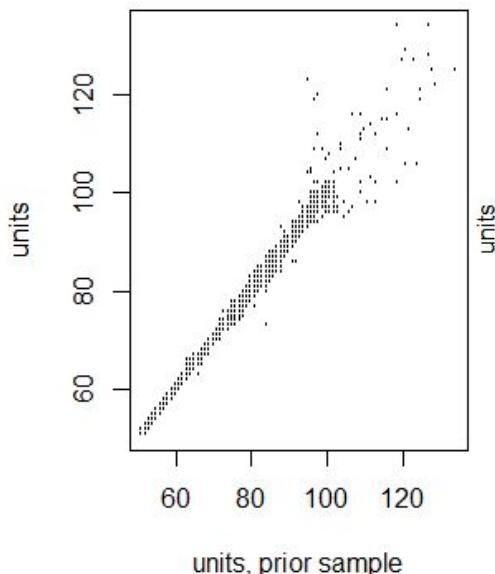
# Univariate Exploratory Graphing

Specific Conductance ( $\mu\text{S}/\text{cm}$ )

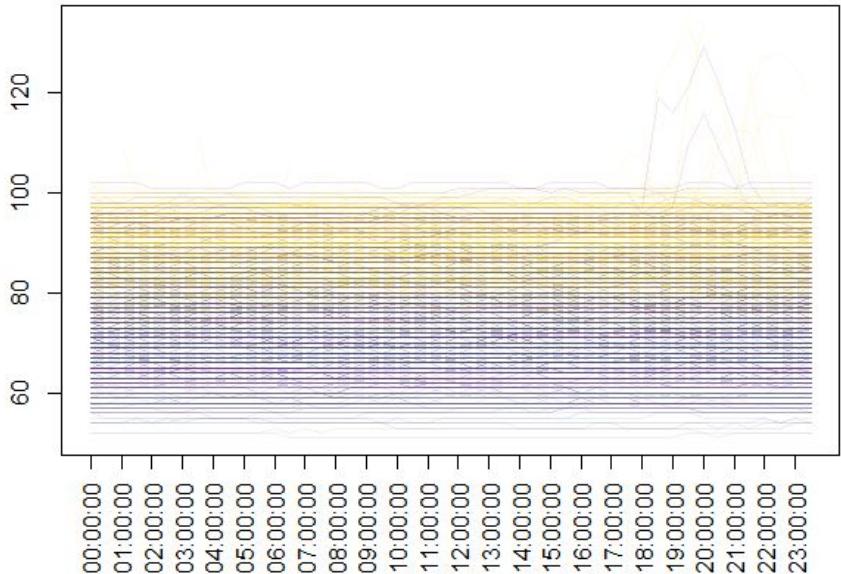
Time Series



Scatterplot



Specific Conductance ( $\mu\text{S}/\text{cm}$ ) by Day



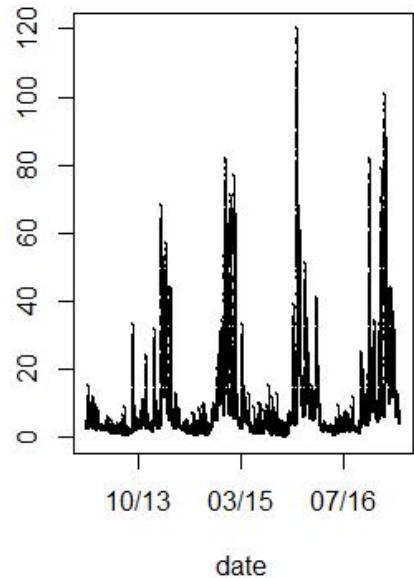
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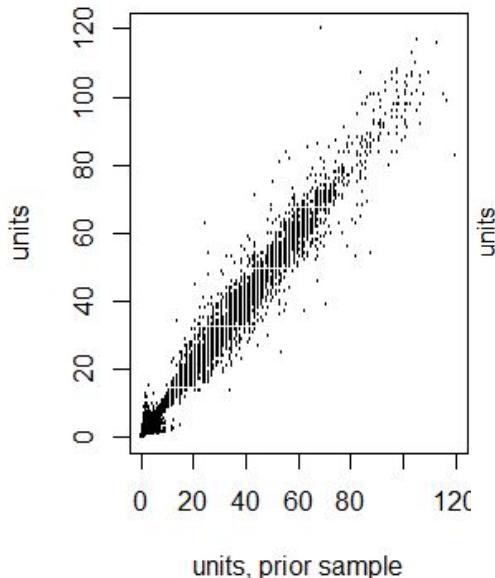
# Univariate Exploratory Graphing

Turbidity (FNU)

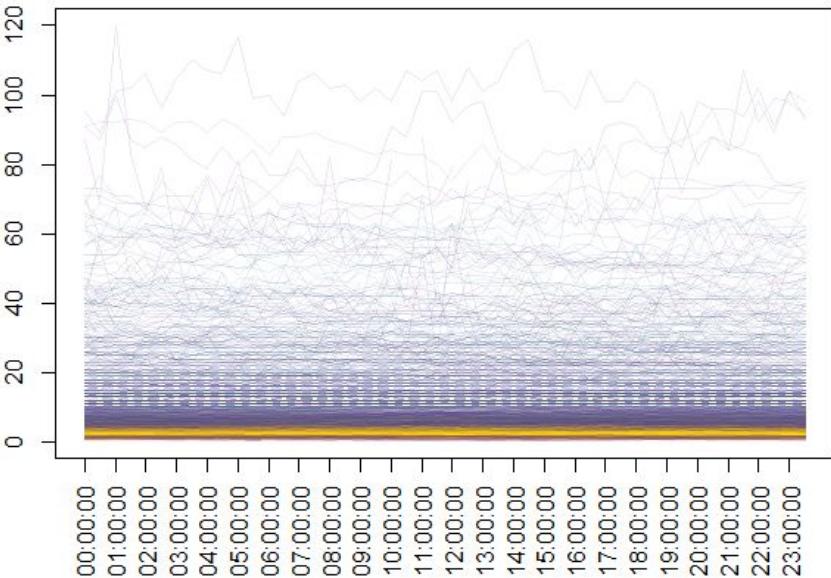
Time Series



Scatterplot



Turbidity (FNU) by Day



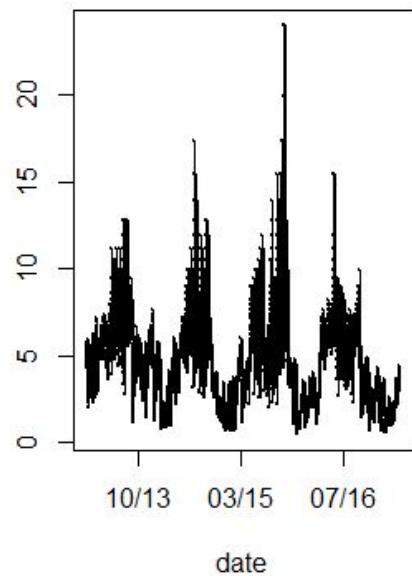
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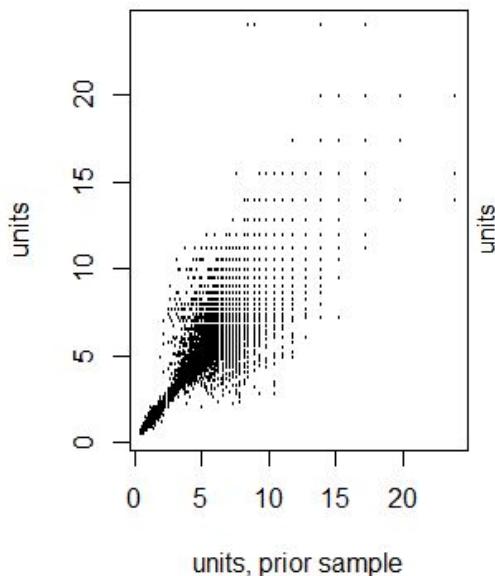
# Univariate Exploratory Graphing

Estimated Secchi Depth (feet)

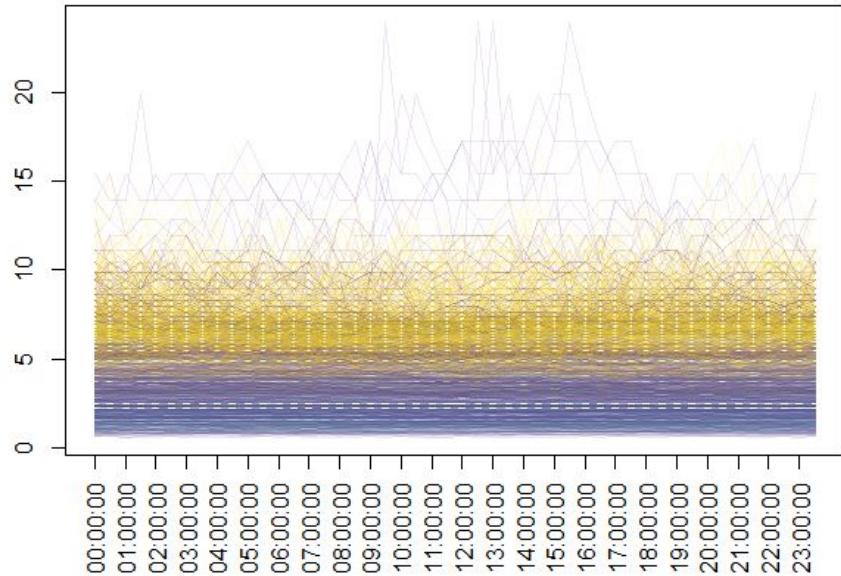
Time Series



Scatterplot



Estimated Secchi Depth (feet) by Day



Left: measurements over time

Right: current sample vs. prior sample

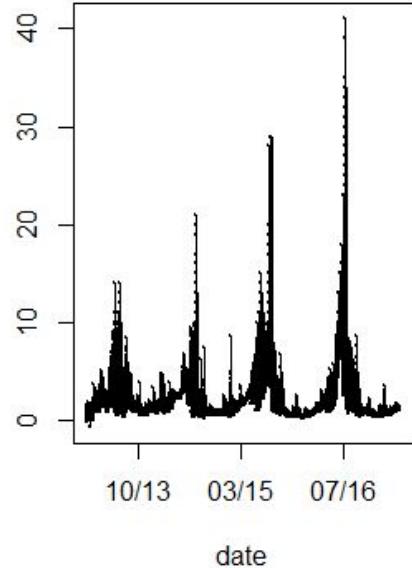
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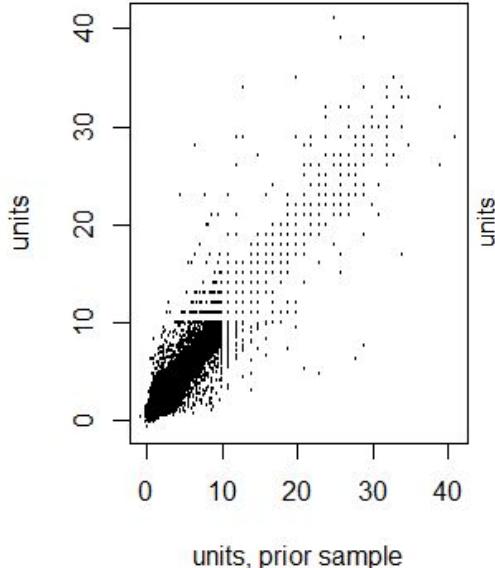
# Univariate Exploratory Graphing

Total Chlorophyll (ug/L)

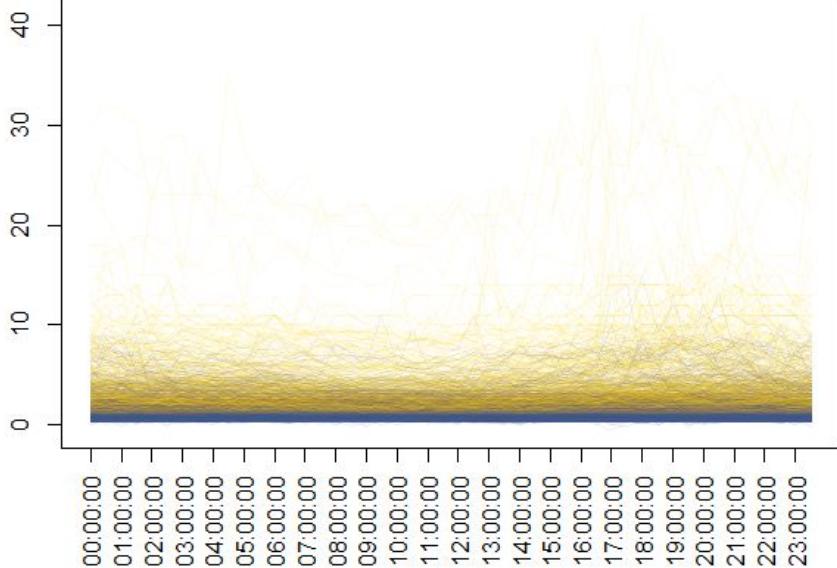
Time Series



Scatterplot



Total Chlorophyll (ug/L) by Day



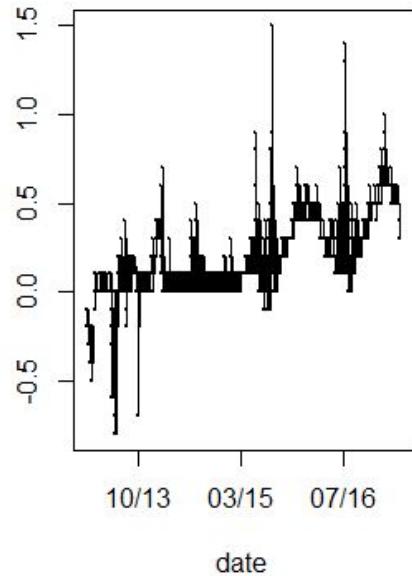
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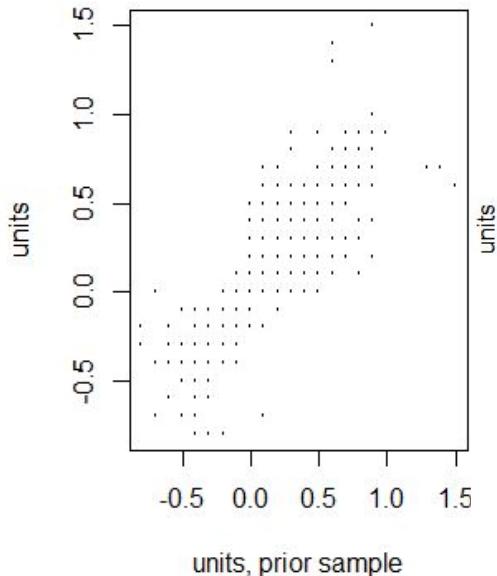
# Univariate Exploratory Graphing

Phycocyanin (ug/L)

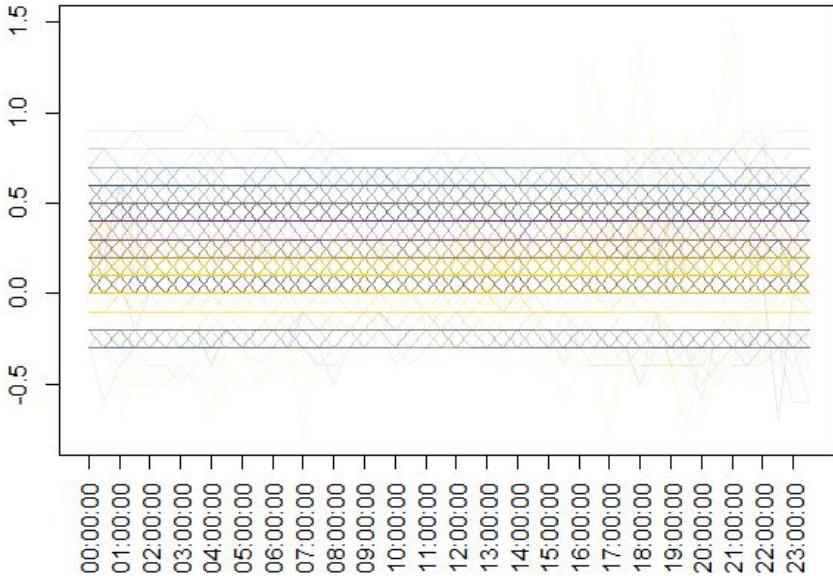
Time Series



Scatterplot



Phycocyanin (ug/L) by Day



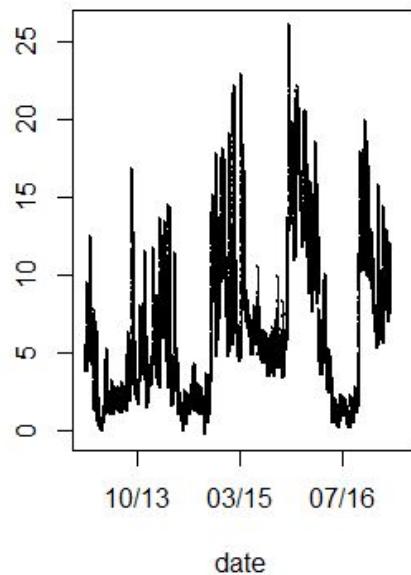
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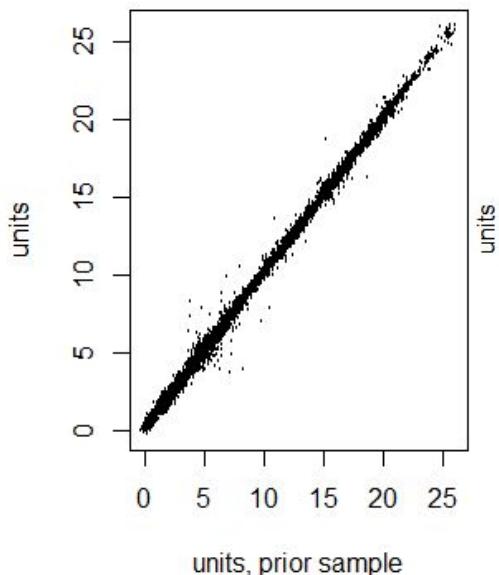
# Univariate Exploratory Graphing

fDOM (370/460) (ppb QSE)

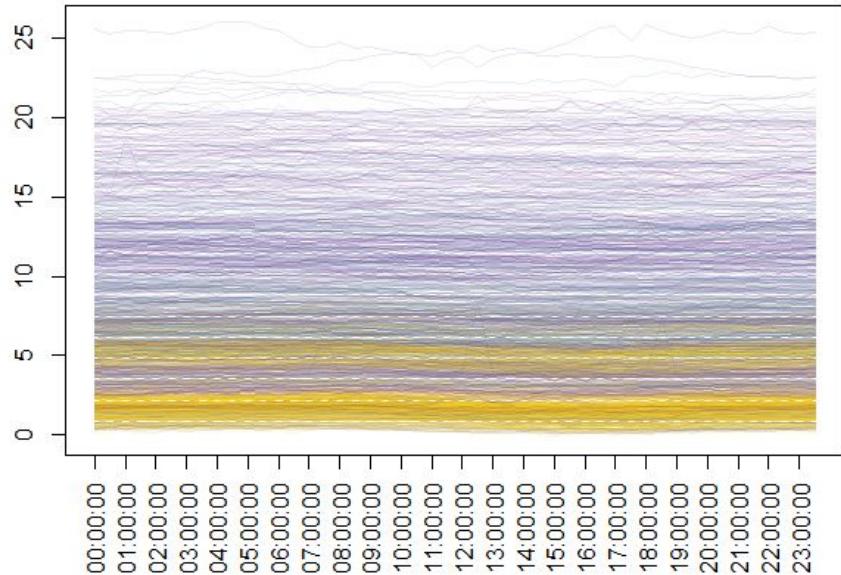
Time Series



Scatterplot



fDOM (370/460) (ppb QSE) by Day



Left: measurements over time

Right: current sample vs. prior sample

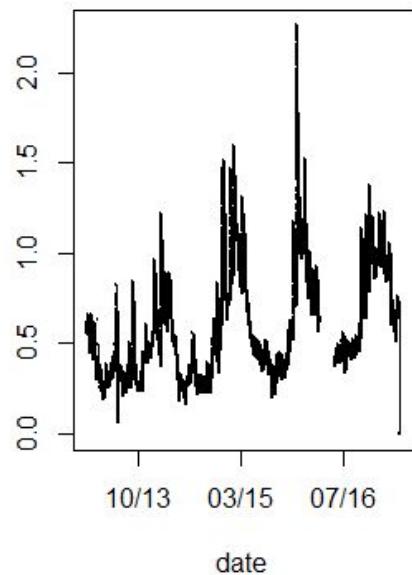
Measurements plotted by time of day.

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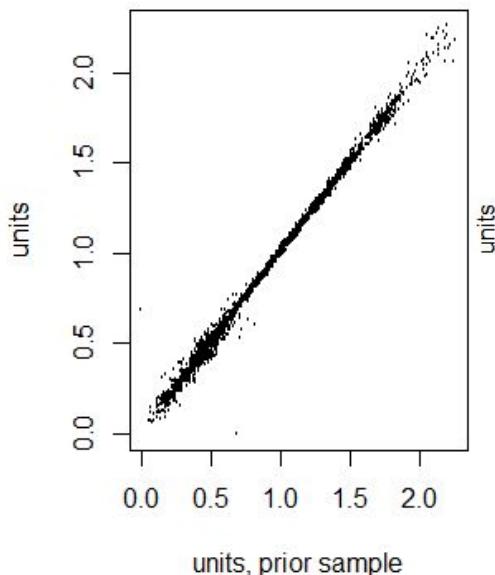
# Univariate Exploratory Graphing

Nitrate (mg/L)

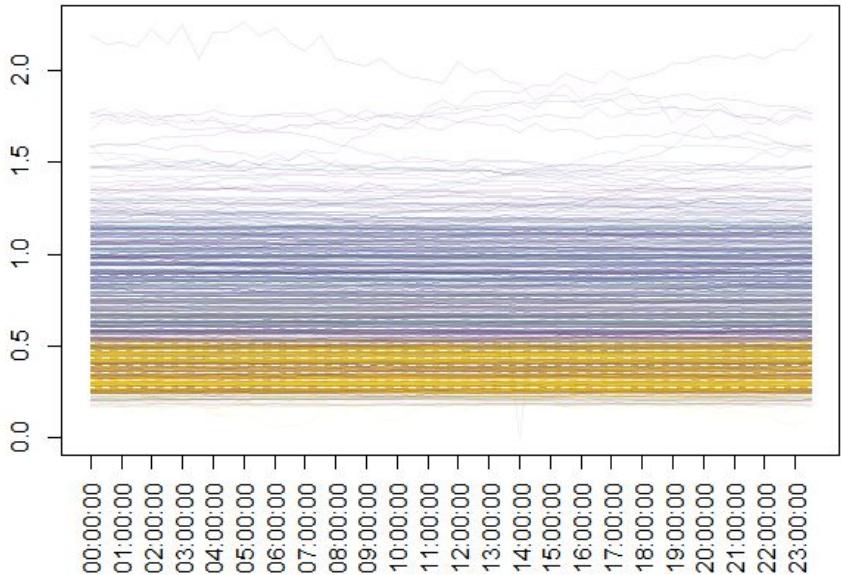
Time Series



Scatterplot



Nitrate (mg/L) by Day



Left: measurements over time

Right: current sample vs. prior sample

Measurements plotted by time of day.  
Q1: Blue, Q2: Brown, Q3: Gold, Q4: Purple

# Discrete Data

# Discrete Data Clean-up

- 319 covariates with at least 90% of data points available across samples.
- 74 observations since 2/15/13
- Eligible covariates were scanned.
- Contaminants of interest were selected, along with degenerate forms.
- Where measurement units allowed, values were summed across relevant forms.
  - DIAZINON
  - FIPRONIL
  - HEXAZINONE
  - METOLACHLOR

# Imputation

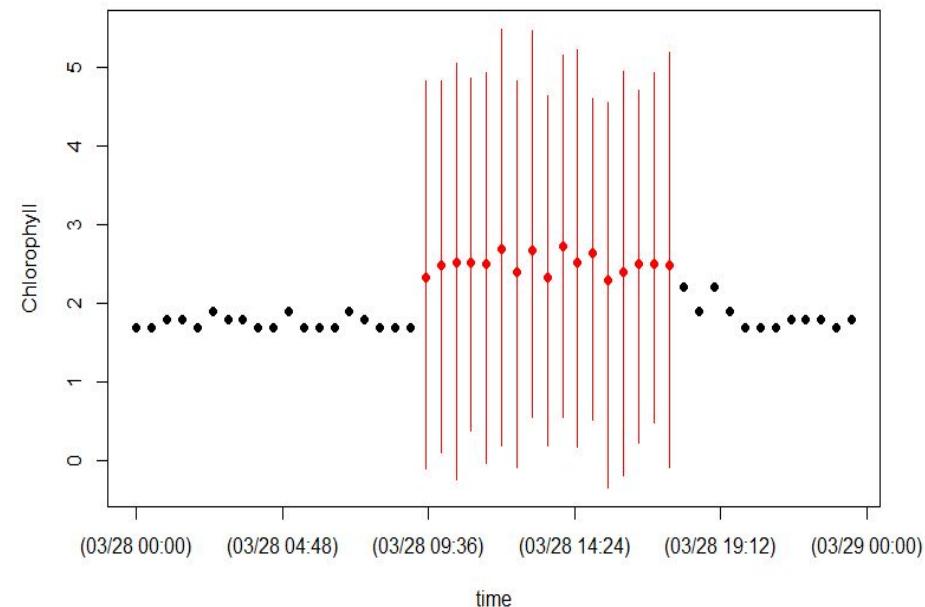
# Using Amelia II

## An 'R' package for imputing data.

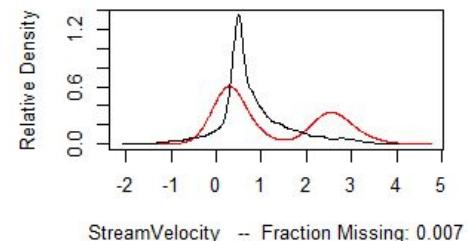
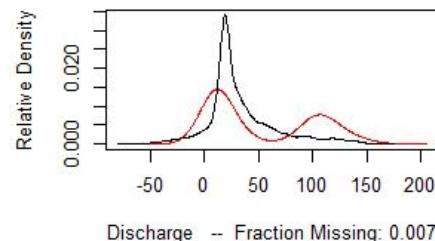
# Amelia II Overview

- Uses a bootstrapping-based algorithm to complete multiple imputations of missing data.
- Allows for trends in time series across observations within a cross-sectional unit.
- Can incorporate priors.
- Amelia II also includes useful diagnostics of the fit of multiple imputation models.
- Data are assumed to be multivariate normal.
- Data are assumed to be missing at random.
- “For each draw, we bootstrap the data to simulate estimation uncertainty and then run the EM algorithm to find the mode of the posterior for the bootstrapped data.”

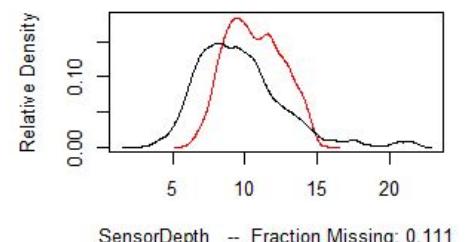
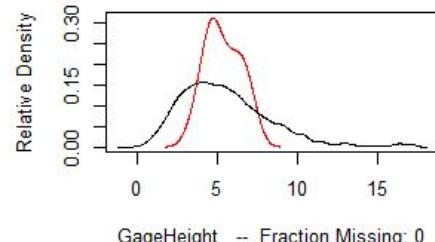
03/28/13



Observed and Imputed values of Dischar  
Observed and Imputed values of StreamVel



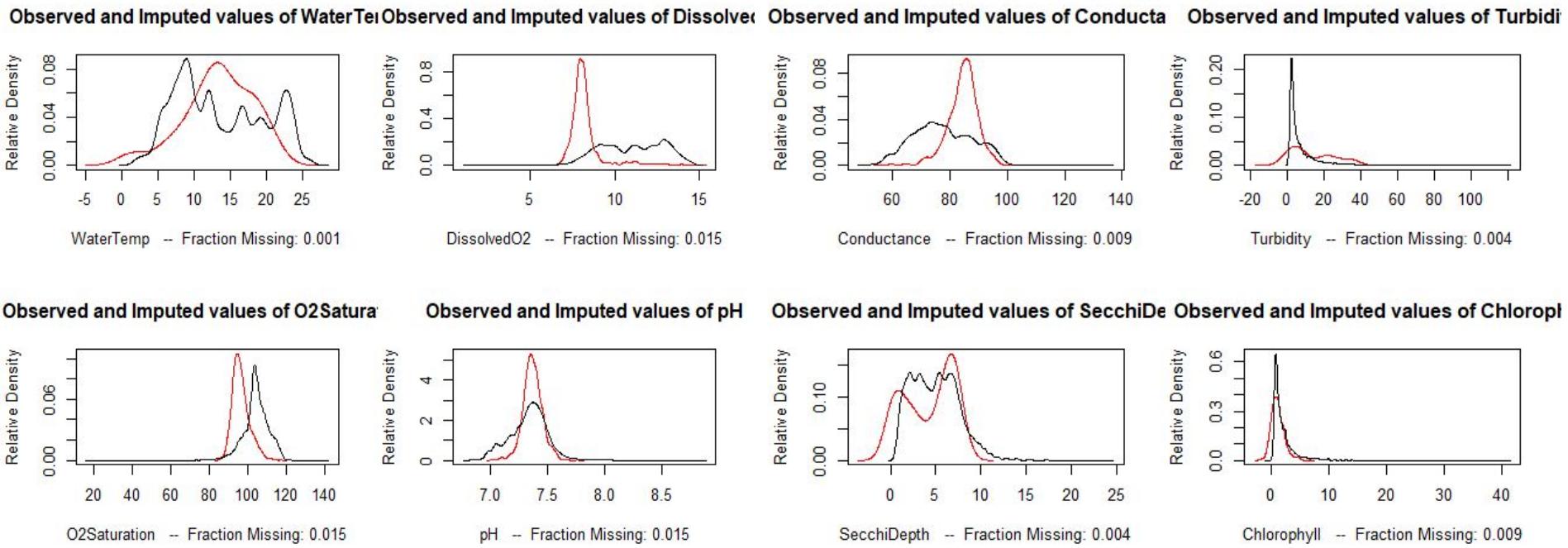
Observed and Imputed values of GageHei  
Observed and Imputed values of SensorDe



## Graphical outputs. Time Series.

Above: Imputed values with 95% confidence intervals for Chlorophyll samples taken on 3/28/13.

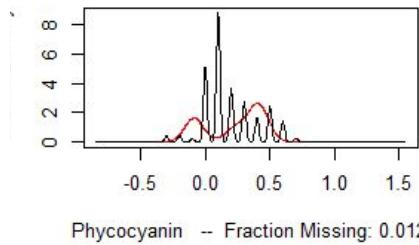
Above: Density curves for observed and imputed samples with:  
Red: mean imputation, Black: observed.



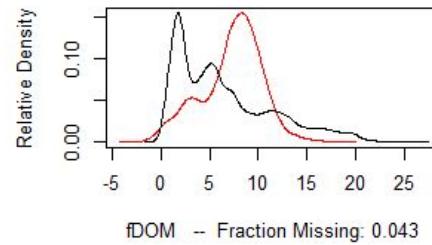
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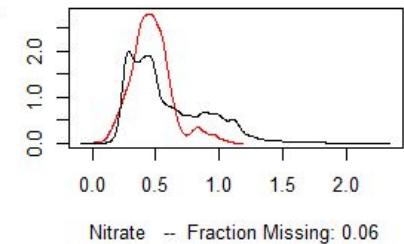
**Observed and Imputed values of Phycocyanin**



**Observed and Imputed values of fDOM**

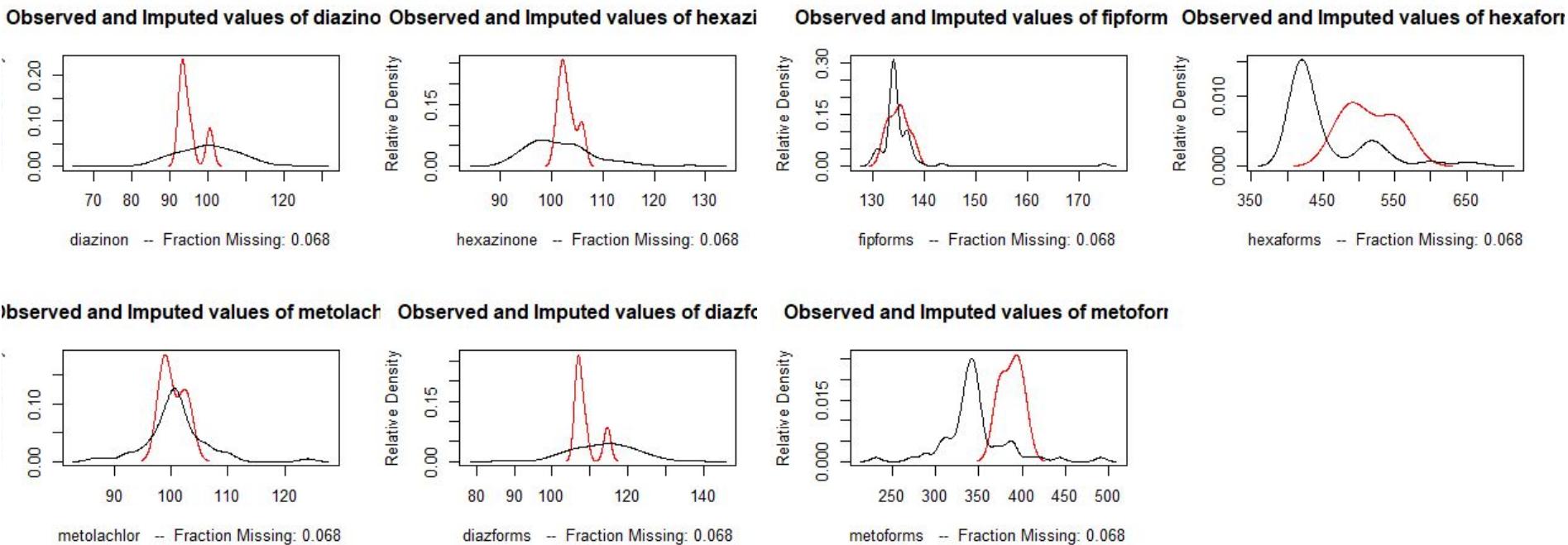


**Observed and Imputed values of Nitrate**



## Graphical outputs. Time Series.

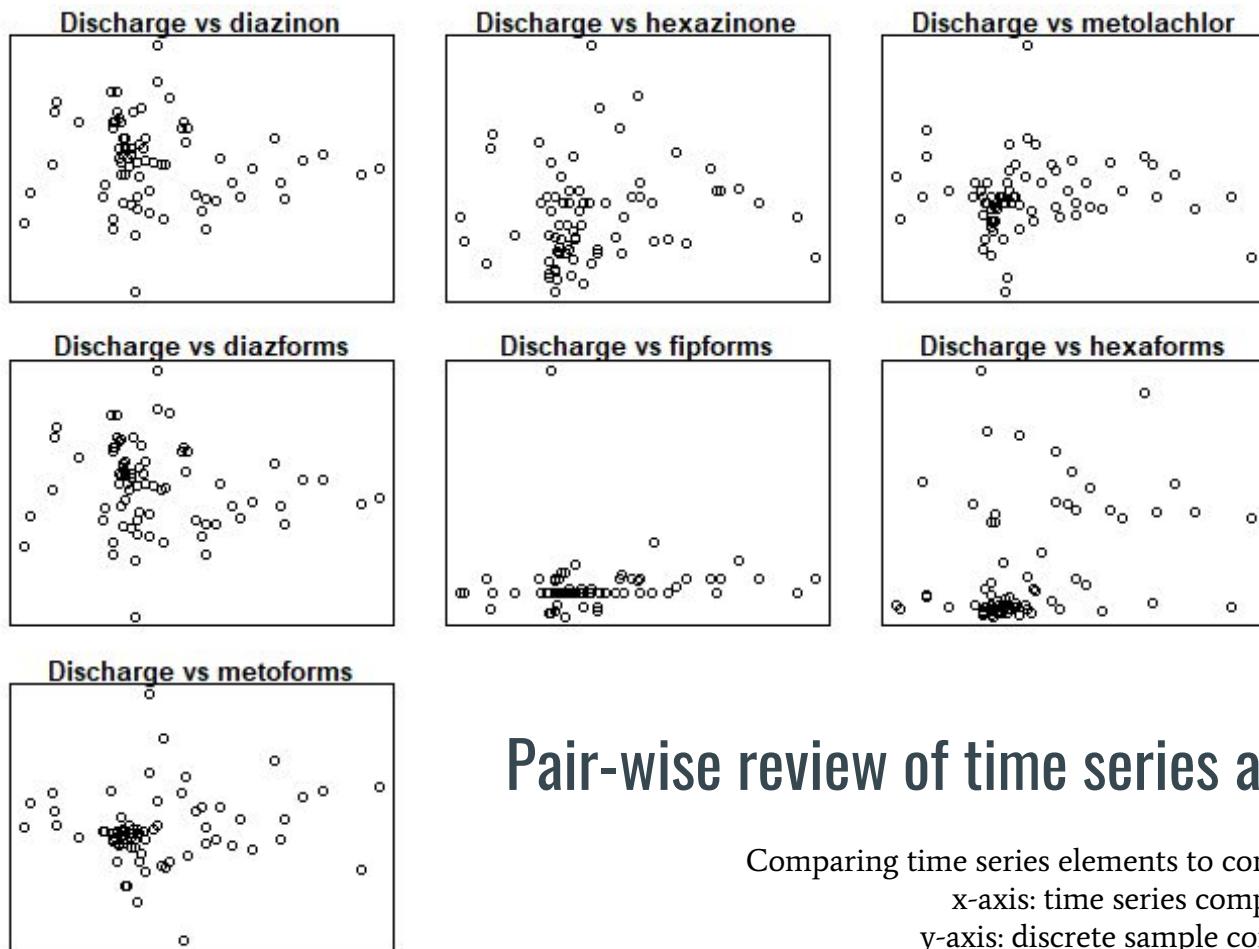
Density curves for observed and imputed samples with:  
Red: mean imputation, Black: observed.



## Graphical outputs. Discrete Elements.

Density curves for observed and imputed samples with:  
Red: mean imputation, Black: observed.

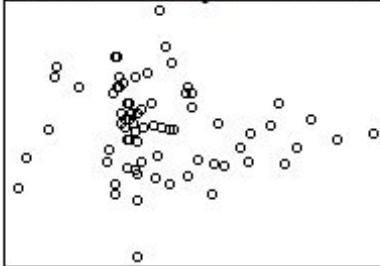
# Bivariate Graphical Analysis



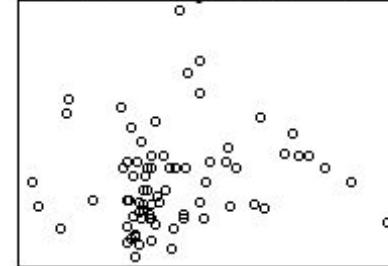
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.  
 x-axis: time series component  
 y-axis: discrete sample component

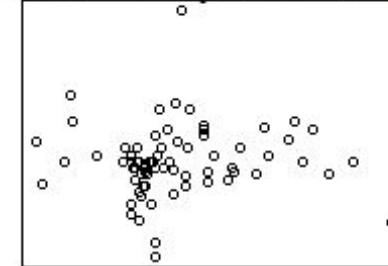
**StreamVelocity vs diazinon**



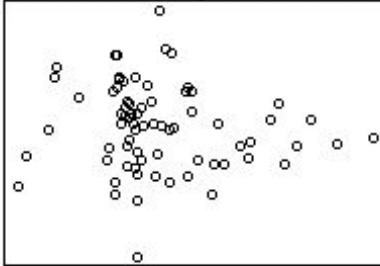
**StreamVelocity vs hexazinone**



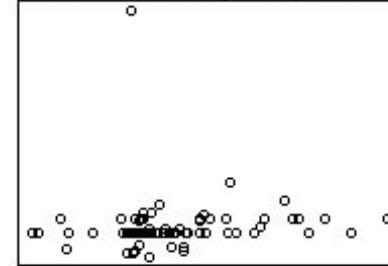
**StreamVelocity vs metolachlor**



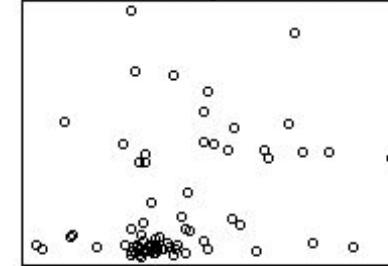
**StreamVelocity vs diazforms**



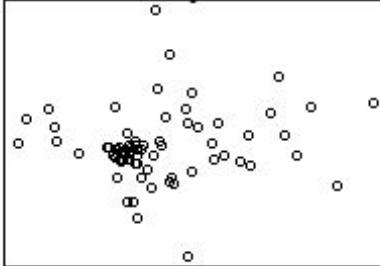
**StreamVelocity vs fipforms**



**StreamVelocity vs hexaforms**



**StreamVelocity vs metoforms**



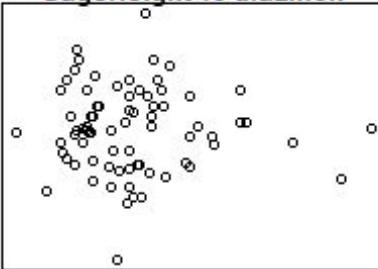
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

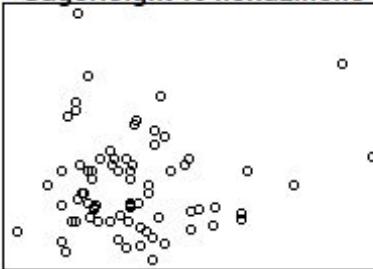
x-axis: time series component

y-axis: discrete sample component

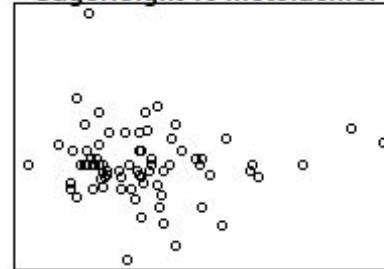
GageHeight vs diazinon



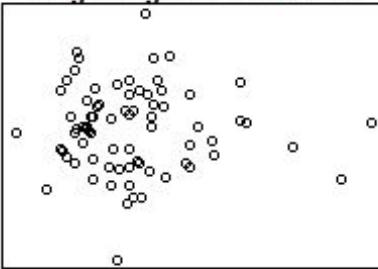
GageHeight vs hexazinone



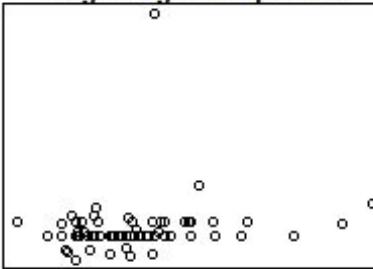
GageHeight vs metolachlor



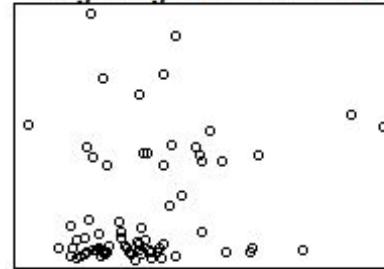
GageHeight vs diazforms



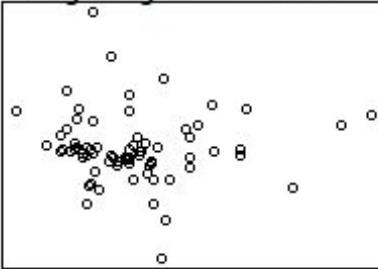
GageHeight vs fipforms



GageHeight vs hexaforms



GageHeight vs metoforms



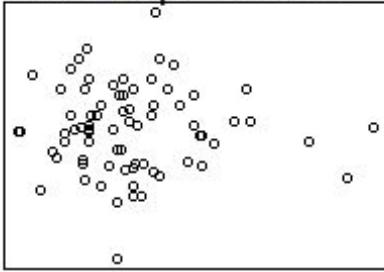
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

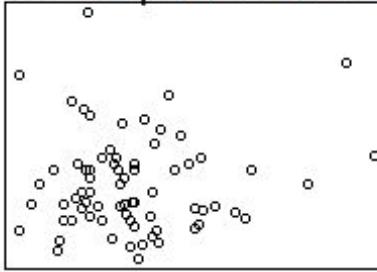
x-axis: time series component

y-axis: discrete sample component

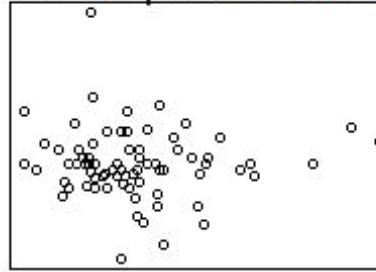
SensorDepth vs diazinon



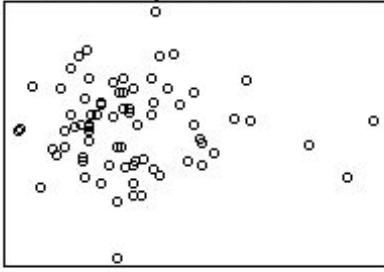
SensorDepth vs hexazinone



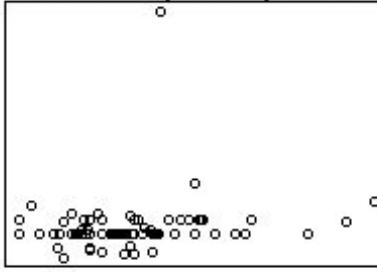
SensorDepth vs metolachlor



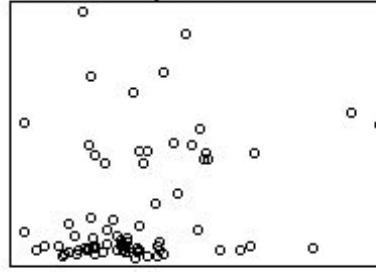
SensorDepth vs diazforms



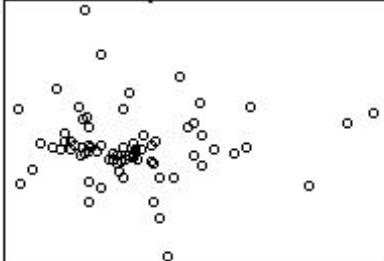
SensorDepth vs fipforms



SensorDepth vs hexaforms



SensorDepth vs metoforms



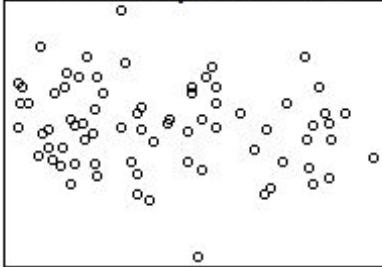
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

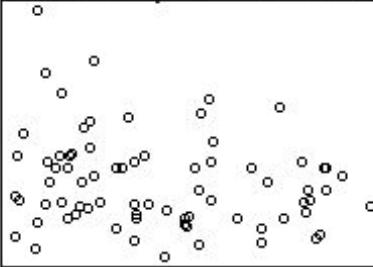
x-axis: time series component

y-axis: discrete sample component

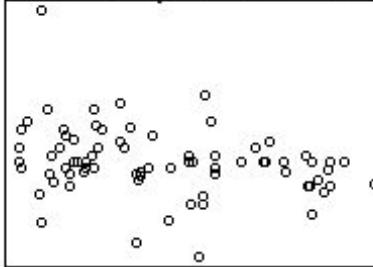
**WaterTemp vs diazinon**



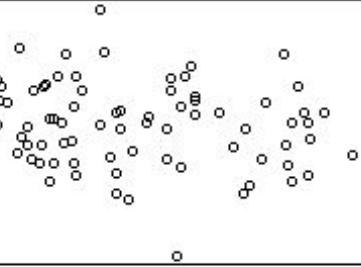
**WaterTemp vs hexazinone**



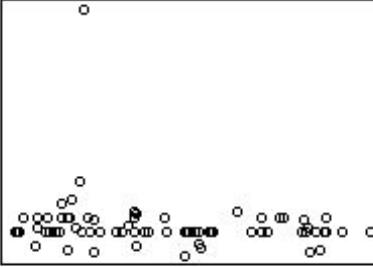
**WaterTemp vs metolachlor**



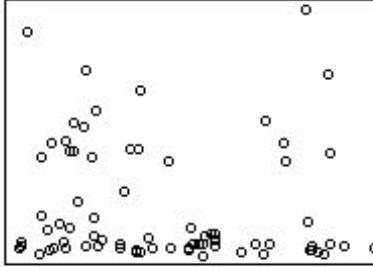
**WaterTemp vs diazforms**



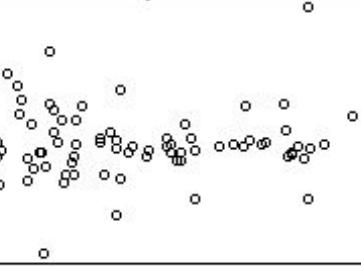
**WaterTemp vs fipforms**



**WaterTemp vs hexaforms**



**WaterTemp vs metoforms**



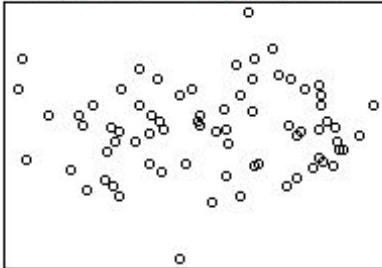
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

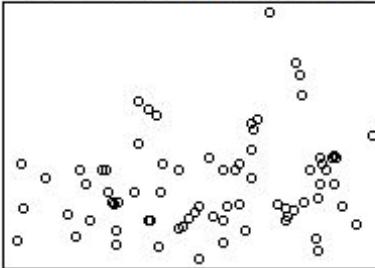
x-axis: time series component

y-axis: discrete sample component

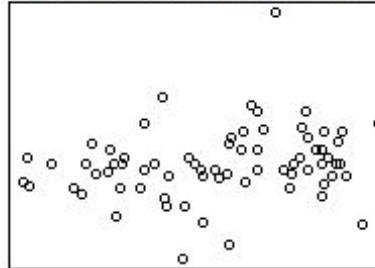
DissolvedO2 vs diazinon



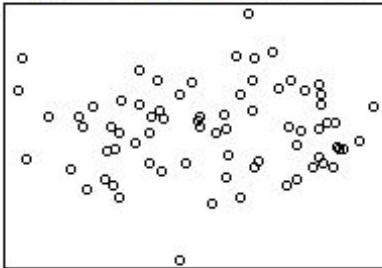
DissolvedO2 vs hexazinone



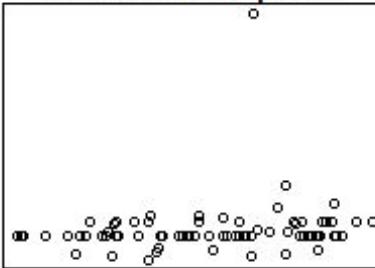
DissolvedO2 vs metolachlor



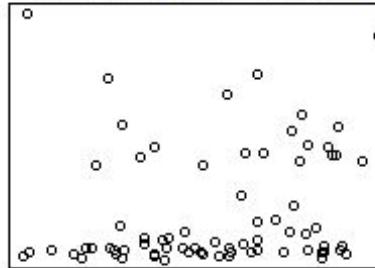
DissolvedO2 vs diazforms



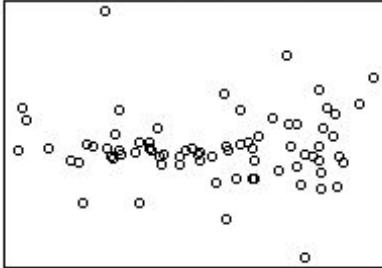
DissolvedO2 vs fipforms



DissolvedO2 vs hexaforms



DissolvedO2 vs metoforms



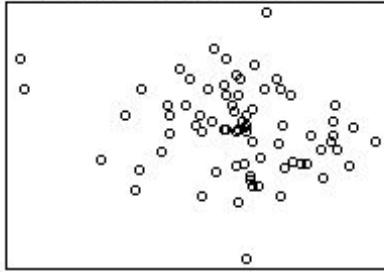
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

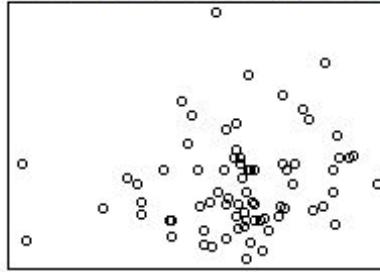
x-axis: time series component

y-axis: discrete sample component

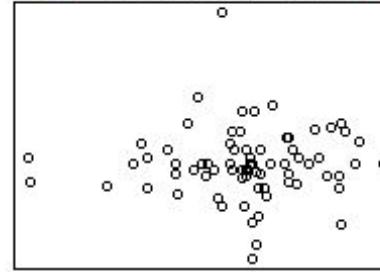
O<sub>2</sub>Saturation vs diazinon



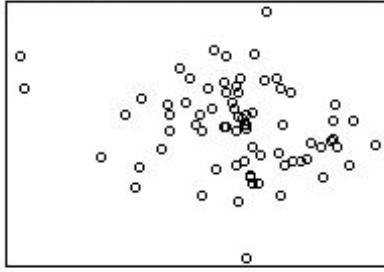
O<sub>2</sub>Saturation vs hexazinone



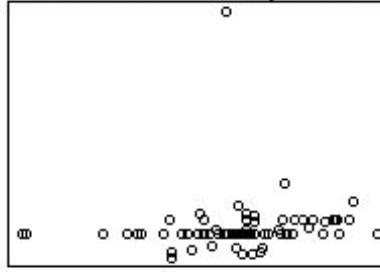
O<sub>2</sub>Saturation vs metolachlor



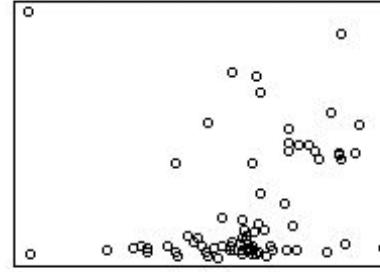
O<sub>2</sub>Saturation vs diazforms



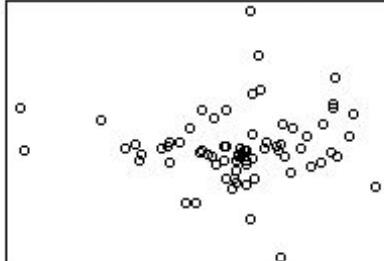
O<sub>2</sub>Saturation vs fipforms



O<sub>2</sub>Saturation vs hexaforms



O<sub>2</sub>Saturation vs metoforms



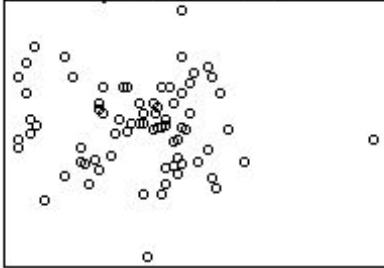
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

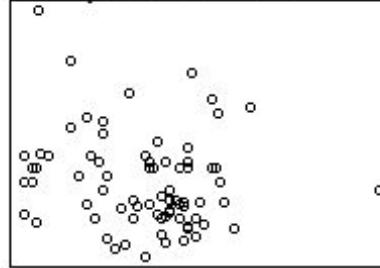
x-axis: time series component

y-axis: discrete sample component

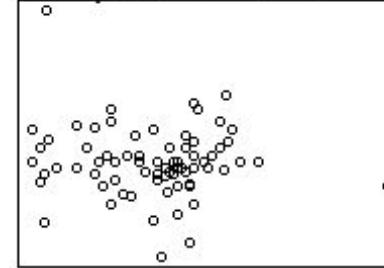
pH vs diazinon



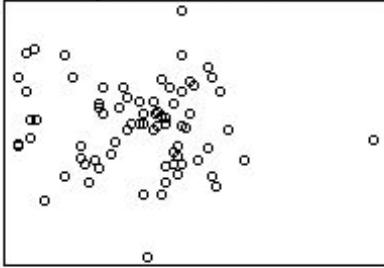
pH vs hexazinone



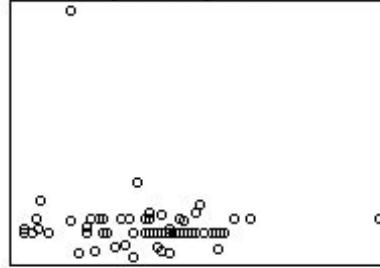
pH vs metolachlor



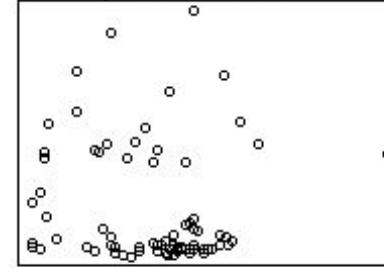
pH vs diazforms



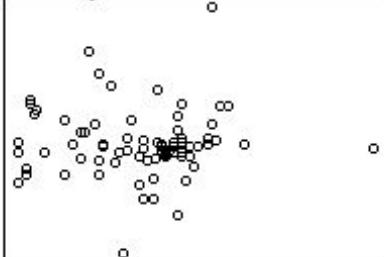
pH vs fipforms



pH vs hexaforms



pH vs metoforms



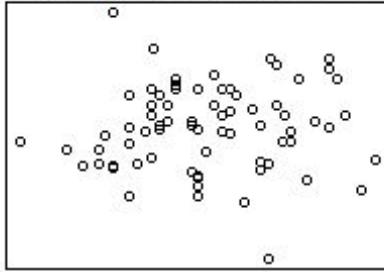
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

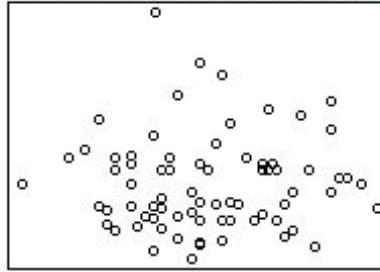
x-axis: time series component

y-axis: discrete sample component

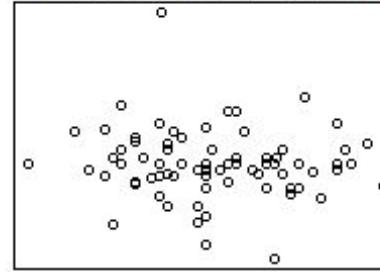
Conductance vs diazinon



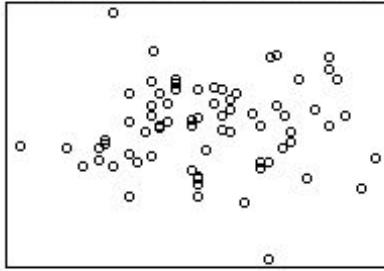
Conductance vs hexazinone



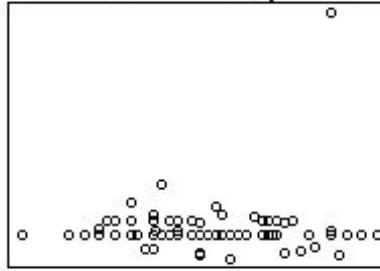
Conductance vs metolachlor



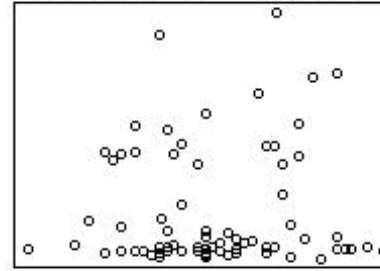
Conductance vs diazforms



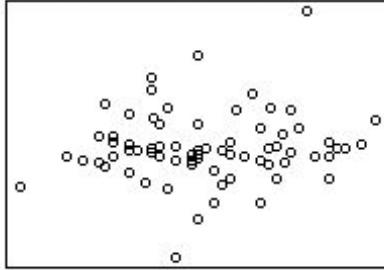
Conductance vs fipiforms



Conductance vs hexaforms



Conductance vs metoforms



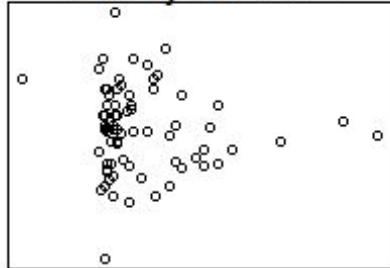
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

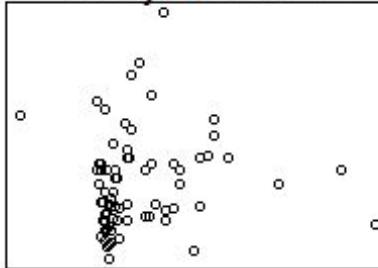
x-axis: time series component

y-axis: discrete sample component

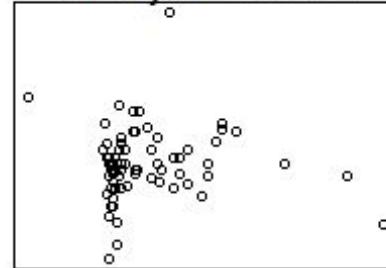
Turbidity vs diazinon



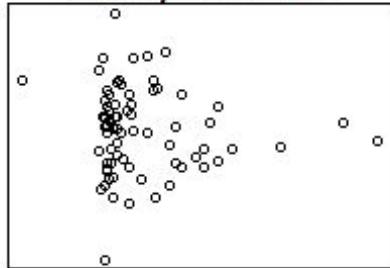
Turbidity vs hexazinone



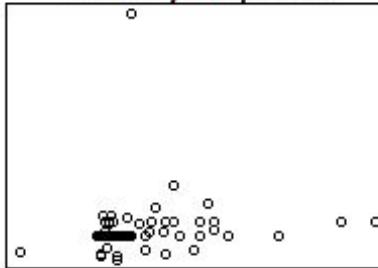
Turbidity vs metolachlor



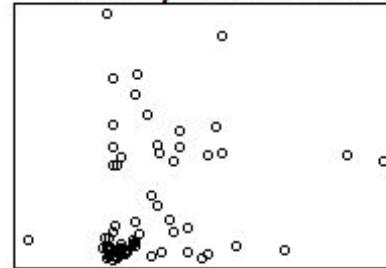
Turbidity vs diazforms



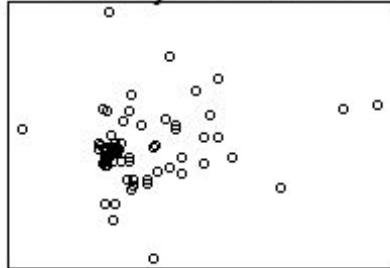
Turbidity vs fipforms



Turbidity vs hexaforms



Turbidity vs metoforms



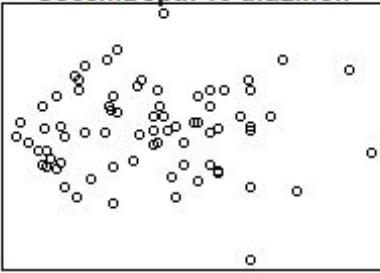
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

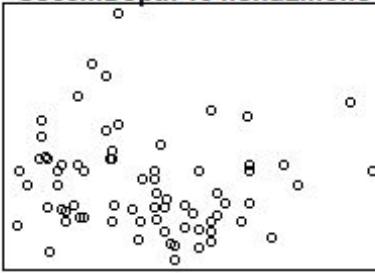
x-axis: time series component

y-axis: discrete sample component

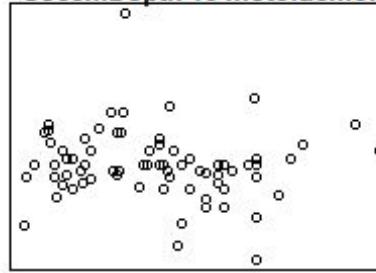
**SecchiDepth vs diazinon**



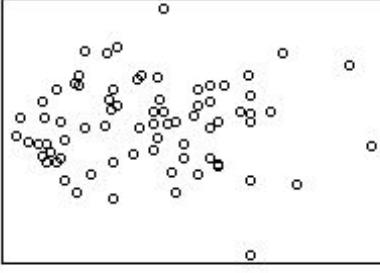
**SecchiDepth vs hexazinone**



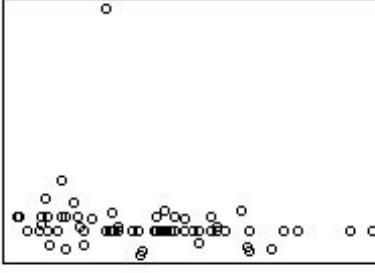
**SecchiDepth vs metolachlor**



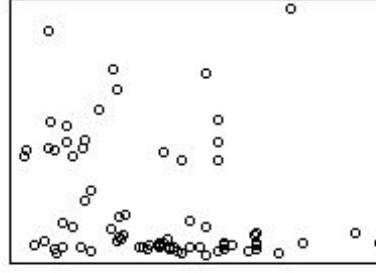
**SecchiDepth vs diazforms**



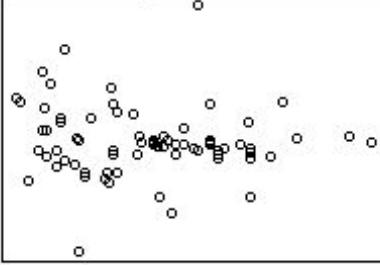
**SecchiDepth vs fipforms**



**SecchiDepth vs hexaforms**



**SecchiDepth vs metoforms**



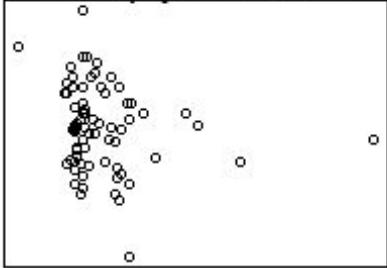
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

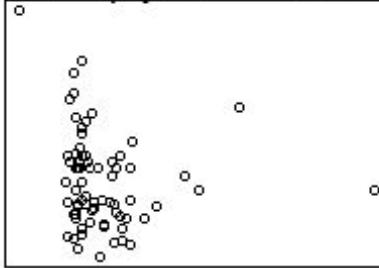
x-axis: time series component

y-axis: discrete sample component

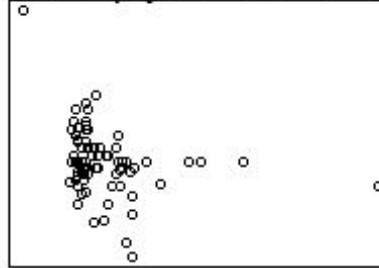
Chlorophyll vs diazinon



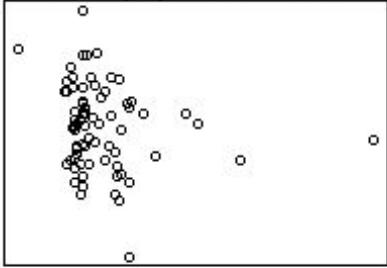
Chlorophyll vs hexazinone



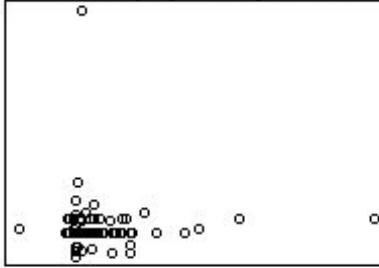
Chlorophyll vs metolachlor



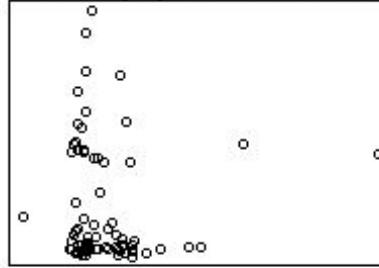
Chlorophyll vs diazforms



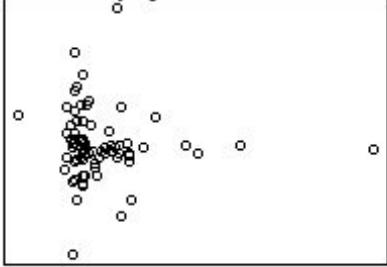
Chlorophyll vs fipforms



Chlorophyll vs hexaforms



Chlorophyll vs metoforms



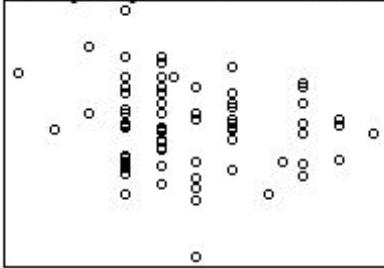
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

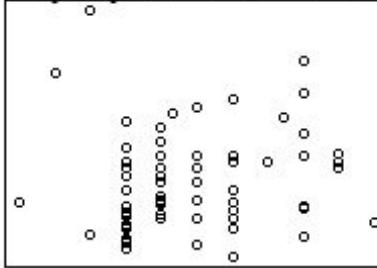
x-axis: time series component

y-axis: discrete sample component

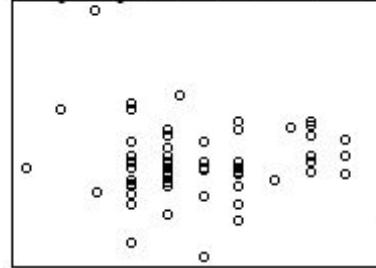
**Phycocyanin vs diazinon**



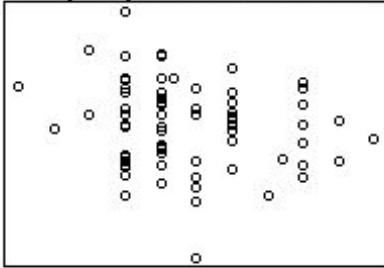
**Phycocyanin vs hexazinone**



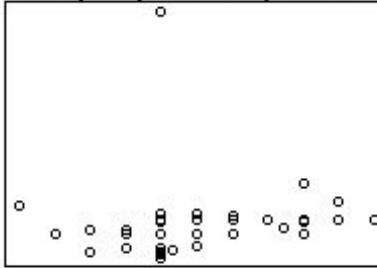
**Phycocyanin vs metolachlor**



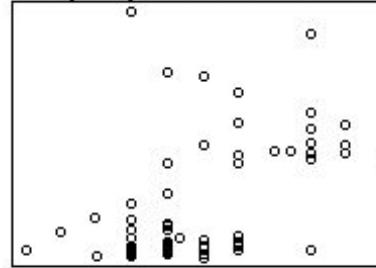
**Phycocyanin vs diazforms**



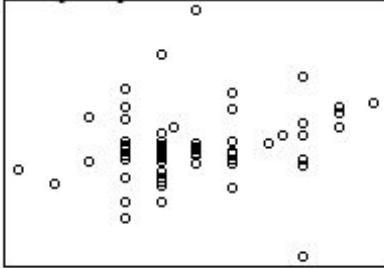
**Phycocyanin vs fipforms**



**Phycocyanin vs hexaforms**



**Phycocyanin vs metoforms**



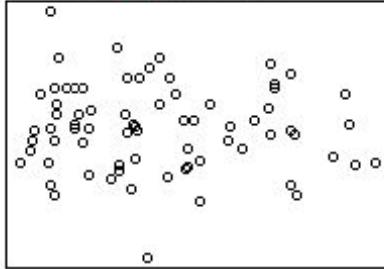
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

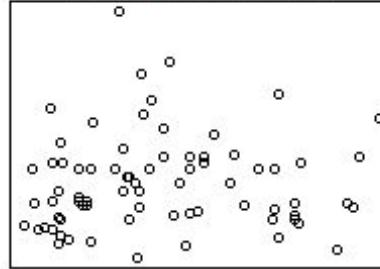
x-axis: time series component

y-axis: discrete sample component

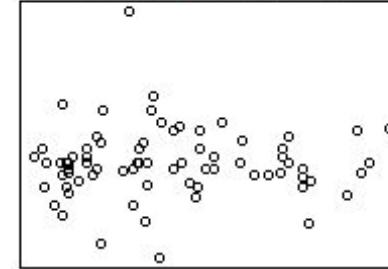
fDOM vs diazinon



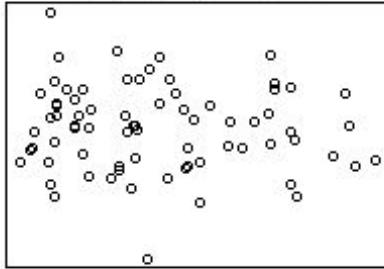
fDOM vs hexazinone



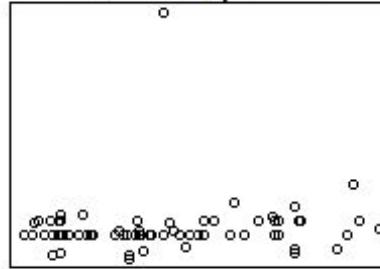
fDOM vs metolachlor



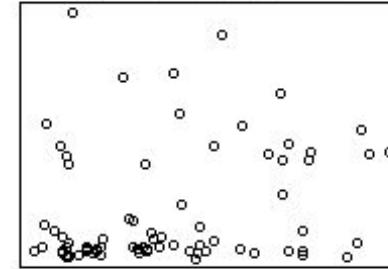
fDOM vs diazforms



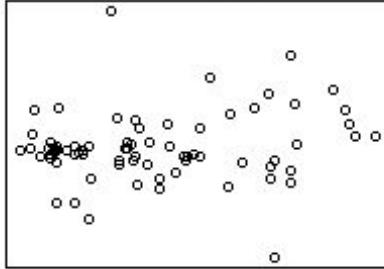
fDOM vs fipforms



fDOM vs hexaforms



fDOM vs metoforms



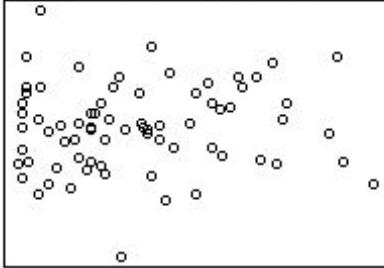
## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

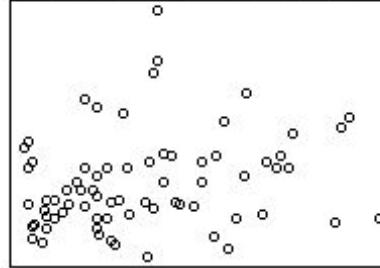
x-axis: time series component

y-axis: discrete sample component

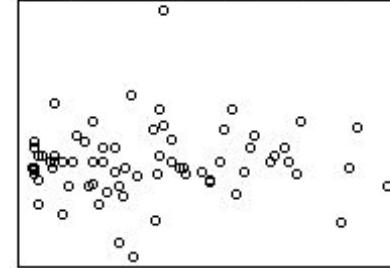
Nitrate vs diazinon



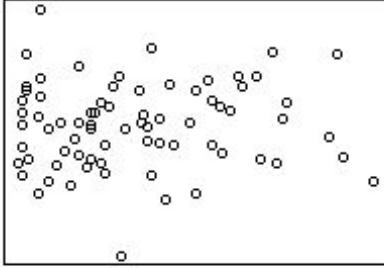
Nitrate vs hexazinone



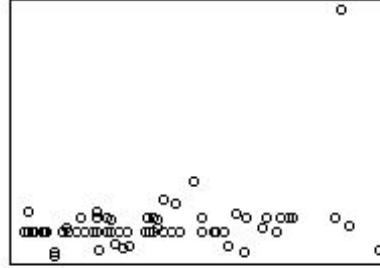
Nitrate vs metolachlor



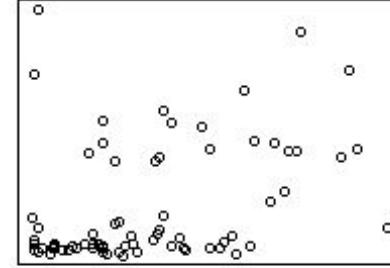
Nitrate vs diazforms



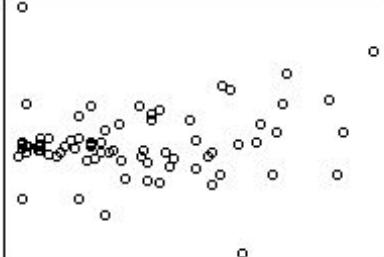
Nitrate vs fipforms



Nitrate vs hexaforms



Nitrate vs metoforms



## Pair-wise review of time series and discrete covariates.

Comparing time series elements to contaminants of interest.

x-axis: time series component

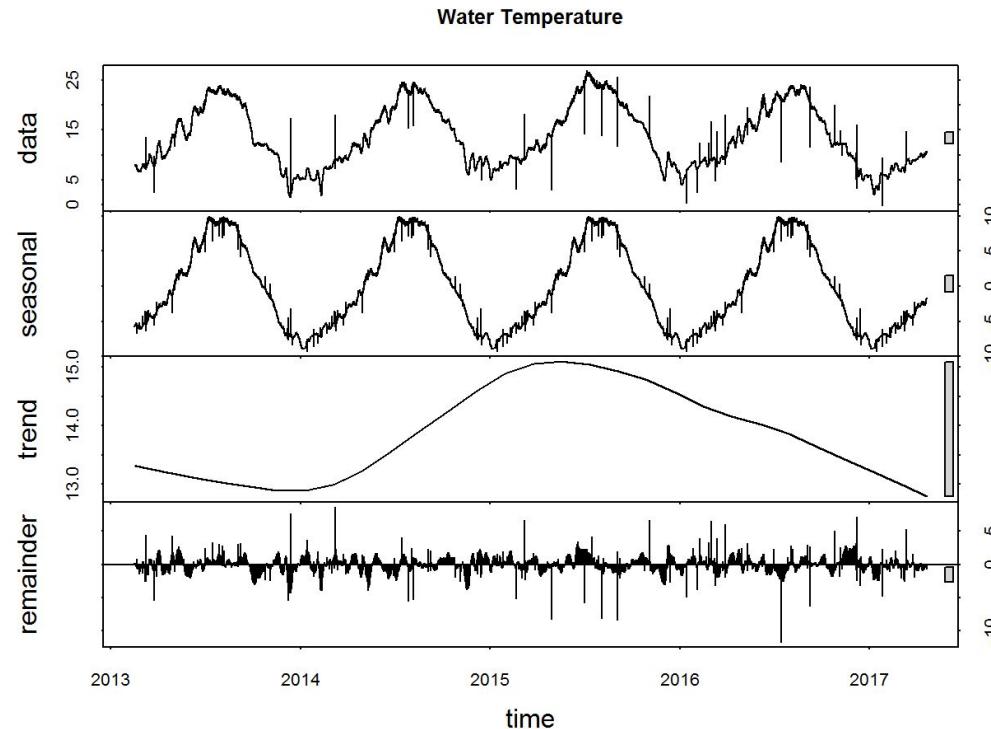
y-axis: discrete sample component

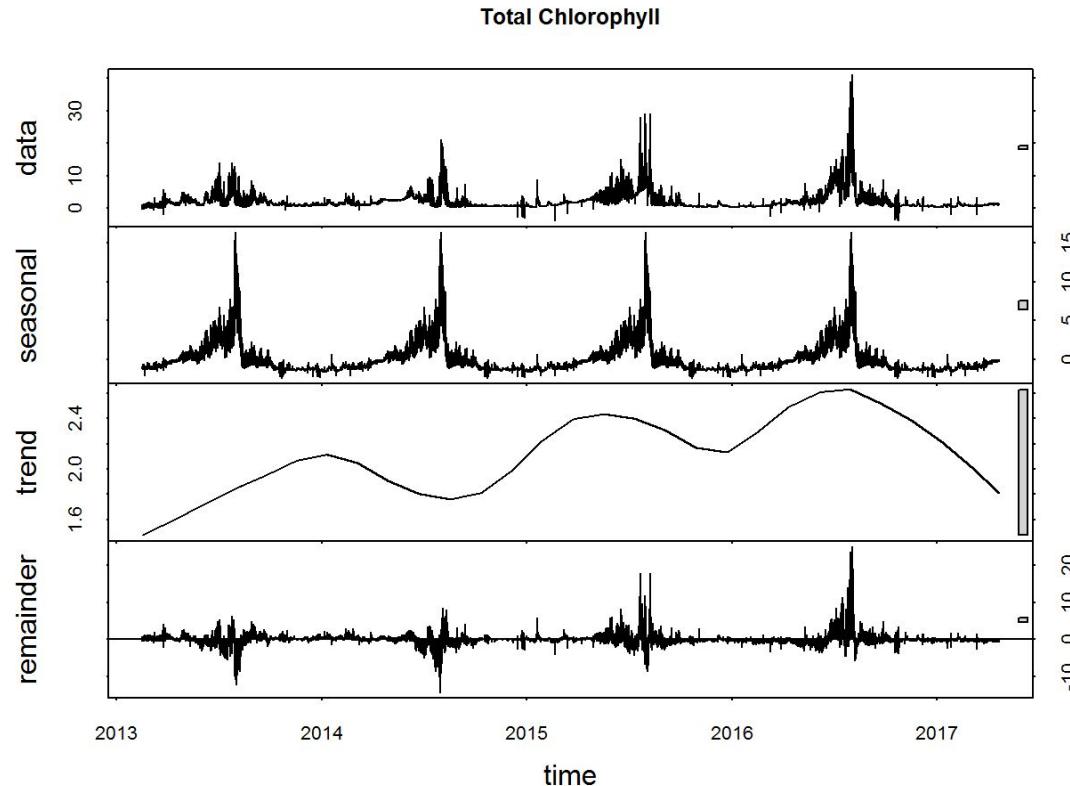
# Time Series Analysis

# Decomposing the Time Series Measurements

- Used additional packages ‘TSA’ and ‘forecast’ to analyze time series objects
- Decomposed all 15 measurements using stl()
  - Seasonal Trend
  - Decomposition Procedure using Loess
- Keep an eye on the units of seasonal vs. trend!

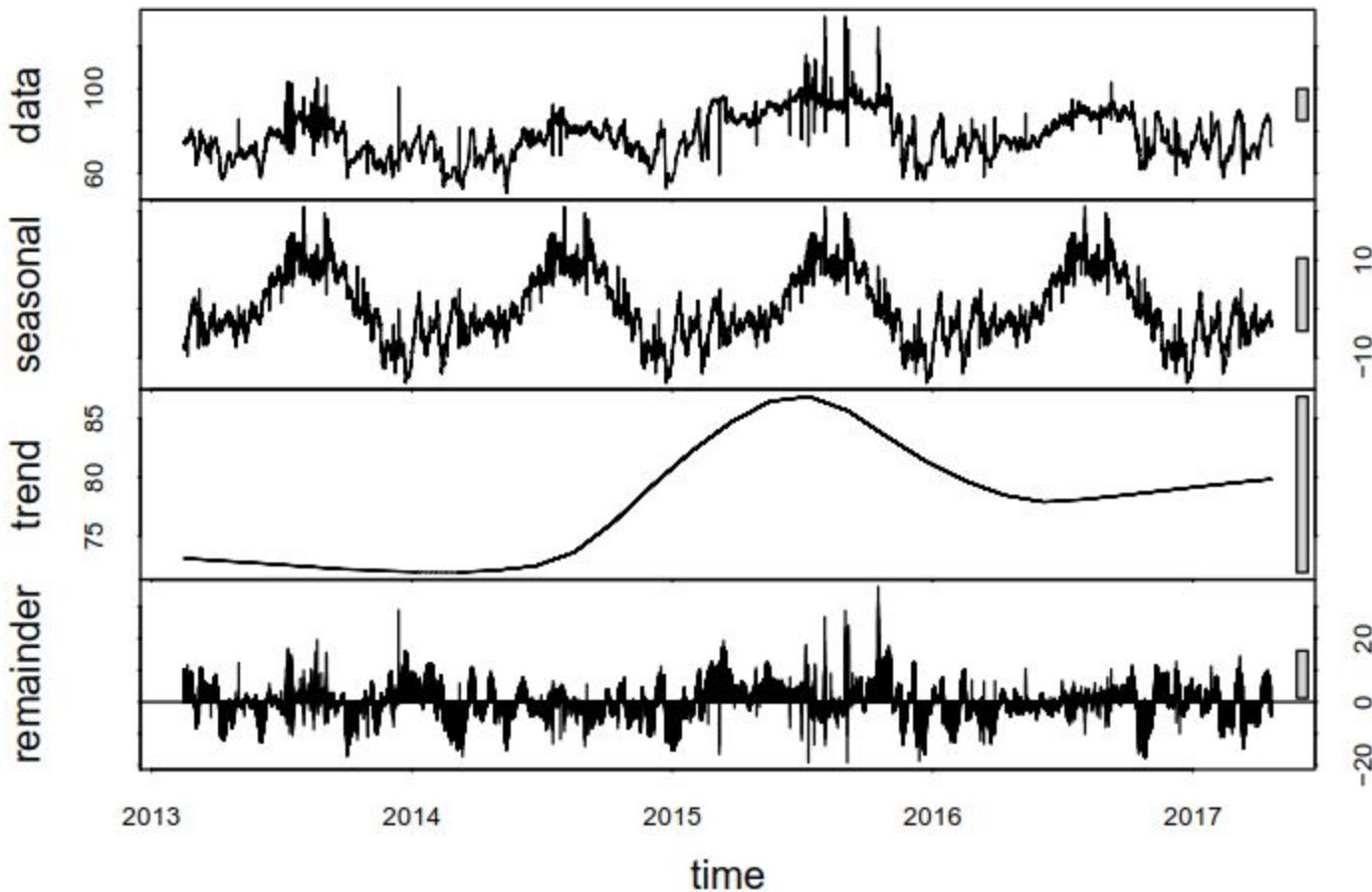
Right: Decomposition of water temperature data to break into seasonal and trend components



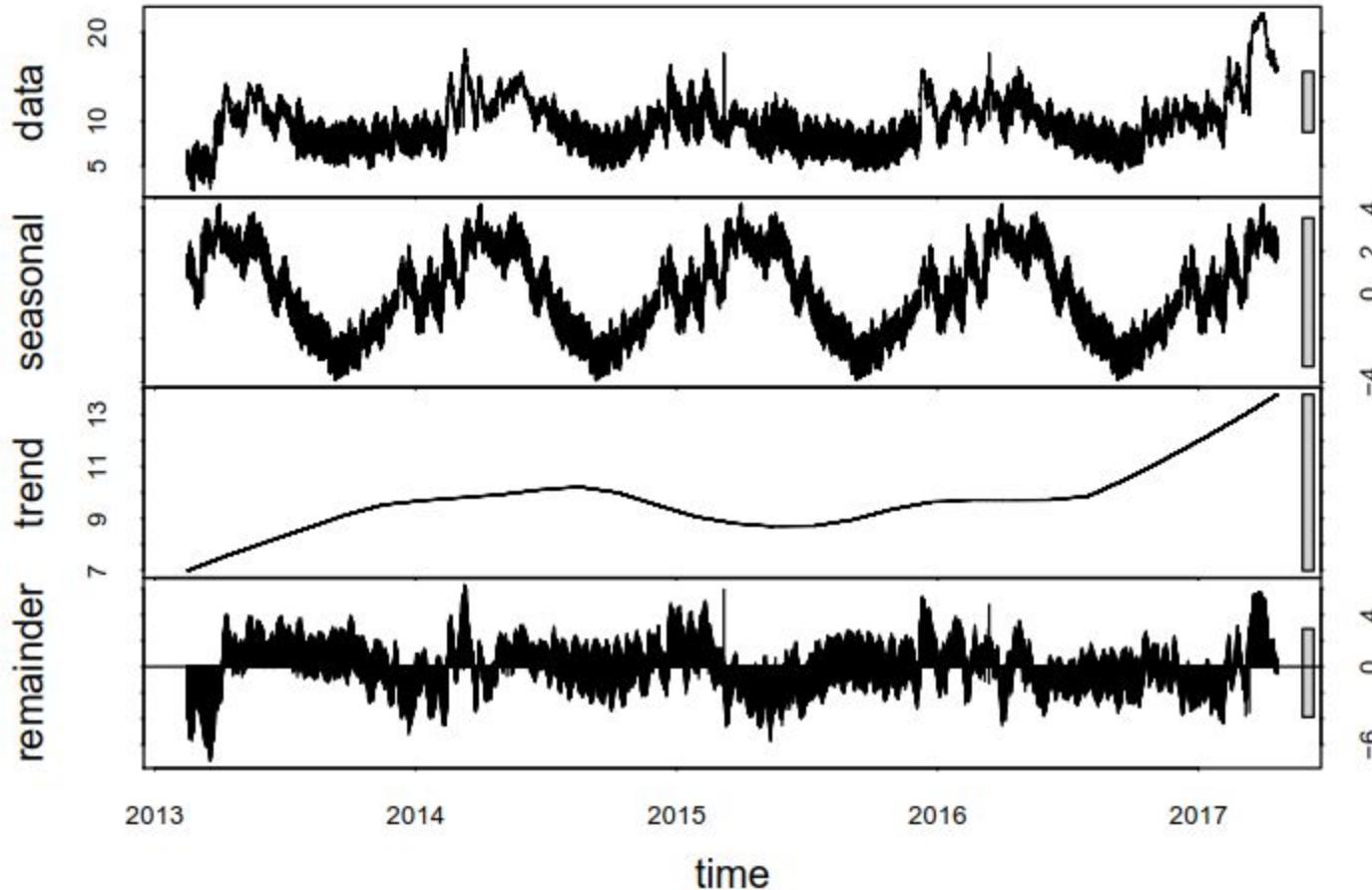


Above: Decomposition of chlorophyll data into  
seasonal, trend components using `stl()`

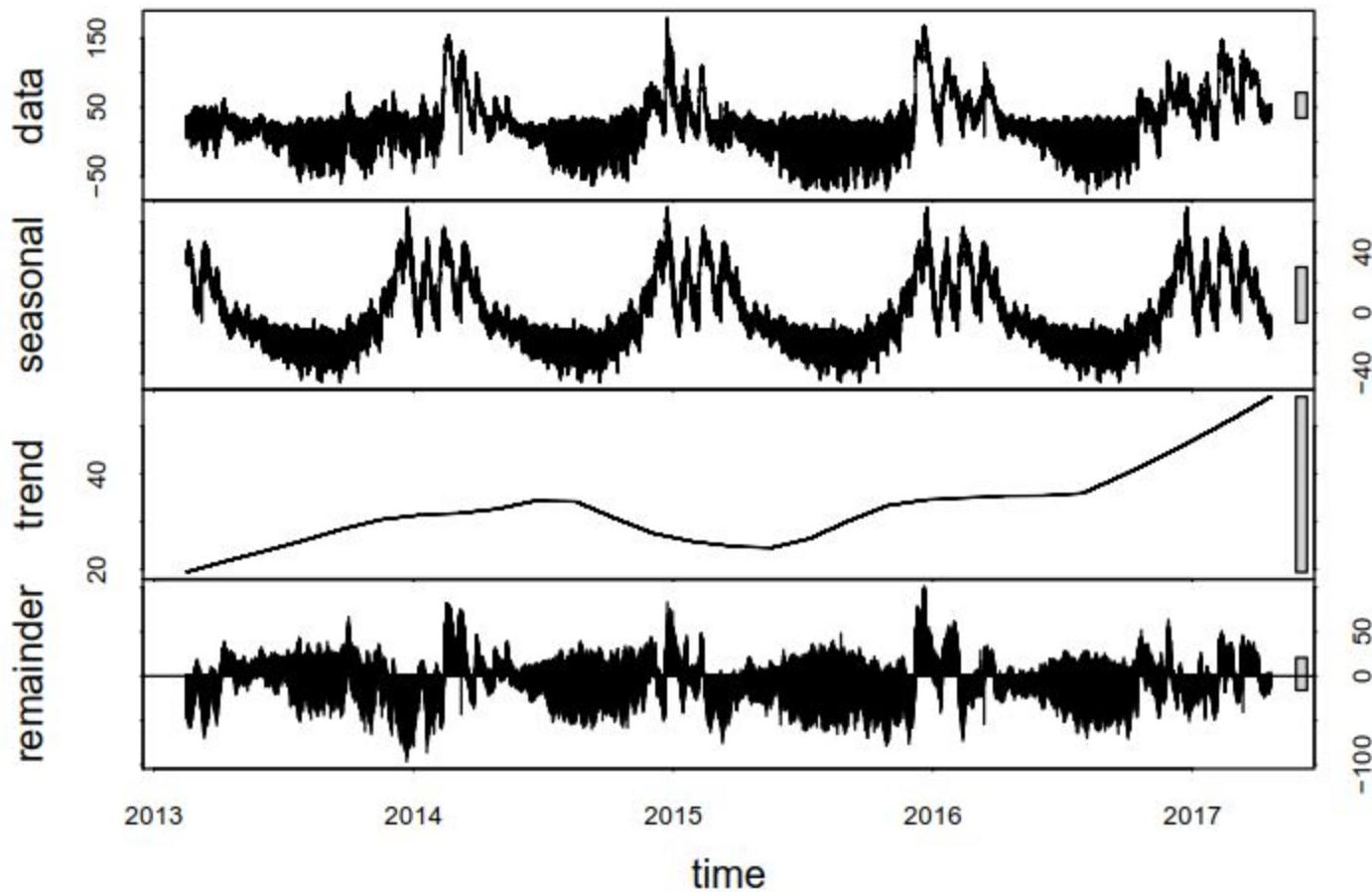
### Conductance



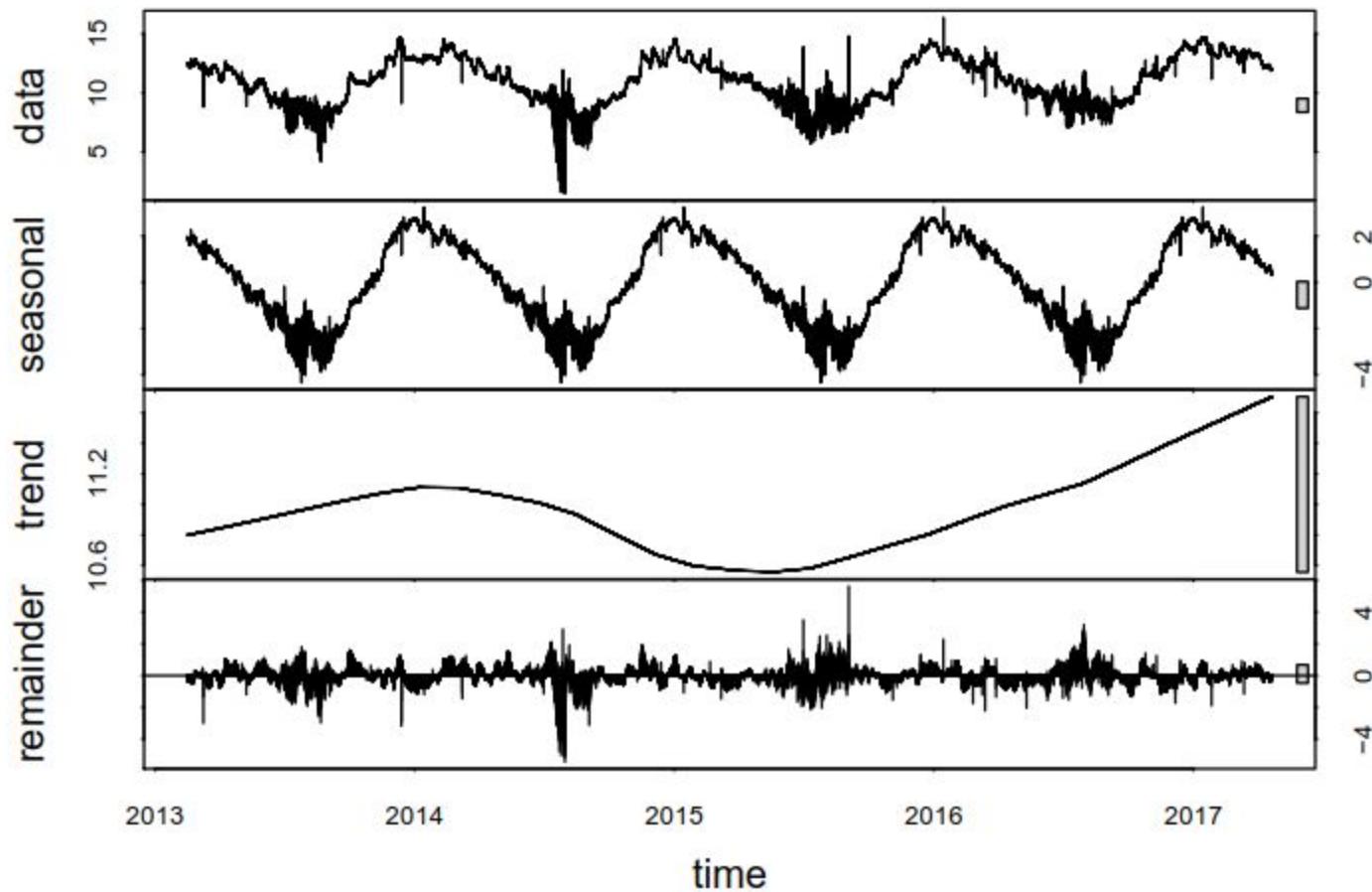
Sensor Depth



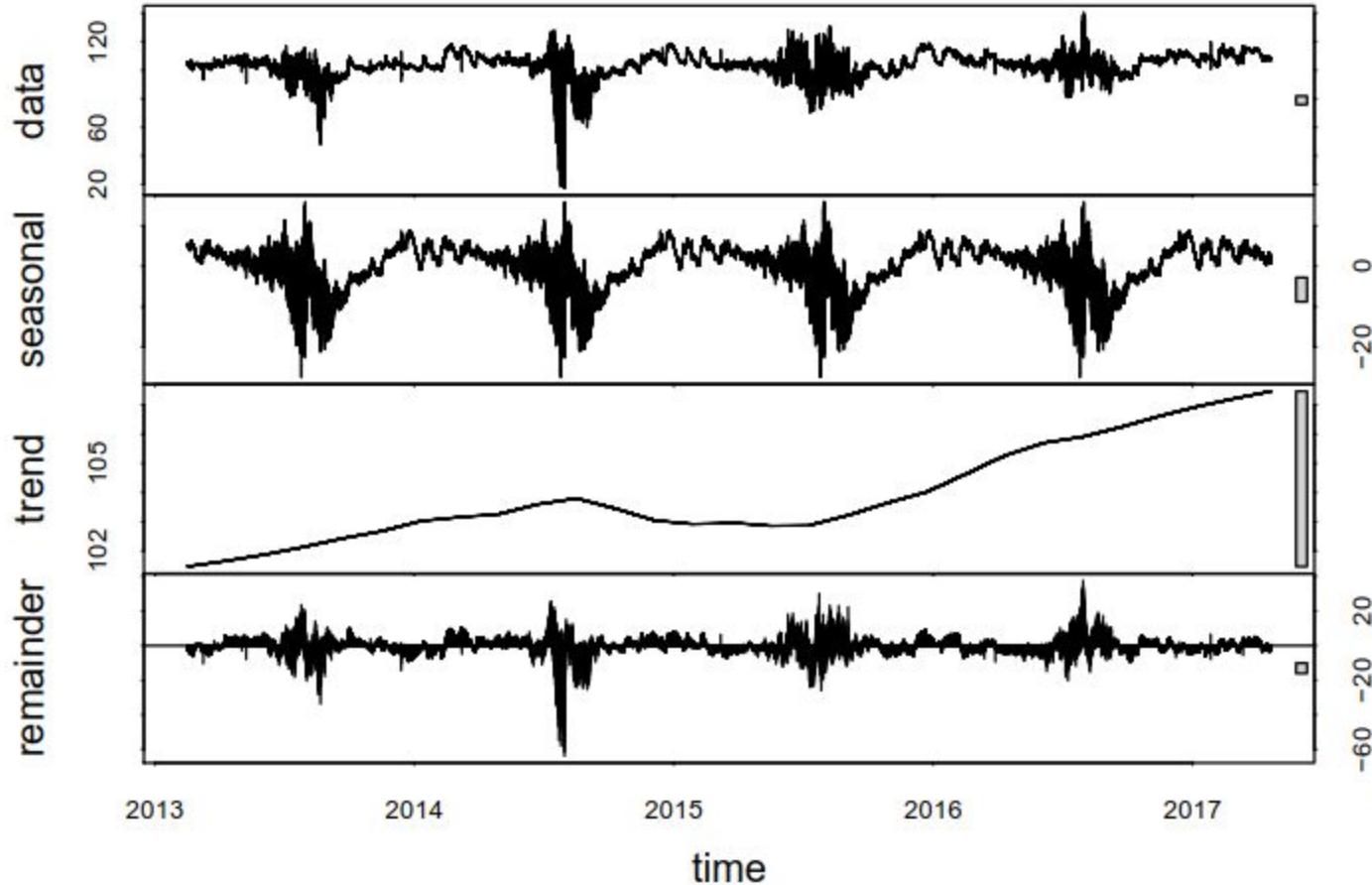
### Stream Discharge



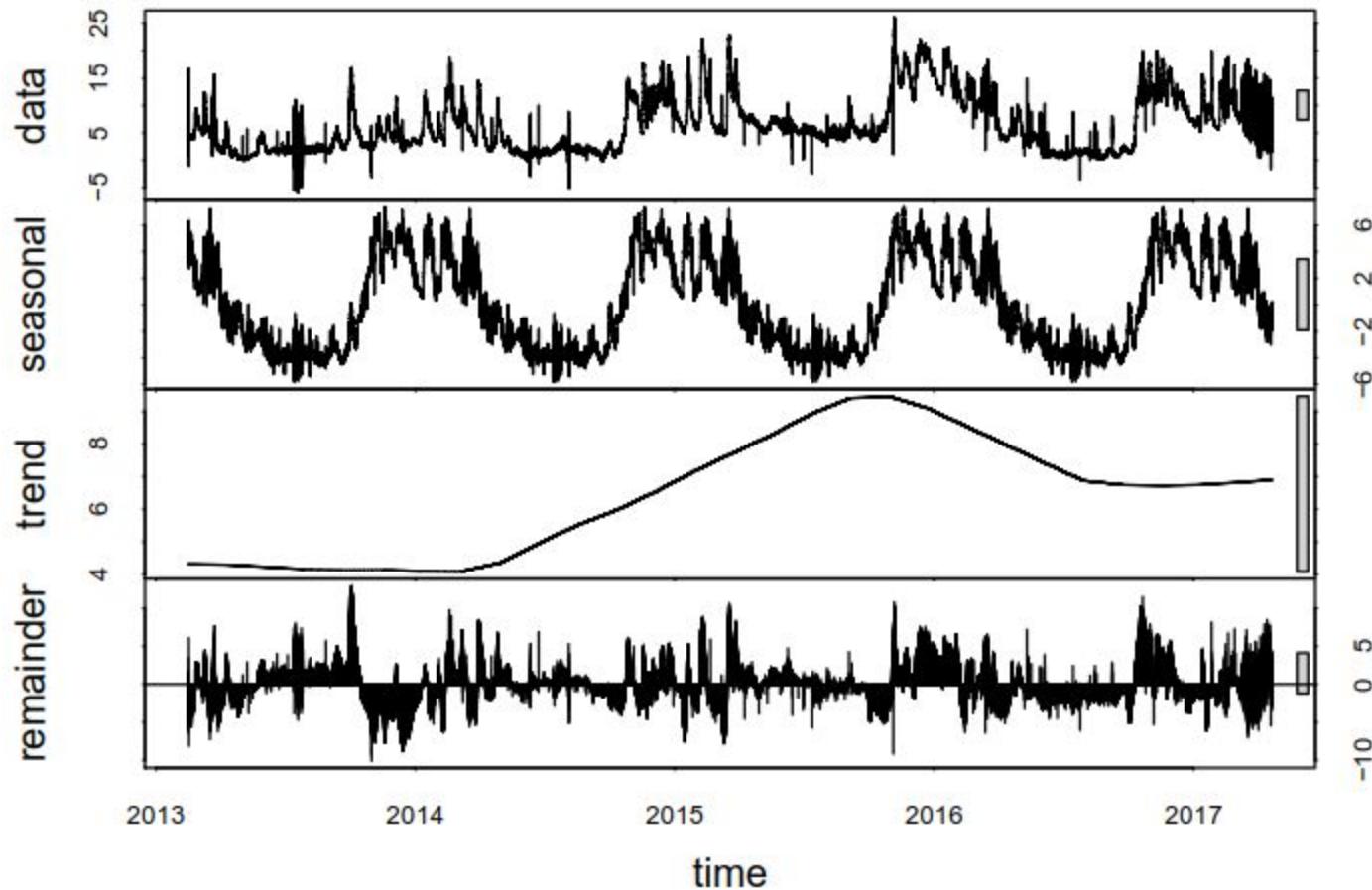
### Dissolved O<sub>2</sub>



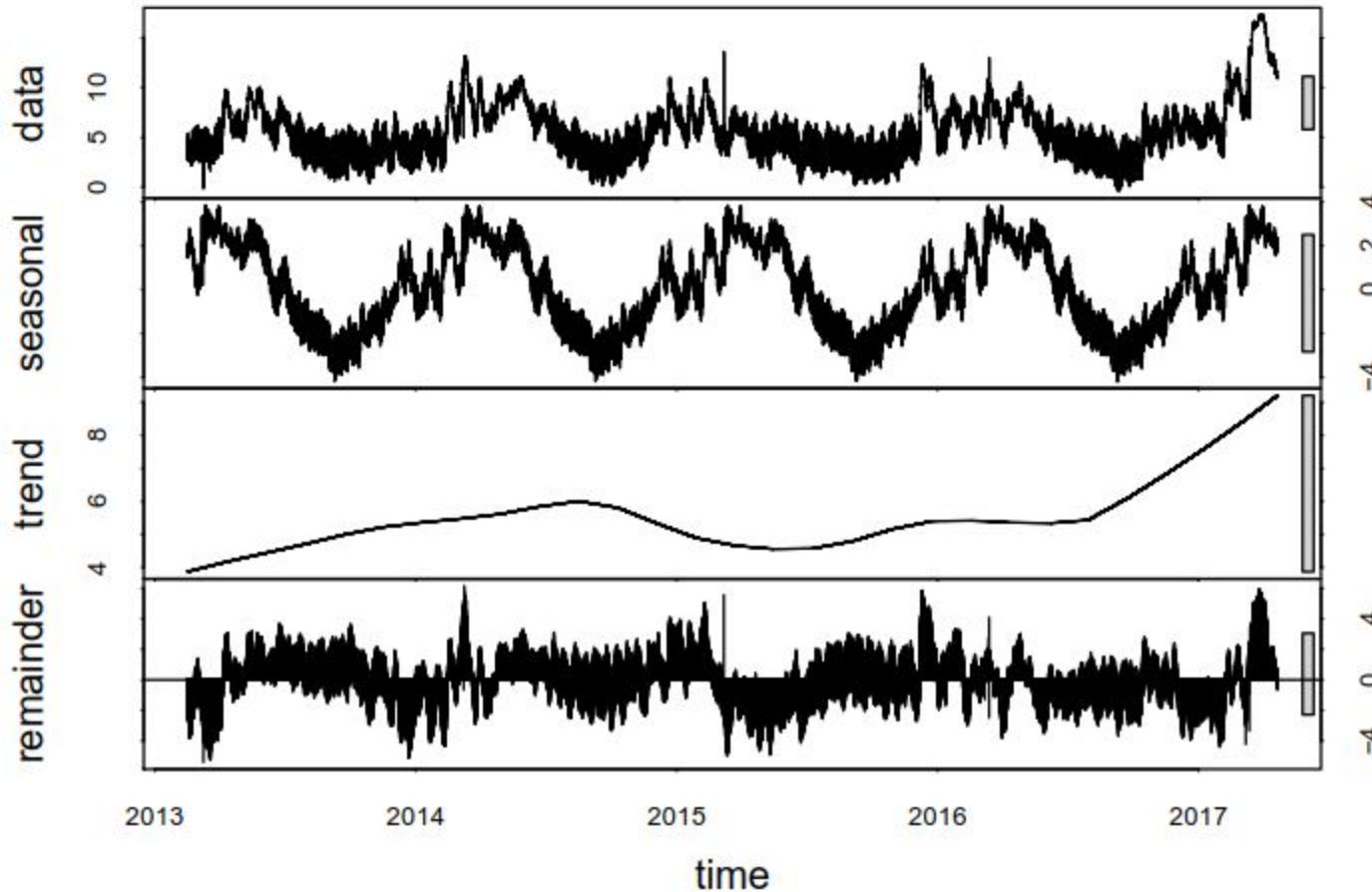
## O2 Saturation



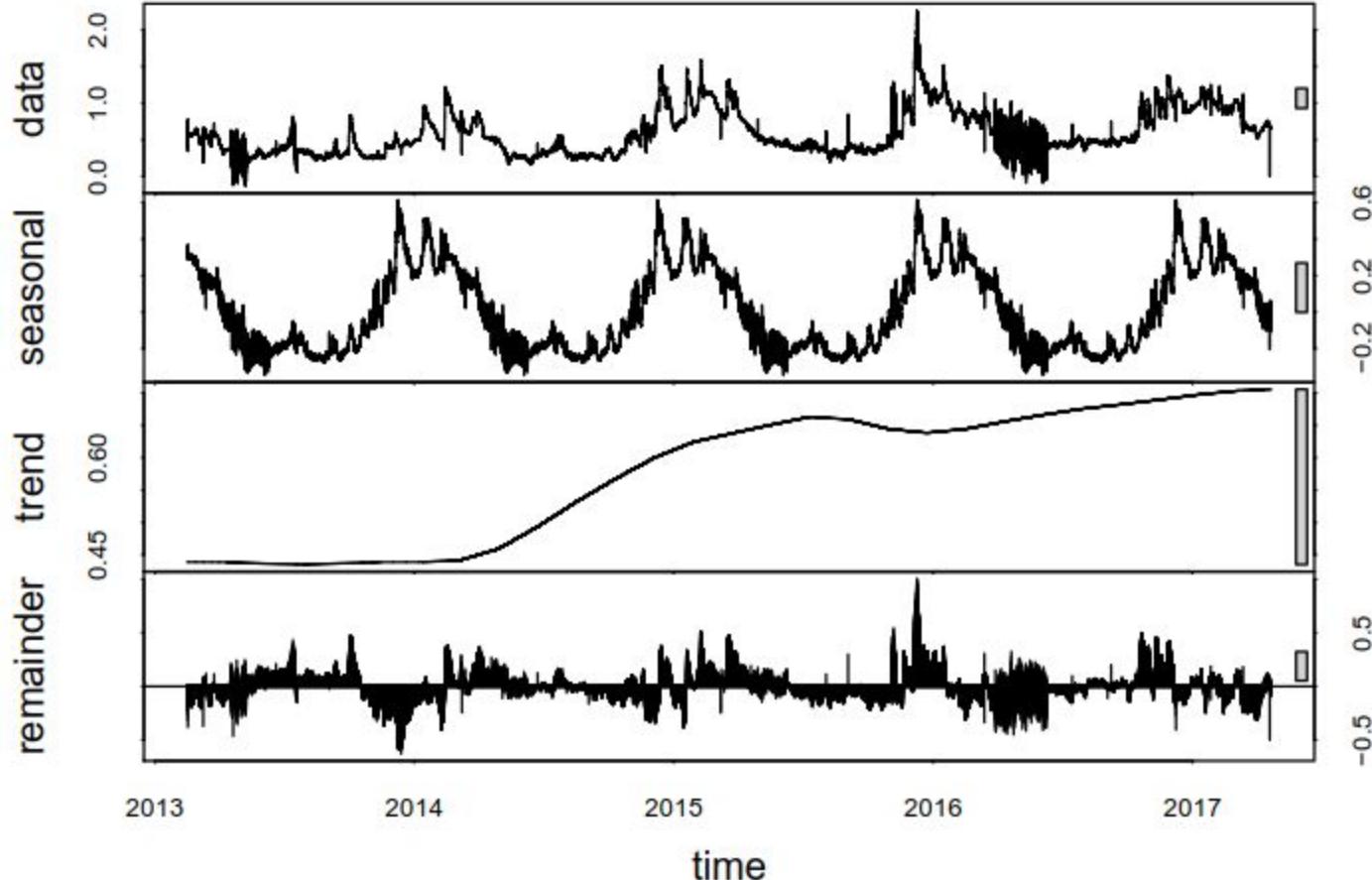
### fDOM

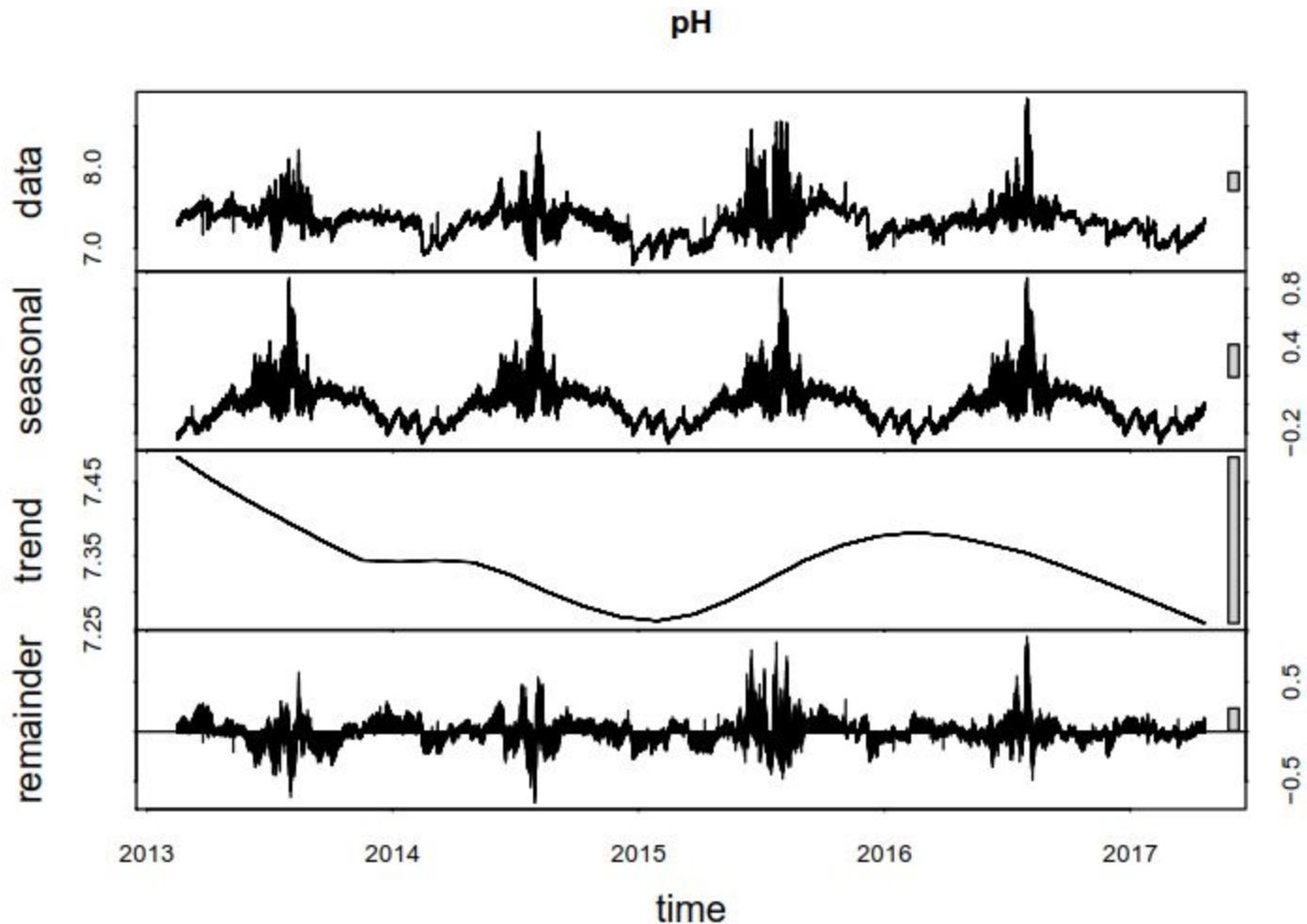


### Gage Height

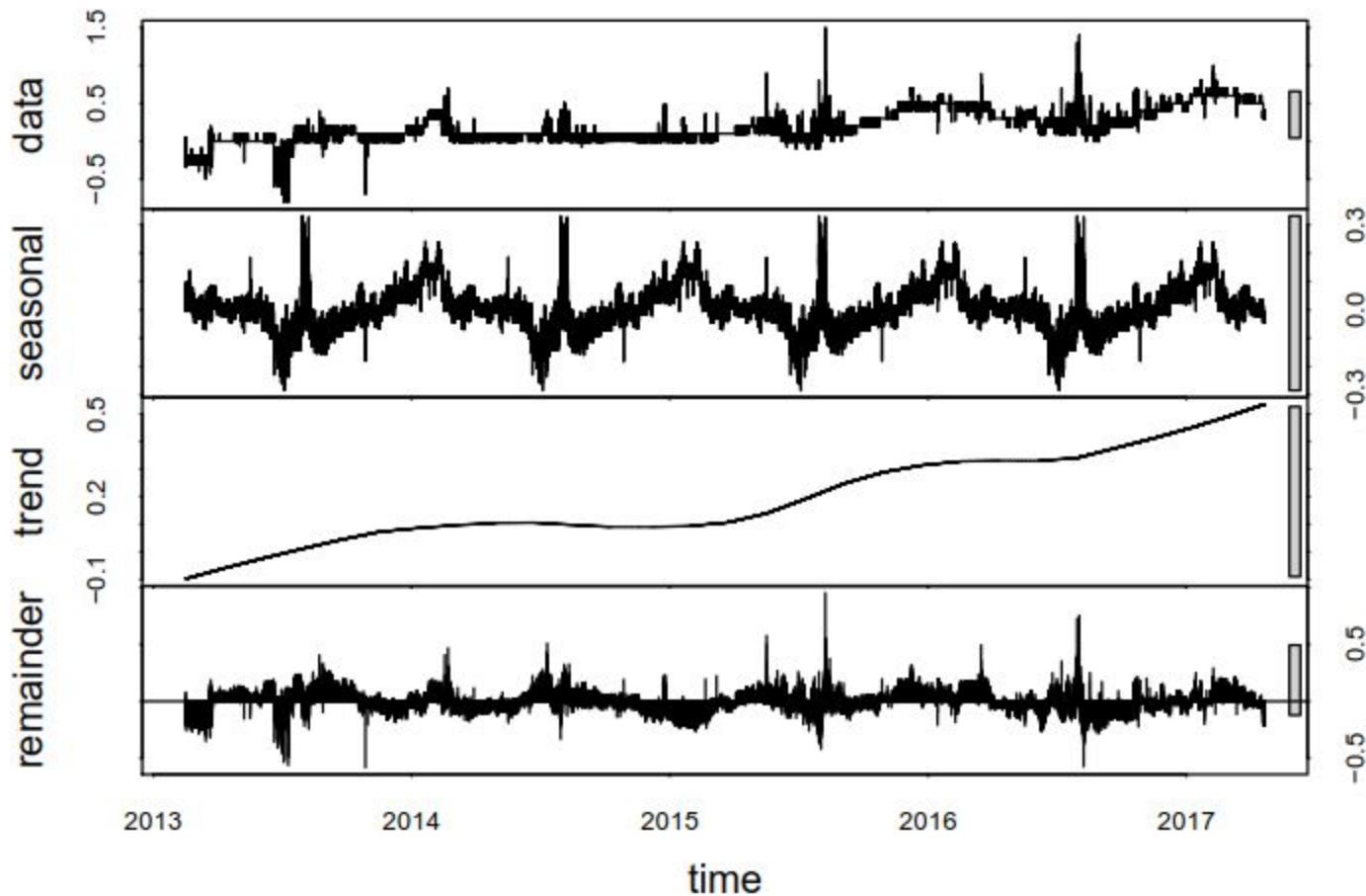


### Nitrate

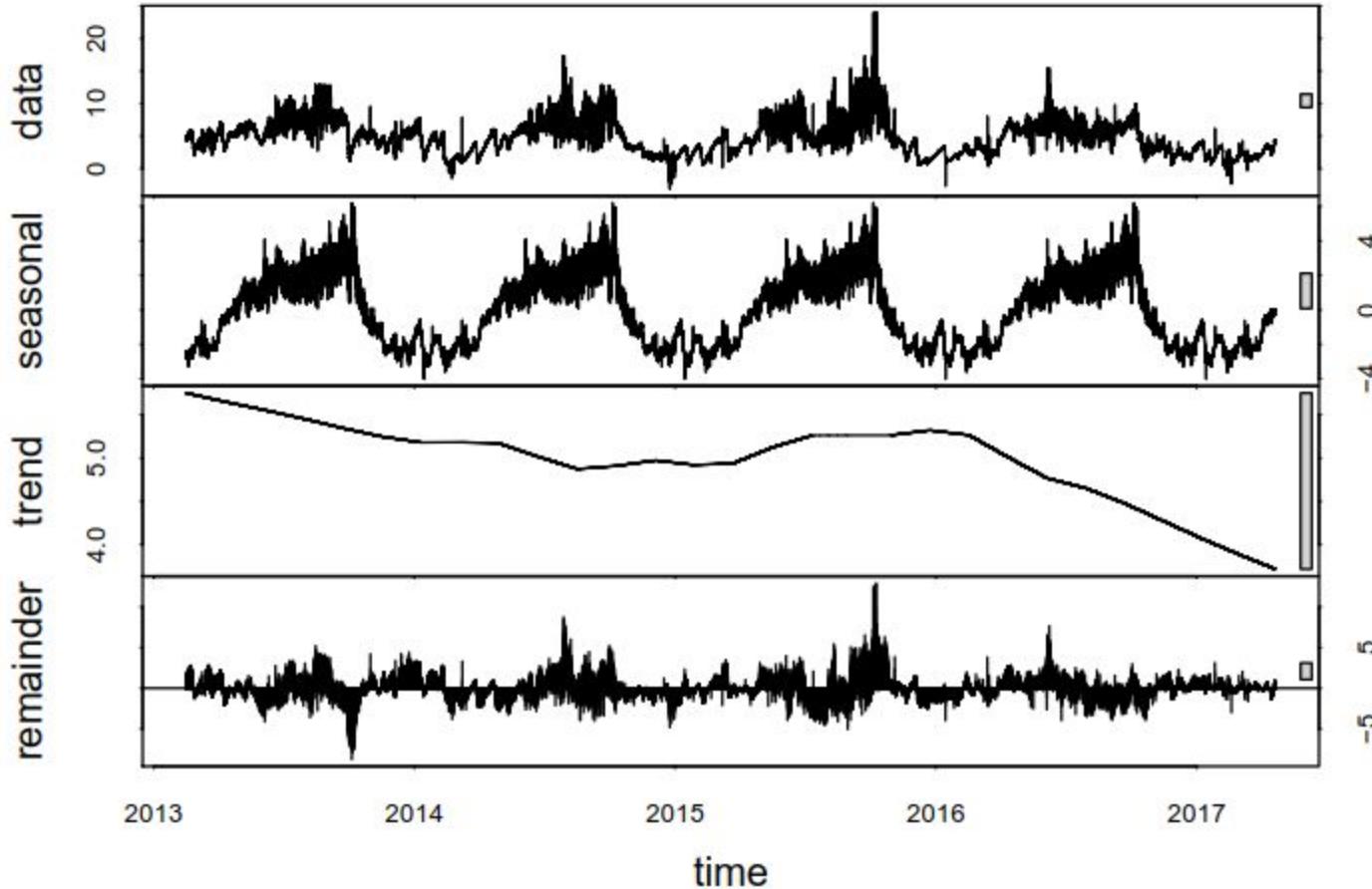




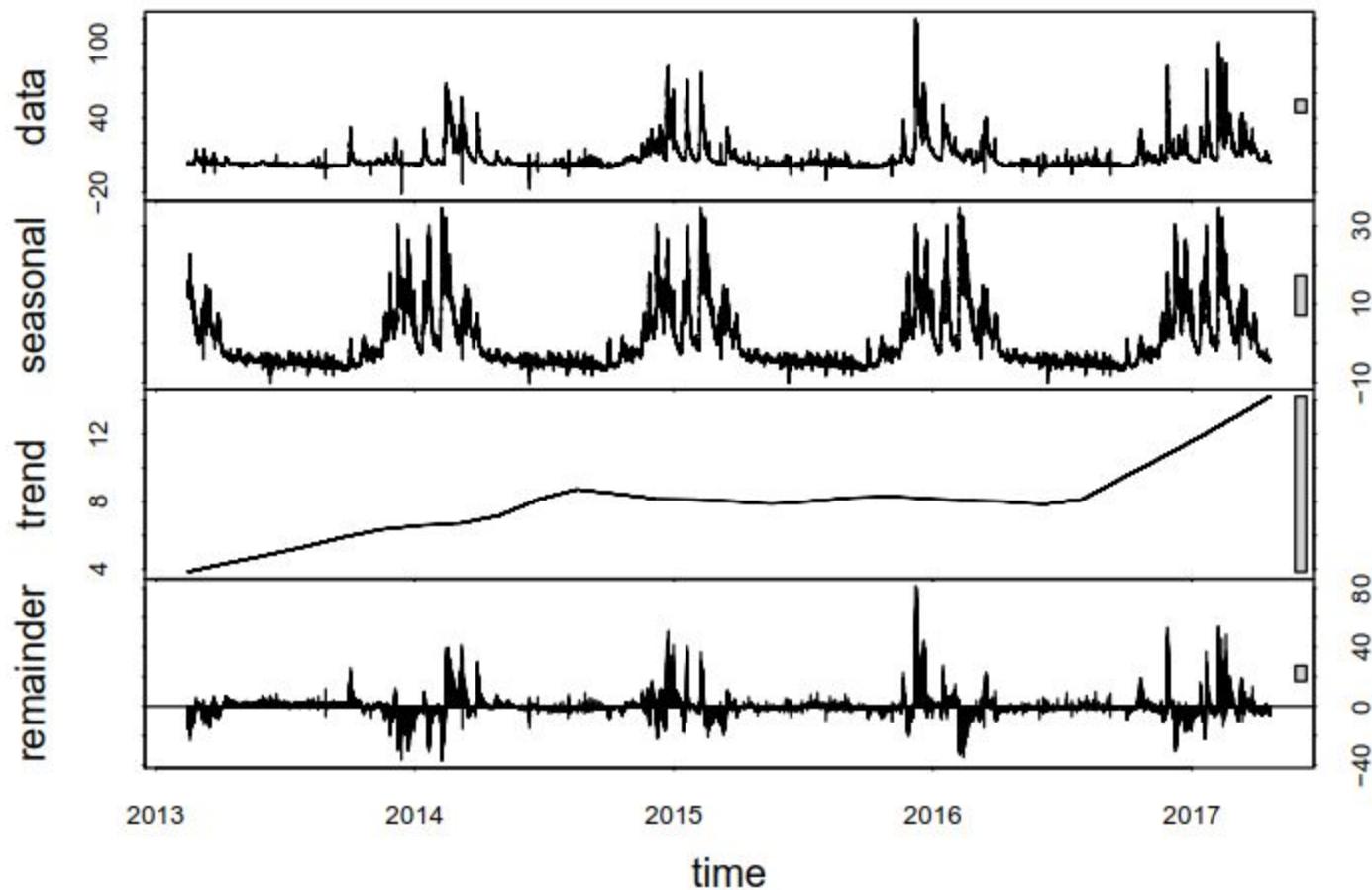
## Phycocyanin



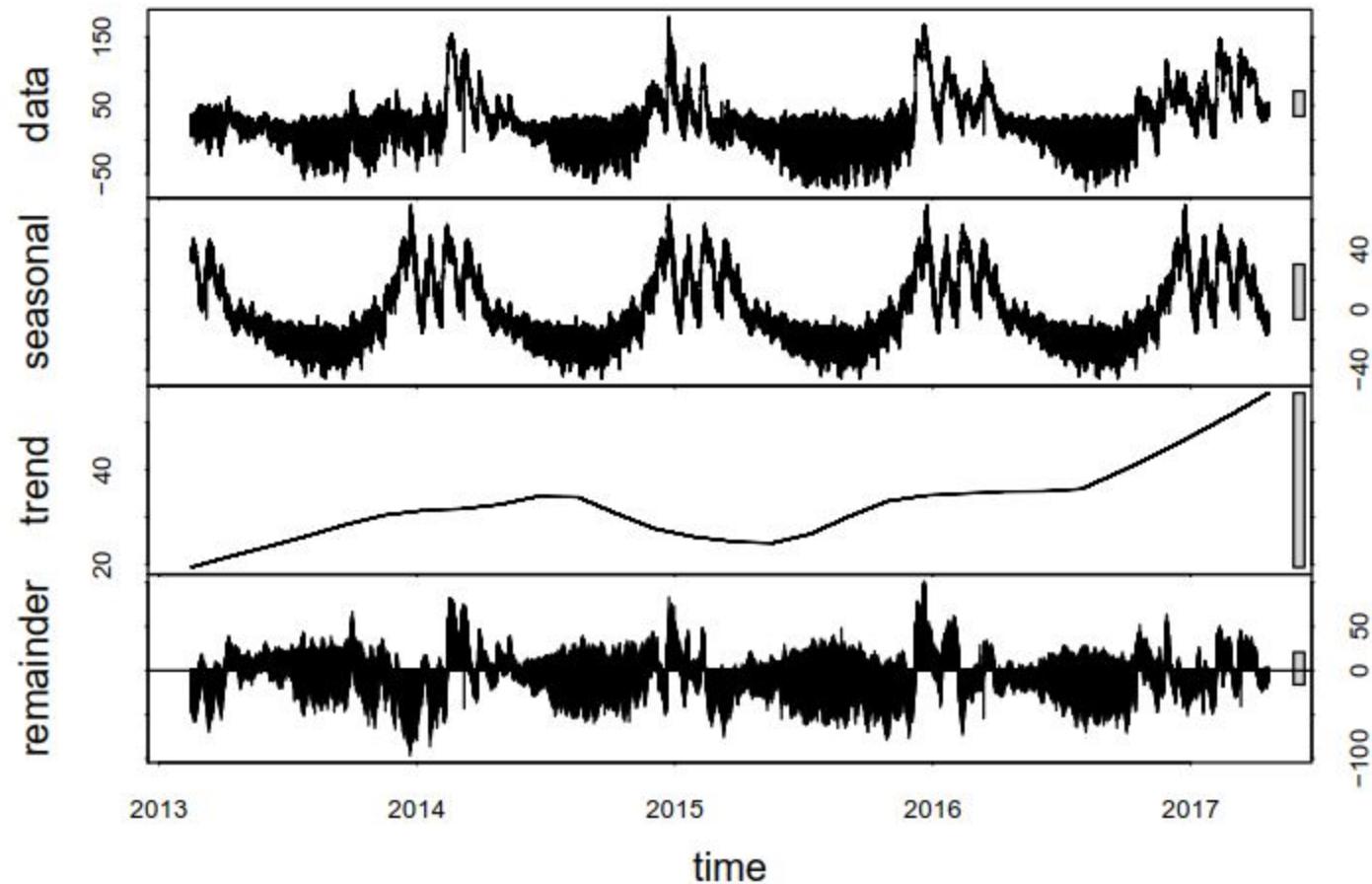
### Secchi Depth



## Turbidity



### Stream Velocity

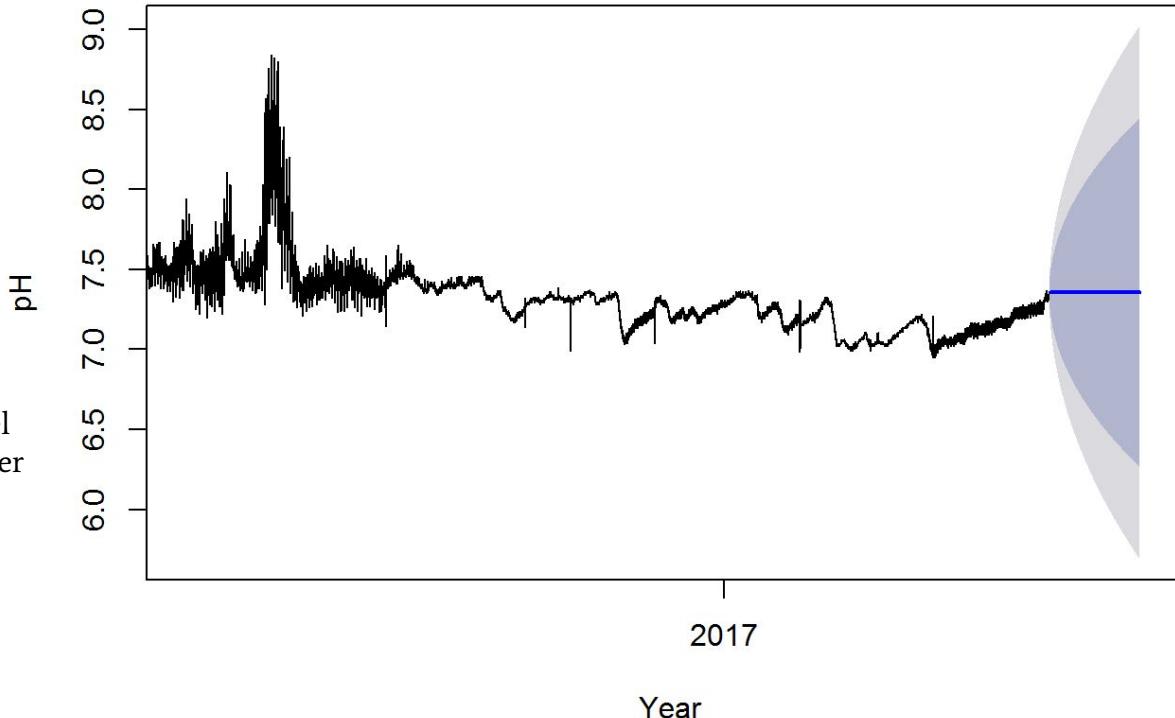


# ARIMA Models

- Autoregressive Integrated Moving Average
- When the current state is dependant on past states
- Requirement of stationarity
  - Constant mean, variance, autocorrelation
  - Augmented Dickey-Fuller Test: `adf.test()`
- Behold `auto.arima!`
  - Handles non-stationarity through auto-differencing
  - Finds the best model by AIC, AICc, or BIC
  - Beware using with huge data sets!

# ARIMA model example: with forecasting

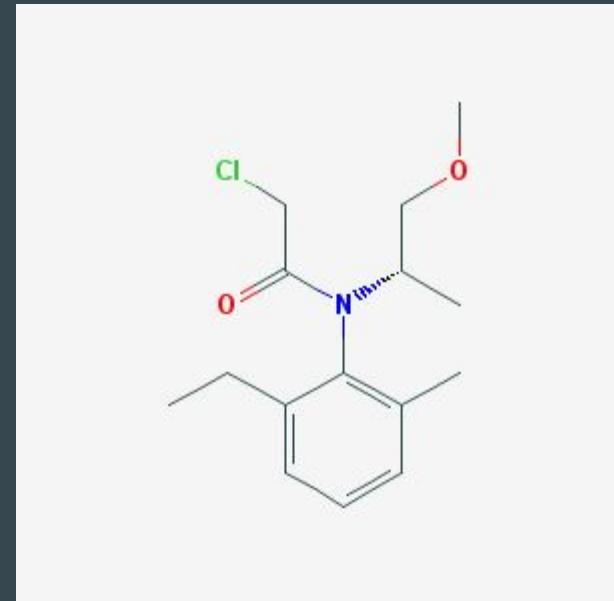
Forecasts from ARIMA(5,1,2)



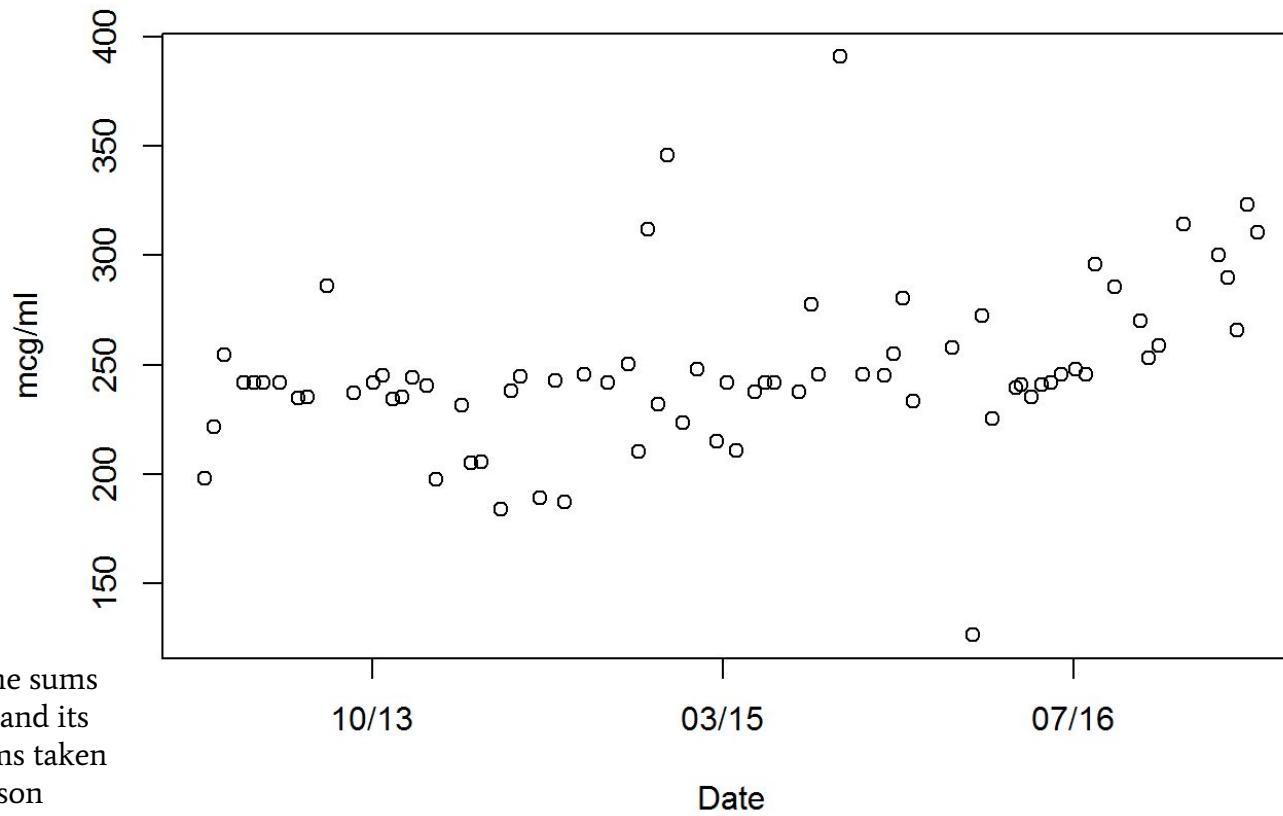
# Regression Model

# Metolachlor

- Herbicide
  - Controls grasses
- Approved in US, but not EU
- By GHS:
  - May cause allergic skin reaction (category 1)
  - Fatal if inhaled (category 1,2)
  - Very toxic to aquatic life (category 1)
  - Very toxic to aquatic life with long lasting effects (category 1)



## **Metolachlor & degenerate forms**

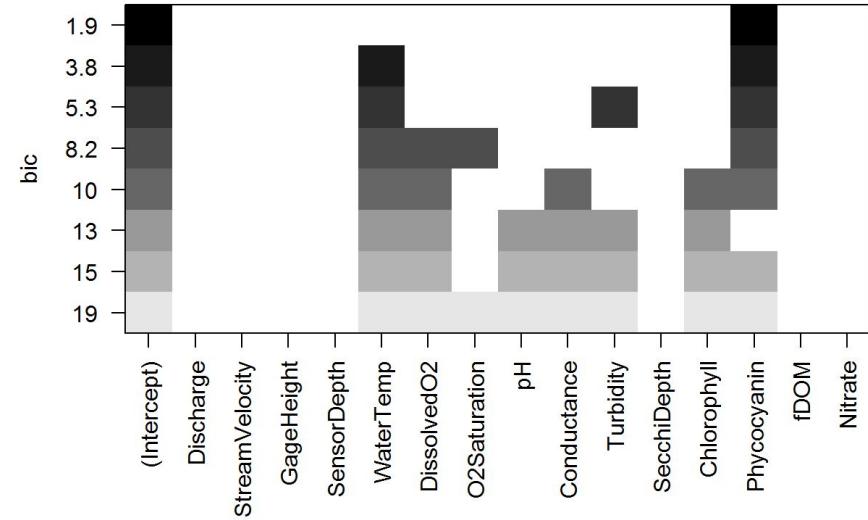
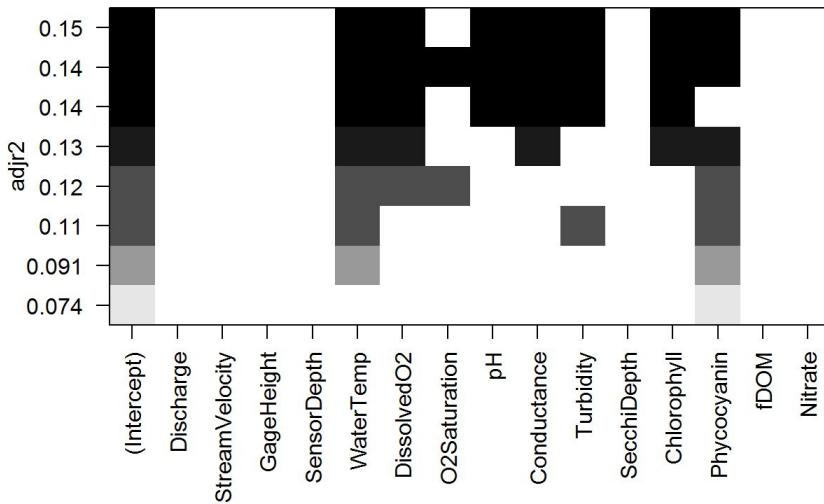


Right: Plot of the sums of Metolachlor and its degenerate forms taken from the Morrison Bridge

# Inconsistent frequency of Measurement

- Cannot treat like a normal time series
- Merging the data sets
- Regression model options
  - Linear Model
  - General Additive Mixed Model
    - `gamm()` function in package ‘mgcv’ created for this purpose
  - Quantile Regression

# Leaps package for model reduction



Above: Output from `plot.regsubsets` using the leaps package for best adjusted r2 (left) and bic (left) with metolachlor as a response

# Model Choice

- Created regression models using 3 methods outlined
  - Full Model
  - Reduced model (adj r<sup>2</sup>)
  - Reduced model (bic)
- Compared fit via AIC

	Reduced LM	Reduced GAMM	Reduced QR	Phycocyanin QR
AIC	745.7691	745.7691	713.1188	711.6929

# Final Model

```
## Call: rq(formula = metoforms ~ WaterTemp + DissolvedO2 + pH + Conductance +
##           Turbidity + Chlorophyll + Phycocyanin, data = data.all)
##
## tau: [1] 0.5
##
## Coefficients:
##              coefficients lower bd   upper bd
## (Intercept) -285.12336  -983.40177 323.35978
## WaterTemp     1.33968    -2.17665   9.43410
## DissolvedO2    0.77693   -11.62171  20.75141
## pH            60.86486   -8.13841 110.82329
## Conductance    0.63455   -0.05009  1.03935
## Turbidity      1.70864    0.03051   2.38374
## Chlorophyll   -4.68017   -6.84272  0.48336
## Phycocyanin   35.00731    1.45508  85.75796
```

This gives us the regression equation:

$$\hat{y} = -285.12336 + 1.33968\beta_1 + .77693\beta_2 + 60.86468\beta_3 + .63455\beta_4 + 1.70864\beta_5 - 4.68017\beta_6 + 35.00731\beta_7$$

Where  $\beta_1 = \text{WaterTemperature}$ ;  $\beta_2 = \text{DissolvedO2}$ ;  $\beta_3 = \text{pH}$ ;  $\beta_4 = \text{Conductance}$ ;  $\beta_5 = \text{Turbidity}$ ;  $\beta_6 = \text{Chlorophyll}$ ;  $\beta_7 = \text{Phycocyanin}$

# Notes on Model

- The Phycocyanin quantile regression model was best model via AIC
  - However it traded less than 2 points of AIC for dropping 6 parameters
  - So went with the reduced quantile model on last slide
- This tells us that Phycocyanin is the overall strongest predictor for Metolachlor
- Metolachlor + degenerate forms is NOT decreasing!

# Next Steps