Estimating the Reactive Component of Natural Attenuation of Dioxins in Sediments

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Presentation Overview

- Definition of Natural Attenuation (NA)
- The components of NA
- The role of reactive processes
- A multivariate analysis technique for estimating reactive contributions to field patterns
- Dioxin dechlorination patterns in sediments of the Passaic River, NJ
- Uncertainties
- Practical considerations for the technique

Define Natural Attenuation in Contaminated Sediments

Water

Algae

- Decline of contaminant concentrations in important receptors (fish, etc.)
- Decline of contaminant concentrations in sediments contributing to exposure:

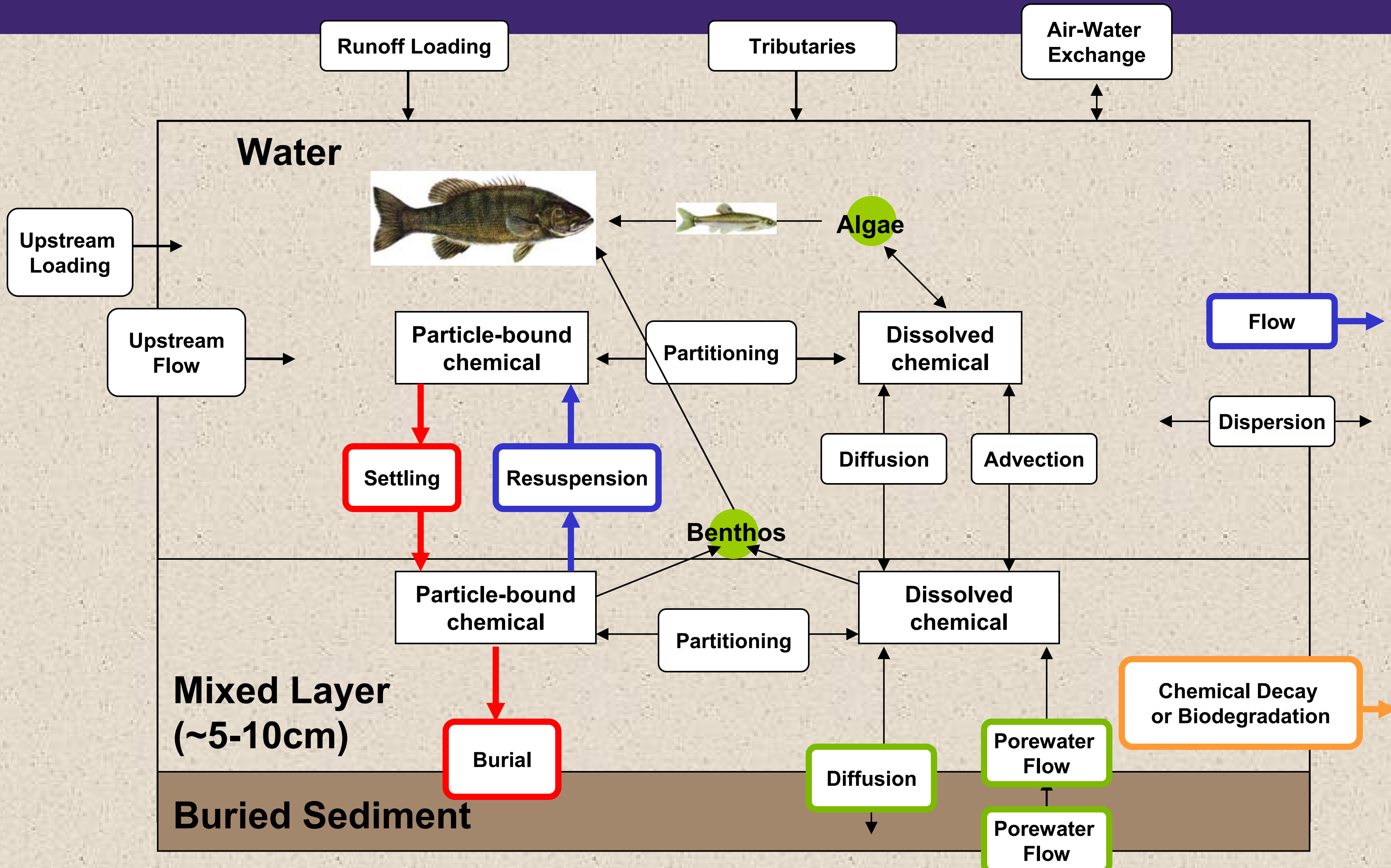
Benthos

surficial

Buried Sediment

Deep (when exposed):

Conceptual Model of Natural Attenuation



Primary modes of attenuation: settling/burial, resuspension/advection, chemical decay/biodegradation, porewater

Current Focus of Natural Attenuation Applications

Observed Media:

- Surficial sediments (remediation studies and fate modeling/forecasting)
- Sediment cores (studies of national trends)
- Fish (remediation studies and studies of national trends)

NA processes:

- Burrial: settling and resuspension

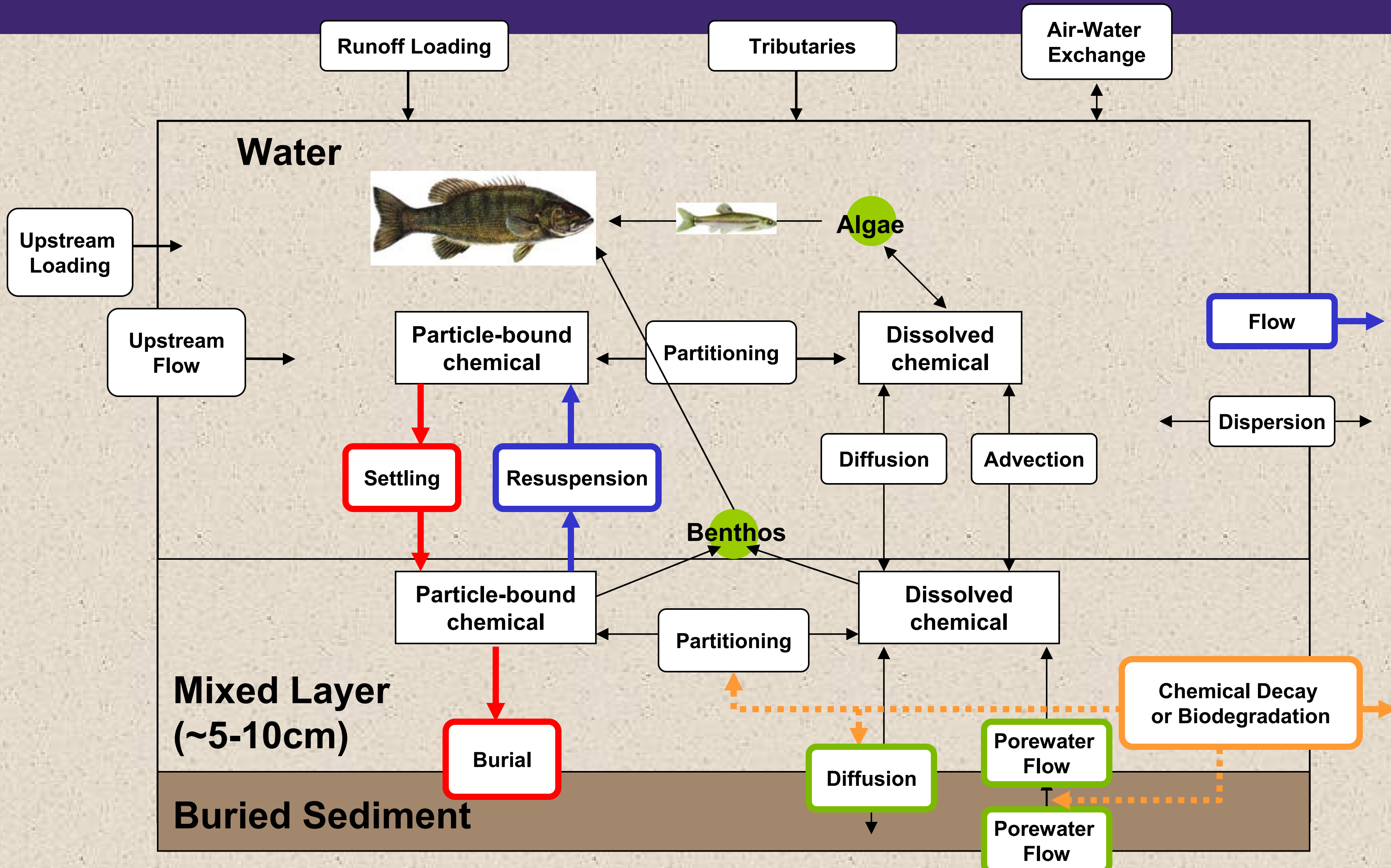
Conclusions:

- Mix of some decreasing trends (half-time ~10 years) and some stabilization in sediments and fish (PCBs, DDT)

Knowledge Gaps in NA Modeling and Application

- Bioavailability is often ignored due to insufficient information
- Biogeochemistry is important determinant of bioavailability:
  - Biogeochemical reactions determine partitioning characteristics and thus, bioavailability.
  - relative importance increases for residual contamination after remedial action.
  - Exposure through extreme events can lead to increased/decreased risk depending on nature of reactions
  - Often assumed negligible for PCBs, Dioxins, persistent chemicals
- How are long-term risks modified by reactive processes during NA? – How prevalent are reactive processes in sediments?

Conceptual Model of Natural Attenuation

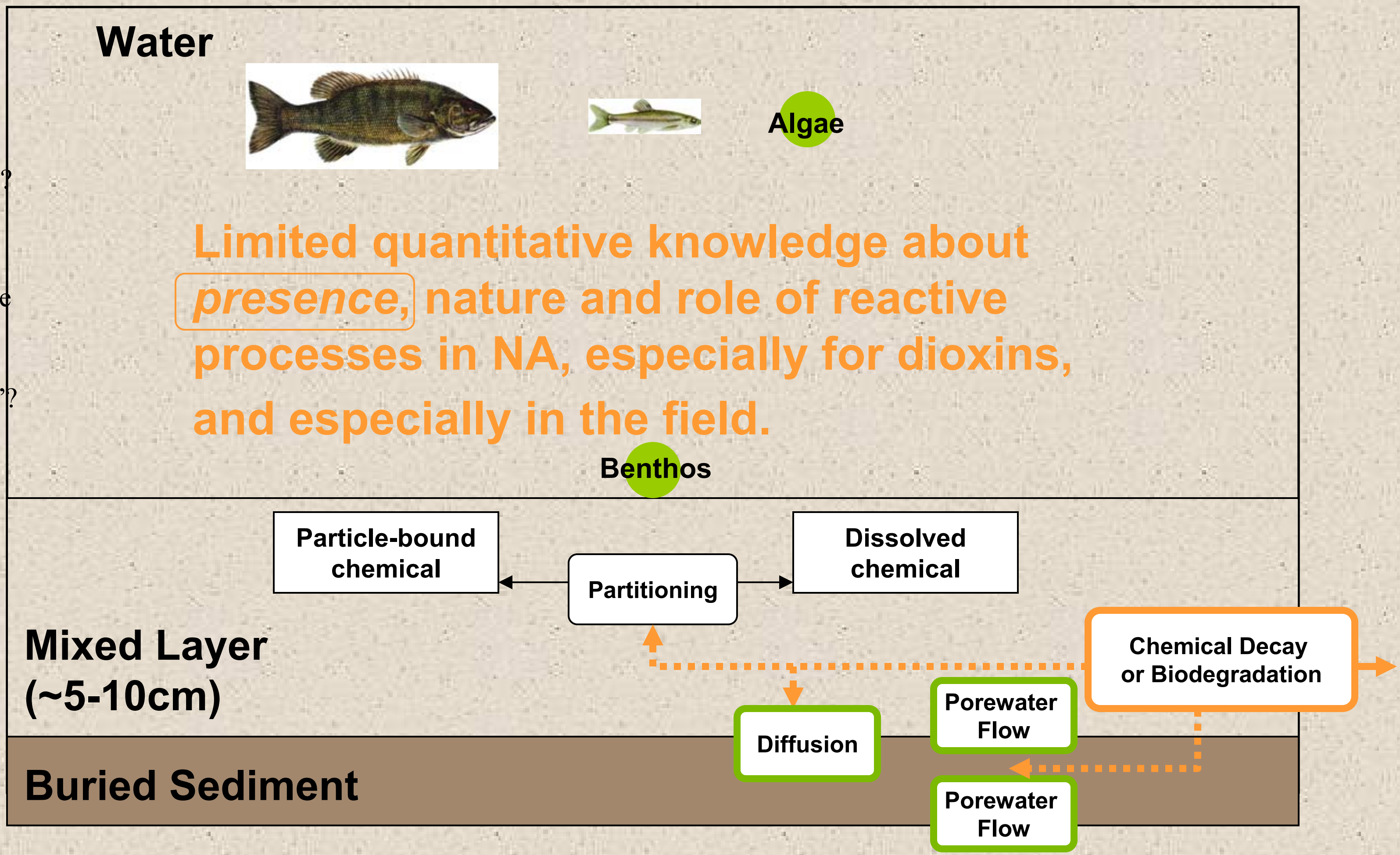


Primary modes of attenuation: settling/burial, resuspension/advection, chemical decay/biodegradation, porewater

Role of Reactive Processes in NA

John Pardue: "presence of starting halorespirers"?

Mike Dybas: "where are the environments that support halorespirers"?



Limited quantitative knowledge about *presence*, nature and role of reactive processes in NA, especially for dioxins, and especially in the field.

Primary modes of attenuation: **chemical decay/biodegradation**

Role of Reactive Processes in NA

Water

Algae

Limited quantitative knowledge about *presence*, nature and role of reactive processes in NA, especially for dioxins, and especially in the field.

Benthos

Polytopic Vector Analysis (PVA) as a tool to detect and estimate dechlorination reactions involving dioxins in sediments.

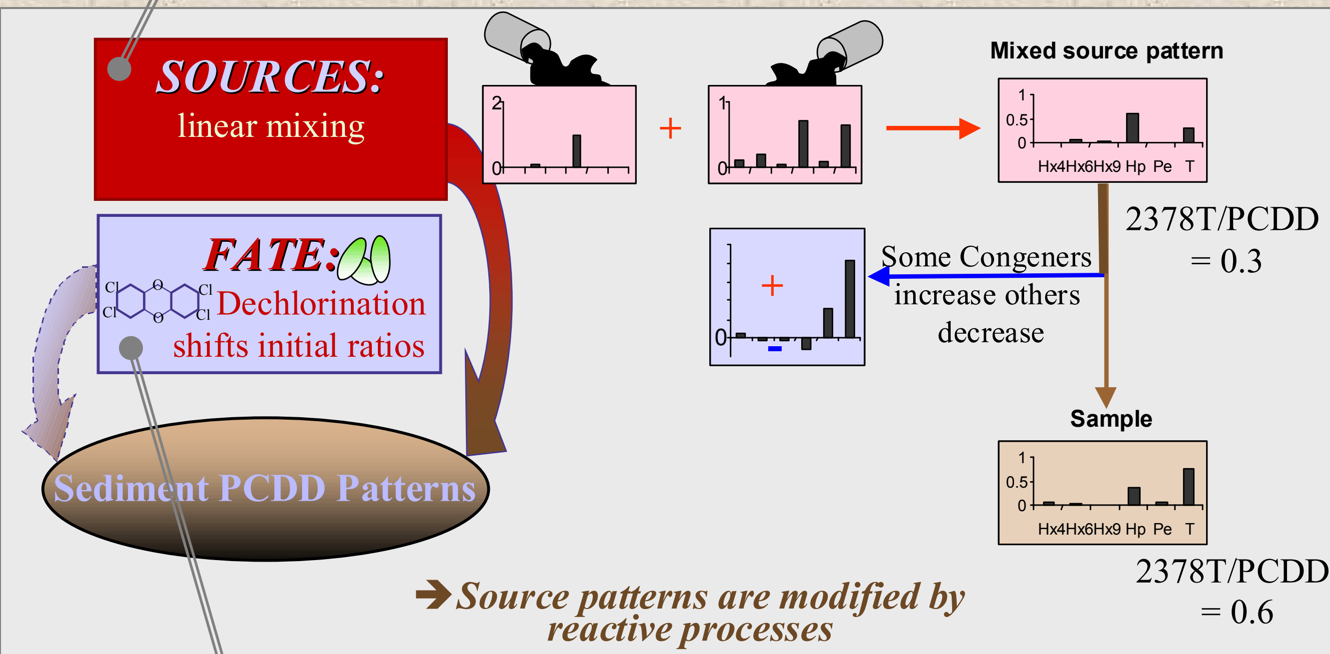
Chemical Decay
or Biodegradation

Buried Sediment

Primary modes of attenuation: chemical decay/biodegradation

PVA-Conceptual Model

Traditionally PVA used to model source patterns



How do we infer this?

PVA

From this?

Modified PVA to model reactive patterns in dioxins/furans (M-PVA)

PVA in the Scientific Literature on Sediments

Algae

- Most applications model PCB sources (Arochlors)
- Some work on the impact of biotic reactions on the ability of PVA to identify Arochlor sources in PCB mixtures

Benthos

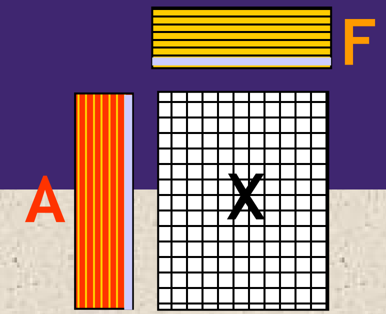
- Some work on identifying dechlorination related PCB signatures
- Fewer applications of PVA to dioxin/furan source patterns.

Chemical Decay or Biodegradation

- No PVA adaptations for estimating dechlorination of dioxins/furans

Modified PVA

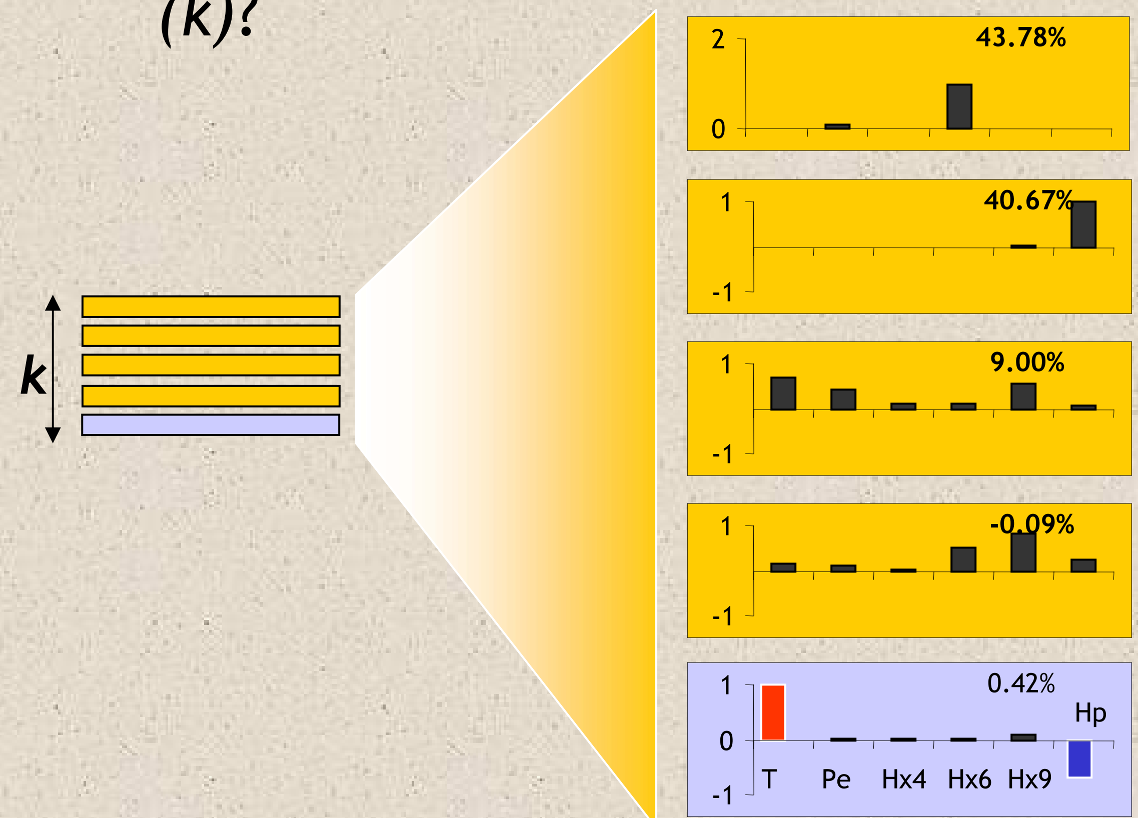
X = AF

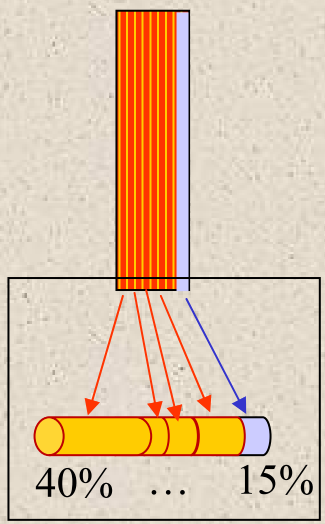


How many end-members *(k)*?

What is their pattern?

How important is each in each sample?





Modified PVA

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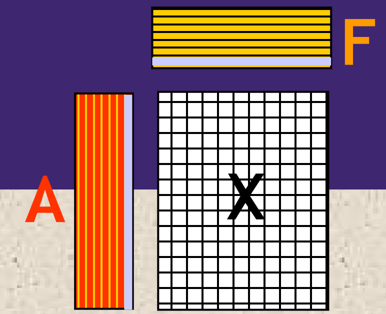
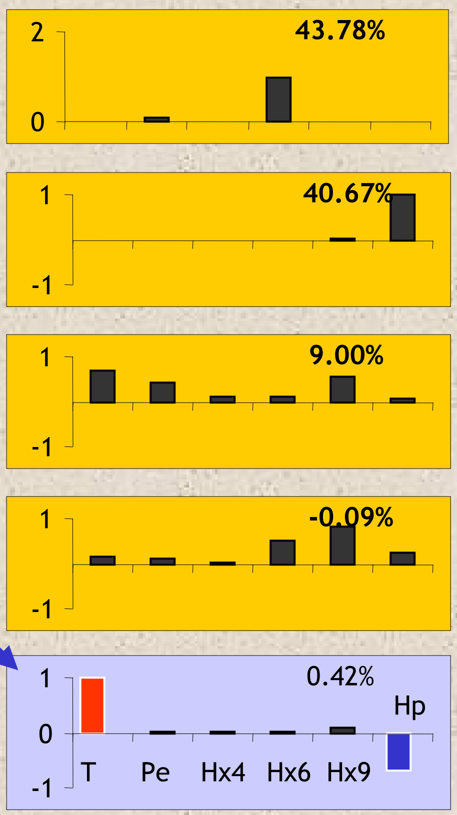
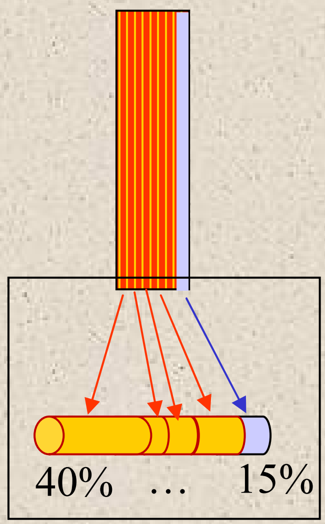


Basic Approach for Modeling Dechlorination

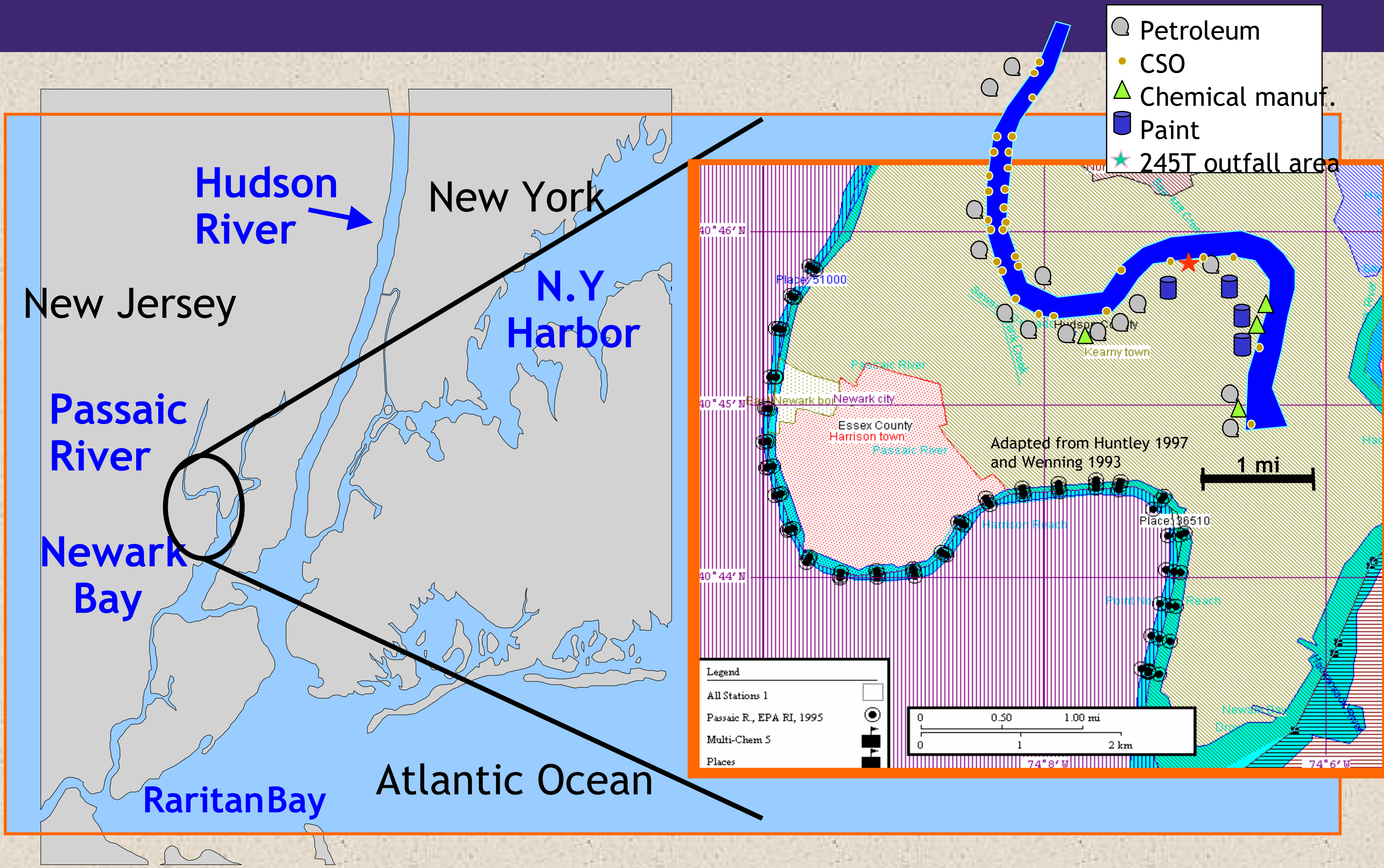
1. Multivariate field data
2. Principal Components Analysis – PCA
3. Outliers? Number of end-members?
4. Rotation of PC axes until all elements of matrices A and F are positive except for elements of $F_{dechlorin}$
5. Compare PVA patterns with known source and dechlorination patterns





(Variance-based)

Dioxins in Passaic River Sediments



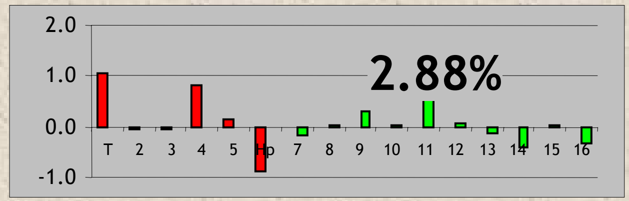
M-PVA: Dechlorination EMs

Model (pos+neg):

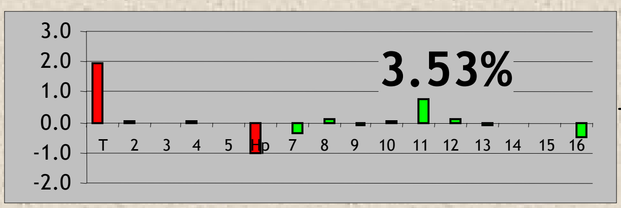
Pattern:

Uncertainty:

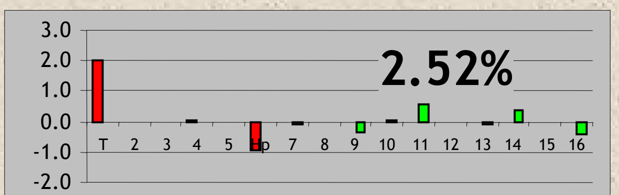
10 + 2:

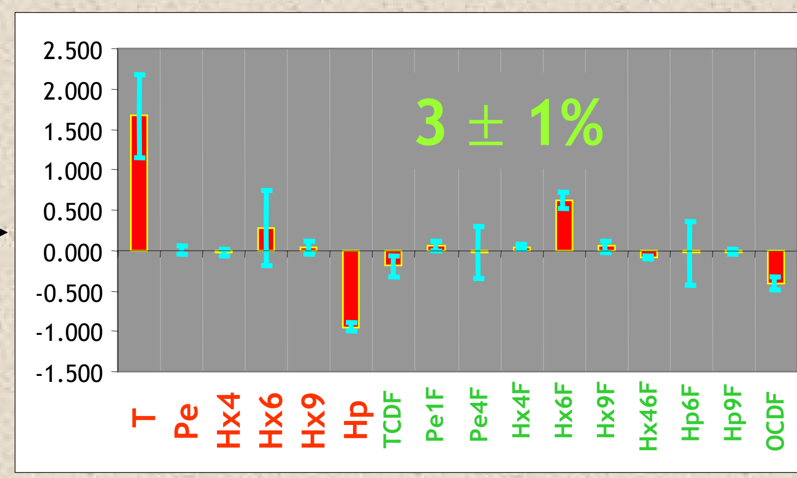


10 + 3:



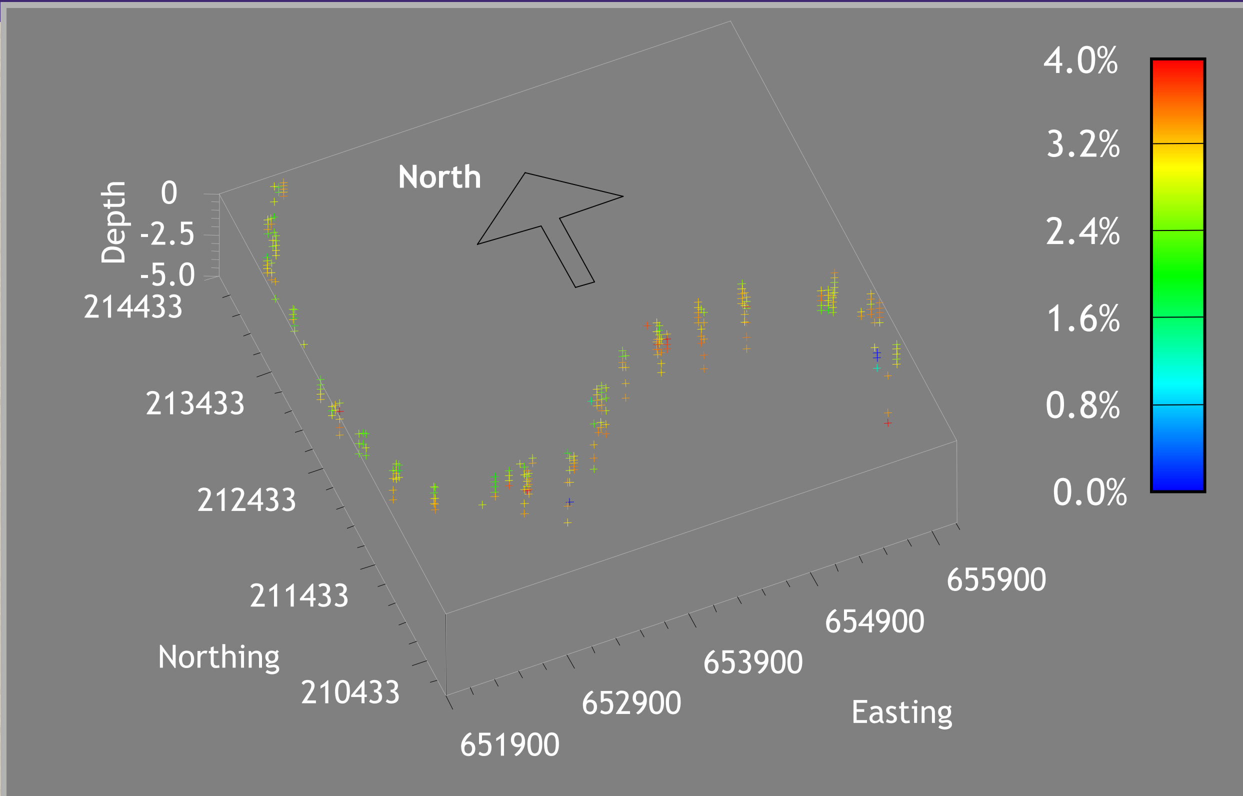
10 + 4:

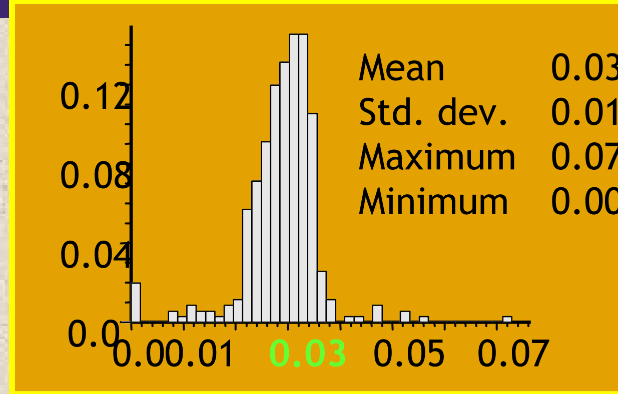




- If variability overestimated by factor of 2, dechlorination contributes at least 1.5% overall.

Map of Dechlorination Loadings



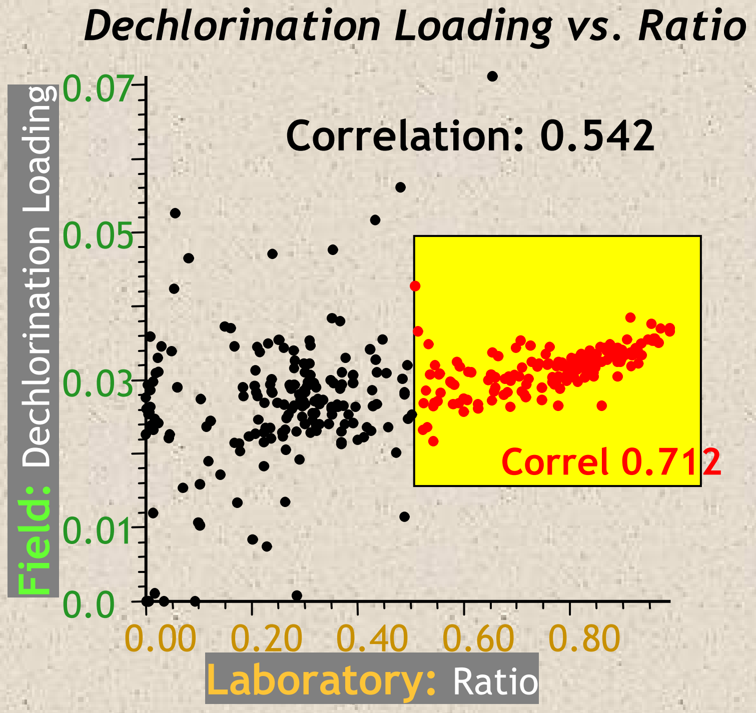


Site-wide contribution to variability: 2.88%

Presence?!

- 3% means a 3% net change in dioxin and furan concentrations in a given sample due to dechlorination (distributed among the different kinds of dioxins).

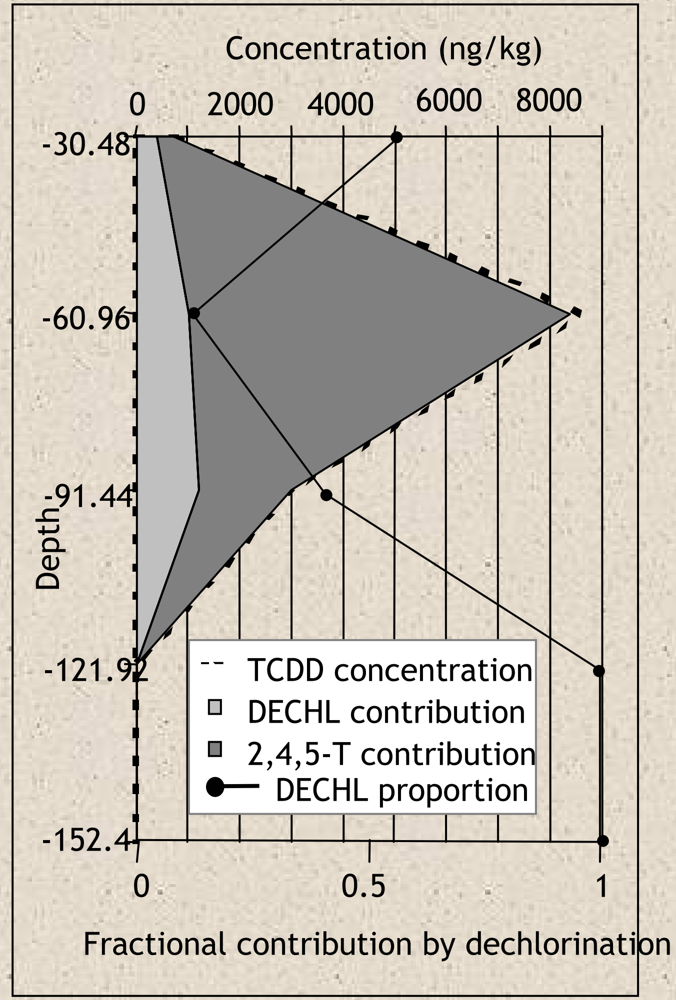
Validation



Consistent with Laboratory Results

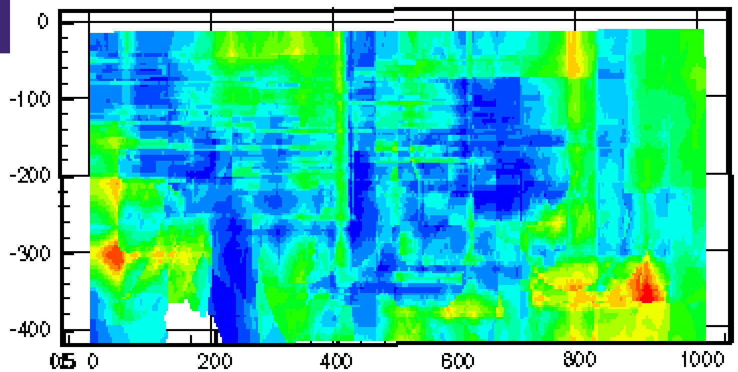
- Convergence of laboratory and field methods:
  - Ratios above 0.5 are indicative of dechlorination activity as indicated by laboratory experiments
  - As such, they correlate well with dechlorination loading derived from field data.

How Has Dechlorination Affected Concentrations??

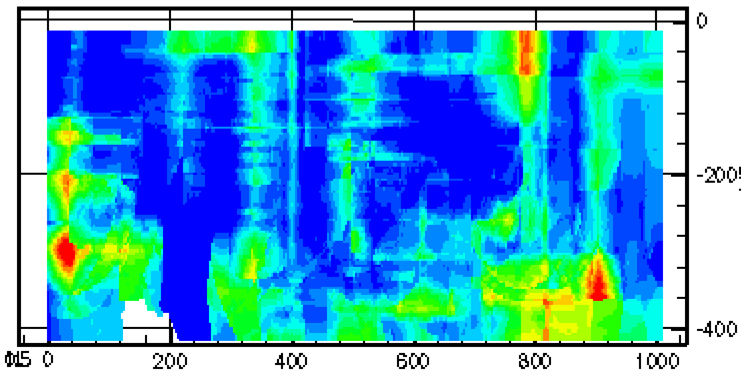


- On average dechlorination contributed 770 ng/kg to TCDD concentrations
- The proportion, can be as high as 100% relative to other sources of TCDD, in samples with low total concentration.
- At 33 ± 25%, dechlorination is the second most important contributor to 2,3,7,8-TCDD concentrations (after 2,4,5-T production, 60 ± 30%).
- Dechlorination is inversely proportional to total dioxin concentration.

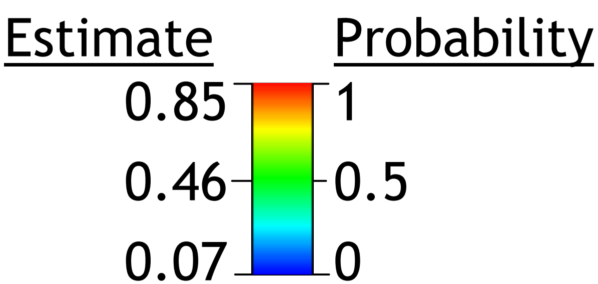
Uncertainty Maps of Dechlorination

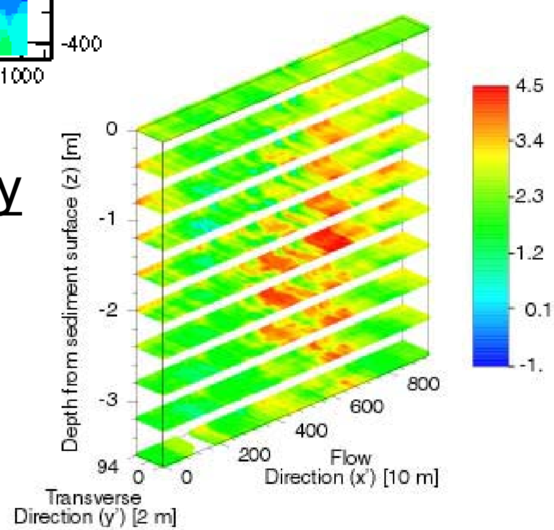


Estimate of contribution to 2,3,7,8-TCDD concentrations



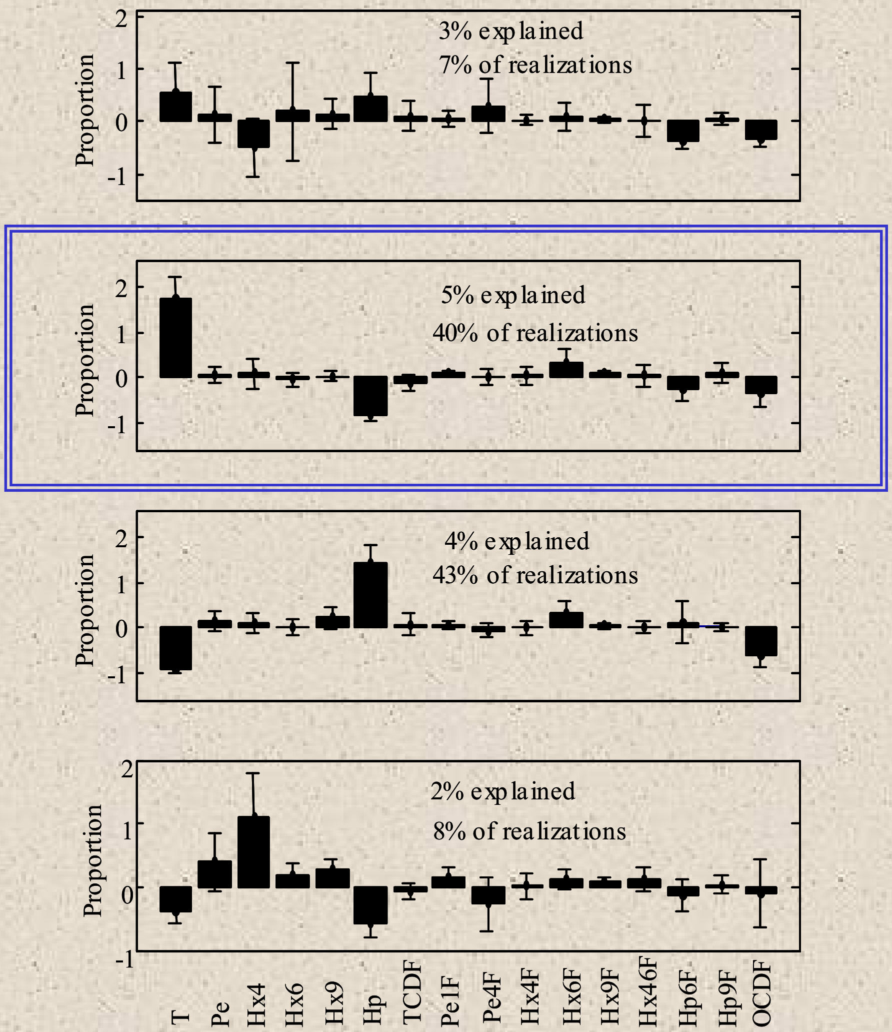
Probability that contribution exceeds 50%





- There are three areas where dechlorination is very important (both maps) and these overlap with "contaminated" and "clean" locations
- Intermediate to high contributions cover about 30% of sediments.
- In the most contaminated areas dechlorination is least important
- "Contaminated" areas with high dechlorination contribution could be candidates for enhancement

Demonstration of Uncertainties with Bootstrap Analysis



- 4 patterns!
- How unique is the dechlorination signature?
- Can the other patterns be interpreted?
- Re-partitioning during transport? Other pathways?

Conditions of Applicability of M-PVA

- Multivariate data set available (multiple congeners, multiple metals etc.)
  - Data-rich situations as opposed to finding similar answer with satelite imagery.
- Candidate source/reactive patterns available for identification (fingerprints)
- Current method requires that sources dominate overall variability pattern (true for persistent contaminants)

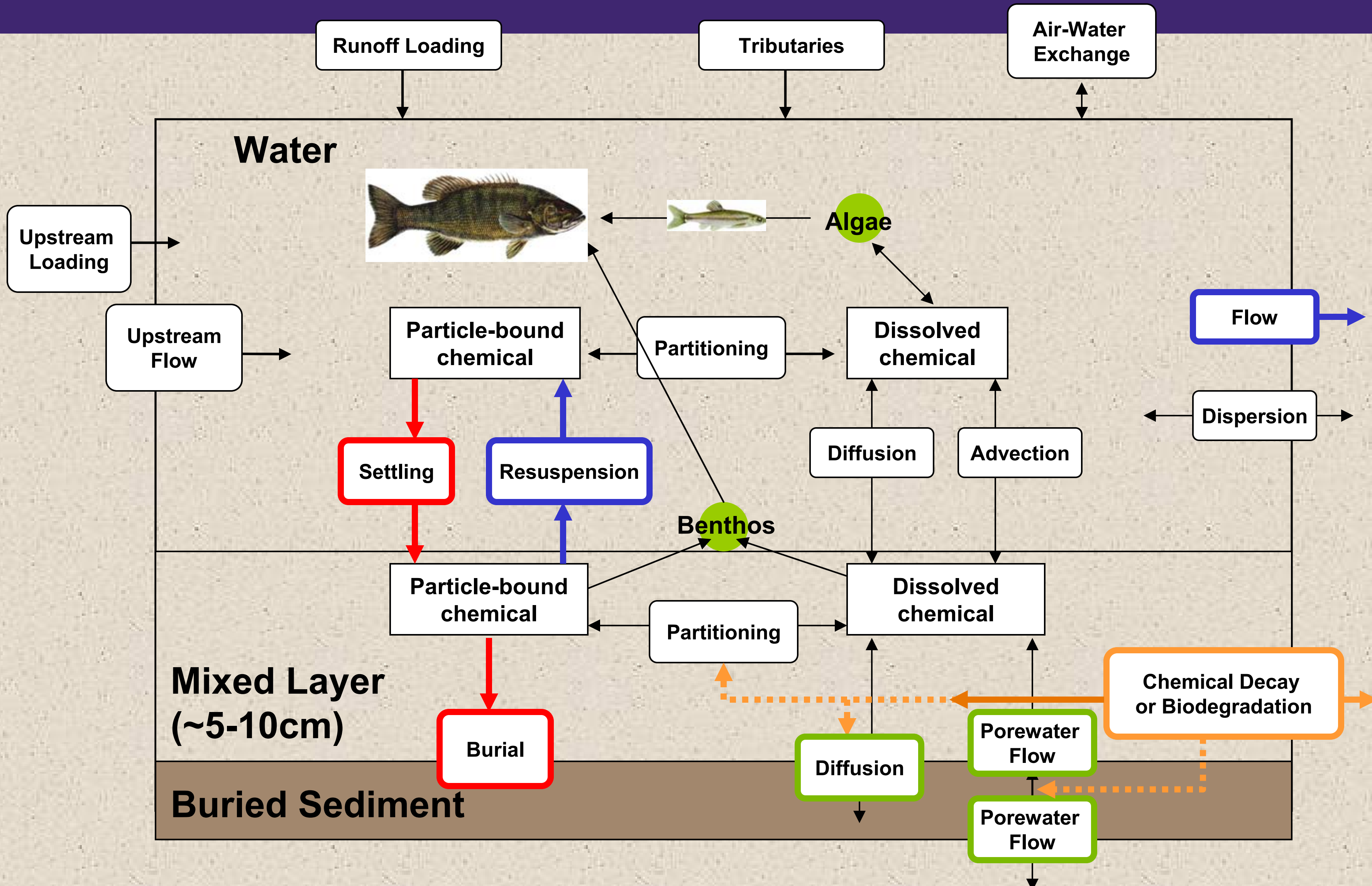
Implementation Considerations for M-PVA

- Can only resolve patterns with differences in variability/patterns => similar patterns are lumped into single categories.
- Does not give information about reaction rates
- Can we distinguish internal from external sources?
- Variance-based approach makes pattern contribution to individual samples most uncertain
- Uncertainty analysis is important component (e.g. Bootstrap, Monte-Carlo)
- To assess performance efficacy, more research needed with artificial data and laboratory experiments to determine:
  - limits of pattern resolution, pattern uncertainty
  - effect of varying levels of dechlorination contribution on uncertainty

Obstacles for Further Development/Use

- Requires implementation by experts familiar with multivariate statistics *and* reactive processes, due to:
  - Computational complexity of method
  - Multiple levels of decisionmaking (statistical and interpretive)
- Availability of code/software
- Application is limited by uncertainties in the types of dechlorination/reactive patterns that can occur.

Conceptual Model of Natural Attenuation



PVA gives partial answer to question about role of reactive processes in NA.

Integration of PVA in Site Assessment

Should be integrated with other methods and lines of evidence: