Department of the Environment

Maryland's Ion Monitoring Plan

Water Quality Standards Section
SSA-MDE

Adam Rettig and Tim Fox

September 2011

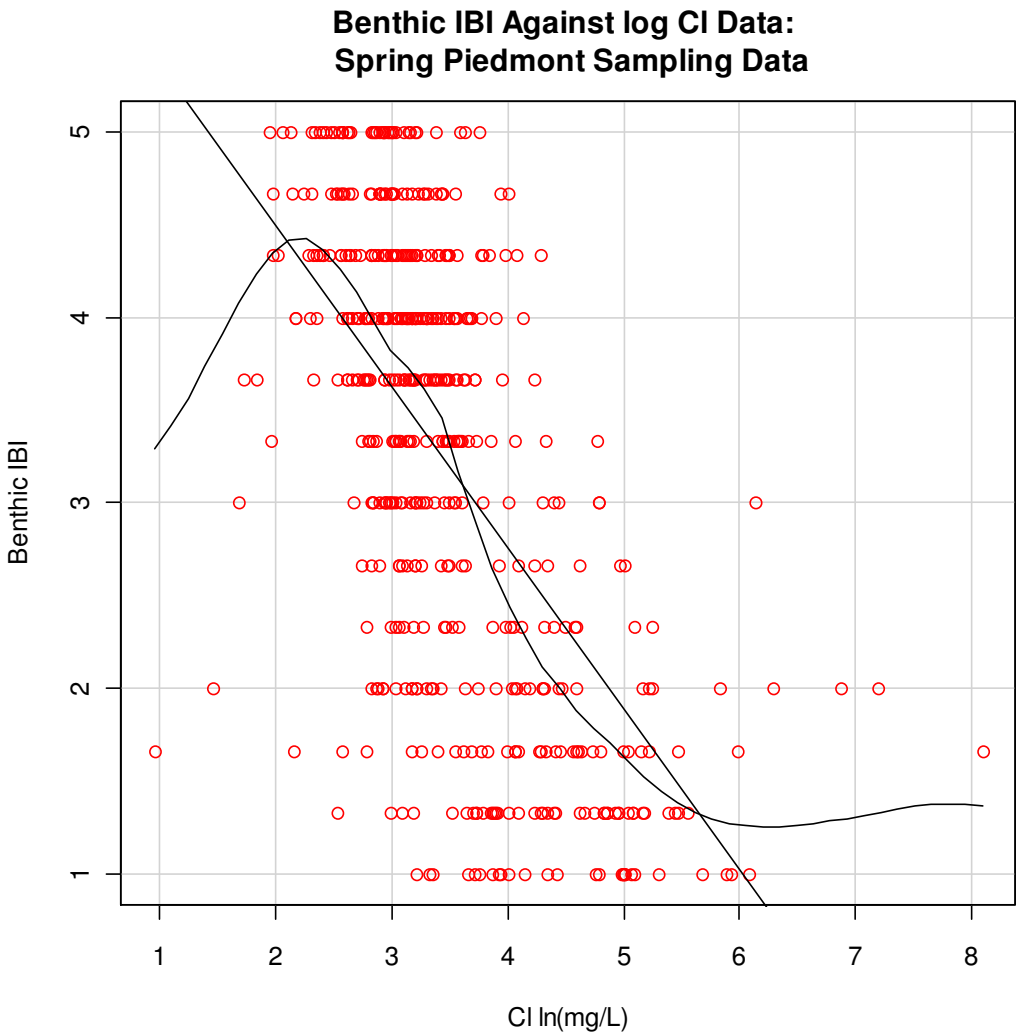
Introduction

$Cl^- = Cl$

- MD Stressor ID Program identified several steams impaired Cl.
- TMDL development has begun, therefore there is a need to develop WQS to support this effort.
- Seek feedback from colleagues in MD.

Introduction

Evidence of a Relationship

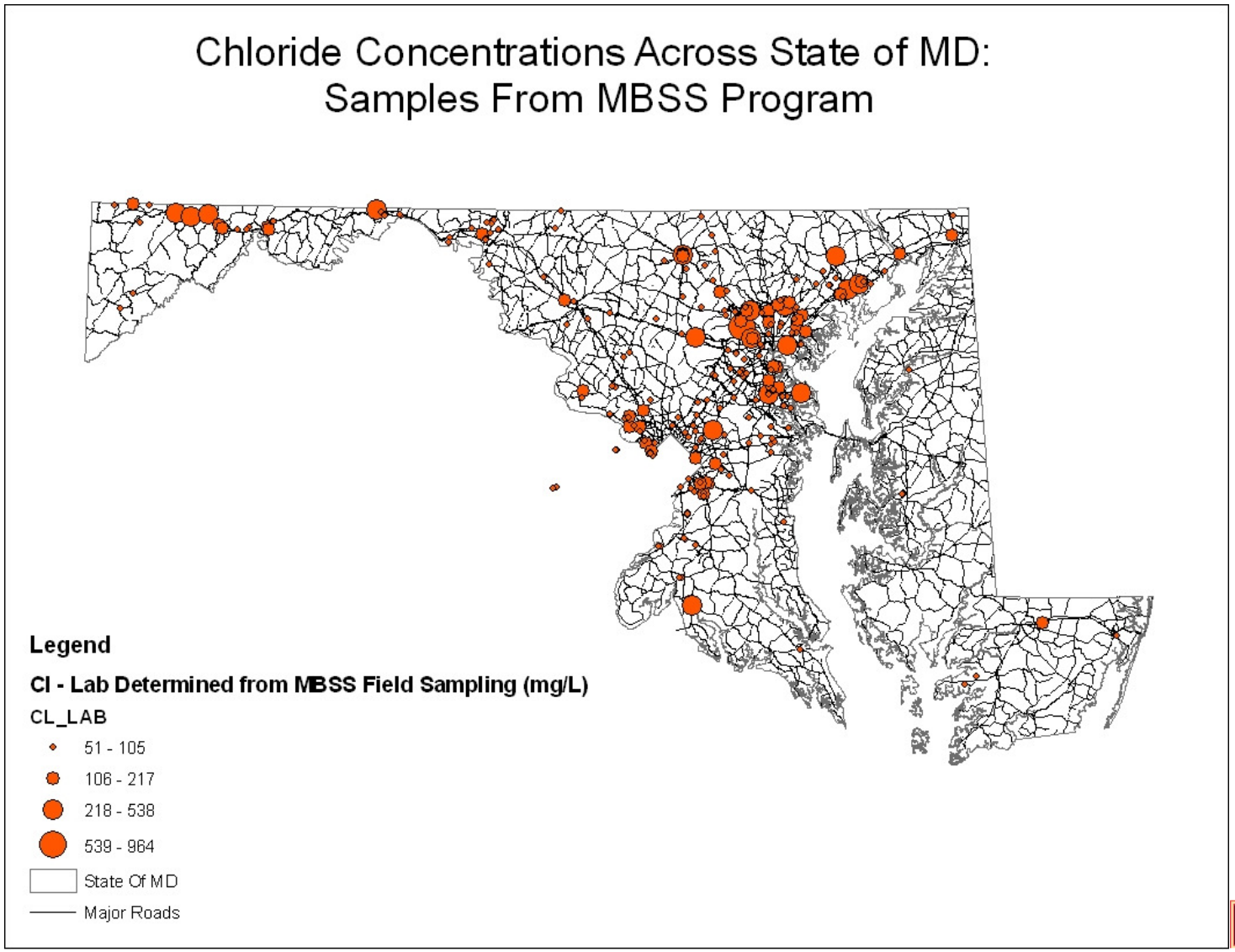


Introduction

Addressing Cl

- Elevated Cl levels in MD:
  - Clearly Associated with transportation
  - Temporally dynamic

Spatial Distribution



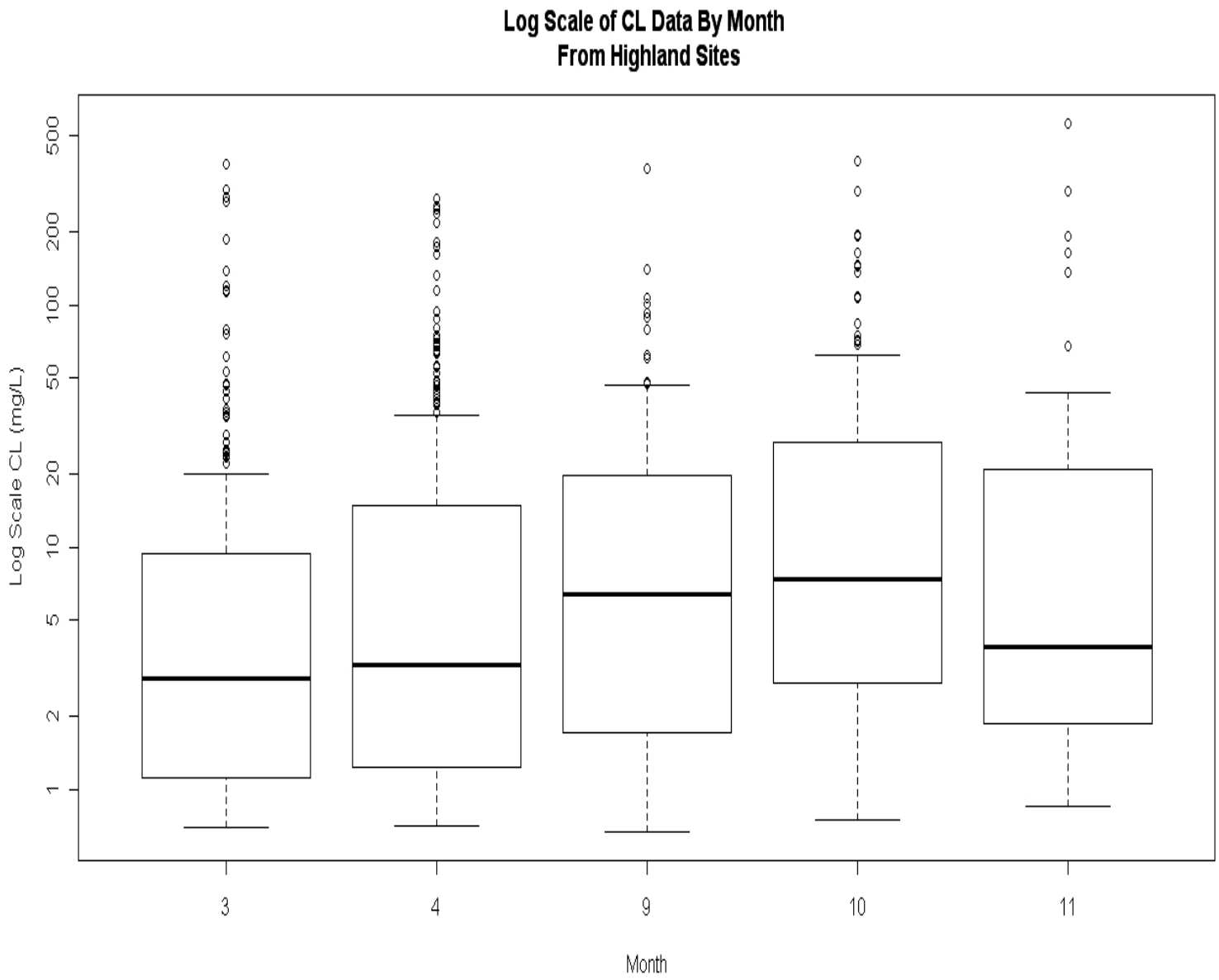
Introduction

Temporally Dynamic

1. Consistent, elevated Cl levels are present during base flow conditions via ground water sources. (Late summer – Fall)

2. Inconsistent, extreme levels of Cl enter streams during snow melt events. (Winter – Early Spring)

Monthly Cl Data: Western MD



Established Cl Thresholds

	EPA Criteria	MD Stressor ID
Threshold (mg/L)	Ac: 860 Ch: 230	50
Account for Variability (Temporal/Spatial)	No	Yes
Level of Confounders in Development	Low	High
Level of Confounders in Application	High	Low
Uses Ecologically Representative Organism(s)	No	Yes
Account For Ion Matrix	**NO**	**NO**

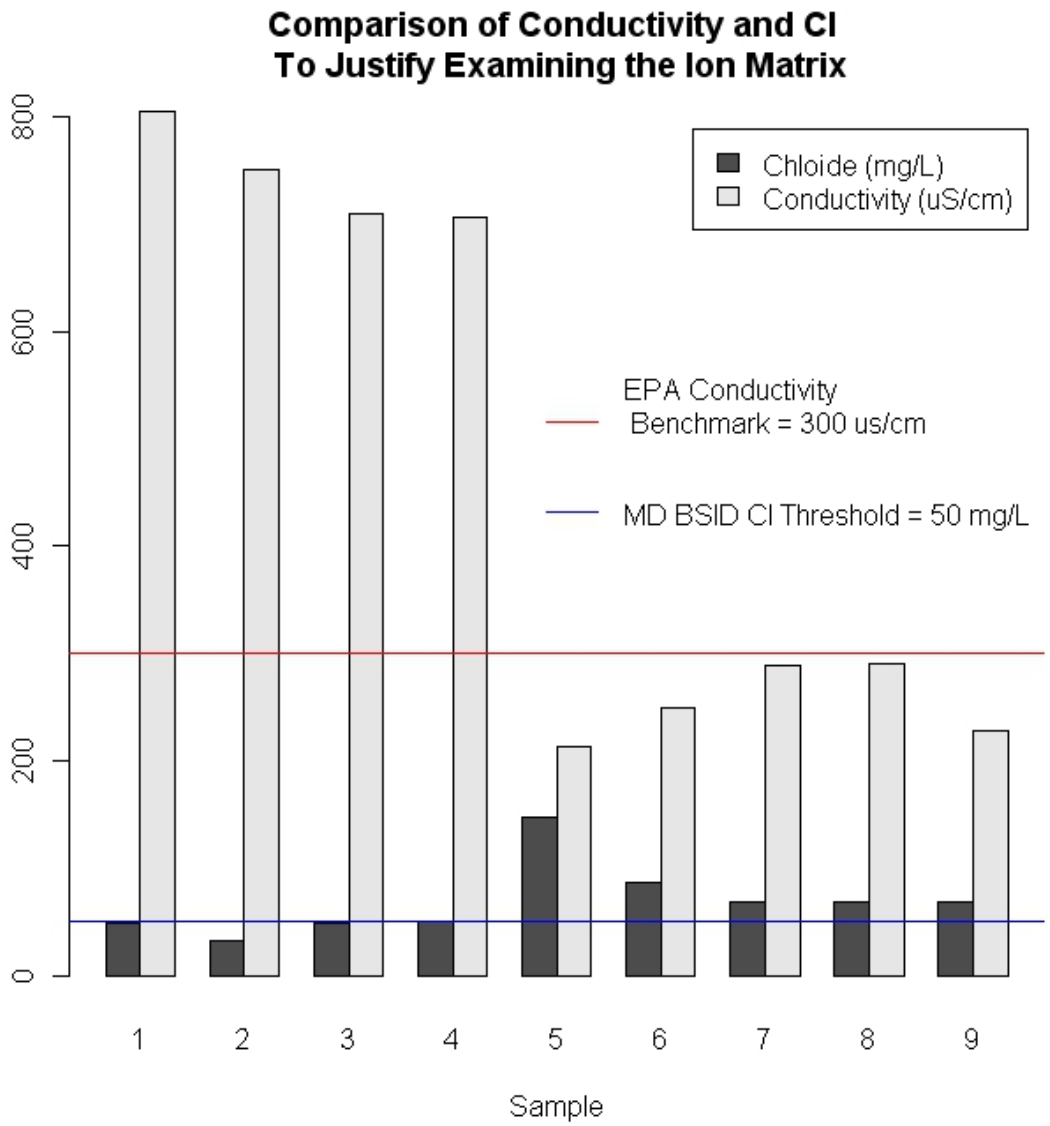
Ion Matrix

- Mixture of all ions and metals in surface waters.

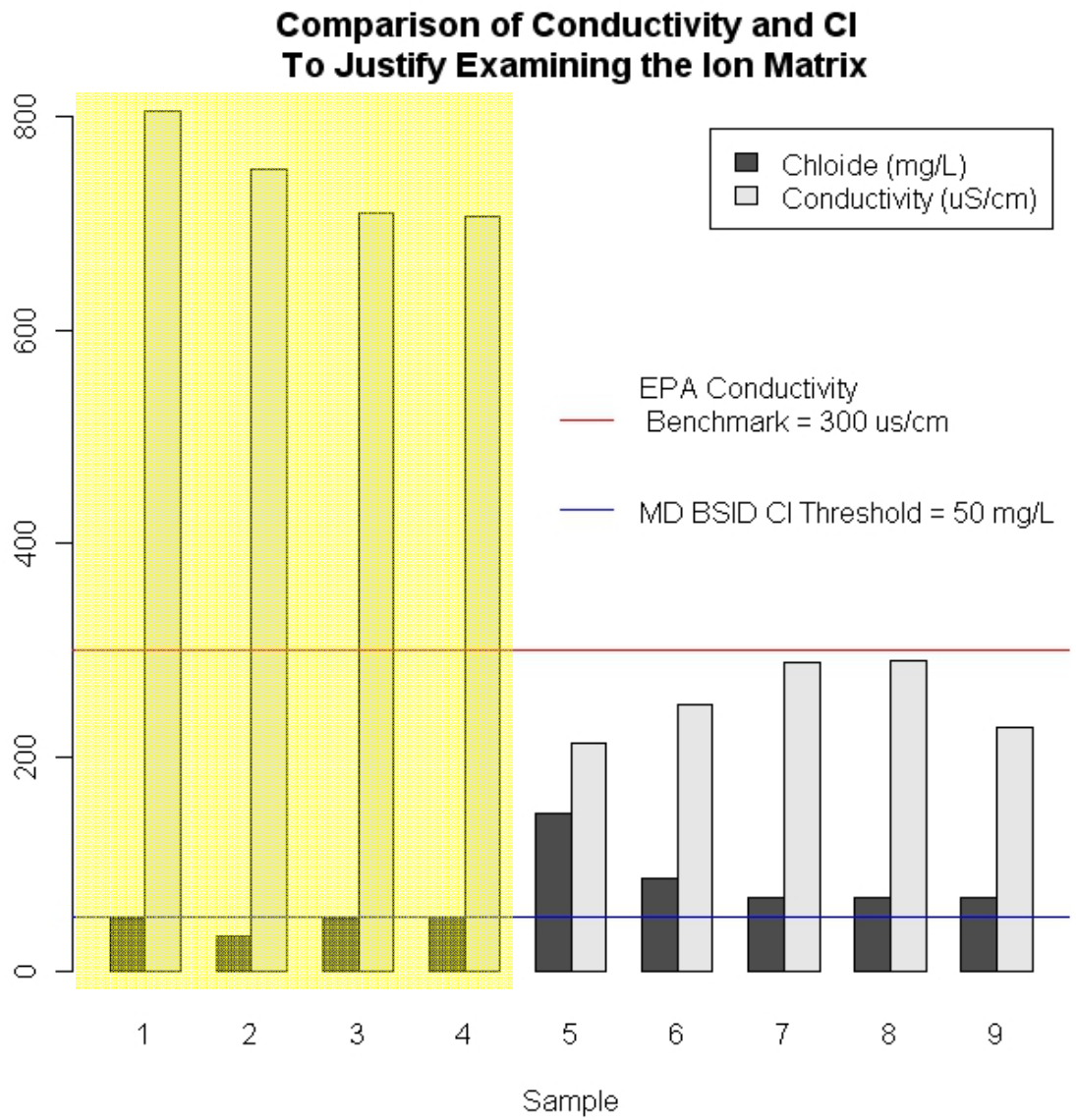
- Importance: Ion matrix has the ability to ameliorate and/or compound the toxicity of particular ions.

Class	Name	Formula
Cations	Calcium	Ca^{2+}
	Magnesium	Mg^{2+}
	Sodium	Na^{+}
	Potassium	K^{+}
	Ammonium	NH_4^{+}
Anions	Chloride	Cl^{-}
	Sulfate	SO_4^{2-}
	Bicarbonate	HCO_3^{-}
	Nitrate	NO_3^{-}
	Nitrite	NO_2^{-}
	Phosphate	PO_4^{3-}
	Bromide	Br^{-}
Metals	Iron	Fe
	Manganese	Mn
	Selenium	Se
	Aluminum	Al
	Strontium	Sr
	Barium	Ba

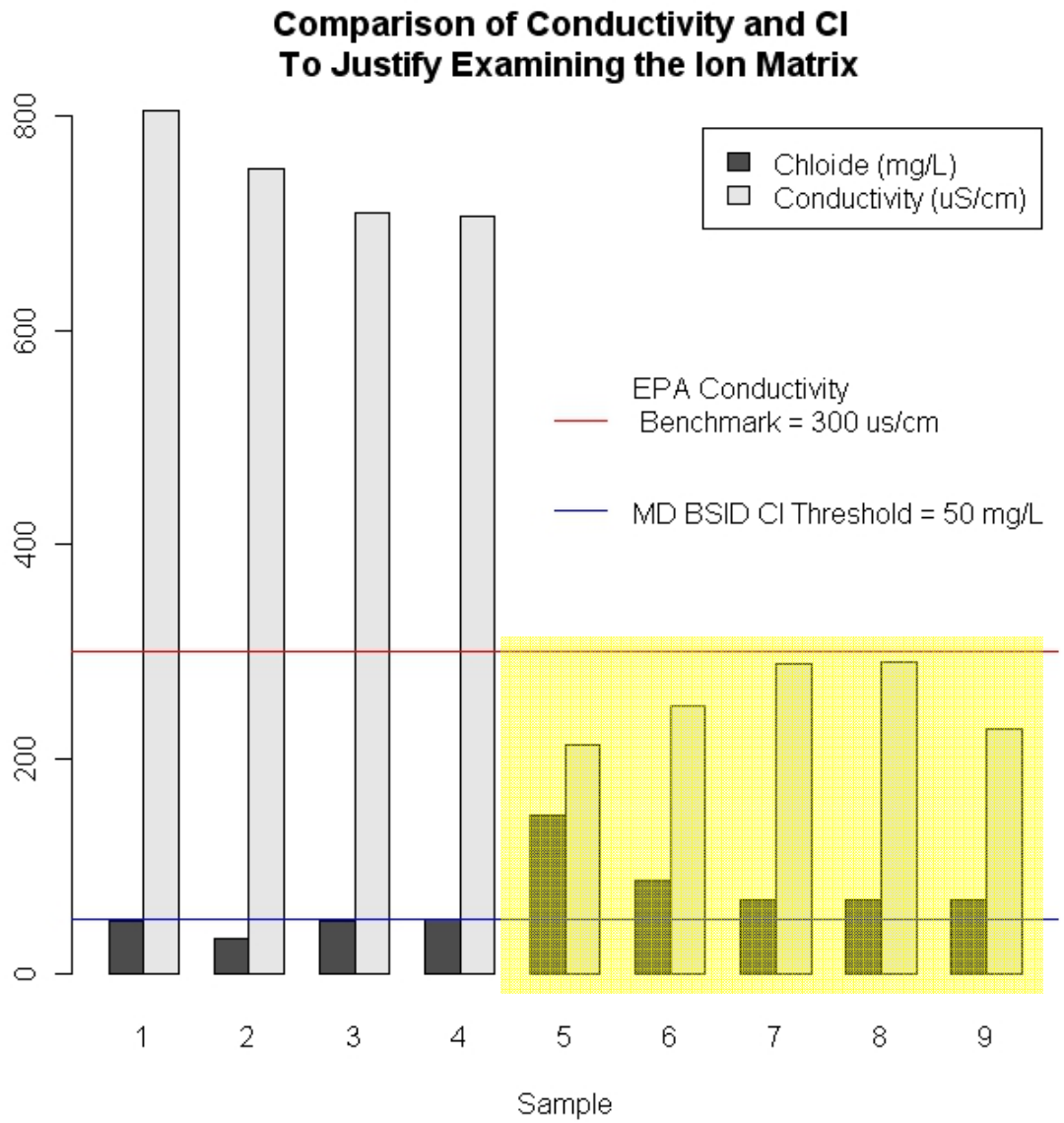
Ion Matrix


Comparison of Conductivity and Cl
To Justify Examining the Ion Matrix
Chloide (mg/L)
Conductivity (uS/cm)
EPA Conductivity
Benchmark = 300 us/cm
MD BSID Cl Threshold = 50 mg/L
0
200
400
600
800
1
2
3
4
5
6
7
8
9
Sample

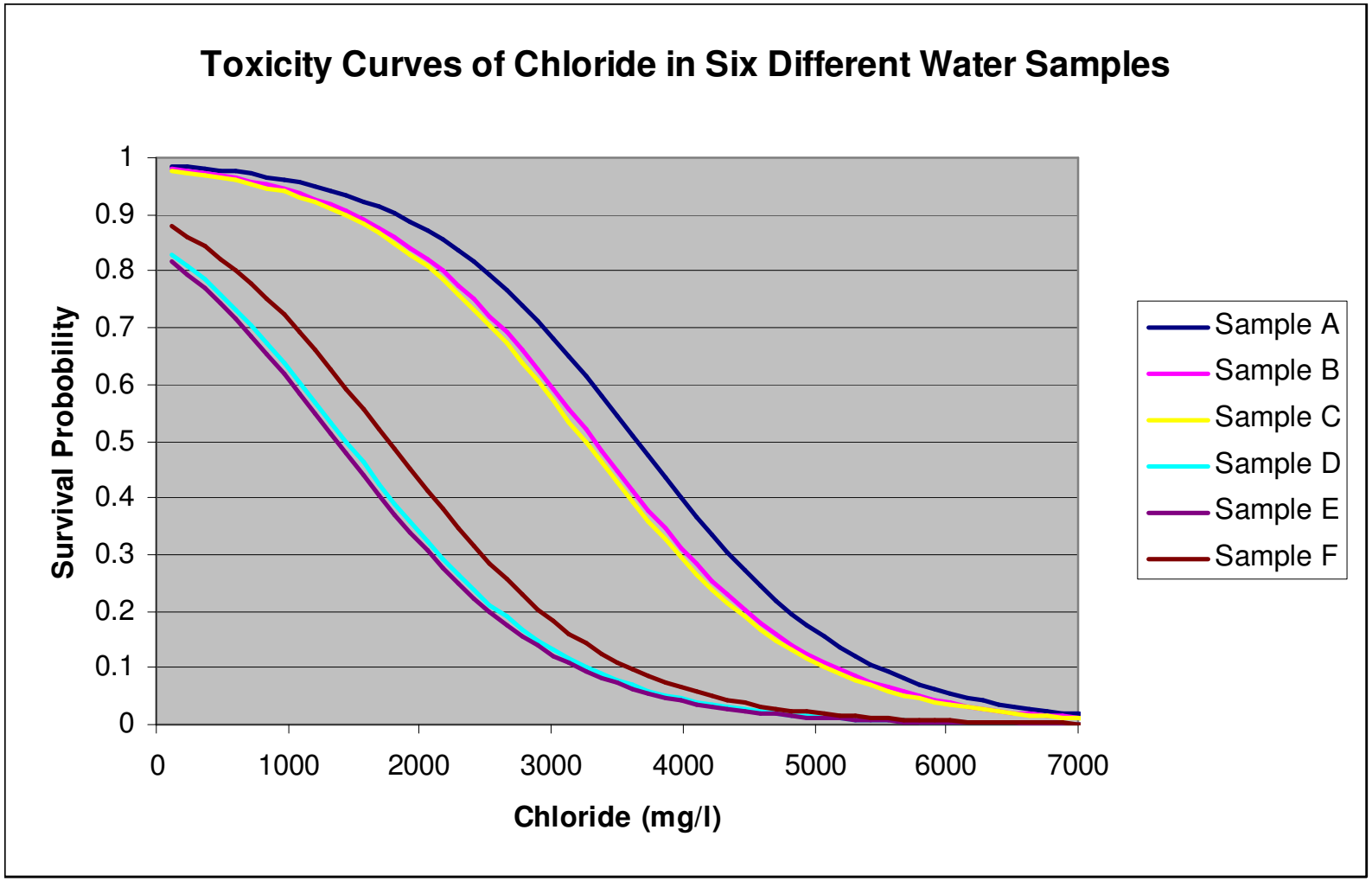
Ion Matrix


Comparison of Conductivity and Cl
To Justify Examining the Ion Matrix
Chloide (mg/L)
Conductivity (uS/cm)
EPA Conductivity
Benchmark = 300 us/cm
MD BSID Cl Threshold = 50 mg/L
0
200
400
600
800
1
2
3
4
5
6
7
8
9
Sample

Ion Matrix


Comparison of Conductivity and Cl
To Justify Examining the Ion Matrix
Chloide (mg/L)
Conductivity (uS/cm)
EPA Conductivity
Benchmark = 300 us/cm
MD BSID Cl Threshold = 50 mg/L
0
200
400
600
800
1
2
3
4
5
6
7
8
9
Sample

Ion Matrix: Mount et al. 1997



Proposed Objectives

A. Identify the natural, background ion matrix in streams within each ecoregion across Maryland at base flow, and identify how these background ion matrices affect the toxicity of chloride.

B. Identify the ion matrix in a stream that has been documented as being impaired by chloride, and identify how that matrix affects the toxicity of the maximum chloride concentration achieved during storm flows.

Objective A

Identify the Natural/Background Ion Matrix

1. What is the ion matrix, in its natural state (IBI > 4), within each ecoregion in MD?
2. What is the ion matrix associated with streams that meet the biological criteria (IBI >3) within each ecoregion within MD?
3. How is this ion matrix affected by changes in landuse composition?

Objective A

Field Methods

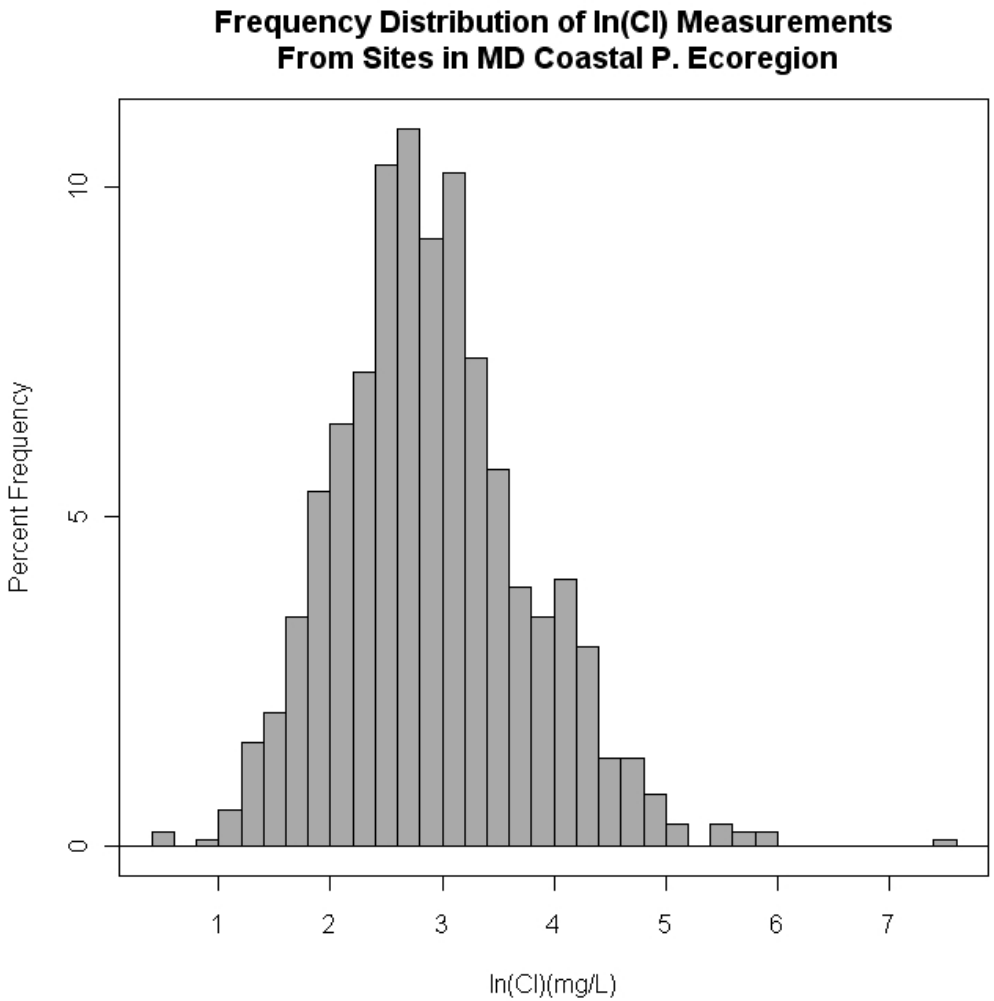
- Sample streams with a bug and fish IBI >3 and >4.
- Sample sites located at bridge crossings for ease of access.
- Grab samples during base flow (summer and/or fall seasons)
- Also measure: Hydro-lab data and discharge.

Objective A

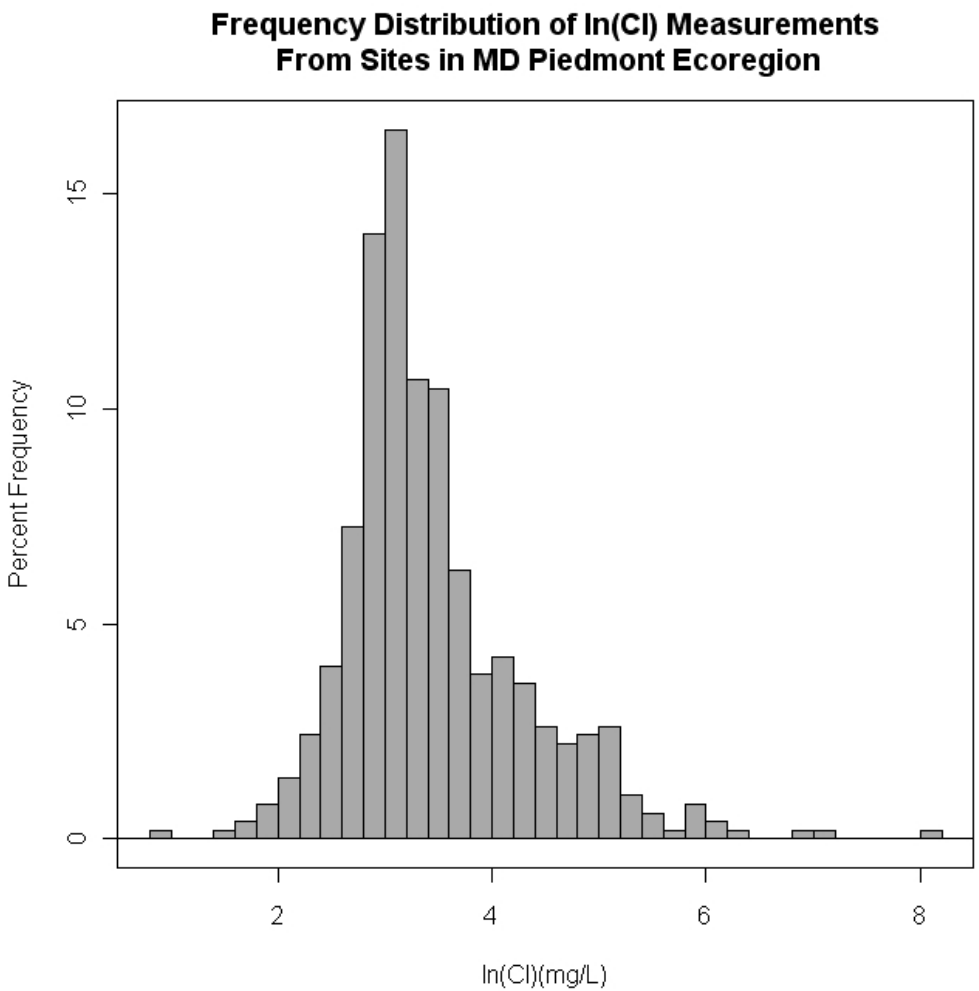
Sample Size Estimates

- Total = 400
  - Coastal Plain: 50
  - Piedmont: 50
  - Highlands: 300

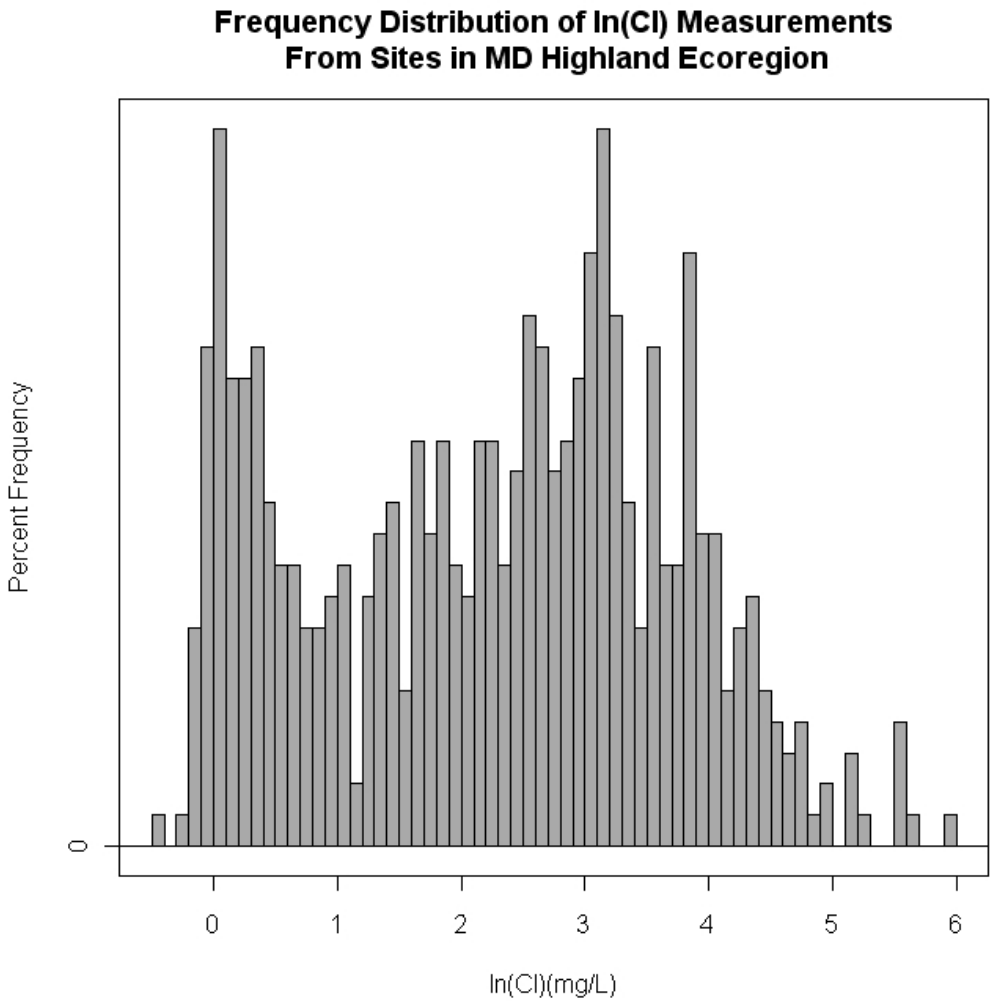
Percent frequency of Cl Data: Coastal Plain



Percent frequency of Cl Data: Eastern Piedmont



Percent frequency of Cl Data: Highlands



Site Selection

- Sample sites located at bridge crossings for ease of access.
- Identified stream reaches associated with IBI > 3 and >4
- Located road crossings with those reaches.

Objective B

Identify ion matrix in a stream that is impaired by chloride

1. What is the maximum chloride concentration possible during storm flows in a stream that is known to be affected by elevated chloride concentrations?

2. What are the characteristics of the ion matrix associated with this maximum chloride concentration?

Objective B

Field Methods

- Coordinate with TMDL Development Program's sampling effort.
- Sample flow (or conductivity) - triggered stream discharge samples.
- Number of samples:
  - As many as possible, up to 10

Objective A and B

Lab Methods

- Assess ion and metal concentrations in grab samples
- Lab analysis performed by CBL and SERC

Class	Name	Formula
Cations	Calcium	Ca^{2+}
	Magnesium	Mg^{2+}
	Sodium	Na^{+}
	Potassium	K^{+}
	Ammonium	NH_4^{+}
Anions	Chloride	Cl^{-}
	Sulfate	SO_4^{2-}
	Bicarbonate	HCO_3^{-}
	Nitrate	NO_3^{-}
	Nitrite	NO_2^{-}
	Phosphate	PO_4^{3-}
	Bromide	Br^{-}
Metals	Iron	Fe
	Manganese	Mn
	Selenium	Se
	Aluminum	Al
	Strontium	Sr
	Barium	Ba

Objective A and B

Application of New Data to Identify Chloride Thresholds

- Relationships between chloride and measures of the ion matrix will be applied to historical dataset to identify negative biological responses.
  - Old data (MBSS Data): Extensive chloride concentration, conductivity, and biological data.
  - New data (from this proposed study): Natural (and elevated) chloride concentrations relative to ion matrix, and its' effect on conductivity or TDS
- Adapt future synoptic sampling to incorporate the ion matrix.

MDE

Three Big Mathematical / Statistical Challenges

- Dev. Relationship between CI and IM
- Classify Streams
- Identify Biological Response

MARYLAND

Overview

Objective	A: Background Ion Matrix, By Ecoregion	B: Extreme/Stormflow Concentrations
Field Methods	400 Grab samples Summer Fall	AMAP Automated Storm Samples
Sites Selection	High Quality Streams: IBI >4 (random) Unimpaired Streams: IBI >3 (random)	Stream known to be impaired for Cl (targeted)
Lab Analysis	Ion matrix (Including Cl and Metals)	Ion matrix (Including Cl and Metals)
Data Analysis	Apply newly established relationships b/t Cl and ion matrix to historical data to identify biological response.	Apply documented concentrations to ion toxicity models.

Time Frame

- Objective A: Summer / Fall 2011
- Objective B: Spring 2012

Additional Benefits

- Other ions and metals can be examined from this newly gathered data.
- Aid in setting baseline information regarding up coming potential WQ threats. (e.g. Sr and Ba).

Questions?

Extra Stuff

Objective B

Application of New Data to Identify Chloride Thresholds

- Relationships between chloride and measures of the ion matrix will be applied to historical dataset to identify negative biological responses.

- Toxicity Models will also be employed

MDE

Necessary Sample Size Estimates

Recommended Sample Sizes for Sites that Meet the Biological Criteria to Meet a Given Preciscon Around the Mean Using Natural Log Transformed Chloride Data.

Ecoregion	Mean	Standard D.	N	CV	Proposed Sample Size for Given Preciscion			
					25%	20%	10%	5%
Coastal Plain	2.7	0.7	393	0.254	4	6	26	103
Eastern Piedmont	3.1	0.5	246	0.160	2	3	10	41
Highlands	1.9	1.3	243	0.705	32	50	199	794

Recommended Sample Sizes for High Quality Sites to Meet a Given Preciscon Around the Mean Using Natural Log Transformed Chloride Data.

Ecoregion	Mean	Standard D.	N	CV	Proposed Sample Size for Given Preciscion			
					25%	20%	10%	5%
Coastal Plain	2.6	0.6	136	0.236	4	6	22	89
Eastern Piedmont	2.9	0.4	94	0.142	1	2	8	32
Highlands	1.5	1.3	96	0.893	51	80	31[illegible]	[illegible]

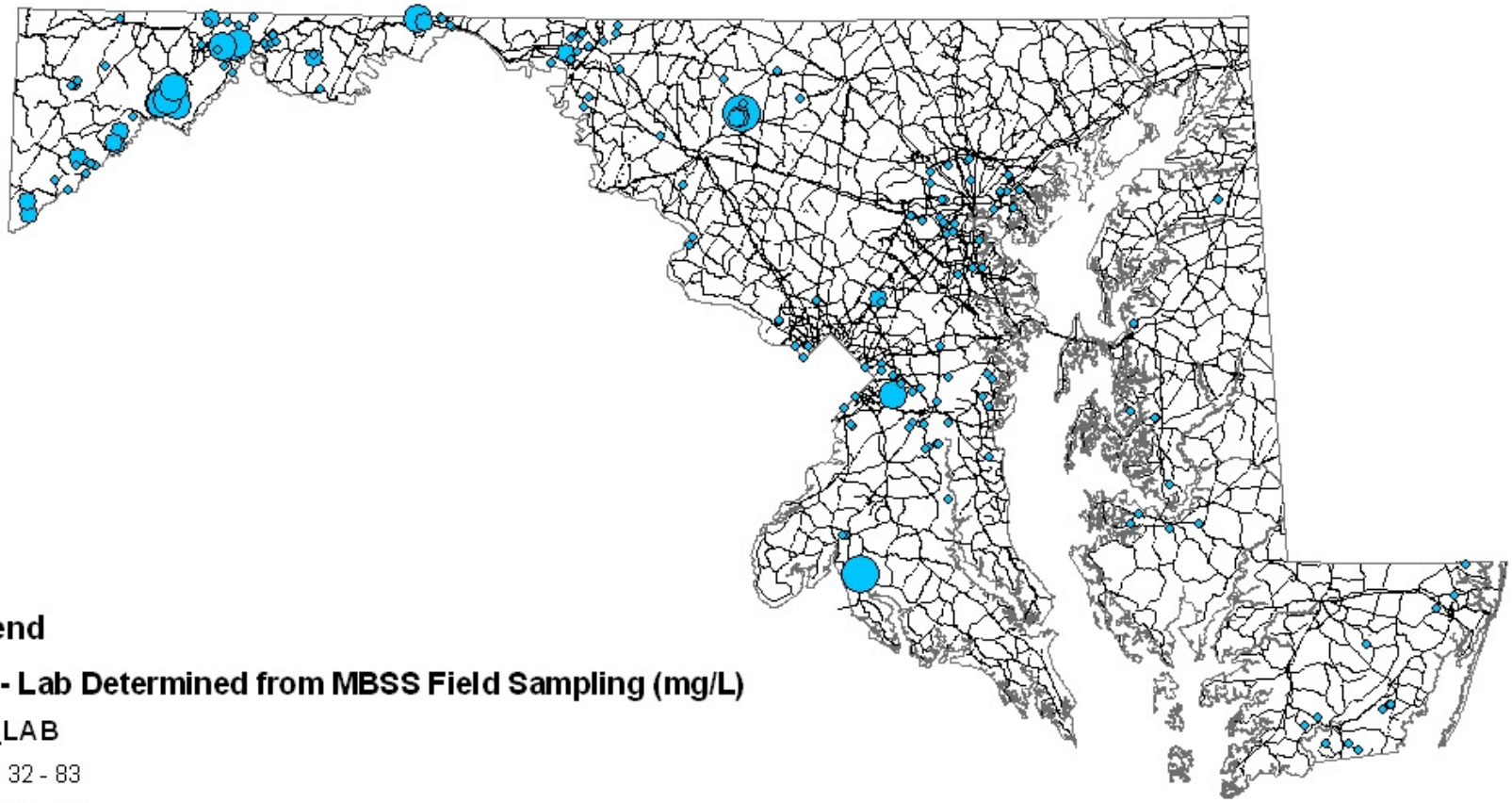
MARYLAND

Introduction: SO4

SO4 can be justifiably derived from current data sets.

- Regional pollutant
- Ecoregions used to develop EPA benchmark are present in MD.

Sulfate Concentrations Across State of MD: Samples From MBSS Program



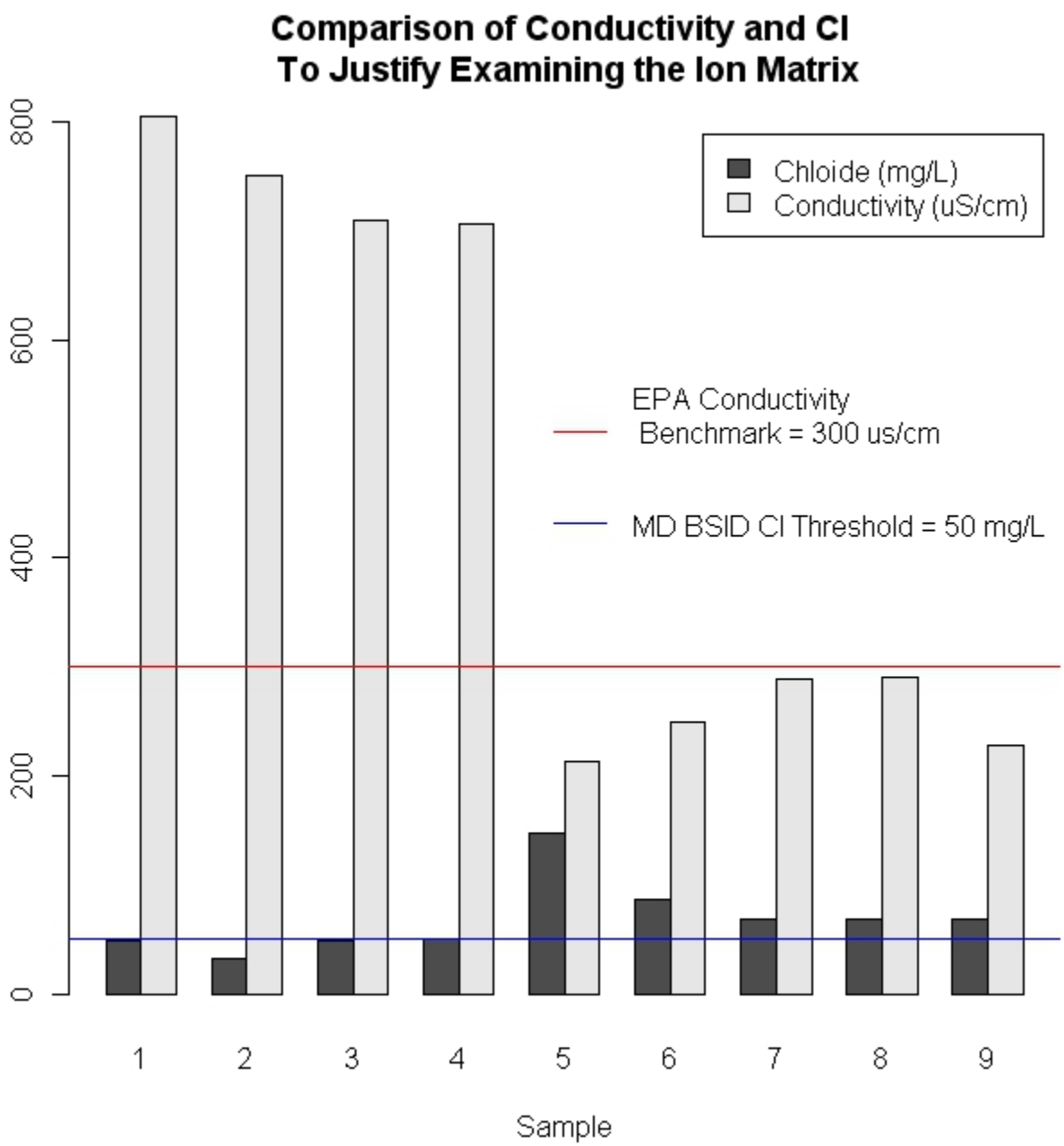
Legend

SO4 - Lab Determined from MBSS Field Sampling (mg/L)

SO4_LAB

- 32 - 83
- 84 - 174
- 175 - 350
- 351 - 798
- State Of MD
- Major Roads

MDE



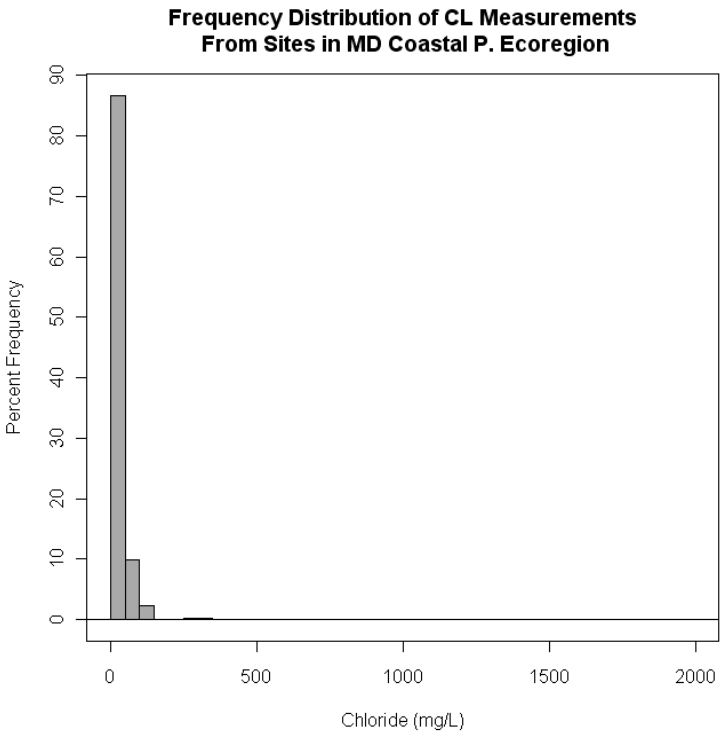
MARYLAND

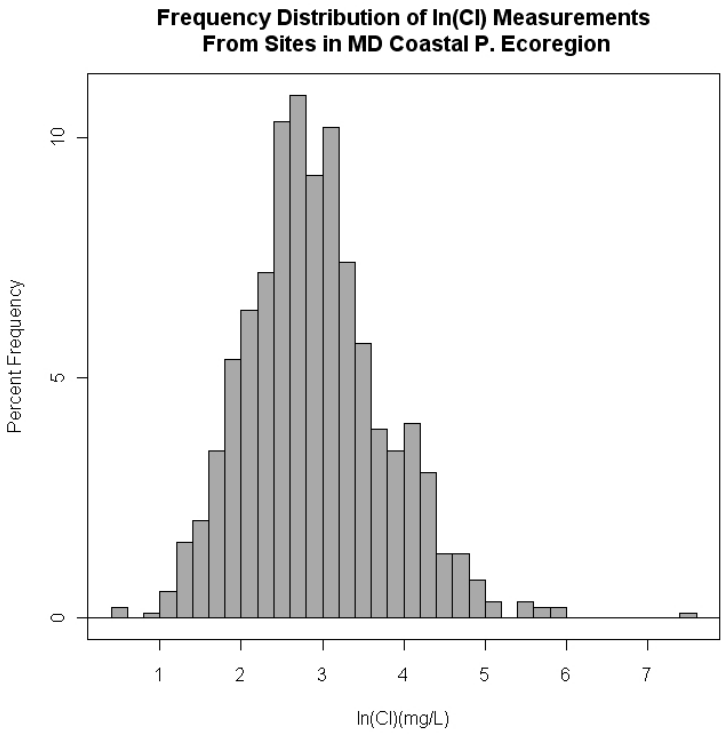
Objective A

Sample Size Estimates

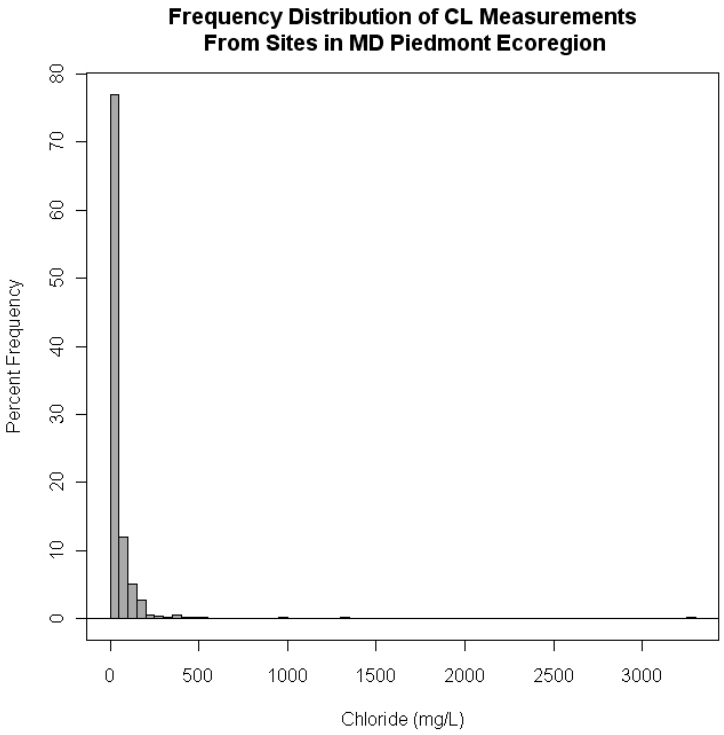
- Total = 400
- Sites that meet biological criteria (Fish and Bug IBI > 3)
  - Coastal Plain: 50
  - Piedmont: 50
  - Highlands: 200
- High-quality sites (Fish and Bug IBI > 4)
  - Coastal Plain: 25
  - Piedmont: 25
  - Highlands: 300

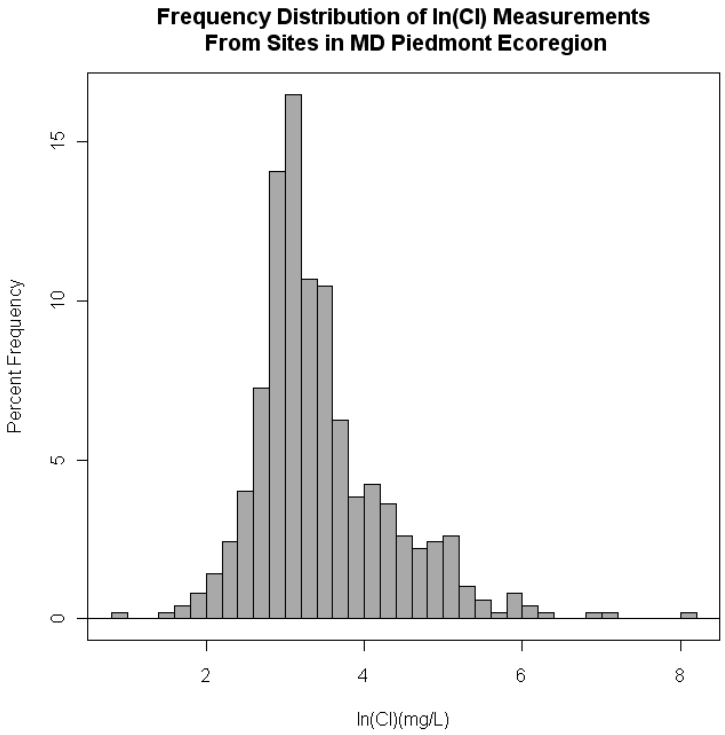
Percent frequency of Cl Data: Coastal Plain



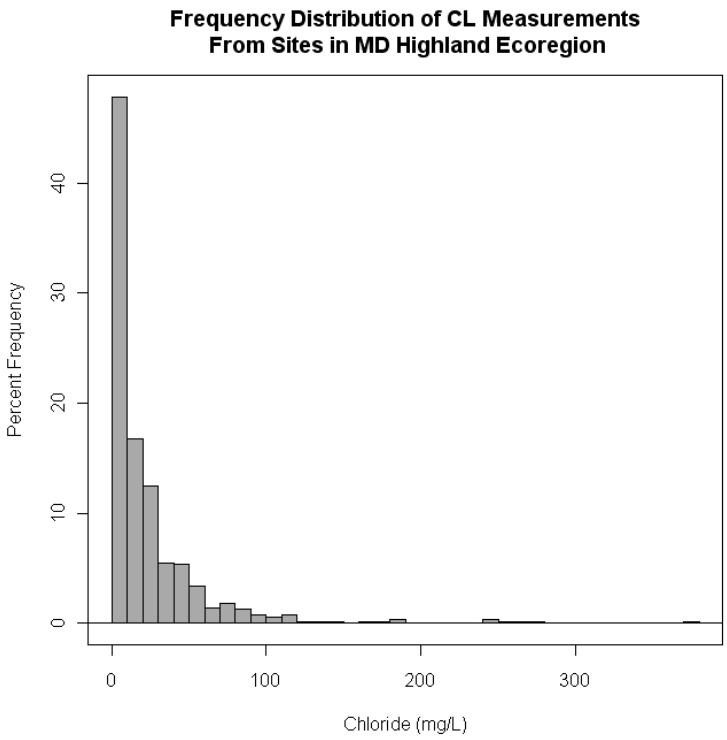


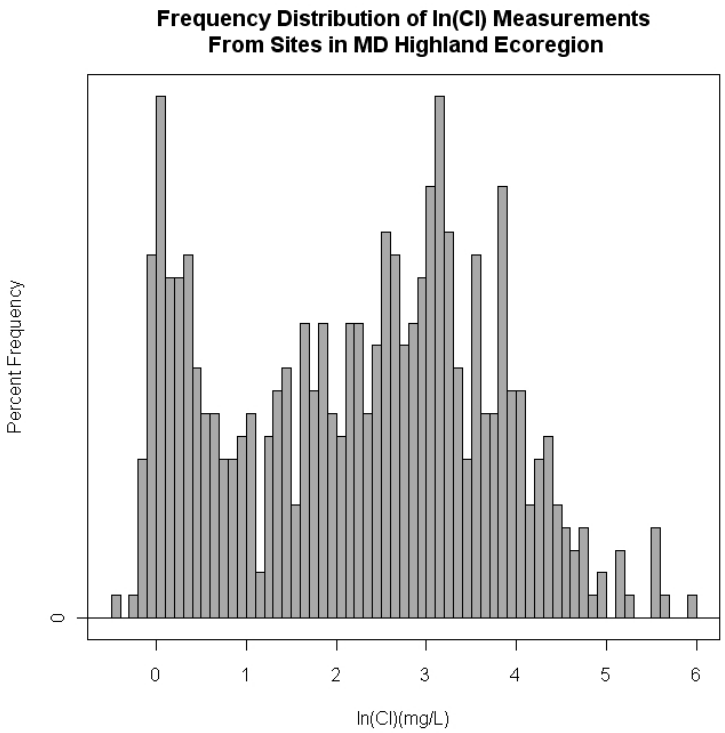
Percent frequency of Cl Data: Eastern Piedmont



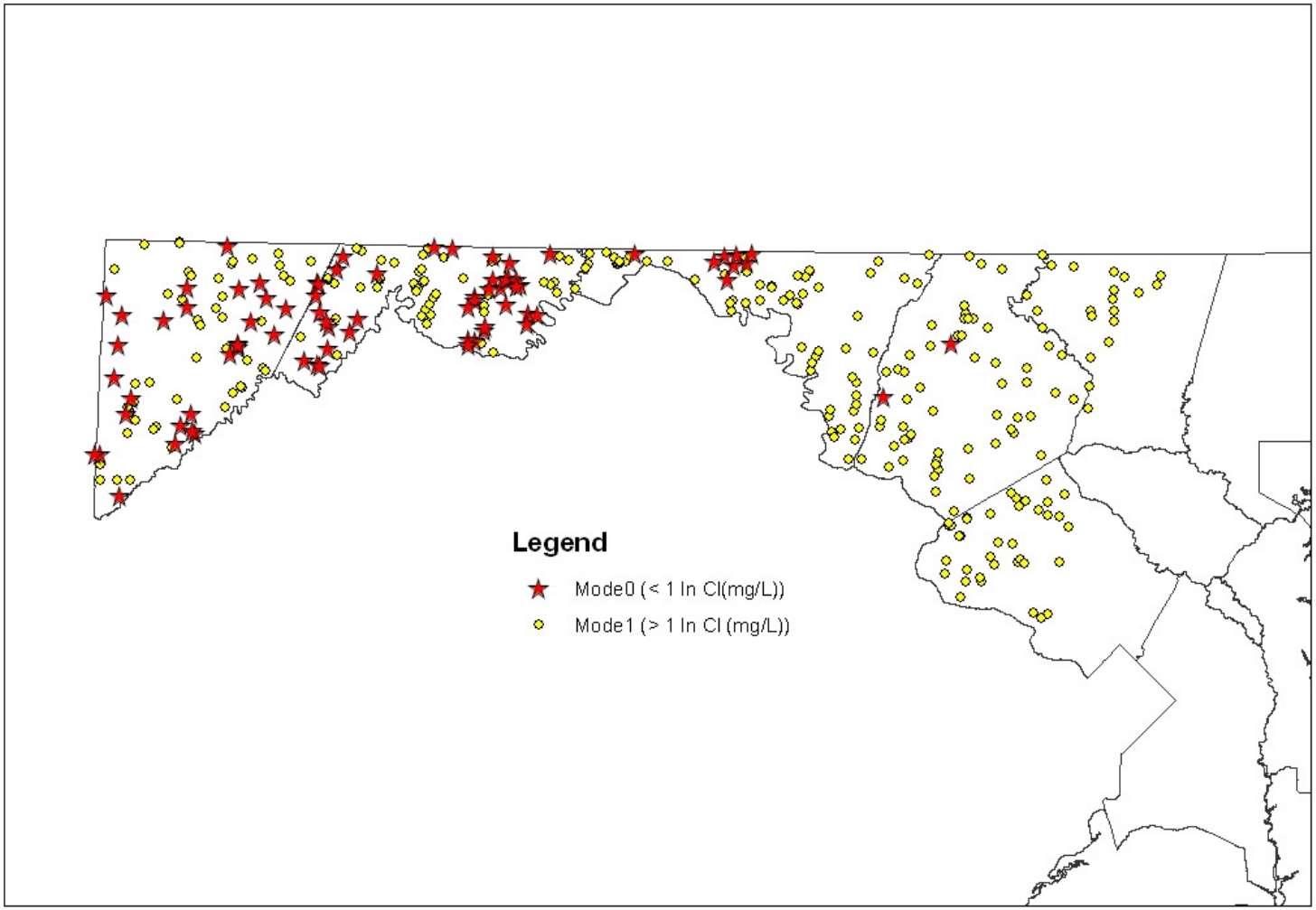


Percent frequency of Cl Data: Highlands



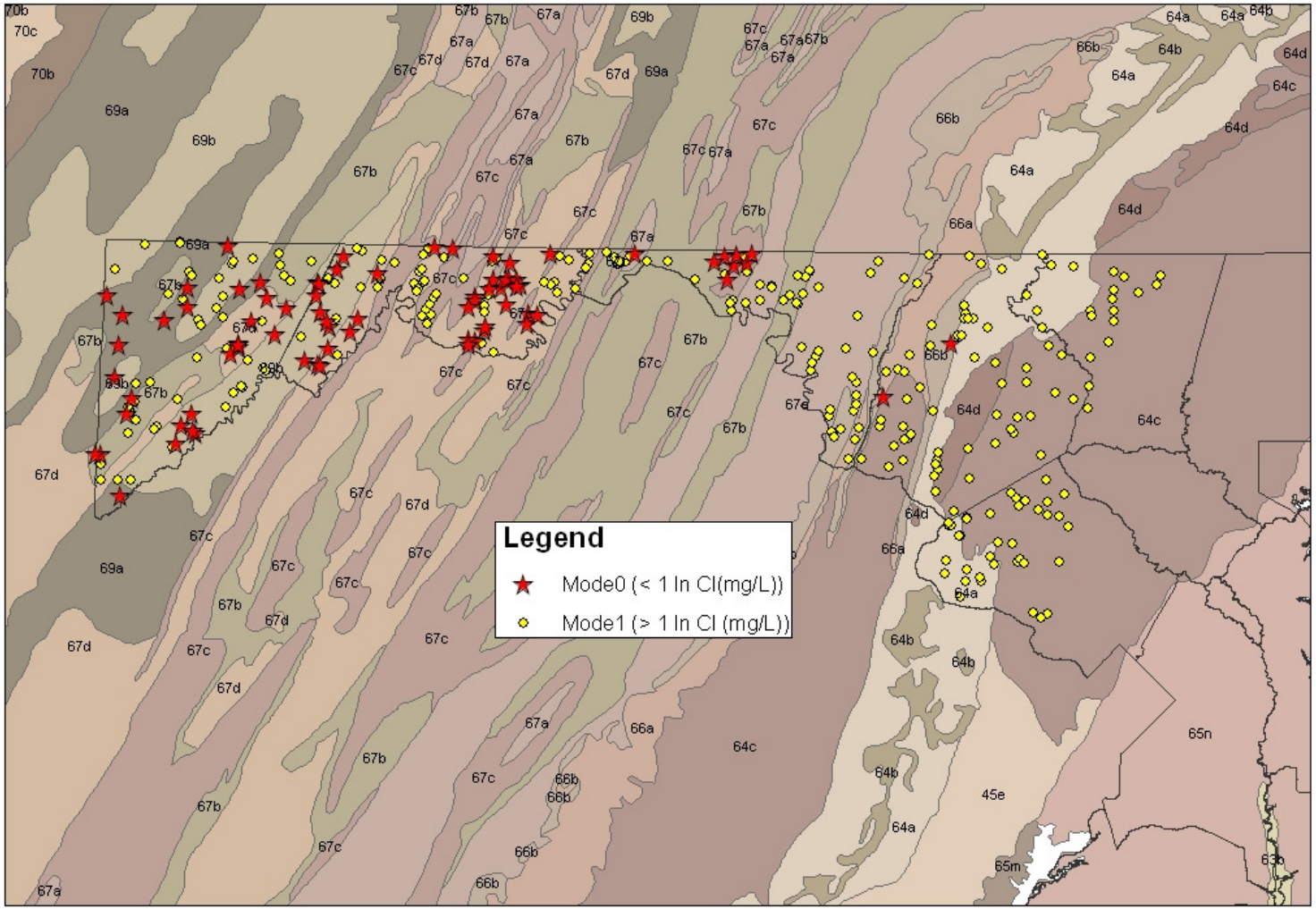


MDE



MARYLAND

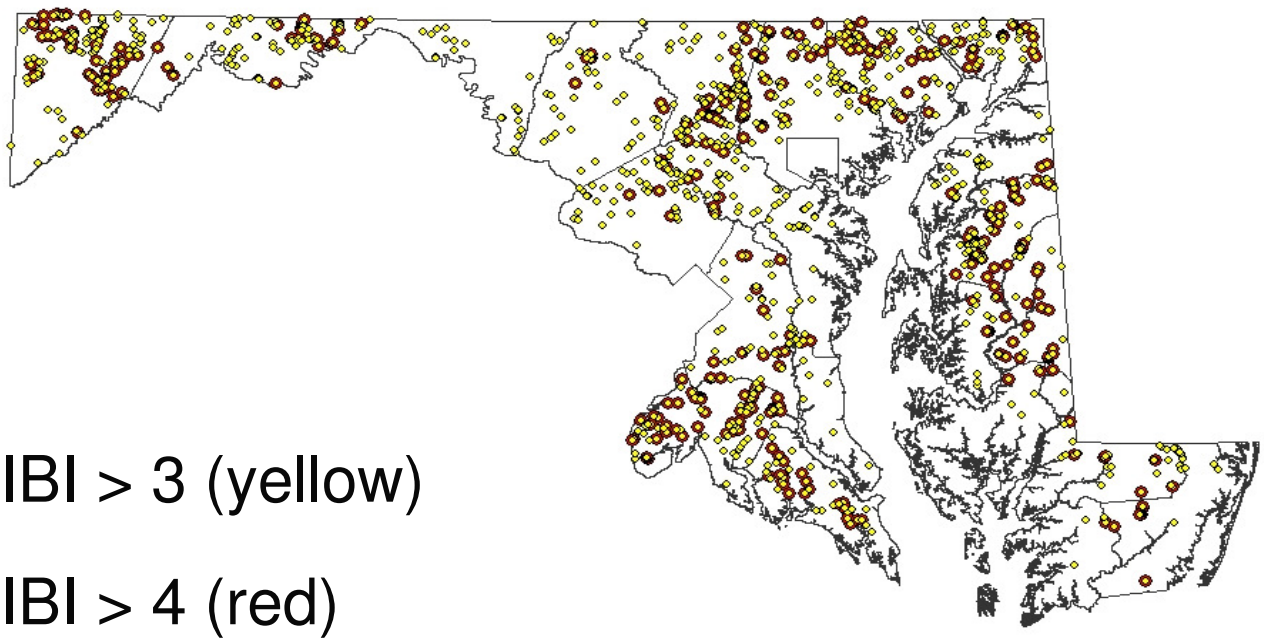
MDE

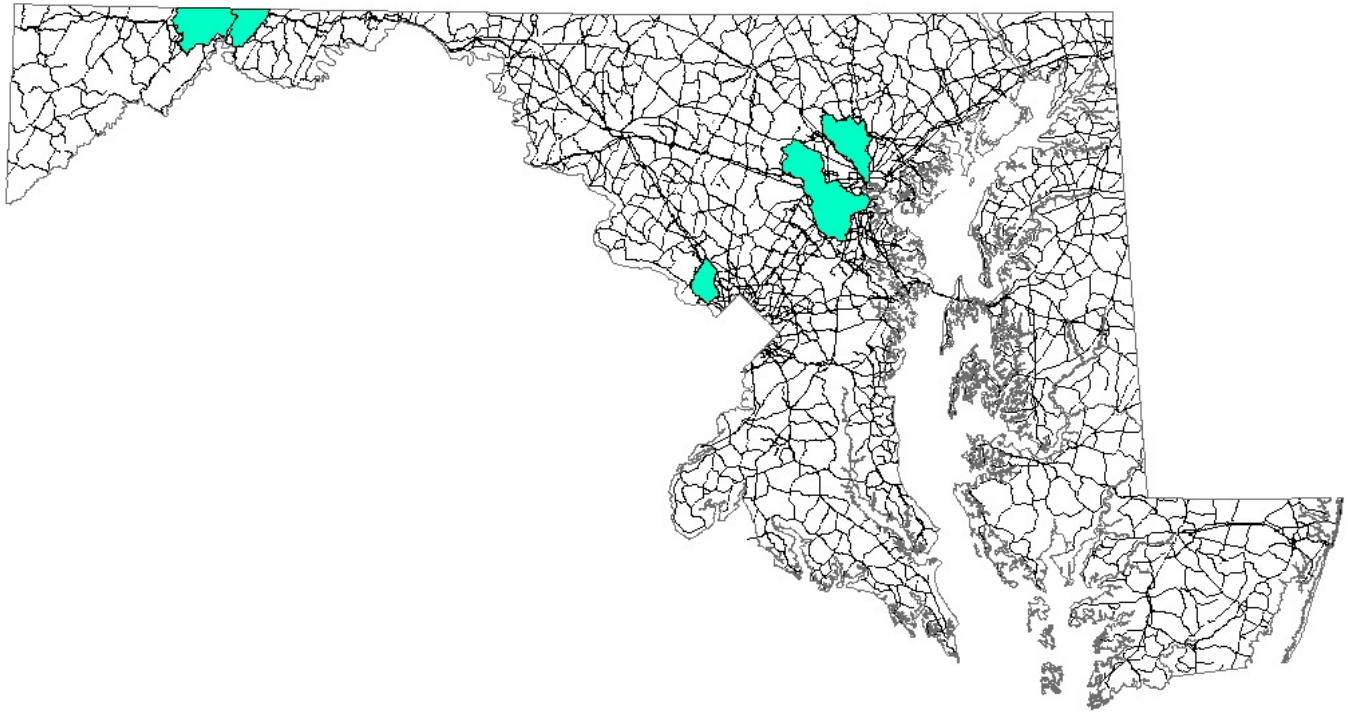


MARYLAND

Objective A: Field Methods

Examination: Potential CI Monitoring Sites



- IBI > 3 (yellow)
- IBI > 4 (red)

Listed Watersheds