Using a conductivity-alkalinity relationship as a tool to identify surface waters in reference condition across Canada

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Environment and Climate Change Canada

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INTRODUCTION

ASSESSING NATURAL VARIABILITY

- Inorganics occur naturally in the environment
- Natural concentration in the environment
  - i.e. “Background Concentration Range”
  - Variations with geology
  - e.g. Highly mineralized Canadian Shield Ecozone

INTRODUCTION

BACKGROUND CONCENTRATION RANGES (BCR)

- Elevated concentration ~ Anthropogenic activity
- Aid in predictive modelling
- Ecological Assessment Division (ECCC)
  - Approach to quantify BCR
  - Inform ecological risk assessments
  - Chemical Management Plan initiative
- General Approach
  - Reference Condition Data/ Management Area

<u>CHALLENGE</u>

Identify sites in Reference Condition

REFERENCE CONDITION

- Land cover: minimal % disturbance
  - Upstream catchment of site
  - Inaccuracies from small point-source inputs (e.g. mine)
  - Limited by:
    - Data availability, Spatial resolution, Time/cost

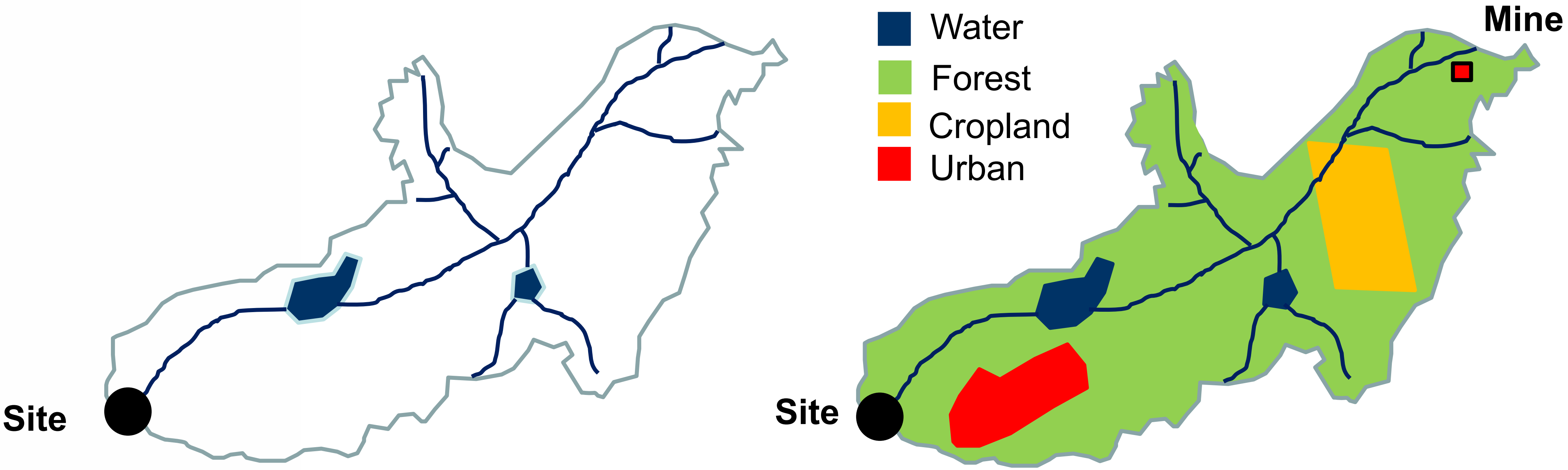


Figure 1. Assessment of reference condition based on anthropogenic disturbances in the upstream catchment.

REFERENCE CONDITION

- Conductivity-Alkalinity (Bodo 1993)
  - Natural relationship
  - Independent assessment of RC (water chem)

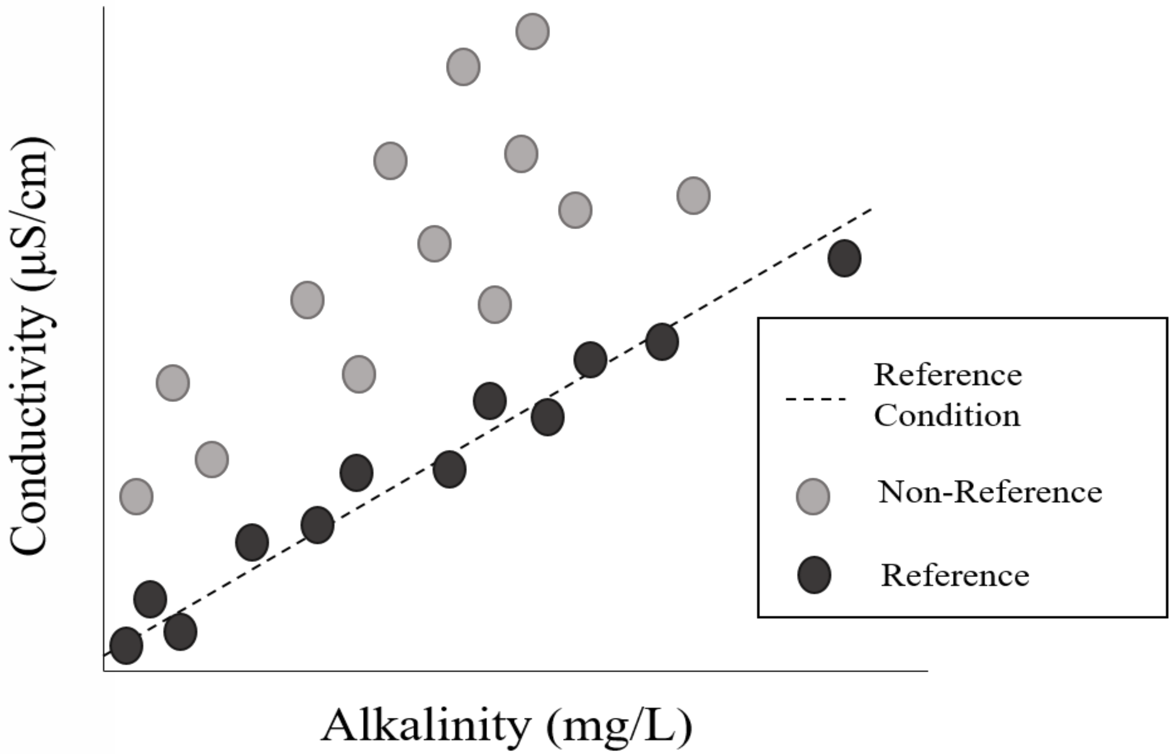


Figure 2. Conceptual diagram for the assessment of reference condition

Robust:

- Point Source; e.g. Mine Tailings (metals)
- Non Point Source; e.g. Cl- & Na (road salts)

OBJECTIVES

TEST CONDUTIVITY~ALKALINITY RELATIONSHIP

1. Collect available WQ data
2. Model relationship with data
3. Validate relationship with land cover data
4. Establish optimal Cutoff Value

DATA COLLECTION

FRESHWATER MONITORING PROGRAMS

Program	Agency	Location(s)
Freshwater Quality Monitoring and Surveillance (FQMS)	Environment and Climate Change Canada	**BC**, **YT**, ON, QC, **NB**
Provincial Water Quality Monitoring Network (PWQMN)	Ontario Ministry of the Environment and Climate Change	**ON**
Banque de Données sur la Qualité du Milieu Aquatique (BQMA)	Ministère du Développement durable, Environnement et Lutte contre les changements climatiques du Québec	**QC**
Regional Aquatics Monitoring Program (RAMP)	Alberta Environment & Other (Multi-stakeholder)	**AB**

Data Sharing Agreements:

Manitoba Long-Term Water Quality Monitoring Network Data

Saskatchewan Baseline Monitoring & Long Term Lakes Monitoring

COMPILED DATABASE

2005-2015

15 [inorganics]

40,513 samples from 3,535 sites

30,357 samples from 864 sites with conductivity and alkalinity data

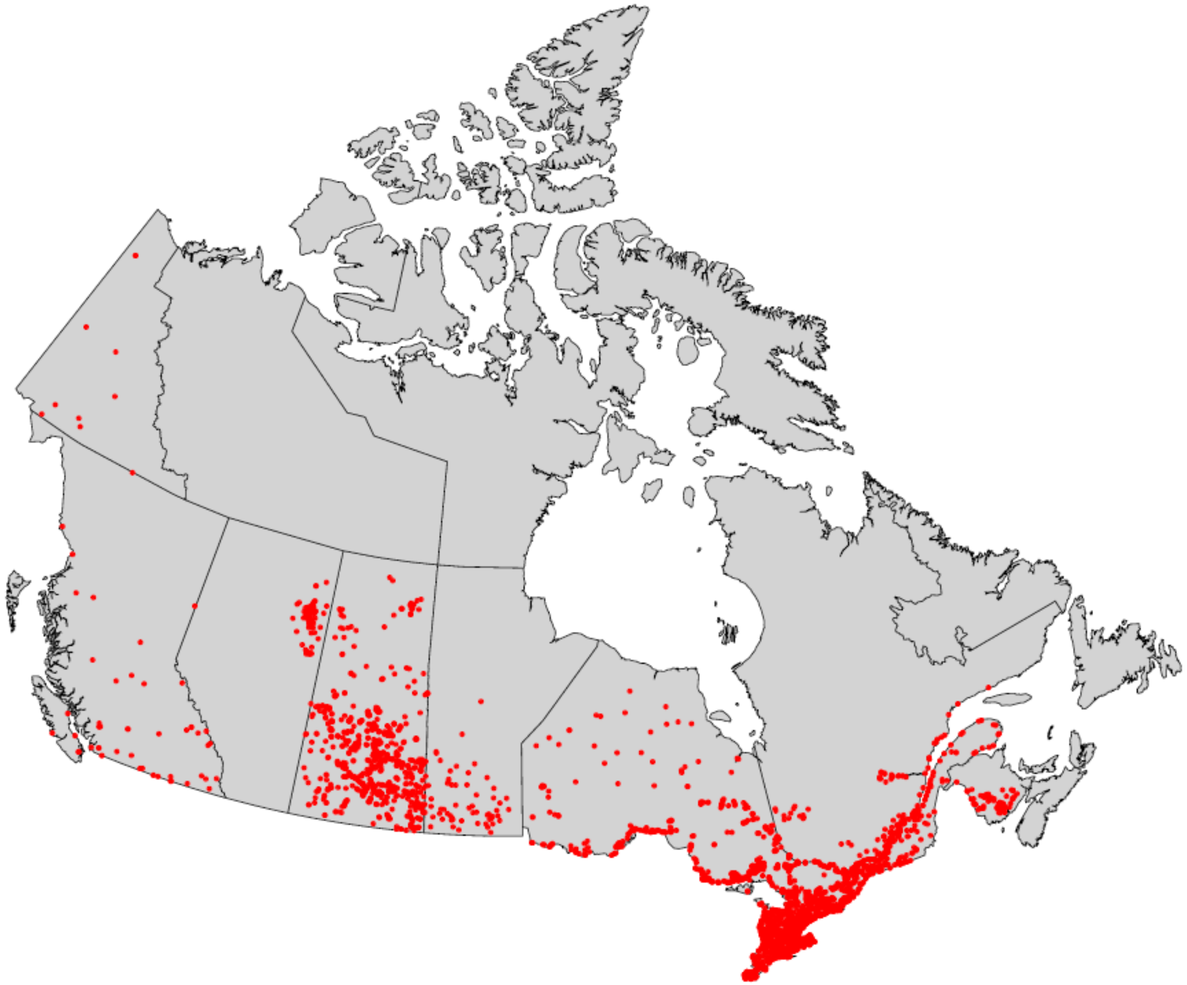


Figure 3. Surface water quality monitoring stations.

STATISTICAL ANALYSES

CONDUCTIVITY-ALKALINITY RELATIONSHIP

- Quantile Regression (Koenker and Basset 1978)
- Estimate limits of data extremes
- Lower 10th quantile

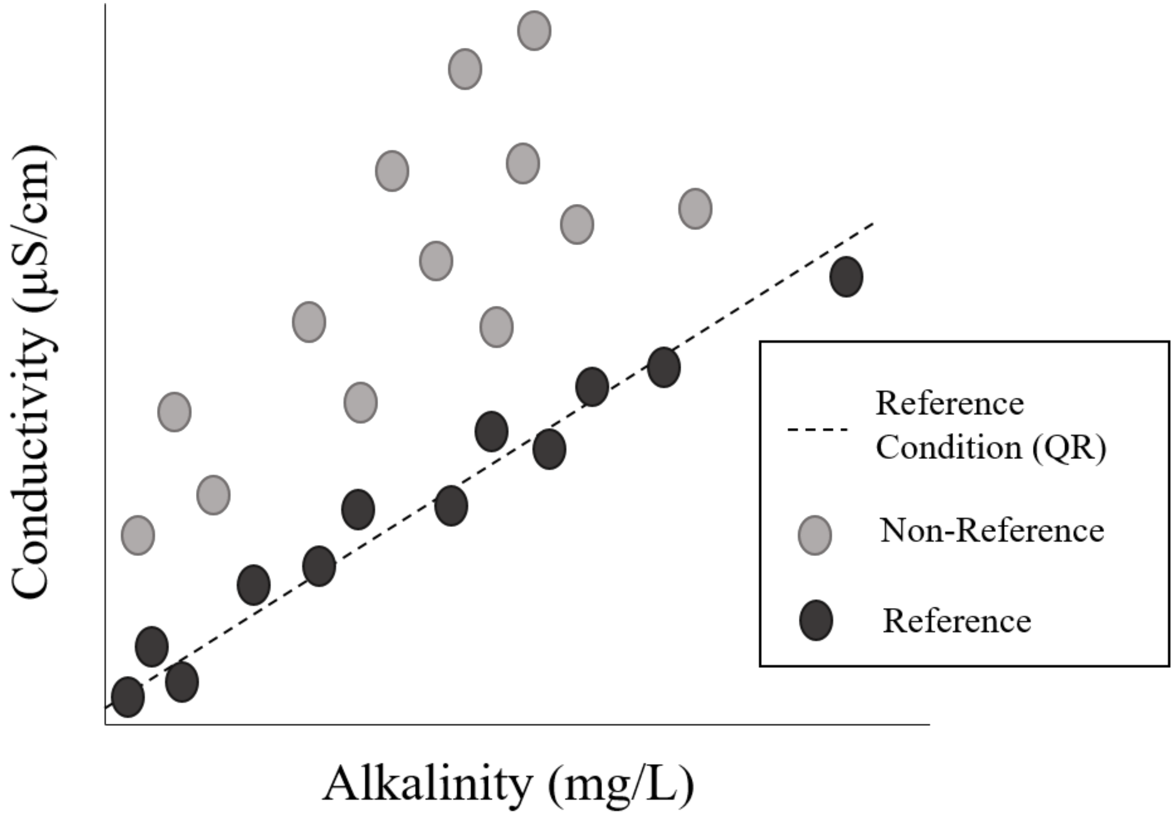


Figure 4. Relationship between conductivity and alkalinity under reference condition estimated by lower 10th quantile

COND ~ ALK RELATIONSHIP

$$Conductivity = 7.76 + 2\ (Alkalinity)$$

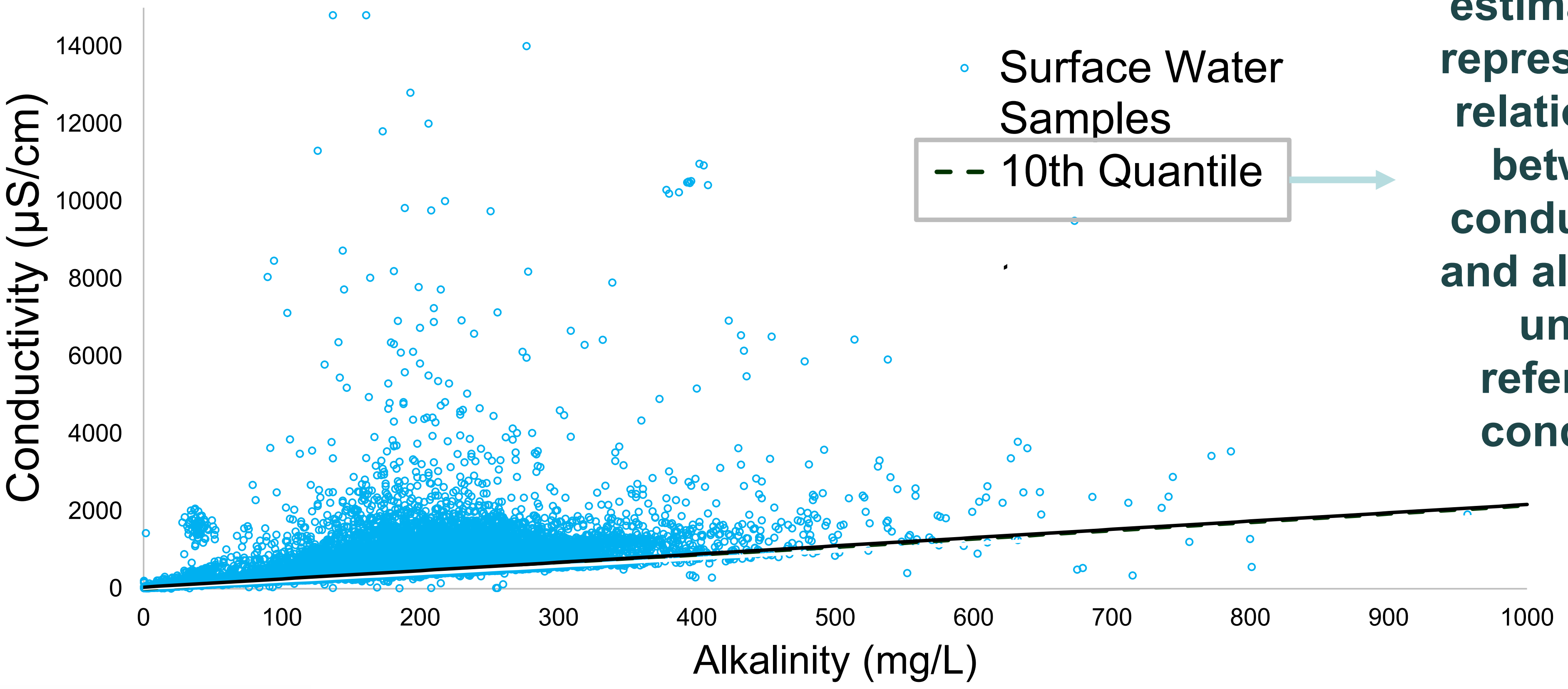


Figure 5 Relationship between conductivity and alkalinity for freshwater samples collected across Canada

The extreme lower 10th quantile was **estimated to represent the relationship between conductivity and alkalinity under reference condition**

COND ~ ALK RELATIONSHIP

$$Conductivity = 7.76 + 2\,(Alkalinity)$$

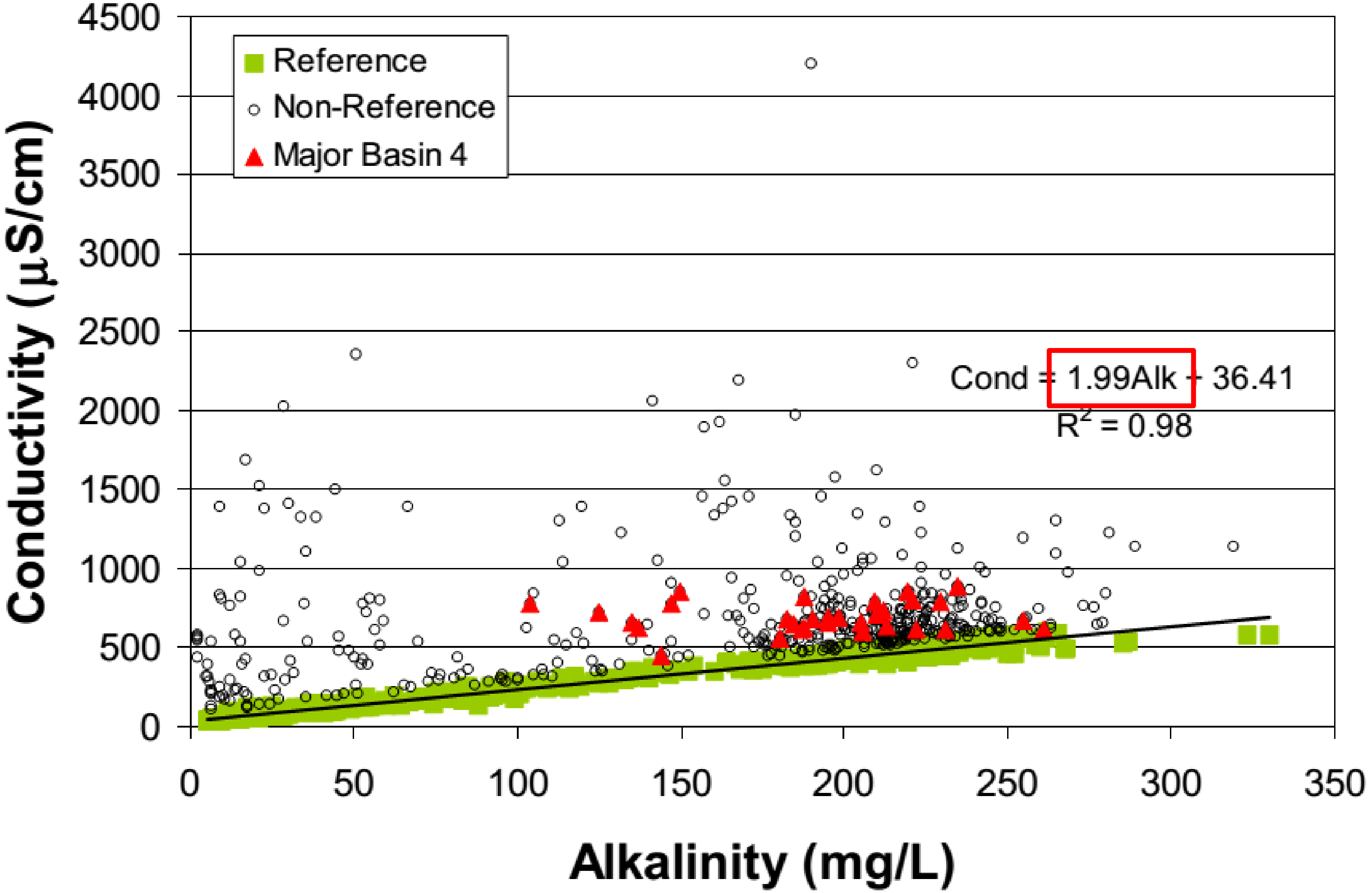


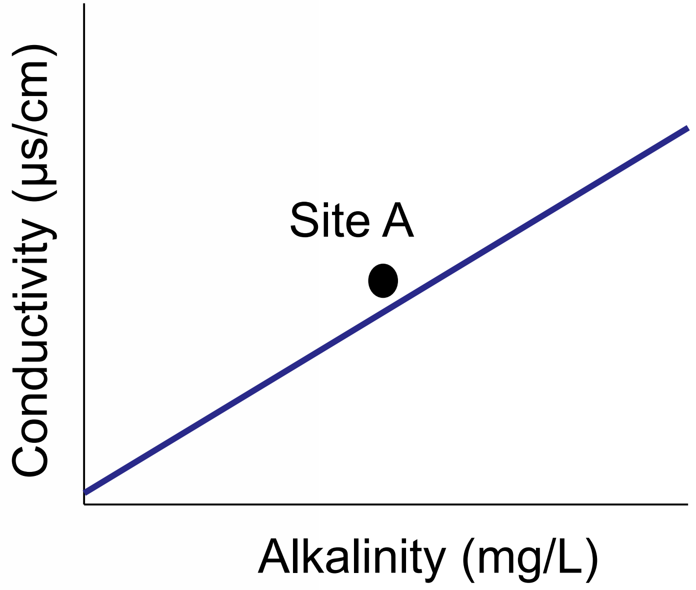
Figure 6 Relationship between conductivity and alkalinity for riverine water samples collected across Ontario (Kilgour et al. 2002).

VALIDATION

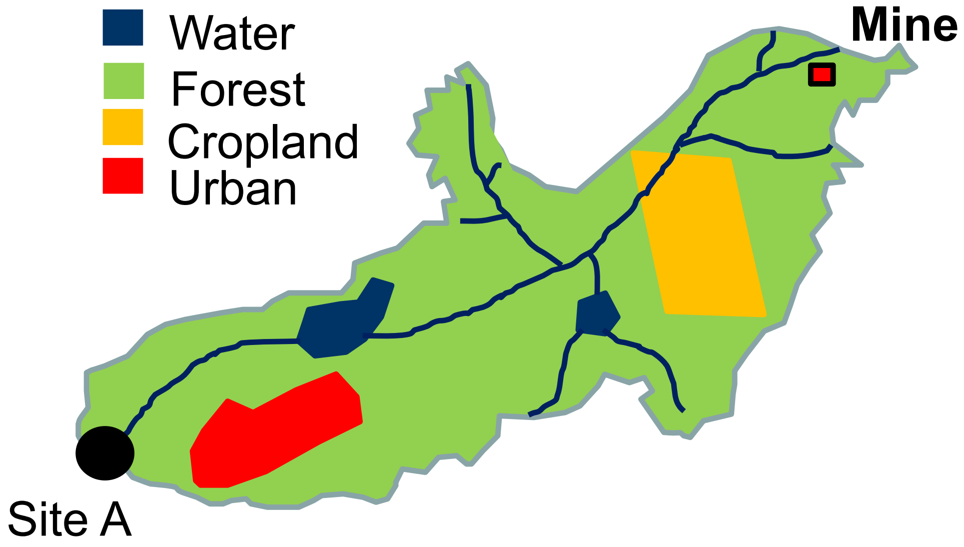
REFERENCE CLASSIFICATION (N=85)

- Relationship vs. Land Cover
  a. Classify based on relationship
     - Ref = modeled line
  b. Classify based on disturbance
     - Ref = minimally disturbed (<2.5%)

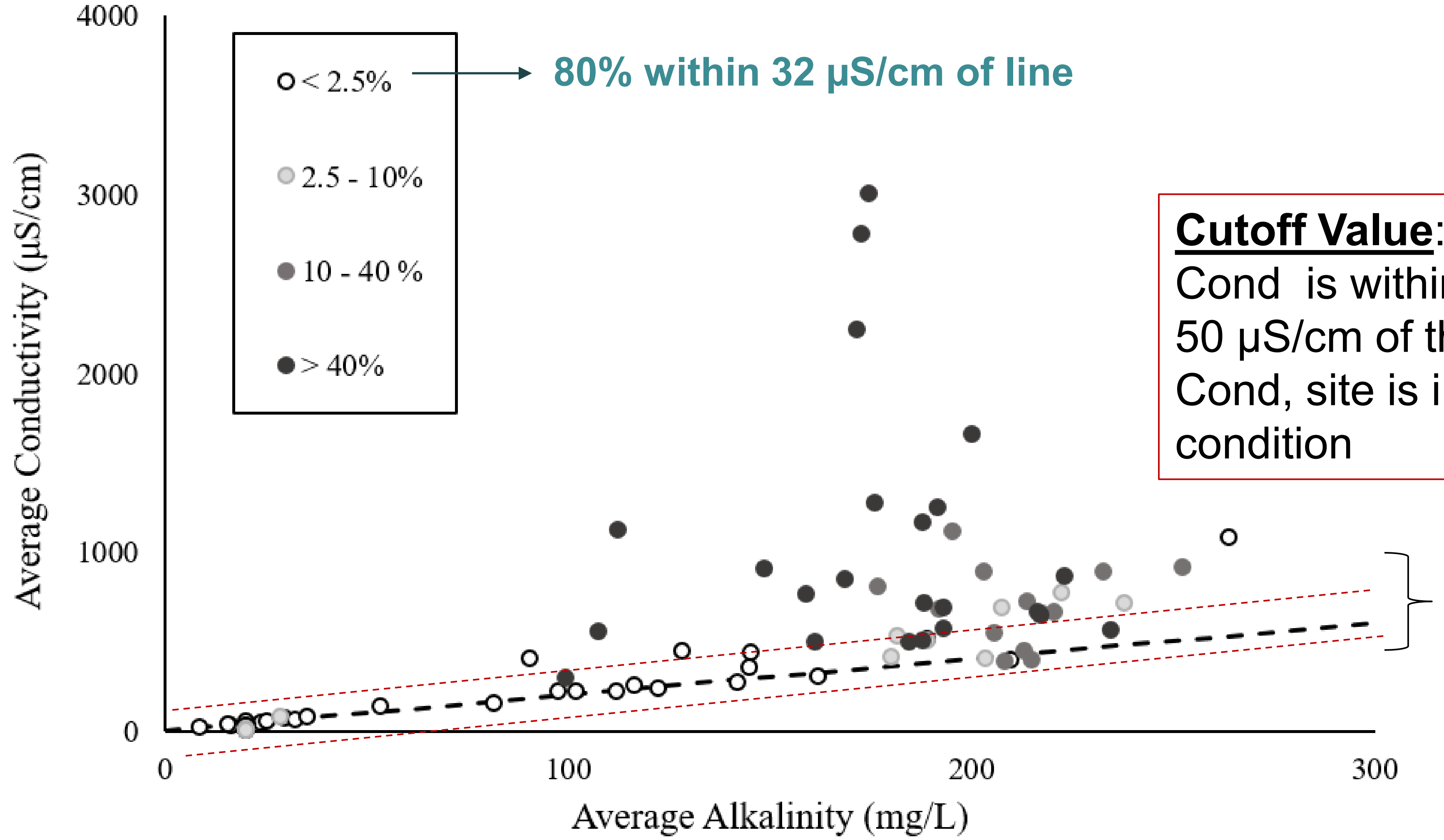
Figure 7. Reference classification of site A with relationship compared to land cover disturbance



VS.



VALIDATION



<u>Cutoff Value</u>: if observed Cond is within, for e.g., 50 µS/cm of the predicted Cond, site is in reference condition

Figure 8. Mean conductivity and alkalinity of sites (N = 85) based on land disturbance within their catchment.

VALIDATION & CUTOFF

RELIABILITY OF RELATIONSHIP

- Signal Detection Theory (Murtaugh 1996)

Predictive Ability: of an **indicator** estimated from equal-sized sample of **positive** (i.e. Reference) and **negative** (i.e. Non-Reference) responses defined by a **true measurement** (i.e. land cover)

		Conductivity-Alkalinity	
		Reference	Non-Ref.
Disturbance	Reference	TP	FN
	Non-Ref.	FP	TN

Figure 9 Modified from Murtaugh 1996

VALIDATION & CUTOFF

PREDICTIVE VALUE

- Sensitivity

$$\boldsymbol{Sensitivity = \frac{TP(c)}{TP(c) + FN(c)}}$$

- Specificity

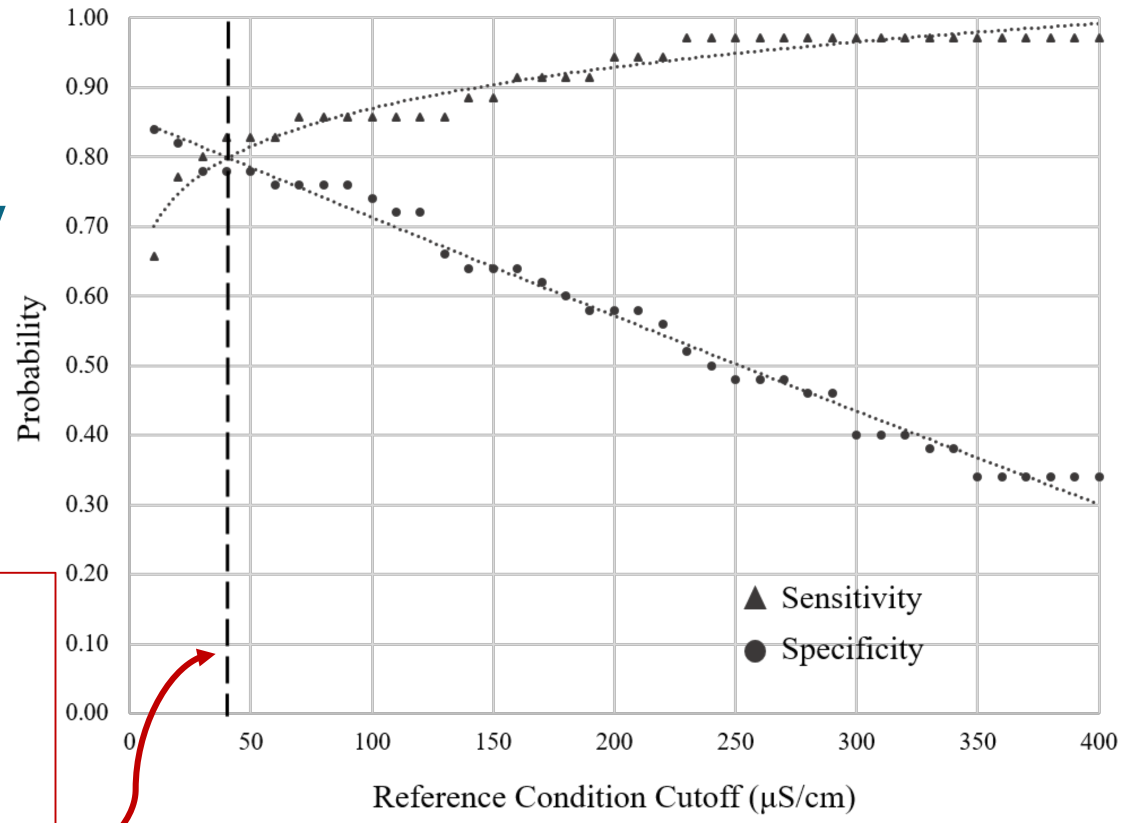
$$\boldsymbol{Specificity = \frac{TN(c)}{TN(c) + FP(c)}}$$

VALIDATION & CUTOFF

PREDICTIVE VALUE

- Probability true positive vs. true negative
- Maximize reliability of indicator at optimal cutoff

Figure 10. Indicator reliability for different cutoff values for assessing reference condition with conductivity-alkalinity relationship



predicted conductivity ± C µs/cm

Optimal Cutoff = 41 µS/cm

SUMMARY

- Quantile Regression
- Conductivity = [7.76 + 2(Alk)] ± 41µS/cm
- 41µS/cm → Maximizes TP & TN
- Validated with Land Cover

REFERENCE SITES

2005-2015

11,756 samples of 30,357 in RC based on

Cond = [7.76 + 2(Alk)] ± 41

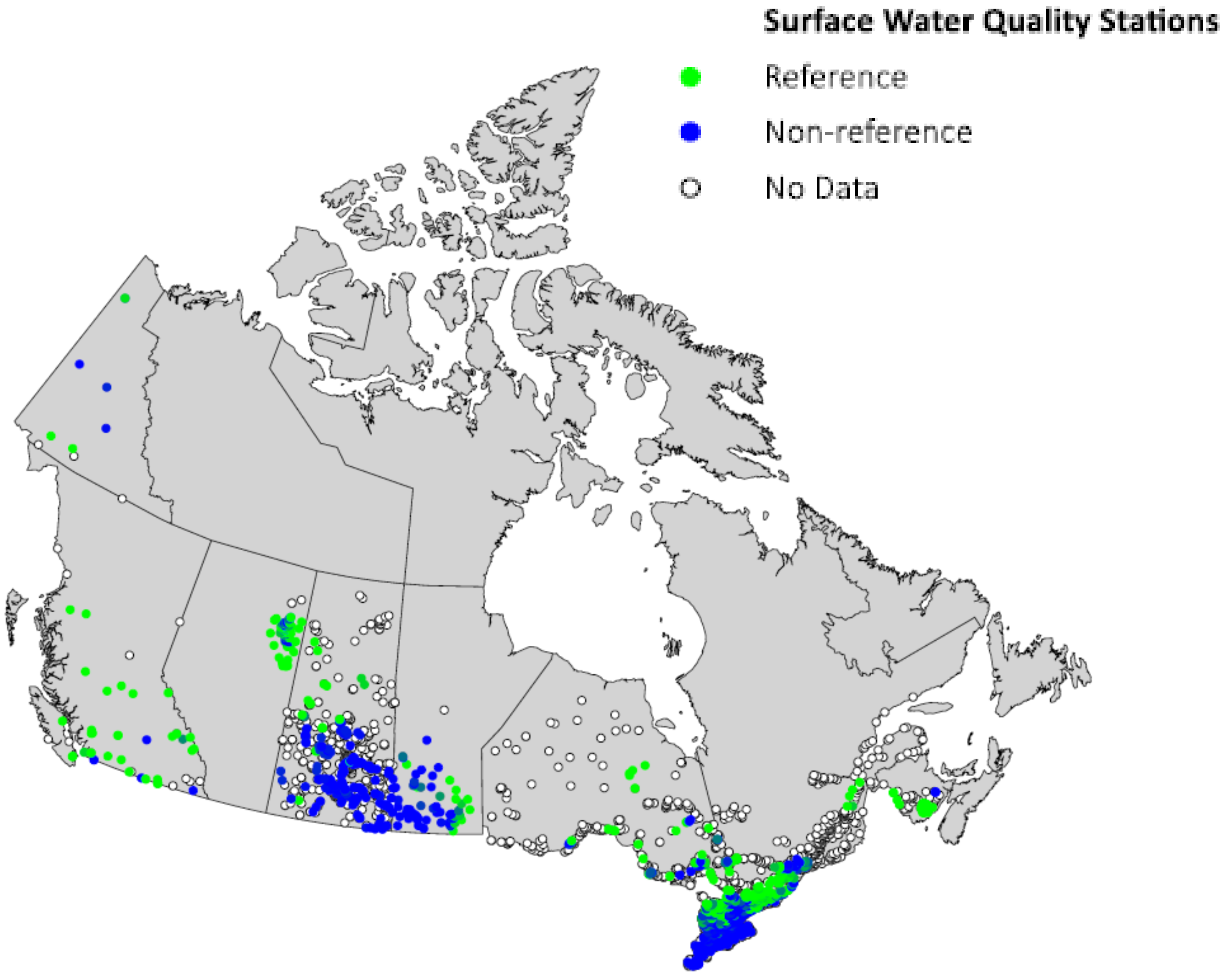


Figure 11. Reference condition of surface water quality monitoring stations with available alkalinity and conductivity data (N=850).

APPLICATION

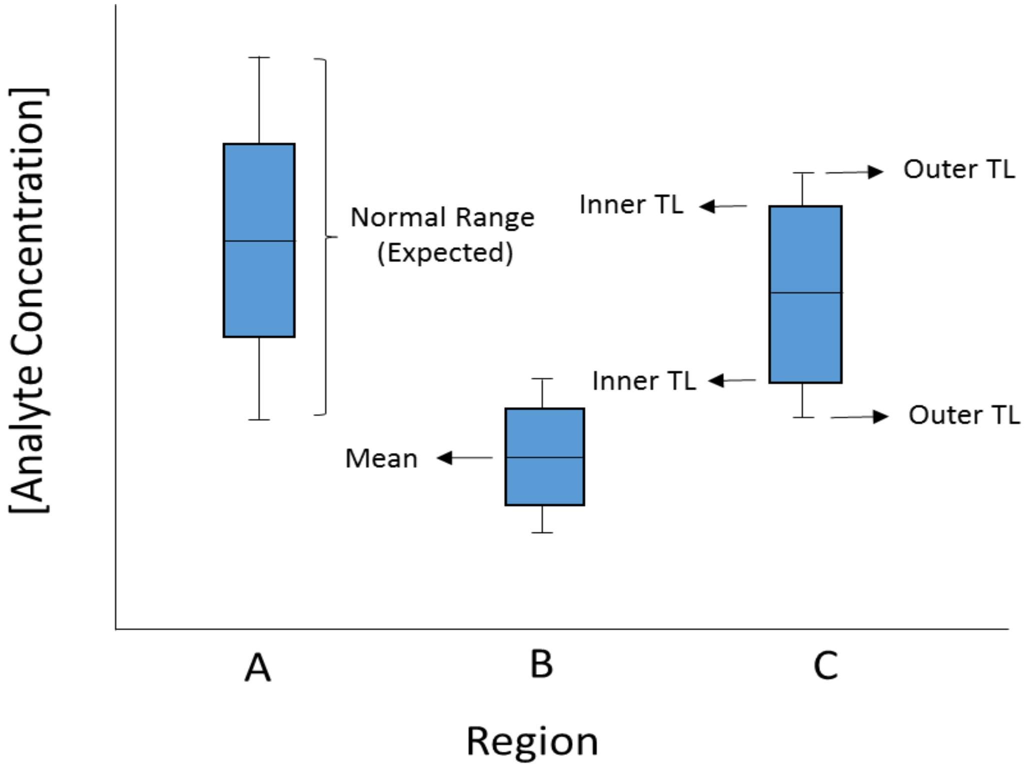
BACKGROUND RANGES

- Surface water from sites in reference condition
- Normal range of variation for 15 analytes
  - E.g. Al, Ba, Be, Bi, Cu, Li, Mn, Mo, Se, Ag, Zn
    "***ranges of values that analyte concentrations might be expected to vary within, given the conditions of the site***"
- Range of values that include 95% of possible observations using the mean
- The limits of the normal range were calculated using the 5^{th} and 95^{th} percentiles

INTERPRETATION OF NORMAL RANGES

- [Analyte] inside inner 5th – not unusual (i.e. expected)
- [Analyte] outside 95th – unusual (i.e. not expected)
- [Analyte] between inner/outer limits – uncertainty
  - May require further investigation

Figure 12. Conceptual diagram of normal ranges of background concentrations of an analyte



PRELIMENARY RESULTS

Aluminum Example

Table. Outer Tolerance Limits for various Ecozones

Analyte (µg/l)	Form	Ecozone										CCME
		6	7	8	9	10	11	12	13	14	15	
Aluminum	D	161	45.7	234	188.4	277			266	17.7		5-100
	E	352		758					765	1088		
	T	1612			5816	3680	2594	6435	2019	1438		
	TU	620		446	920	7311					228	

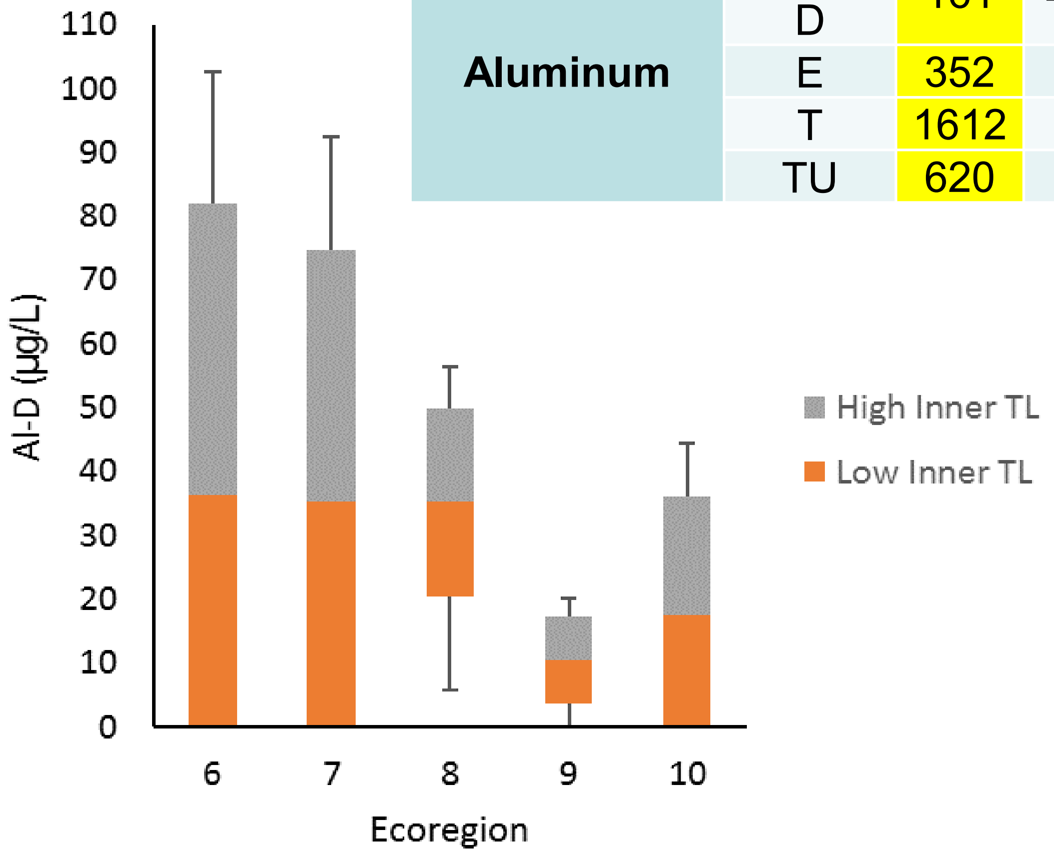


Figure 13. Normal ranges of background concentrations of aluminum in 5 Ecozones across Canada; Boreal Shield (6), Atlantic Maritime (7), Mixewood Plains (8), Boreal Plains (9), Prairies (10)

CONCLUSION

- Cond/Alk commonly measured in monitoring
- Widely applicable approach
- Assessment of reference condition allows to assess natural variability of inorganics with normal ranges

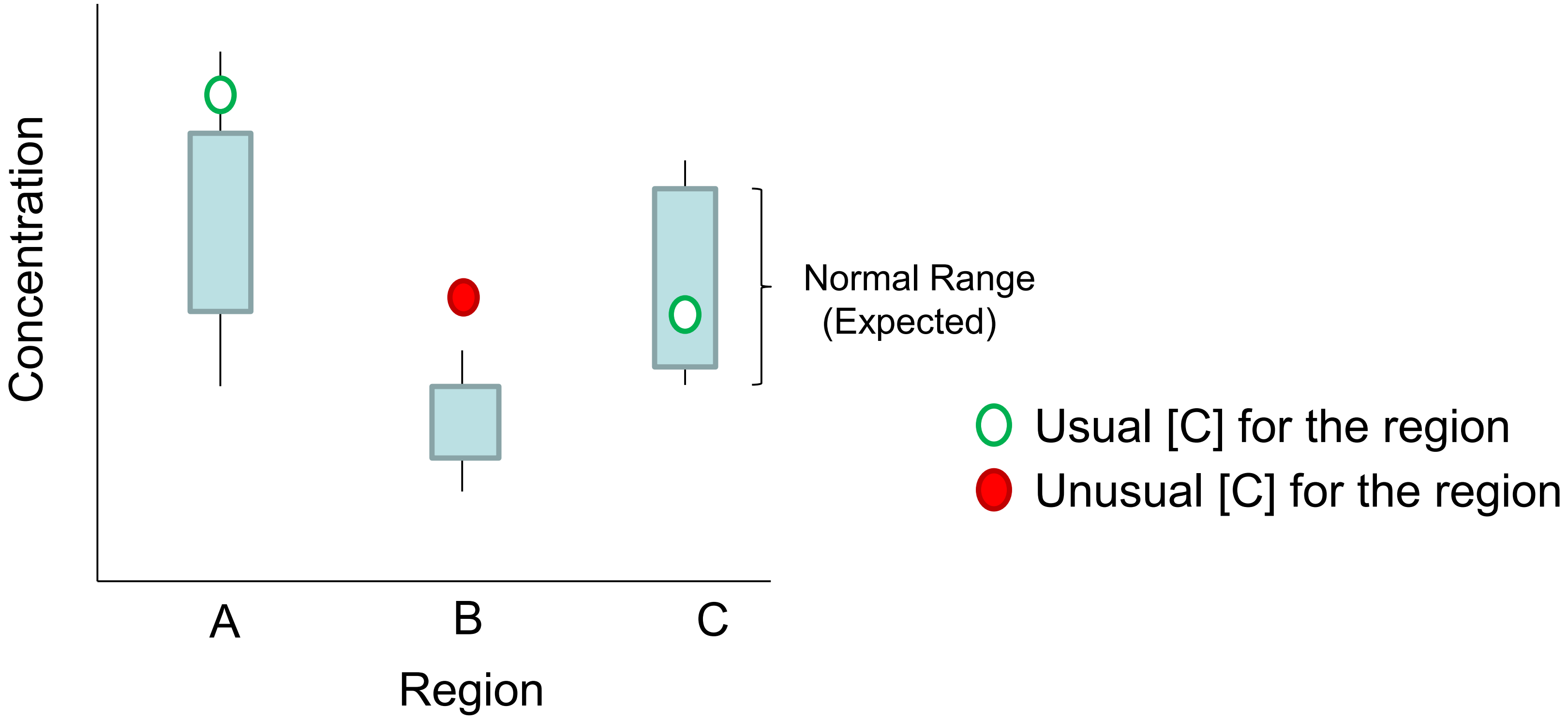


Figure 14. Conceptual diagram for comparison of chemical concentrations to natural concentrations in the same region.

Thank You.

Questions?

ROBUST STUDY SUMMARIES

- Robust Study Summaries
  - Determine *reliability* and *applicability* of study
  - QA/QC procedure implemented
- Assumptions
- E.g. Field data were measured correctly using calibrate equipment and recorded accurately
- E.g. Proper field procedures, labelling & shipment

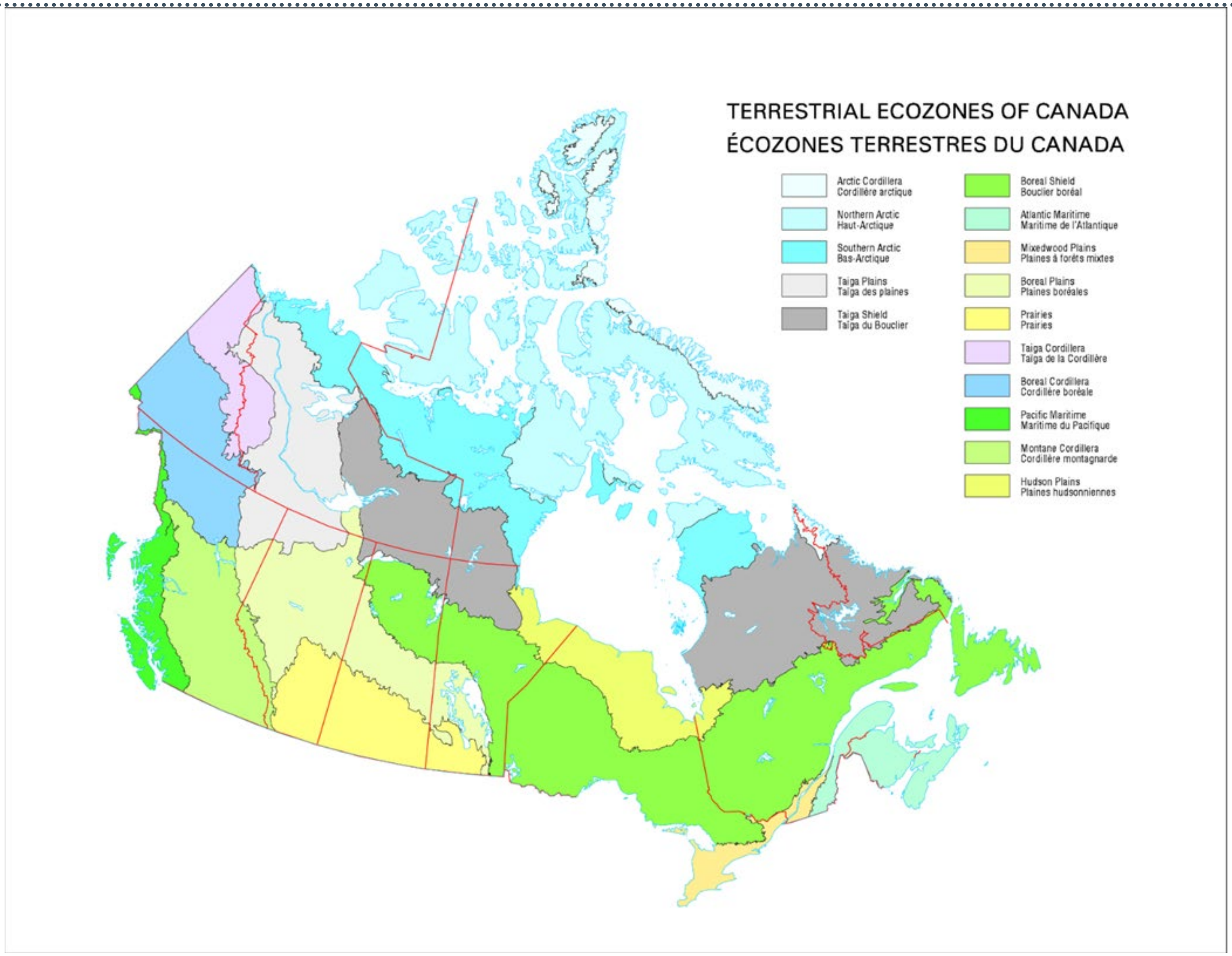
QUANTILE REGRESSION

Table 4. Results from the quantile regressions estimating the relationship between conductivity and alkalinity under reference condition using all available data for Canada.

Quantile	Intercept	Slope
1st	5.96	1.80
2.5th	6.85	1.83
5th	7.67	1.83
10th	7.76	2.00

SPATIAL VARIATION

An Ecozone is defined as **“an area of the earth’s surface representative of large and very generalized ecological units characterized by interactive and adjusting abiotic and biotic factors”** (ESWG 1995).



Ecozones of Canada as defined by the National Ecological Framework of Canada (from AAFC, 2013).

SPATIAL VARIATION

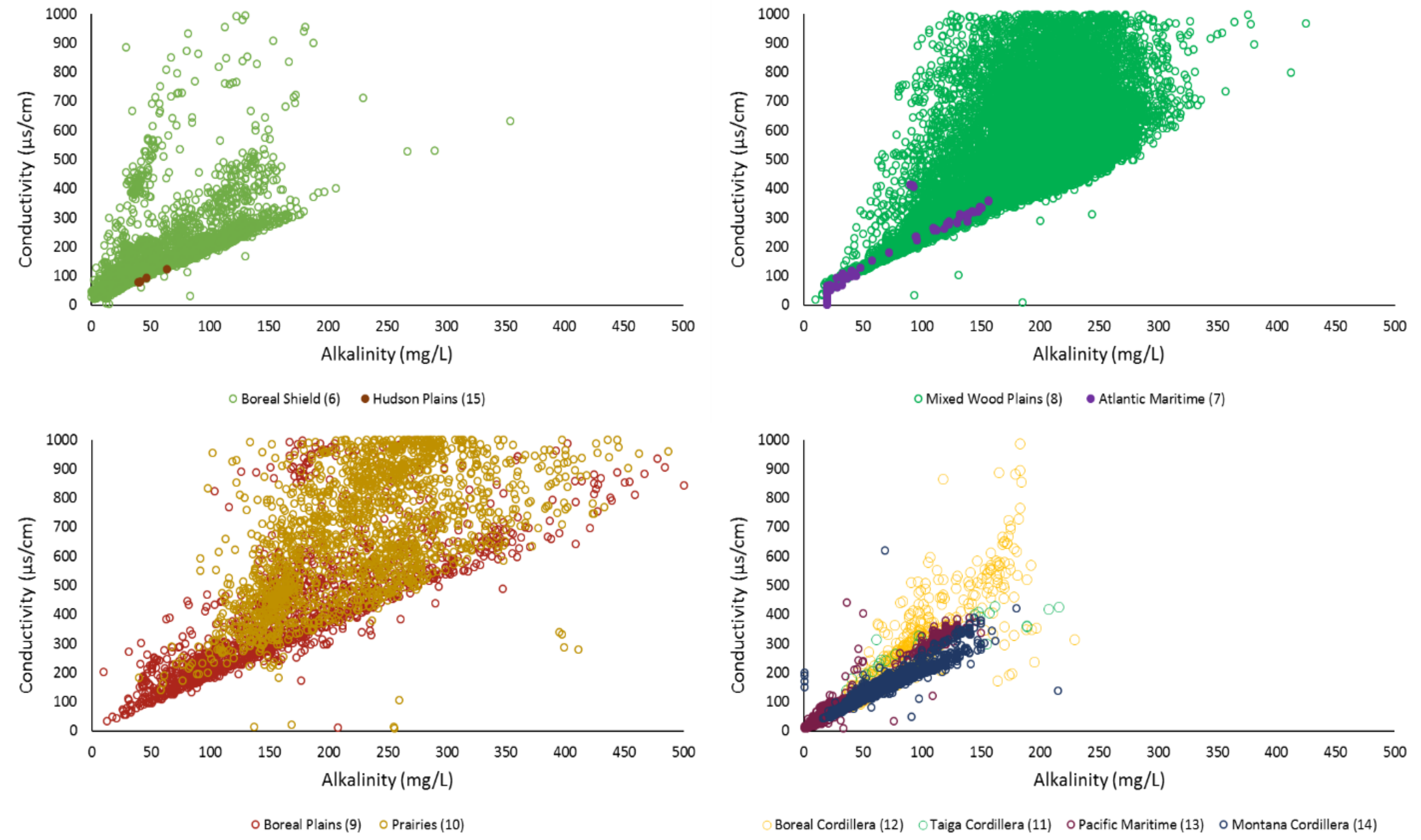


Figure 6. Underlying relationship between conductivity and alkalinity for surface water samples across various ecozones, assessed using 10th quantile regressions.

Table 5. Results from the quantile regressions estimating the relationship between conductivity and alkalinity under reference condition for each ecozone.

Ecozone	N	Quantile Regression (10th)	
		Intercept	Slope
Boreal Shield (6)	3,141	19.5	1.70
Atlantic Maritime (7)	130	-34.9	2.44
Mixed Wood Plains (8)	17,980	24.5	1.96
Boreal Plains (9)	1,755	16.5	1.73
Prairies (10)	2,879	29.6	2.02
Taiga Cordillera (11)	39	36.7	1.71
Boreal Cordillera (12)	604	10.3	1.97
Pacific Maritime (13)	1,738	4.3	2.22
Montane Cordillera (14)	2,076	14.1	1.83
Hudson Plains (15)	5	-2.2	1.96

SPATIAL VARIATION

$$Match\ (\%) = \frac{\#\ samples\ with\ matching\ classification}{total\ \#\ samples}$$

Table 6. Comparison of the results from the determination of the reference condition of surface water samples using the national and individual ecozone relationships between conductivity and alkalinity.

Ecoregion	N	Samples in Reference Condition		Match (%)
		National	Ecoregion	
Boreal Shield (6)	3141	2223	2155	97
Atlantic Maritime (7)	130	127	118	93
Mixed Wood Plains (8)	17980	5111	5600	97
Boreal Plains (9)	1755	930	742	89
Prairies (10)	2879	365	459	97
Taiga Cordillera (11)	39	21	22	97
Boreal Cordillera (12)	604	317	317	100
Pacific Maritime (13)	1738	1496	1559	96
Montane Cordillera (14)	2076	2010	1989	99
Hudson Plains (15)	5	5	5	100
Total	30,347	12,605	12,966	97

DISTURBANCE %

Table 7. Comparison of the number of sites classified as being in reference and non-reference condition based on different levels of disturbance cover representing a minimally disturbed catchment.

Disturbance Cover (%)	Reference Site (N)	Non-Reference Sites (N)	Cutoff
0	18	67	<10 µs/cm
2.5	35	50	41 µs/cm
5	40	45	62.5 µs/cm
10	44	41	84 µs/cm

Table Notes: Optimal cutoff values are provided based on the sensitivity and specificity curves.

DISTURBANCE %

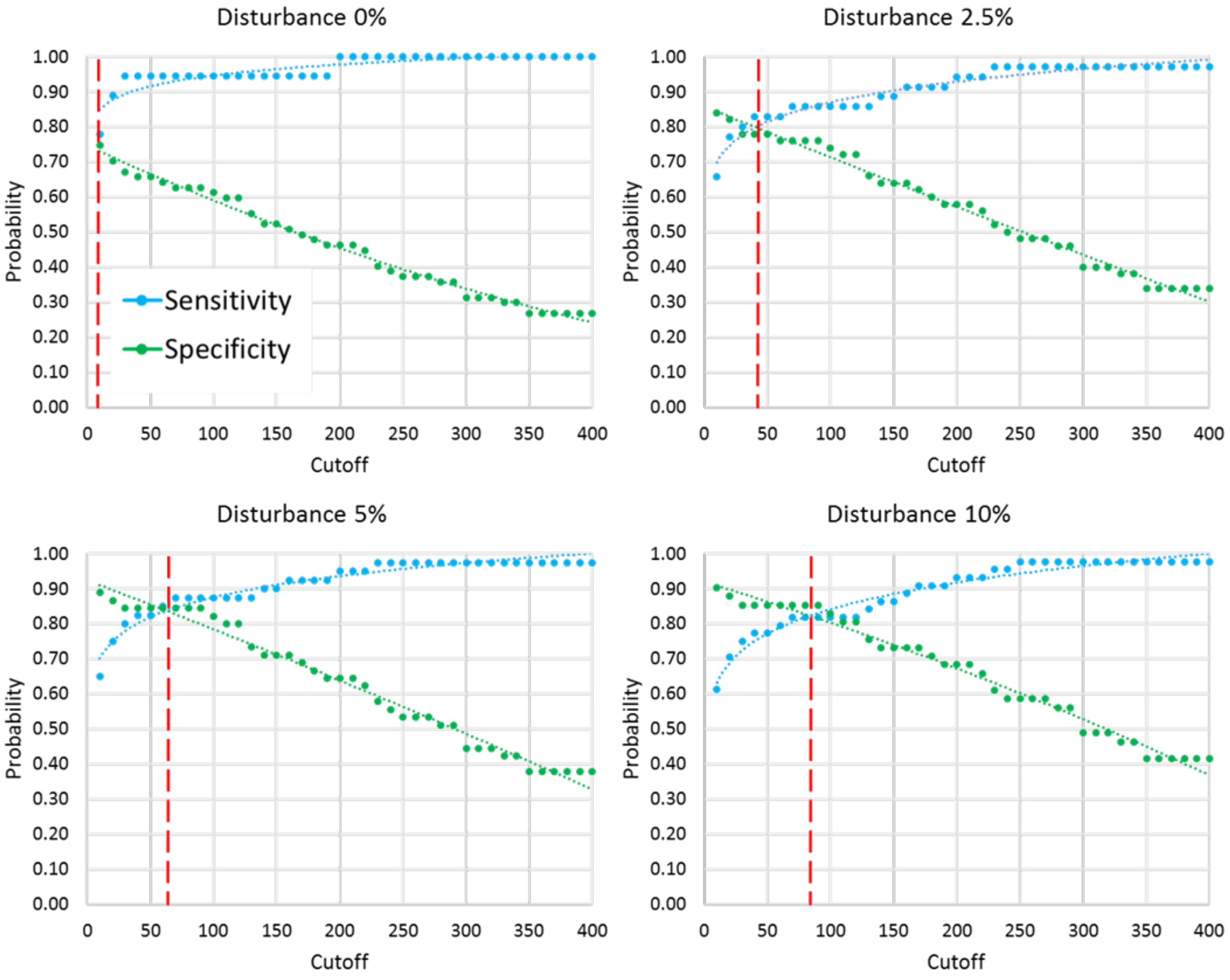


Figure 10. Sensitivity and specificity curves for different levels of anthropogenic disturbances (cropland and urban).