

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

C. L. Proulx, B. W. Kilgour, A. P. Francis, R. F. Bouwhuis and J. R. Hill

ABSTRACT

The underlying natural relationship between conductivity and alkalinity was used to identify surface water quality monitoring sites that are in a 'reference' or minimally disturbed condition. Data from over 40,500 freshwater samples from 1,230 sites were combined for the time period of 2005–2015 from various federal, provincial, and joint federal–provincial/territorial freshwater monitoring programs (e.g., Freshwater Quality Monitoring and Surveillance Program, Ontario's Provincial Water Quality Monitoring Network). Of the samples, 30,347 provided conductivity and alkalinity data. Surface water samples with a measured conductivity that deviated (by more than 41 $\mu\text{S}/\text{cm}$) from the predicted conductivity calculated from the sample's alkalinity were deemed to be non-representative of a reference condition, while samples within 41 $\mu\text{S}/\text{cm}$ of the predicted value were deemed representative of a reference condition. The 41 $\mu\text{S}/\text{cm}$ cutoff value was determined using signal detection theory. The conductivity–alkalinity model was validated through a comparison with land cover data by demonstrating that samples identified as 'reference' were typically from catchments that had minimal anthropogenic disturbances. The proposed approach provides a rapid means of evaluating the reference condition of a watercourse, and of identifying data that provide an estimate of reference condition.

Key words | alkalinity, background ranges, ecozone, land cover, reference condition, specific conductance

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INTRODUCTION

The use of data from sites in reference condition is common when establishing normal range criteria for water, sediment, soils, and biota (Furse *et al.* 1984; Wright *et al.* 1984; Hughes *et al.* 1986; Hughes & Gammon 1987; Larsen *et al.* 1986; Davis & Simon 1995; Parsons & Norris 1996; Kilgour *et al.* 1998, 2017). The regional-reference approach to characterizing background concentration ranges involves the use of data from several reference locations, which represent acceptable or unimpaired conditions, within a specified management area (Kilgour & Somers 2017). Political boundaries often do not provide a consistent geographic basis for

the management of surface water chemistry, which varies primarily with bedrock and surficial geology (Bodo 1993). Alternatives to political boundaries are ecological boundaries such as ecozones which can further be broken down into ecoregions and ecodistricts. These ecological boundaries are based on the variation in climatic and geologic characteristics which will likely also influence variations in aquatic ecology. For example, highly mineralized areas may have naturally elevated background concentration ranges of inorganics which are higher than water quality standards (Runnells *et al.* 1992). Ecoregions have been used

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as the management area to examine the distribution of water quality parameters such as nutrients (Larsen *et al.* 1986), metals (Bodo 1993; Kilgour *et al.* 2002), and pH in lakes (Shilts & Kettles 1989). A significant challenge with using a regional-reference approach to establish normal range criteria for water remains in identifying a set of sites deemed to be sufficiently in a reference condition (Bailey *et al.* 2004).

The reference condition of a catchment can be inferred from land cover and land use data. Upstream catchments with minimal to no disturbance may be characterized as being in a reference condition (Bailey *et al.* 2004). Using land cover information (% disturbance within a catchment) to infer reference condition, however, is associated with inaccuracies arising from small point-source inputs into the aquatic environment, such as mines whose impact to water quality can be larger than expected if based only on the physical space they occupy in the landscape. Additionally, detailed land cover data are not always available and their manipulation and assessment can be time-consuming when numerous sites are being assessed at a large spatial scale. Bodo (1993) and then Kilgour *et al.* (2002) proposed an independent means of identifying sites in reference or minimally disturbed condition based solely on water chemistry. Bodo (1993) and Kilgour *et al.* (2002) demonstrated a strong association between hardness and alkalinity and between conductivity and alkalinity in baseline (reference) conditions. The association between conductivity and alkalinity is robust, detecting contributions to watercourses from mine tailings (which would contribute various metals), as well as non-point-sources of chloride and sodium (i.e., road salts). Sites with anthropogenically derived inputs of inorganic chemicals typically have unusually high conductivity given the alkalinity (Bodo 1993; Kilgour *et al.* 2002).

Conductivity reflects the concentrations of negatively and positively charged monovalent and divalent ions (McCleskey 2011; McCleskey *et al.* 2011). Ions that contribute significantly to the electrical potential of surface water include both positively charged (e.g., Ca^{2+} , Mg^{2+} , Na^+ , K^+ , H^+ , HN_4^+) and negatively charged (e.g., HCO_3^- , Cl^- , SO_4^{2-} , NO_3^- , CO_3^{2-} , OH^-) ions (Bodo 1993). Various positively charged metals (e.g., Zn^{2+} , Cu^{2+} , Fe^{2+} , Ni^{2+}) also contribute to conductivity. The conductivity–alkalinity relationship, therefore, should be robust to the detection of

influences from a variety of land cover disturbances. Mines typically release effluents that have elevated conductivity associated with high concentrations of metals. Generally, mine effluents are acidic and therefore require treatment with lime to be neutralized prior to release into the environment. This treatment also increases conductivity (because of associations with Ca^{2+} , Mg^{2+} , and OH^-), and to a lesser extent, contributes to higher alkalinity. Effluent from the Garson Mine in Sudbury, for example, typically has a conductivity $>2,000 \mu\text{S}/\text{cm}$, while alkalinity is $<50 \text{ mg}/\text{L}$ (Kilgour & Associates Ltd & AquaTox 2014). Effluents with a high conductivity–alkalinity ratio may alter the water chemistry of the mixing zone towards a ‘non-reference’ condition. Agricultural lands contribute nutrients (nitrogen compounds including nitrate and nitrite, and phosphates) which will also produce a high conductivity signal given alkalinity (Chambers *et al.* 2012). Finally, urban areas where road salts are used can be anticipated to produce similarly elevated conductivity values given the alkalinity (Kilgour *et al.* 2014). The conductivity–alkalinity relationship, therefore, should pick up signals for most of the land cover changes in the Canadian landscape.

The purpose of this study was to test whether the underlying relationship between specific conductivity and alkalinity can be used to identify watercourses in reference or minimally disturbed condition using surface water data from freshwater monitoring programs across Canada. More specifically, the objectives were to: (1) model the relationship between conductivity and alkalinity using available surface water samples across Canada; (2) validate the conductivity–alkalinity model as a means of identifying reference sites through comparison to land cover data; (3) investigate spatial variation in the conductivity–alkalinity relationship; and (4) determine the optimal cutoff value for deviation from the conductivity–alkalinity relationship that detected departure from a reference condition.

METHODOLOGY

Data collection

Specific conductance and alkalinity data were compiled from a large proportion of available Canadian surface

Table 1 | Chosen databases of surface water quality data collected by major reporting agencies through various ongoing monitoring programs across Canada

Reporting agency	Monitoring program	Data source	Available location(s)
Environment and Climate Change Canada (ECCC)	Fresh Water Quality Monitoring and Surveillance (FWQMS)	http://genie.qc.ec.gc.ca/wqmsd_en.aspx	ON, QC, NB
Environment and Climate Change Canada (ECCC)	Long Term Trend Monitoring (PYLTM)	http://aquatic.pyr.ec.gc.ca/webdataonlinenational/	BC, YK
Ontario Ministry of Environment and Climate Change (OMECC)	Provincial Water Quality Monitoring Network (PWQMN)	https://www.ontario.ca/data/provincial-stream-water-quality-monitoring-network	ON
Ministre du Développement durable, de l'Environnement et de la Lutte contre les changements climatiques (MDDELCC)	Banque de Données sur la Qualité du Milieu Aquatique (BQMA)	http://www.mddelcc.gouv.qc.ca/eau/Atlas_interactif/donnees_recentes/donnees_iqbp.asp	QC
Regional Aquatics Monitoring Program (RAMP)	Regional Aquatics Monitoring Program (RAMP)	http://www.ramp-alberta.org/data/Water/waterquality/water.aspx	AB
Government of Manitoba Water Quality Management Division	Long-Term Water Quality Monitoring Network (MLTWQMN)	Data sharing agreement	MB
Saskatchewan Water Security Agency	Primary Sites Monitoring (SKPSM)	Data sharing agreement	SK
Saskatchewan Water Security Agency	Long-Term Lakes Baseline Monitoring (SKBM)	Data sharing agreement	SK

Sampling locations in bold represent locations included in the database.

water quality data repositories from various government agencies and government-affiliated websites (see Table 1) and reports into a single database to characterize the relationship between conductivity and alkalinity. Four freshwater monitoring programs were identified as reliable sources of surface water quality data that were publicly available (Table 1). Each of the freshwater monitoring programs listed provided geo-referenced sampling locations with concentrations of various metals, in addition to conductivity and alkalinity. In addition to the data obtained online, additional data were provided by provincial monitoring programs through data-sharing agreements with ECCC. Because of resource constraints, sites were chosen to maximize the geographic extent of the database rather than to include all available surface water quality data from sites across the country. Since detection limits change over time due to improved analytical equipment and methodologies, the data compiled were limited to those collected from 2005 to 2015.

Statistical analysis

Conductivity–alkalinity relationship

Quantile regression was used to estimate the linear relationship between conductivity and alkalinity under reference condition. Unlike a standard linear regression equation which represents the mean relationship between the independent and response variables, a quantile regression estimates a desired conditional q^{th} quantile of the response variable (Koenker & Bassett 1978). Quantile regressions are useful when there is interest in estimating the limits of data extremes. The extreme lower 10th quantile was estimated to represent the relationship between conductivity and alkalinity under reference condition.

Validation of the conductivity–alkalinity relationship

The conductivity–alkalinity relationship is used here as an indication of whether samples were collected from areas

that were in a reference condition. The relationship between the two parameters had been previously demonstrated with data from watercourses from across Ontario (e.g., Kilgour et al. 2001, 2002). Reference condition is more normally inferred on the basis of land cover and land use data (Bailey et al. 2004). Here then, reference classification based on the alkalinity–conductivity method was compared to classifications based on upstream land cover disturbance. The validation was carried out with a subset of sites ($N = 85$) from various ecozones (i.e., 6, 7, 8, 9, 13, 14). Using a 1:50,000 Canadian Digital Elevation Model (NRCan 2012), the upstream catchment of each site was delineated in Manifold GIS (version 8.0.28). The percent land disturbance was then estimated for each catchment based on Moderate Resolution Imaging Spectroradiometer (MODIS) land cover data at a 250-m spatial resolution (Friedl et al. 2010) by reclassifying cropland and urban land cover tiles as ‘disturbed’. The percent of land cover disturbed was calculated from the total catchment area in Manifold GIS. Each site’s catchment was categorized as being minimally disturbed if less than 2.5% of the upstream catchment was disturbed. For each of the $N = 85$ validation sites, the means (of available data) of conductivity and alkalinity were computed, and compared to the national 10th quantile regression equation.

Based on methods from signal detection theory (Murtaugh 1996), the reliability of the conductivity–alkalinity indicator for correctly classifying the reference condition of a site given the predicted conductivity was determined. Murtaugh (1996) proposed that the predictive ability of an indicator can be estimated from an equal-sized random sample of positive (i.e., reference) and negative (i.e., non-reference) responses defined by a true response measurement (i.e., here land cover). For any indicator cutoff value (e.g., predicted conductivity + $X \mu\text{S/cm}$), results from the classification of sites is divided into four categories, based on the indicator and true response value (Figure 1): (1) true positive (TP): both the land cover and conductivity–alkalinity approaches agree that the site is in reference condition; (2) false positive (FP): conductivity–alkalinity approach indicates that the site is in reference condition, but is not (based on land cover); (3) true negative (TN): both the land cover and conductivity–alkalinity approaches agree that the site is not in reference condition;

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

Figure 1 | Table for classifying results for a given indicator cutoff value (modified from Murtaugh 1996).

and (4) false negative (FN): conductivity–alkalinity approach indicates that the site is not in reference condition, but it is (based on land cover).

From the true positives, false positives, true negatives, and false negatives, the indicator’s sensitivity and specificity was calculated. Sensitivity represents the probability of obtaining a positive result (i.e., reference) when the true response is positive (Equation (1)), while specificity represents the probability of obtaining a negative result (i.e., non-reference) when the true response is negative (Equation (2)). Together these properties determine the indicators predictive value (Murtaugh 1996):

$$\text{Sensitivity} = \frac{TP(c)}{TP(c) + FN(c)} \quad (1)$$

$$\text{Specificity} = \frac{TN(c)}{TN(c) + FP(c)} \quad (2)$$

The probability of classifying a site as being in reference condition when it is (i.e., true positive) was calculated for cutoff values ranging from 0 to 400 $\mu\text{S/cm}$. Similarly, the probability of classifying a site as not being in a reference condition when in fact it is not (i.e., true negative) was calculated for cutoff values ranging from 0 to 400 $\mu\text{S/cm}$. A plot of these values representing the sensitivity and specificity curves, respectively, was used to determine the optimal cutoff value for each level of disturbance at which the reliability of the conductivity–alkalinity relationship as an indicator is maximized.

Spatial variation in the alkalinity–conductivity relationship

Quantile regression was used to estimate the coefficients of the 10th percentile of data for each of Canada's ecozones, in order to determine whether there was spatial variation in the conductivity–alkalinity relationship under reference condition. There are 15 terrestrial ecozones in Canada, as defined by the National Ecological Framework for Canada (ESWG 1995). 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). These abiotic and biotic factors include geomorphology (e.g., physiographic landforms), soils (e.g., soil order group), vegetation (e.g., physiognomic types), and climate. The ecozones are further classified into 194 ecoregions and 1,021 ecodistricts (ESWG 1995). Ecozones are at the top of the hierarchical land classification scheme and represent the broadest ecological classification unit. The ecozone class was selected here as the unit of analysis in order to maximize the amount of data used to assess spatial variability in the conductivity–alkalinity relationship under reference condition. All quantile regression equations were estimated using the statistical package 'quantreg' (Koenker & Bassett 1978) in the R Project for Statistical Computing. The results from both the national and ecoregion approach were compared by classifying each water sample as being either in reference or non-reference condition using both equations and then compared the number of water samples in reference condition.

RESULTS AND DISCUSSION

Specific conductance and alkalinity values were available for 30,347 of the 40,503 surface water quality samples collected from select freshwater monitoring programs for the period of 2005 to 2015. These samples were collected from 864 sites spread across ten ecozones, including seven provinces and one territory. For the water samples used for this analysis, the majority of data for southern Québec and south-central Saskatchewan did not provide conductivity and/or alkalinity measurements (Table 2).

Table 2 | Specific conductivity and alkalinity measured from surface water samples collected for freshwater monitoring programs across Canada during the period of 2005 to 2015, used to identify sites in reference condition

Database	Samples (N)	Range		No data ^a
		Conductivity (µS/cm)	Alkalinity (mg/L)	
BQMA	1,047	19–137	10–38	1,022
FWQMS	137	0.5–414	20–156.4	12
MLTWQMN	2,865	85.5–3,420	37.4–1,330	183
PWQMN	21,211	8–23,700	0.5–1,480	262
PYLTM	9,124	8–1,200	0.5–715	4,667
RAMP	1,024	35–7,910	9.8–3,920	20
SKBM	4,211	3.8–20,070	11.2–786	3,096
SKPSM	894	NA	NA	894
Total	40,513	0.5–23,700	0.5–3,920	10,156

^aEither no conductivity and/or no alkalinity data were provided for the water sample.

The range of conductivity and alkalinity values measured from water samples varied in most provinces, and consequently, in most ecozones as well. The national-scale conductivity–alkalinity relationship was defined, using 10th quantile regression, as $\text{conductivity} = 7.76 + 2 \times \text{alkalinity}$ (Figure 2). The slope of that line describing the national-scale relationship is similar to the slope obtained by Kilgour *et al.* (2002; slope = 1.99) for surface waters in Ontario, and similar to the equation provided by Bodo (1993; slope ~2.4) also for surface waters in Ontario but for an earlier data set than used by Kilgour *et al.* (2002).

Overall, the relationship between conductivity and alkalinity in reference condition corresponded well to the level of disturbance in the upstream catchment of sites used in the validation exercise. Sites with elevated average conductivity, given average alkalinity, tend to have higher levels of anthropogenic disturbances in their upstream catchment (Figure 3). Sites with minimal levels of land cover disturbance in their upstream catchment (i.e., <2.5%) generally produced conductivity values that were on or near the conductivity–alkalinity reference condition regression line (i.e., 80% of sites $\pm 32 \mu\text{S/cm}$ of the line). Based on water chemistry, some catchments with 2.5–10% disturbed land cover still produced conductivity values that would imply a 'minimally disturbed' condition, potentially indicating that

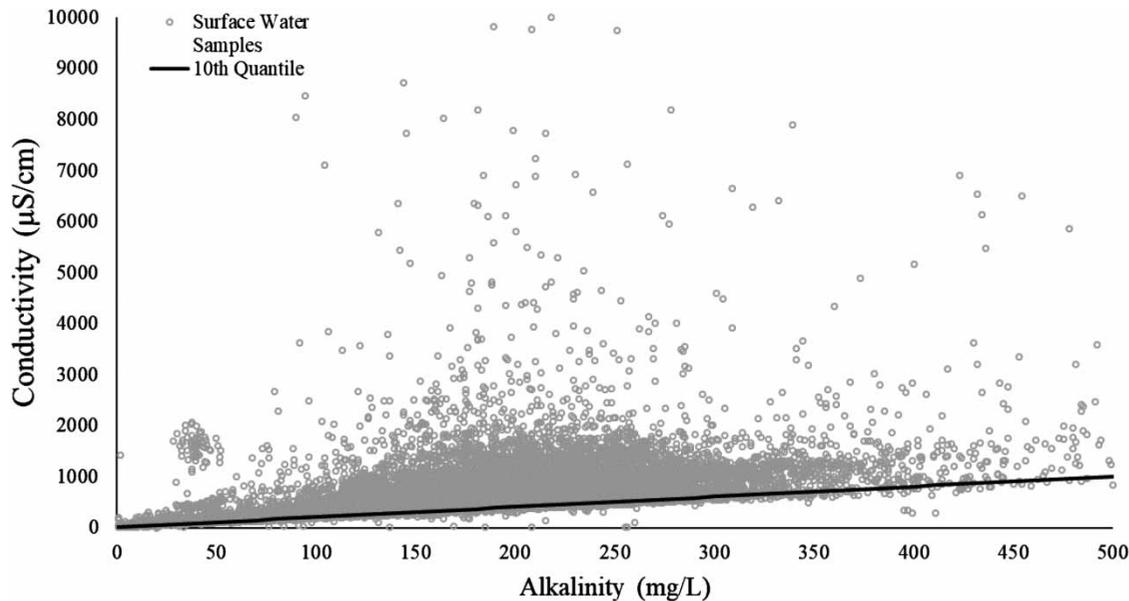


Figure 2 | National-scale conductivity–alkalinity relationship defined using the 10th quantile regression for surface water samples collected across Canada. *Note:* Full spread of data not shown.

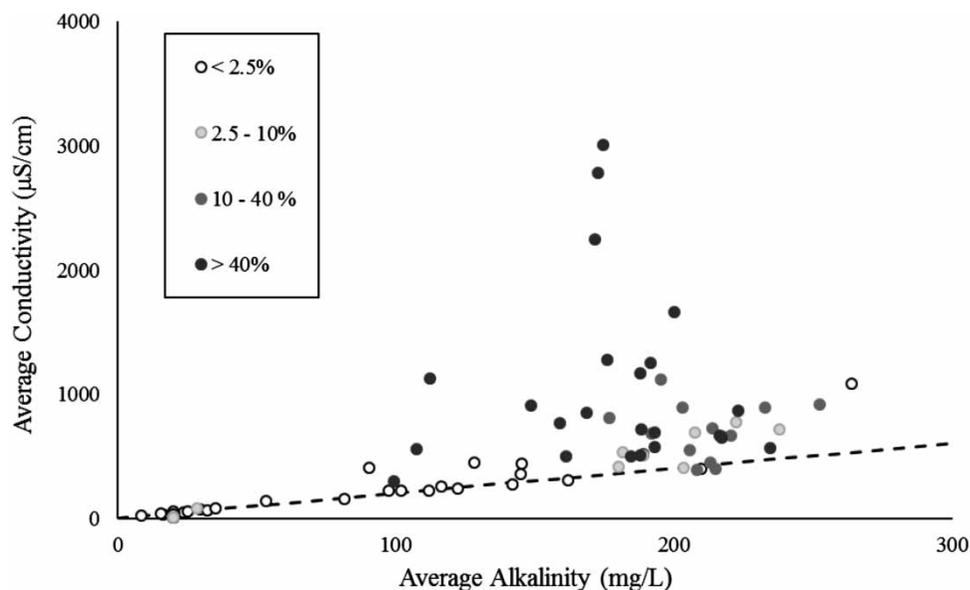


Figure 3 | Relationship between mean conductivity and mean alkalinity at 85 sites for varying levels of adjacent land disturbance in their upstream catchment.

designating land cover with <2.5% disturbed land as a reference is potentially conservative. Six sites with minimal land cover disturbance (<2.5%) had elevated conductivity with respect to the corresponding alkalinity and would be thus classified by the conductivity–alkalinity relationship as not being in reference condition. Those kinds of observations

(high conductivity when land cover has low physical disturbance) may reflect important localized water quality disturbances resulting from activities that have small physical footprints (e.g., small mines).

The probability of classifying a waterbody as being in reference condition when it is (i.e., land disturbance

<2.5% cover; true positive), was maximized ($P = 97\%$) at a cutoff value of 230 $\mu\text{S}/\text{cm}$ above the 10th quantile regression equation (Figure 4). The specificity of the indicator, which is the probability of classifying a waterbody as not being in reference condition when in fact it is not (i.e., true negative), was maximized ($P = 84\%$) at a cutoff value of 10 $\mu\text{S}/\text{cm}$ above the 10th quantile regression line (Figure 4). The overall reliability of the conductivity–alkalinity indicator was maximized at the intersection of the sensitivity and specificity curves, where there was an 80% probability of correctly assessing the reference condition of a waterbody. The optimal cutoff value associated with this 80% probability was 41 $\mu\text{S}/\text{cm}$ above the 10th quantile regression equation (Figure 4).

Of the 30,347 surface water samples, 11,756 samples had conductivity values that did not deviate from the predicted conductivity by more than 41 $\mu\text{S}/\text{cm}$ with the national-scale conductivity–alkalinity relationship (Figure 5). In each ecozone, the proportion of sites for which all samples were in a reference condition for the period of 2005 to 2015 ranged from 0 to 100% (Table 3). The ecozones with the highest proportion of sites always in a reference condition were Hudson Plains (100%),

Atlantic Maritime (93%), Montane Cordillera (70%), and Pacific Maritime (58%). None of the sites from the Taiga Cordillera were always in reference condition and only a few sites from both the Prairies (3%) and Mixed Wood Plains (8%) were always in reference condition. Both the Prairies and Mixed Wood Plains represent high population density areas.

The ecozone-scale conductivity–alkalinity relationships were also defined using 10th quantile regression. Little variation was observed in the slopes of the lines representing the conductivity–alkalinity relationship under a reference condition in the different ecozones (range of slopes: 1.7 to 2.4, Table 4). The intercepts, however, varied from -35 to 37 (Table 4), potentially due to differences in the spread of data which varied within each ecozone (Table 2). Of the 30,347 surface water samples, 12,109 samples were deemed in reference condition using the ecozone-scale approaches. Only 1% of samples (361 out of 30,347) were classified as non-reference with the national conductivity–alkalinity equation, but classified as reference with the eco-region equations. In general, both approaches provided similar results, with 93 to 100% reference condition classifications matching (Table 5).

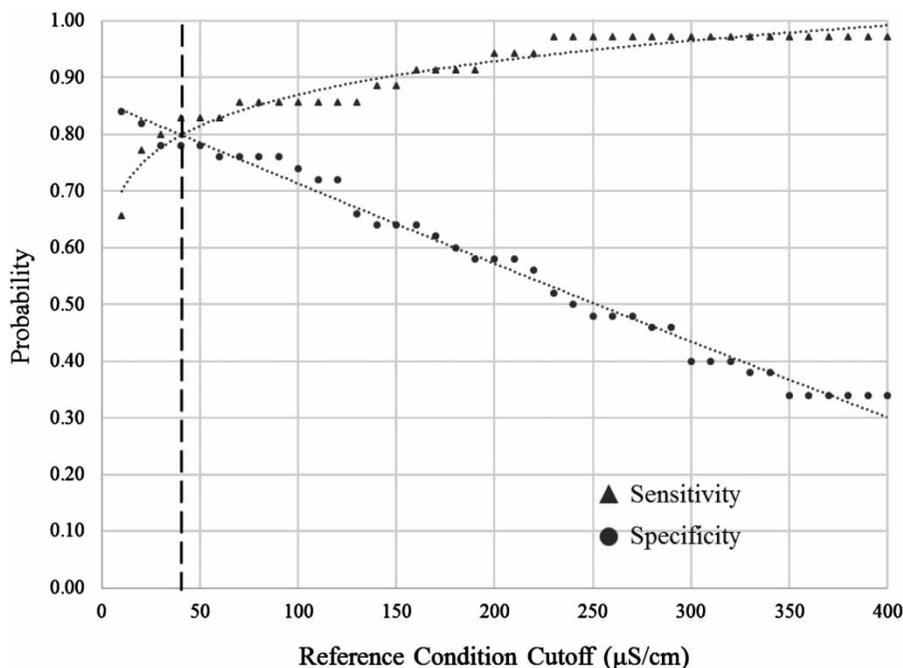


Figure 4 | Relationship between the conductivity–alkalinity indicator reliability and different cutoff values for assessing the reference condition of waterbodies.

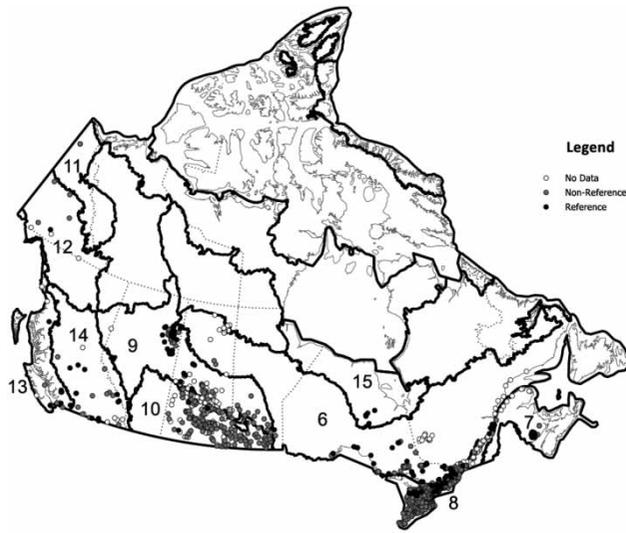


Figure 5 | Reference condition of waterbodies with freshwater monitoring sites across Canada. Note: 'No Data' means there were no conductivity or alkalinity data on which to base a reference classification.

Table 3 | Proportion of surface water sampling sites in each ecozone for which all samples were in a reference condition (RC), based on the national conductivity–alkalinity relationship

Ecozone	Total no. sites	Total no. samples	No. sites with all samples in RC	Proportion (%)
Boreal Shield (6)	81	3,141	39	48
Atlantic Maritime (7)	44	130	41	93
Mixed Wood Plains (8)	393	17,980	30	8
Boreal Plains (9)	110	1,755	46	42
Prairies (10)	165	2,879	5	3
Taiga Cordillera (11)	2	39	0	0
Boreal Cordillera (12)	5	604	1	20
Pacific Maritime (13)	12	1,738	7	58
Montane Cordillera (14)	23	2,076	16	70
Hudson Plains (15)	5	5	5	100

CONCLUSION

The underlying natural relationship between conductivity and alkalinity is a potential tool for rapidly screening sites that may be in a reference condition. The association between conductivity and alkalinity is appropriate for detecting contributions to watercourses from mine tailings

Table 4 | Results from the quantile regressions estimating the relationship between conductivity and alkalinity under reference condition across different ecozones

Ecozone (ID)	N	Quantile regression (10th)			
		Intercept	CI ^a	Slope	CI ^a
Boreal Shield (6)	3,141	19.5	±0.76	1.70	±0.02
Atlantic Maritime (7)	130	−34.9	±1.6	2.44	±0.05
Mixed Wood Plains (8)	17,980	24.5	±1.2	1.96	±0.01
Boreal Plains (9)	1,755	16.5	±4.1	1.73	±0.04
Prairies (10)	2,879	29.6	±29	2.02	±0.14
Taiga Cordillera (11)	39	36.7	±29	1.71	±3.26
Boreal Cordillera (12)	604	10.3	±9.4	1.97	±0.38
Pacific Maritime (13)	1,738	4.3	±0.6	2.22	±0.04
Montane Cordillera (14)	2,076	14.1	±1.4	1.83	±0.02
Hudson Plains (15)	5	−2.2	±3.58	1.96	±3.58

Ecozone name and ID as defined by the National Ecological Framework for Canada (ESWG 1995).

^aCI = confidence interval, calculated as the coefficient ±2 (standard error).

Table 5 | Comparison of the results from the determination of reference condition of surface water samples using the national and individual ecozone relationships between conductivity and alkalinity

Scale	N	Samples in reference condition		
		National	Ecoregion	Match (%)
Boreal Shield (6)	3,141	2,225	2,155	97
Atlantic Maritime (7)	130	127	118	93
Mixed Wood Plains (8)	17,980	5,111	5,600	97
Boreal Plains (9)	1,755	930	742	89
Prairies (10)	2,879	365	459	97
Taiga Cordillera (11)	39	21	22	97
Boreal Cordillera (12)	604	317	317	100
Pacific Maritime (13)	1,738	1,496	1,559	96
Montane Cordillera (14)	2,076	2,010	1,989	99
Hudson Plains (15)	5	5	5	100

(which would contribute various metals), as well as non-point-sources of chloride and sodium (i.e., road salts), such that sites with anthropogenically derived inputs of inorganic chemicals typically have unusually high conductivity given the alkalinity (Bodo 1993; Kilgour *et al.* 2002). The conductivity–alkalinity relationship, therefore, should be robust to the detection of influences from a variety of

land cover disturbances in the Canadian landscape. The conductivity–alkalinity relationship is also appropriate for establishing normal range criteria for inorganic analytes which will perturb the relationship, using data from sites representative of a reference condition. Surface water samples having a measured conductivity that deviates (by more than 41 $\mu\text{S}/\text{cm}$) from that predicted by the sample's alkalinity are deemed to be non-representative of a reference condition. Samples having a measured conductivity within 41 $\mu\text{S}/\text{cm}$ of the predicted value are deemed representative of a reference condition. The cutoff value reflects roughly that conductivity in lakes and rivers with naturally low alkalinity tend to naturally vary up to 50 $\mu\text{S}/\text{cm}$ (e.g., Selinger et al. 2006; and see Table 3).

This approach to identifying reference condition was validated by demonstrating that samples that produced 'reference' samples were typically from catchments that had minimal anthropogenic disturbances (i.e., <2.5%). Using land cover information to infer reference condition is a common approach, however inaccuracies in analysis may arise from small point-source inputs into the aquatic environment, such as mines. Additionally, current and detailed land cover data are not always available and their manipulation and assessment can be time-consuming when numerous sites are being assessed at a large spatial scale.

Ecozones, which are the broadest ecological classification, are not the only or ideal polygon within which to compute the relationship between conductivity and alkalinity, but were used for this exploratory exercise. Going forward, and assuming sufficient data, the relationship between conductivity and alkalinity may be characterized by watersheds, sub-watersheds, and quaternary watersheds, since the geology and thus background chemistry will be more homogenous at smaller spatial scales.

As conductivity and alkalinity values are commonly measured in water monitoring programs, this approach has the potential to be widely applicable. Given the availability of sufficient data, this approach allows efficient assessment of the reference condition of a large number of waterbodies. Water quality data from reference samples can then be used to estimate background concentration ranges of inorganic analytes.

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