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A probabilistic hazard assessment for cyanobacterial toxins accounting for regional geography and water body trophic status

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ABSTRACT

Under climate change scenarios freshwater eutrophication is expected to increase, and with it the occurrence of cyanobacterial toxin-producing harmful algal blooms. In the current study, microcystin toxin occurrence data from literature sources and a long-term provincial monitoring program were used to conduct a probabilistic hazard assessment for Alberta, Canada. The large temporal and spatial range of data makes Alberta a model system for identifying regional geography and water body trophic status factors driving toxin concentrations. Environmental exposure distributions of microcystin concentrations were plotted and used to identify the likelihood of a given sample exceeding water guideline values as a function of regional geography, total phosphorus and chlorophyll-a concentration. This process identified regions with intensive cultivation and those most prone to water deficits associated with climate change to be most associated with exceedances of regulatory guideline values. Elevated phosphorus and chlorophyll-a concentrations were also drivers of toxin occurrence. This assessment can be used to identify water bodies of greatest risk to human and animal populations from cyanotoxins and thereby inform regulators as to most effective monitoring strategies.

1. Introduction

Factors such as fertilizer application, changes in livestock management, and sewage disposal, may result in extensive nutrient enrichment of surface waters and an overall degradation of water quality (Reynolds 2006; Rockström et al., 2009). One consequence of the eutrophication of water bodies, in particular elevated water phosphorus, is increased algal growth (Downing et al., 2001), which can lead to algal bloom events. When these blooms include cyanobacteria capable of producing cyanotoxins, then this represents a risk to wildlife and human health, particularly when the water body is a potential source of drinking water.

Microcystins are the most commonly-reported sub-group of cyanotoxins in freshwater systems (Svirčev et al., 2019), and of these, microcystin-LR (MCLR) is the variant of greatest environmental concern, owing to its prevalence in eutrophic waters and its high toxicity (Massey et al., 2018). When ingested, MLCR is readily accumulated in the liver, wherein it inhibits hepatic protein phosphatases (Billam et al., 2008). Because of the importance of these enzymes in a number of cellular cascades, liver function may be altered (Falconer and Humpage 2005), leading to hepatocyte necrosis, tumor promotion and ultimately,

liver failure (Billam et al., 2008; Falconer and Humpage 2005). In humans specifically, exposure to microcystins is often linked to symptoms such as nausea, vomiting, diarrhea, and convulsions (Pouria et al., 1998), and can lead to kidney and gastrointestinal damage (Kotak and Zurawell 2007). Recently, the ecotoxicological effects of cyanotoxins on aquatic life were summarized from over 150 published articles (Mehinto et al., 2021). These authors concluded that recreational water quality guidelines (8 µg/L) within the United States are likely to be protective of acute mortality in aquatic wildlife; however, guideline values were not necessarily protective of chronic adverse effects to aquatic organisms.

The magnitude and frequency of eutrophic events are predicted to increase in coming years, necessitating enhanced water quality monitoring programs (Hallegraeff 1993; Winter et al., 2011). In the Canadian province of Alberta, MCLR is the most commonly occurring microcystin analogue in lakes, rivers and other major water bodies (Zurawell et al., 1999). Consequently, Alberta has developed an extensive monitoring program for this specific microcystin variant (Kotak and Zurawell 2007; Rashidi et al., 2021). This monitoring began in 2005 and has continued on a routine basis since, leading to an extensive record of MLCR occurrences and concentrations across a broad temporal and spatial range.

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Based on the monitoring results to date, MCLR concentrations vary as a function of the type of aquatic system (lentic/lotic), season, time of day, and regional geography (i.e., prevailing natural land cover) (Kotak et al., 1995; Orihel et al., 2012; Schneider 2013).

Owing to the increased prevalence of harmful algal blooms (HAB) and their potential toxic effects on humans, guideline values (GV) for the maximum allowable microcystins in inland surface waters have been developed in many jurisdictions (Rashidi et al., 2021). For example, in Canada a tolerable daily MCLR intake value of 0.04 μ g/kg body weight per day has been established (Health Canada 2002). In effect, this allows for a maximum acceptable concentration of 1.5 μ g/L in drinking waters. It should be noted that, although this concentration is specific to MCLR, it is also often applied for exposure to other microcystin variants and pertains to both intracellular and extracellular toxin levels (i.e., whole-water). This value is comparable to the World Health Organization (WHO) provisional guideline value for total MCLR concentrations in water (1.0 μ g/L; World Health Organisation, 1998). Canada has also instituted a maximum allowable concentration for microcystins in recreational water (10 μ g/L; Health Canada 2022).

Although HABs, and the toxins they produce, are increasing in prevalence, there are few detailed reports regarding general trends of exceedance relative to current regulations. In one such study, Orihel et al. (2012) detailed microcystin occurrences across Canada using measurements taken between 2001 and 2011. These authors found that 18% of samples surpassed the WHO drinking water quality guideline of 1.0 μg/L and 14% of water bodies exceeded the Canadian drinking water guideline of 1.5 µg/L. This indicates that the risk of microcystins to human health is of concern, and highlights the need for enhanced monitoring efforts. Of particular value is the development of probabilistic hazard assessments, which can identify factors leading to elevated water microcystin concentrations, and which can result in more targeted monitoring efforts. In the current study, we conducted a probabilistic hazard assessment in which concentrations of microcystins in surface water in Alberta were collated from the peer-reviewed literature and monitoring data conducted by the provincial government. This dataset was chosen because of the extensive temporal and spatial coverage of the monitoring conducted to date, providing a sufficiently large dataset from which to delineate trends. Environmental exposure distributions of microcystin concentrations were plotted and used to identify the likelihood of exceeding water guideline values (GVs) as a function of factors such as trophic status, other water body characteristics, and regional geography. Although this model is specific for the province of Alberta, the factors responsible for elevated water microcystin concentrations are likely to be conserved, and so our general approach and resulting assessment is likely to be broadly applicable across multiple jurisdictions.

2. Materials and methods

Microcystin data were collated from two sources: the province of Alberta monitoring program, and Google Scholar. With respect to the latter, a comprehensive literature search was performed to examine microcystin occurrence in surface waters in Alberta. Searching was conducted between May-June 2020 using terms such as "cyanotoxin", "microcystin", "surface water", "lake", "monitoring", "reservoir", "bioaccumulation", "aquaculture", "environmental detection", "coastal", "benthic", "extracellular", "intracellular", "Great Lakes", "biota" and "Alberta" to obtain peer-reviewed scientific journal articles relevant to microcystins detected in Canadian surface water. In these sources, quantitative microcystin data from toxins measured inside cells (intracellular), released into the water (extracellular), or both (whole-water) and per cyanobacterial mass (phytoplankton) were collated along with the study parameters, analytical instrumentation, and regional geography (Aranda-Rodriguez et al., 2015; Lovin and Brooks 2019; Massey et al., 2020; Saari et al., 2017). Since microcystins are comprised of different isomers, data were categorized based on microcystin type (e.g.,

total microcystins, MCLR, or MCLR equivalents). Microcystin occurrence was broken down according to the nature of the aquatic system (i. e., lentic, lotic, reservoirs, rivers, creeks). Occurrence values were also categorized according to the prevailing natural geography according to previous published classifications (Natural Regions Committee 2006; Schneider 2013). Briefly, the broad classification of ecological landscapes is commonly used for resource management and help place biophysical patterns into a geographical context (Natural Regions Committee 2006). In Alberta, the broad ecological landscapes are divided into six natural regions called the Foothills, Rocky Mountain, Grassland, Parkland, Boreal Forest, and Canadian Shield regions (Natural Regions Committee 2006; Schneider 2013). Each natural region has distinguishing ecosystem characteristics such as climate, geology, vegetation, and land use patterns.

Data values were further categorized based on the trophic status of the water body corresponding to the occurrence value. The trophic state of water indicates the degree of primary productivity in a water body. Total phosphorus and chlorophyll-a are common trophic state metrics that have a range of values indicating where a water body lies on a scale from oligotrophic to hypereutrophic (Government of Alberta 2019). Oligotropic, mesotrophic, eutrophic and hypereutrophic water bodies are so classified based on water total phosphorus values of <10 µg/L, $10-35 \mu g/L$, $35-100 \mu g/L$, and $>100 \mu g/L$, and water chlorophyll-a water concentrations of <2.5 μ g/L, 2.5–8.0 μ g/L, 8.0–25.0 μ g/L, and >25.0 µg/L, respectively (Government of Alberta 2019). Chlorophyll-a is a direct measurement of algal biomass and is commonly used to indicate trophic state. Therefore, microcystin occurrence values were paired, if reported, with their corresponding total phosphorus, chlorophyll-a, and water body trophic state as potential factors to inform assessment results.

Since analytical methods and detection limits varied significantly among studies, only measurements above detection limits were used in the hazard assessment. After microcystin data were collated, environmental exposure distributions were created from maximum environmental concentrations for each sample matrix, microcystin type, and aquatic system within each Alberta natural region when greater than five occurrence measurements were available per dataset. Maximum environmental concentrations were chosen because of differential summary statistics for data reporting and to represent conservative or worst-case scenarios surface water conditions. All graphs were created using SigmaPlot 11.0 (Systat Software, Inc.). Maximum environmental concentrations were ranked in ascending order and assigned a percentile using the following Weibull formula:

$$j = (i \times 100) \div (n+1)$$

where j is the percent rank, i is the rank assigned to each maximum environmental concentration value and n is the number of values examined. In the equation, n+1 accounts for the assumption that there is always one less than all occurrences measured (Posthuma et al., 2001). Environmental exposure distributions were created with microcystin concentration on the x-axis and corresponding Weibull rank on the y-axis. The y-axis was then converted to probability. Linear regression analyses were then performed, and the linear equation slope and y-intercept derived from each environmental exposure distribution was used to calculate the centile values with the following equation:

Centile value =
$$NORMDIST((bx log_{10}(x)) + a)$$

where *NORMDIST* refers to the return of a selected value back to a standard normal cumulative distribution function, b and a are indicative of the slope and y-intercept from the linear regression, and x is the microcystin concentration of interest (e.g., drinking water guidance value), similar to previous published assessments (Corrales et al., 2015; James et al., 2011; Lovin and Brooks 2019; Saari et al., 2017). Water concentrations of interest (x) were entered into the centile value equation to determine the percent exceedance of each GV and corresponding

regressions were plotted with microcystin water GV concentrations from North American jurisdictions and WHO (Table 1). These GVs represent those for human and canine recreational activities, in addition to drinking water GVs. The GVs represent whole-water microcystin concentrations only and toxin concentrations quantified by mass were not used in the analysis due to inconsistent units and variable sample matrices.

3. Results

3.1. Occurrence of microcystins by natural region

The searches resulted in over 16,800 Google Scholar hits and a total of 332 articles were saved and reviewed for further relevancy to water bodies of Alberta. Together with data sourced directly from provincial monitoring programs, a total of 1988 data points were extracted. An environmental exposure distribution generated from all total microcystin and whole-water (extracellular, intracellular + extracellular) detection values is shown in Fig. 1. This combined dataset exceeded the lowest canine recreational GV (0.2 μ g/L; Oregon) by 63.7% and the lowest human recreational GV (0.8 μ g/L; California) by 27.5% (Table 2). The lowest drinking water GV (1.0 μ g/L; WHO lifetime value) was exceeded by 22.7% but there was only a minimal exceedance of 0.17% at the highest GV (24.0 μ g/L; WHO recreational value; Table 2).

Using the geographic location of all reported microcystin values, environmental exposure distributions were generated for five out of six regional geographic classifications in Alberta including Boreal Forest, Foothills, Grassland, Parkland, and Rocky Mountain (Fig. 2). The Canadian Shield natural region comprises only a very small portion of land in Alberta's northeast and there are insufficient data available for generating environmental exposure distributions for this region. The GV exceedances associated with each of the data-viable natural regions are listed in Table 2. In the Boreal Forest natural region, total microcystin exceedance for the lowest GVs (0.2 $\mu g/L$) were 64.7% for canine recreational value, 23.5% for the drinking water value (0.8 μ g/L), and 0.19% exceedance at the highest GV (24.0 $\mu g/L$). The Boreal Forest had the greatest number of occurrence values of any natural region and represented \sim 68% of all reported values. However, the Parkland natural region occurrence values exceeded the lowest canine recreational and drinking water GV by the greatest percentage, 71.7% and 33.2%, respectively, but exhibited minimal exceedance (0.76%) for the highest

Table 1
Summary table of different water microcystin guideline values across multiple geographic regions in North America (e.g., United States, Canada) and the world (e.g., World Health Organization; WHO).

Water microcystin concentration (µg/L)	Geographic Region	Guideline Value Type
0.2	Oregon, United States	State canine recreational guideline
0.8	California, United States	State human recreational guideline
1.0	World	WHO lifetime drinking water guideline
1.5	Canada	Canadian drinking water guideline
8.0	United States	USEPA water quality criteria/ swimming advisory
10.0	Canada	Canadian recreational water quality guideline
12.0	World	WHO short-term drinking water guideline
24.0	World	WHO recreational water guideline

California guideline value consists of a general warning that toxic cyanobacteria (e.g., microcystin) might be present in a waterbody and advises the population to stay away from impacted areas. USEPA: U.S. Environmental Protection Agency.

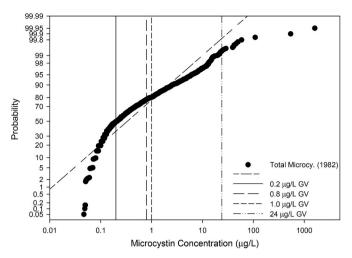


Fig. 1. Environmental exposure distribution of the maximum reported total microcystins (μ g/L) in all whole-water samples. GV, guideline value; Total Microcy., total microcystins; (##), reported values per distribution.

recreational GV. The Rocky Mountain natural region microcystin values exceeded the lowest canine recreational (17.7%), lowest drinking water (0.03%), and highest recreational (0.00%) the least frequently.

3.2. Occurrence of microcystins by trophic status

3.2.1. Total phosphorus

Total microcystin values were categorized by their total phosphorus trophic state corresponding with each detection. Across all total phosphorus trophic states the data exceeded the lowest canine recreational GV by a minimum of 5.22% and maximum of 58.3% (Table 3). Among the natural regions, the canine recreational value was exceeded by a minimum of 33.6% (Boreal Forest, 10–35 $\mu g/L$ total phosphorus) and maximum of 58.3% in the Foothills (Table 3). Regardless of the total phosphorus category in either natural region, very few microcystin occurrences in Alberta exceeded the U.S. Environmental Protection Agency water quality criteria/swimming advisory (8 µg/L). Indeed, only Boreal Forest waters with total phosphorus $<10 \mu g/L$ and Foothills sampling locations with total phosphorus between 35 and 100 µg/L showed any measurements where total microcystin concentrations exceeded the GV. Only one natural region (Boreal Forest with total phosphorus <10 $\mu g/L$) had any total microcystin data that exceeded the highest recreational GV (24.0 µg/L), and even then, this represented only 0.02% of all such measurements.

3.2.2. Chlorophyll-a

Total microcystin values were also categorized by their water chlorophyll-a trophic state corresponding with each detection. Across all chlorophyll-a classifications, data exceeded the lowest canine recreational GV by a minimum of 5.19% or a maximum of 90.8% (Table 4). Among the natural regions, the Foothills had the highest minimum exceedance percentage at 31.3% (2.5–8.0 μ g/L) and Parkland had the highest maximum exceedance at 90.8% (>25.0 μ g/L) by reference to the canine recreational GV (Table 4). Approximately 44.4% of chlorophyll-a categories among either natural region exceeded the U.S. Environmental Protection Agency water quality criteria/swimming advisory GV (8.0 μ g/L), and six chlorophyll-a categories from natural regions reported an exceedance percentage (0.01–4.20%) at the highest recreational GV (24.0 μ g/L).

3.3. Aquatic system type

Total microcystin values geographically located within the Alberta natural regions were categorized based on aquatic system type (e.g.,

 Table 2

 Summary table of microcystin guideline value exceedances for total microcystins reported in Alberta categorized according to natural region from all aquatic systems.

	n	r ²	No.	Centil	e Value ((μg/L)			Percentage exceedance of GVs									
				5	10	20	50	95	0.2 μg/ L	0.8 μg/ L	1.0 μg/ L	1.5 μg/ L	8.0 μg/ L	10.0 μg/ L	12.0 μg/ L	24.0 μg/ L		
All Regions	1982	0.87	164	0.03	0.05	0.10	0.33	3.70	63.7	27.5	22.7	15.2	1.49	0.26	0.71	0.17		
Boreal	1339	0.88	90	0.03	0.05	0.10	0.35	3.87	64.7	28.5	23.5	15.9	1.62	1.09	0.78	0.19		
Forest																		
Foothills	72	0.88	6	0.04	0.06	0.08	0.14	0.5	34.4	1.10	0.47	0.08	~0.00	~0.00	~0.00	~0.00		
Grassland	179	0.87	29	0.03	0.04	0.08	0.25	2.20	56.2	18.8	14.6	8.72	0.46	0.27	0.17	0.03		
Parkland	319	0.91	28	0.04	0.06	0.13	0.50	6.88	71.7	38.4	33.2	24.5	4.10	3.01	2.31	0.76		
Rocky Mtn	73	0.80	12	0.04	0.05	0.06	0.11	0.32	17.7	0.10	0.03	~0.00	~0.00	~0.00	~0.00	~0.00		

n: number of reported values; r²: regression coefficient; No.: number of waterbodies; GVs: guideline values; Rocky Mtn.: Rocky Mountain.

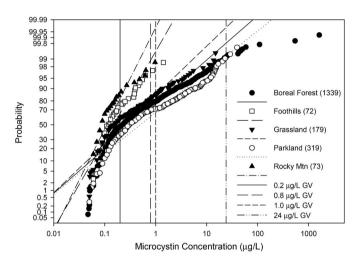


Fig. 2. Environmental exposure distribution of the maximum reported total microcystins (μ g/L) in whole-water samples from each natural region in Alberta, Canada. GV, guideline value; Total Microcy., total microcystins; (##), reported values per distribution.

lotic, lentic, reservoir). Lentic total microcystin occurrences were the most prevalent in all natural regions. The GV exceedances among natural regions are listed in Table 5. The lowest canine recreational GV was

exceeded by a minimum of 8.01% and a maximum of 72.4% among the lentic systems (Table 5). While the most lentic occurrence values were from the Boreal Forest (1339), the Parkland natural region exceeded the lowest (canine $0.2\,\mu g/L$) and highest GV (recreational 24.0 $\mu g/L$) 72.4% and 0.80%, respectively. Similar to trophic state classifications, the Rocky Mountain natural region minimally exceeded either GVs, which ranged between 8.01 and $\sim 0.00\%$ (Table 5). The Grassland region contained the only reported lotic total microcystin values. Sufficient data were available for reservoirs from three natural regions including Grassland, Parkland, and Rocky Mountain. Grassland GV exceedances ranged between 57.7 and 0.01%. The Rocky Mountain and Parkland natural regions exceeded the canine GV by 28.0% and 5.56%, respectively; however, neither region exceeded GVs >8.0 μ g/L.

4. Discussion

To understand how natural region and trophic state influence the occurrence of a common cyanobacterial toxin, a probabilistic hazard assessment with microcystin water values from the province of Alberta was performed. Alberta serves as an excellent model to examine the key drivers of microcystin occurrence in water bodies more generally, owing to the extensive sampling program that has collated thousands of measurements from waters with different characteristics from distinct geographies across a wide temporal and spatial scale.

From the comprehensive dataset some notable patterns emerged. Most of the occurrence data represented measurements of total microcystins (i.e., samples that do not distinguish between toxin that is

Table 3
Summary table of microcystin guideline value exceedances for total microcystins reported in Alberta and categorized by trophic state based on total phosphorus values according to natural region. Occurrence values reported were from lentic and reservoir aquatic systems.

	-																	
	n	r ²	TP	No.	Centil	e Value ((μg/L)		•	Percentage exceedance of GVs								
					5	10	20	50	95	0.2 μg/L	0.8 μg/ L	1.0 μg/ L	1.5 μg/ L	8.0 μg/ L	10.0 μg/L	12.0 μg/L	24.0 μg/L	
BF	16	0.68	<10	11	0.02	0.03	0.05	0.16	1.55	42.8	12.0	9.13	5.23	0.24	0.14	0.09	0.02	
BF	386	0.84	10-35	51	0.04	0.05	0.08	0.14	0.51	33.6	1.27	0.58	0.11	~0.00	~0.00	$\sim \! 0.00$	~0.00	
BF	369	0.95	35-100	57	0.06	0.08	0.11	0.19	0.55	45.8	1.37	0.55	0.08	~0.00	~0.00	$\sim \! 0.00$	$\sim \! 0.00$	
BF	120	0.99	>100	33	0.07	0.09	0.13	0.22	0.65	55.8	2.57	1.12	0.19	~0.00	~0.00	$\sim \! 0.00$	~0.00	
Foothills	5	1.00	<10	3	0.06	0.08	0.09	0.15	0.34	27.5	0.05	0.01	~0.00	~0.00	~0.00	$\sim \! 0.00$	~0.00	
Foothills	54	0.87	10-35	6	0.04	0.06	0.08	0.15	0.49	33.3	1.04	0.45	0.08	~0.00	~0.00	$\sim \! 0.00$	~0.00	
Foothills	8	0.97	35-100	3	0.04	0.06	0.10	0.25	1.45	58.3	13.8	9.71	4.67	0.06	0.03	0.01	$\sim \! 0.00$	
Grassland	16	0.82	<10	6	0.03	0.04	0.05	0.08	0.22	6.49	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	
Grassland	70	0.84	10-35	16	0.03	0.05	0.06	0.13	0.46	27.7	0.91	0.41	0.08	~0.00	~0.00	~0.00	~0.00	
Grassland	24	0.85	35-100	7	0.05	0.07	0.08	0.13	0.34	24.2	0.08	0.02	~0.00	~0.00	~0.00	$\sim \! 0.00$	~0.00	
Grassland	9	0.98	>100	5	0.05	0.07	0.09	0.16	0.46	35.4	0.61	0.22	0.03	~0.00	~0.00	$\sim \! 0.00$	~0.00	
Parkland	7	0.95	<10	2	0.03	0.04	0.05	0.08	0.2	5.22	~0.00	~0.00	~0.00	~0.00	~0.00	$\sim \! 0.00$	~0.00	
Parkland	90	0.88	10-35	9	0.05	0.06	0.09	0.18	0.69	44.4	3.46	1.85	0.50	~0.00	~0.00	$\sim \! 0.00$	$\sim \! 0.00$	
Parkland	46	0.97	35-100	13	0.07	0.09	0.11	0.16	0.36	33.3	0.05	0.01	~0.00	~0.00	~0.00	~0.00	~0.00	
Parkland	28	0.88	>100	14	0.06	0.08	0.11	0.21	0.72	52.1	3.78	1.92	0.46	~0.00	~0.00	~0.00	~0.00	
RM	19	0.74	<10	5	0.03	0.04	0.05	0.11	0.45	24.0	0.99	0.48	0.11	~0.00	~0.00	~0.00	~0.00	
RM	32	0.92	10-35	8	0.04	0.05	0.07	0.10	0.26	12.1	0.01	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	
RM	20	0.73	35-100	3	0.03	0.04	0.06	0.13	0.55	30.4	2.00	1.07	0.30	~0.00	~0.00	~0.00	~0.00	

n: number of reported values; r^2 : regression coefficient; TP: total phosphorus category; No.: number of waterbodies; GVs: guideline values; BF = Boreal Forest; RM = Rocky Mountain.

Table 4
Summary table of microcystin guideline value exceedances for total microcystins reported in Alberta and categorized by trophic state based on chlorophyll-a values according to natural region. Occurrence values reported were from lentic, lotic and reservoir aquatic systems.

	n	r^2	Chl-a	No.	Centile	e Value (μg/L)			Percentage exceedance of GVs								
					5	10	20	50	95	0.2 μg/L	0.8 μg/ L	1.0 μg/ L	1.5 μg/ L	8.0 μg/ L	10.0 μg/L	12.0 μg/L	24.0 μg/L	
BF	76	0.79	< 2.5	24	0.04	0.05	0.06	0.11	0.34	19.7	0.17	0.05	0.01	~0.00	~0.00	~0.00	~0.00	
BF	390	0.89	2.5-8	62	0.05	0.06	0.08	0.15	0.52	36.3	1.30	0.57	0.1	~0.00	~0.00	~0.00	~0.00	
BF	376	0.93	8-25	68	0.05	0.08	0.12	0.28	1.5	62.9	15.2	10.6	5.02	0.05	0.02	0.01	~0.00	
BF	485	0.97	>25	62	0.07	0.12	0.24	0.86	10.9	82.9	52.0	46.2	36.0	7.40	5.57	4.36	1.54	
Foothills	17	0.75	< 2.5	4	0.02	0.03	0.05	0.13	0.78	35.5	4.78	3.04	1.21	0.01	~0.00	~0.00	~0.00	
Foothills	28	0.91	2.8 - 8	4	0.05	0.06	0.08	0.14	0.45	31.3	0.69	0.27	0.04	~0.00	~0.00	~0.00	~0.00	
Foothills	20	0.86	8-25	3	0.05	0.07	0.09	0.15	0.43	33.1	0.43	0.15	0.02	~0.00	~0.00	~0.00	~0.00	
Foothills	5	0.96	>25	2	0.05	0.07	0.11	0.30	1.92	63.4	19.1	14.2	7.66	0.19	0.10	0.06	0.01	
Grassland	34	0.88	< 2.5	13	0.04	0.05	0.06	0.09	0.20	5.19	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	
Grassland	63	0.89	2.5-8	20	0.04	0.05	0.07	0.13	0.45	28.6	0.82	0.35	0.06	~0.00	~0.00	~0.00	~0.00	
Grassland	40	0.93	8-25	16	0.05	0.08	0.14	0.42	3.72	70.8	31.1	25.5	16.8	1.32	0.85	0.58	0.12	
Grassland	30	0.99	>25	10	0.07	0.12	0.25	0.93	12.4	83.7	53.9	48.3	38.2	8.60	6.58	5.22	1.95	
Parkland	14	0.88	< 2.5	4	0.04	0.05	0.06	0.11	0.30	15.4	0.06	0.02	~0.00	~0.00	~0.00	~0.00	~0.00	
Parkland	89	0.79	2.5-8	17	0.04	0.05	0.08	0.17	0.73	42.4	4.05	2.30	0.72	~0.00	~0.00	~0.00	~0.00	
Parkland	93	0.92	8-25	21	0.06	0.08	0.14	0.37	2.45	70.4	25.1	19.4	11.2	0.37	0.21	0.12	0.01	
Parkland	121	0.98	>25	22	0.12	0.22	0.43	1.61	21.1	90.8	67.2	61.9	51.8	15.3	12.2	9.97	4.22	
RM	26	0.74	< 2.5	8	0.03	0.04	0.06	0.11	0.38	21.5	0.42	0.17	0.03	~0.00	~0.00	~0.00	~0.00	
RM	26	0.93	2.5-8	9	0.04	0.05	0.06	0.10	0.21	6.28	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	
RM	9	0.84	8-25	3	0.03	0.05	0.07	0.14	0.59	34.9	2.28	1.20	0.32	~0.00	~0.00	~0.00	~0.00	
RM	12	0.69	>25	2	0.02	0.03	0.05	0.12	0.66	31.5	3.31	1.99	0.72	~0.00	~0.00	~0.00	~0.00	

n: number of reported values; r²: regression coefficient; TP: total phosphorus category; No.: number of waterbodies; GVs: guideline values; BF = Boreal Forest; RM = Rocky Mountain.

Table 5
Summary table of microcystin guideline value exceedances for whole-water total microcystins reported in Alberta lentic, lotic and lotic/reservoir aquatic systems according to natural region. There were no Boreal Forest or Foothill water types classified as lotic.

	AST	n	r ²	No.	Centile Value (µg/L)					Percentage exceedance of GVs							
					5	10	20	50	95	0.2 μg/L	0.8 μg/ L	1.0 μg/ L	1.5 μg/ L	8.0 μg/ L	10.0 μg/L	12.0 μg/L	24.0 μg/L
Boreal Forest	LE	1346	0.88	90	0.03	0.05	0.10	0.34	3.87	64.5	28.5	23.55	15.95	1.62	1.09	0.78	0.19
Foothills	LE	72	0.88	6	0.04	0.06	0.08	0.14	0.5	34.5	1.10	0.47	0.08	~0.00	~0.00	~0.00	~0.00
Grassland	LE	86	0.83	12	0.02	0.03	0.06	0.23	2.8	53.3	20.6	16.7	10.9	0.98	0.65	0.46	0.11
Parkland	LE	312	0.91	27	0.04	0.07	0.14	0.52	7.12	72.4	39.2	33.9	25.2	4.29	3.16	2.43	0.80
Rocky Mtn	LE	40	0.81	8	0.04	0.05	0.06	0.10	0.23	8.01	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00
Grassland	LO	87	0.90	11	0.03	0.05	0.09	0.25	1.93	57.7	17.6	13.4	7.51	0.26	0.15	0.09	0.01
Parkland	LO	7	0.95	1	0.03	0.04	0.05	0.08	0.21	5.56	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00	~0.00
Rocky Mtn	LO	33	0.86	4	0.03	0.04	0.06	0.13	0.47	28.0	1.02	0.47	0.10	~0.00	~0.00	~0.00	~0.00

AST: aquatic system type; LE: lentic; LO: lotic/reservoir; n: number of reported values; r²: regression coefficient; No.: number of waterbodies; GVs: guideline values; Rocky Mtn.: Rocky Mountain.

intracellular or extracellular; see below). The other key observation was that data were concentrated from certain natural regions. For example, samples collected from water bodies in Boreal Forest comprised the majority of datapoints (~68%), followed by Parkland (16.1%). Ninety different water bodies in the Boreal Forest have reported total microcystin values compared to twenty-eight for Parkland, with the Foothills having the fewest number of water bodies per region with six. The Boreal Forest natural region comprises 58% of the provincial land mass followed by Grassland (14%), Foothills (10%), Parkland (9%) and the Rocky Mountains (6%; Natural Regions Committee 2006). There are a number of additional factors contributing to this pattern of sampling. For example, water quality monitoring programs are subjected to biases including favouring larger lakes with high recreational value, and waters closer in proximity to major population centres (Wagner et al., 2008), which in Alberta would result in a higher sampling in Boreal Forest and Parklands natural regions. Additionally, there is not an even distribution of lakes suitable for sustaining algal populations throughout the province. In the southern Parklands, Grasslands and Foothills regions of Alberta, many lakes have been subjected to evaporation causing lakes to disappear or become highly saline and unsuitable for supporting algal populations (Campbell and Prepas, 1986). Because of their very

low probability of blooms, these lakes are not sampled as part of the provincial microcystin monitoring program.

The land use in each natural region is closely linked with climatic conditions. Subregions of Parkland are highly productive due to a long warm growing season, which makes it the most highly cultivated natural region (Natural Regions Committee 2006). When considering all aquatic systems per region, Parkland had the highest percentage of exceedances across all GVs including both recreational (0.2 $\mu g/L = 71.7\%)$ and drinking water guidelines (1.5 μ g/L = 24.5%; Table 2). Rising temperatures are predicted to cause a moisture deficit in Parkland, which favors cyanobacteria compared to other phytoplankton (Schneider 2013), at least until those lakes become too saline to support algae (Campbell and Prepas, 1986). Warming surface waters increase lake stratification (at least for the deep lakes that support recreational activities and which are key targets for sampling programs; Woolway et al., 2021), and lengthen optimal growth periods for cyanobacteria blooms. When these favorable abiotic factors are paired with nutrient enrichment, cyanobacterial toxins become prevalent (Paerl and Huisman 2008). This suggests that in the province of Alberta, diverting sampling efforts towards water bodies in Parkland regions would be more likely to identify exceedances, and be protective of human and animal health, especially in a warming

climate

Over the past several decades, trophic status has been positively associated with HAB and cyanobacteria occurrences (Kotak and Zurawell 2007). This is driven by dissolved nutrients such as nitrogen, but particularly phosphorus, which is commonly limited in aquatic ecosystems. Our analysis supports this. Parkland lentic and reservoir total phosphorus observations corresponding with total microcystin occurrences indicated a number of impacted water bodies were mesotrophic (moderately nutrient rich; n = 9), eutrophic (high nutrients; n = 13), and hypereutrophic (extreme nutrient enrichment; n = 14). Total microcystin values within each region were also categorized using the chlorophyll-a content taken at the time of sample collection. Chlorophyll-a, an algal pigment, is a trophic status indicator known to be associated with high total microcystin levels (e.g., Kotak and Zurawell 2007). Similar to the lentic and reservoir total phosphorus indicator results, in the current study chlorophyll-a trophic status analysis indicated Parkland water bodies had the highest percent exceedance across all GV including both recreational (0.2 $\mu g/L = 90.8\%$) and drinking water guidelines (1.5 μ g/L = 51.8%; Table 4). Overall, the microcystin levels are concerning due to the common recreational use (e.g., fishing, swimming, hiking) of lentic and reservoir systems. It is worth noting that in the current assessment, 93.4% of whole-water total microcystin values were from lentic aquatic systems, reflecting the more intensive monitoring of these systems and the enhanced likelihood that such waters are most likely to become nutrient-enriched and thus result in HAB (O'Neil et al., 2012).

Another clear outcome of the current analysis is the relative low risk of microcystin exceedance in the Rocky Mountain natural region. Indeed, this region had the lowest percent exceedance across nearly all GVs (~0.00 % for all, except 0.2 μg/L canine for which percent exceedance was 8.01%). This indicates the Rocky Mountain natural region contains aquatic systems of high water quality and microcystins are of minimal risk to humans and wildlife in the region. This likely reflects the limited arable land in this region (in part for logistical reasons, but also because of national park status). This minimizes eutrophication of waters, limiting algal growth and the development of microcystincontaining HAB (Orihel et al., 2012). In contrast to the overall high exceedance associated with Parkland systems more generally, reservoirs sampled within this region, had a very low risk of GV exceedance. However, this risk was assessed on only 7 sampling points from a single water body. More sampling data from Parkland reservoir systems are required to increase confidence in the low-risk status of such systems. Lakes and reservoirs are common potable water supplies and high use recreational areas, and while Rocky Mountain water bodies are of minimal concern, Parkland lentic systems and Grassland reservoirs exceeded the canine GVs 72.4% and 57.7% of the time. Alberta Grassland and its subregions have moderately negative climate moisture index values, the highest number of growing degree days above 5 °C, and are geographically located in the southern latitudes in the province (Schneider 2013). These are all factors that may contribute towards the enhanced risk of these water bodies. The strong association between factors known to generate algal growth in waters and the exceedance percentage calculated in the current study facilitates identification of water bodies where animal and human risks are highest, and therefore where sampling efforts should be most concentrated. Critically, although the hazard assessment conducted is specific to Alberta, the conditions that contribute towards high risk are likely to be conserved globally. Although the factors contributing towards the risk of HAB are well understood, the current study provides empirical evidence in support of these factors over a broad geographical scale, while attributing specific risk values to waters according to key HAB drivers.

Surface water microcystin occurrence data vary in terms of the method of analysis and how these data are reported. This lack of standardization can compromise the quality of a hazard assessment. Microcystins are generally reported in one of three ways: intracellular, extracellular, and total (intracellular + extracellular). Microcystin

analyses include the protein phosphatase enzyme inhibition assay, high performance liquid chromatography, liquid chromatography-tandem mass spectrometry, and enzyme-linked immunoassay. For the purposes of the current study, we were highly fortunate that the majority of samples available (99.4%) were from the same source (Government of Alberta under various different iterations) and were analyzed using the same method. In the province microcystin occurrences are reported as total microcystin and calculated via protein phosphatase enzyme inhibition assay. Total microcystin values encompass all bioactive toxin analogues that exceed the assay limit (0.05-0.09 µg MCLR equivalents/ L; Zurawell 2001). Values are extrapolated from curves plotting inhibition against known MCLR standards and are reported as μg MCLR eq./L. Although liquid chromatography-based approaches are considered the most robust analytical method for quantification of microcystins (Hawkins et al., 2005), they have a number of drawbacks, including the speed of analysis and the availability of isotope standards (Lovin and Brooks 2019). The protein phosphatase enzyme inhibition assay has a high sensitivity, can be rapidly conducted, but is also relatively inexpensive to perform (Hawkins et al., 2005). It is also important to note that most water quality GV are based on total microcystin values, and thus the use of total microcystin data in the current study generated a hazard assessment of direct relevance, without the need to convert from intracellular or extracellular values, which may generate inaccuracies (Dong et al., 2016).

5. Conclusion

Overall, this study highlights the utility of the probabilistic hazard assessment approach in characterizing the prevalence and percent exceedance of microcystin GVs within Alberta surface waters, and serves as a model for similar assessments for this toxin globally. Our work identified local factors such as total phosphorus and chlorophyll-a, and regional factors such as land use as key drivers of elevated microcystins. These outcomes are similar to those identified in previous studies. For example, Loewen et al. (2020) found that total phosphorus, lake elevation, monthly solar radiation, spring air temperature, cropland and pastureland were the factors that explained the most variation in cyanobacterial community composition in northern temperate lakes. The occurrence of these cyanotoxins is clearly a concern worldwide and given the magnitude of detections measured above established guidelines values, especially as this pertains to water quality guidelines for drinking water, is of particular concern in Alberta. Although the method has some limitations (e.g., reliance on a relatively homogenous sampling approach across a wide temporal and spatial scale), it provides a general overview of microcystin occurrence by provincial region and highlights where additional environmental monitoring and assessments may be warranted. Biophysical characteristics of landscapes such as growing degree days and climate moisture index values were associated with the highest GV exceedances and demonstrated how natural regions could be predictive of poor water quality. As HABs continue to increase in frequency due to global climate change and anthropogenic activities, probabilistic hazard assessments present an approach to determine the extent of algal toxins in aquatic systems and predict percent exceedances of water quality guidelines to support monitoring efforts.

Ethical statement

This work does not involve any research on humans or animals and is therefore not conducted any specific institutional ethical approval.

CRediT authorship contribution statement

Diane A. Mielewczyk: Writing – original draft, Investigation, Funding acquisition, Data curation. **Chris N. Glover:** Writing – review & editing, Supervision, Funding acquisition. **Gavin N. Saari:** Writing – review & editing, Supervision, Investigation, Funding acquisition, Data

curation, Conceptualization.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Chris Glover reports financial support was provided by Alberta Conservation Association. Diane Mielewczyk reports financial support was provided by Natural Sciences and Engineering Research Council of Canada. Chris Glover reports financial support was provided by Campus Alberta Innovation Program. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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