Potential recovery of Ca, K, Mg, Br, I, B, and Li from produced water at oil and gas fields, British Columbia

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Introduction

Historically, extracting dissolved solids from formation water was economically motivated. Today, the main drivers are environmental benefits and regulations, as large volumes of water needed for hydraulic fracturing require treatment before reuse or disposal. Element recovery from produced water is not expected to be profitable unless market conditions are favourable, recoverable elements are abundant, and economical recovery methods are established. However, sale of recovered materials could offset recycling and disposal costs.

As of June 2017, more than 60,000 data entries related to British Columbia oil and gas wells were accessible through the AccuMap database. Of these, more than 32,000 entries contain a wide range of information including the chemical composition and physical properties of sampled produced waters. The elements with apparent potential to be extracted and sold, and have records available through AccuMap are Cl, Na, Ca, K, Sr, Mg, Br, Ba, Fe, I, B, and Mn. We test the effects of automated culling on the Accumap database, describe markets for these elements and Li, and their concentrations and distributions in produced water from oil and gas wells in British Columbia.

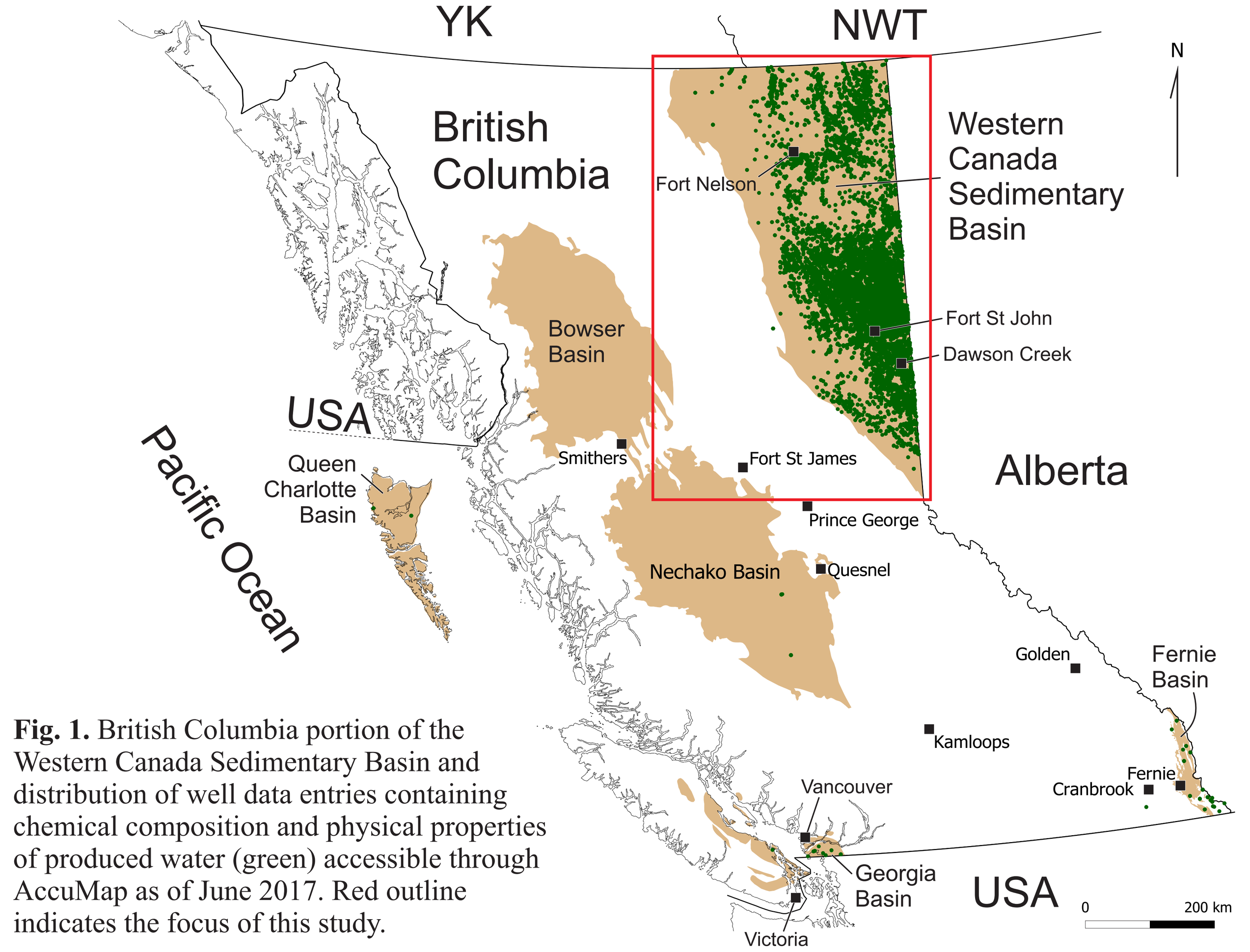

Fig. 1. British Columbia portion of the Western Canada Sedimentary Basin and distribution of well data entries containing chemical composition and physical properties of produced water (green) accessible through AccuMap as of June 2017. Red outline indicates the focus of this study.

Table 1. Elements and related compounds in formation and flowback waters and their uses.

Element or compound	Uses: selected examples
Sodium and chlorine	salt, chlorine (pulp and paper manufacturing, chemical industry), NaOH and Na_2CO_3 (pulp and paper manufacturing, detergents, water treatment, glass)
Calcium compounds	synthetic calcium carbonate, $CaCl_2$ brines (food processing, ice and dust control, refrigeration, concrete setting accelerant)
Potassium-potash	fertilizer, synthetic rubber, food preservatives, insecticides, Zn refining
Strontium	pyrotechnics, magnets, pigments, glass-making
Magnesium and related compounds	MgO (fused, dead-burned, caustic-calcined), Mg metal, $MgCl_2$ (water treatment, road dust control, fertilizer, Sorel cement)
Bromine	flame retardants, disinfectants, water purification
Barium	drilling fluids, filler (plastics, paper, rubber), brake pads
Iodine	liquid crystal displays (LCD), pharmaceuticals, preservatives, iodine tablets
Boron	glass and ceramics, antiseptics, washing powders, boron carbide (body armour)
Lithium	batteries, lubricants, polymer production

Table 2. Recovery potential of Ca, K, Mg, Br, and I is conceptually estimated by comparison of elemental concentrations in produced waters to their regional exploration threshold (**RET**) or detailed exploration threshold (**DET**). For this study, we accept the RET and DET values defined by Hitchon et al. (1995) for a similar study in neighbouring Alberta, except B (Simandl. et al., 2018).

Element	Ca	K	Mg	Br	I	B	Li
RET (mg/l)	20000	5000	3000	1000	40	20	50
DET (mg/l)	60000	10000	9000	3000	100	100	75

Concentrations of elements in produced waters in British Columbia

Elements with records available through AccuMap: Cl, Na, Ca, K, Sr, Mg, Br, Ba, Fe, I, B, and Mn

Table 3. The number of analyses exceeding the detailed and regional exploration thresholds, the total number of analyses for Ca, K, Mg, Br, I, and B, and relative percentages of analyses exceeding the corresponding detailed exploration thresholds (DET) and regional exploration thresholds (RET).

Element	Ca	K	Mg	Br	I	B
≥ DET	102	1115	496	10	30	5
≥ RET	829	2180	1539	93	107	28
Total	30092	21499	29464	1366	1257	275
% ≥ DET	0.34	5.19	1.68	0.73	2.39	1.82
% ≥ RET	2.75	10.14	5.22	6.81	8.51	10.18

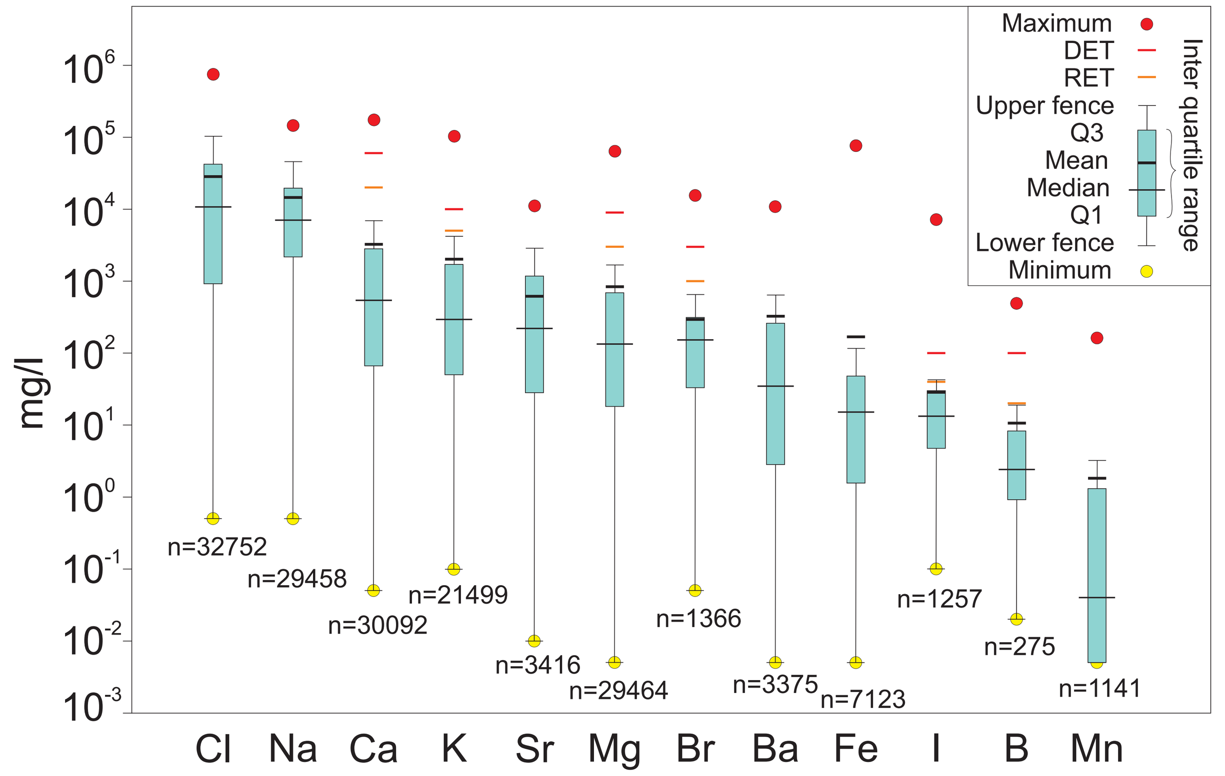

Fig. 2. Concentrations of elements in produced waters in British Columbia. RET- regional exploration threshold, and DET- detailed exploration threshold as established by Hitchon et al. (1995), except B.

Li

There are no data regarding Li in the AccuMap database for British Columbia. However, a study covering the industrial mineral potential of Alberta formation waters contains information from five wells that are within 2° longitude west of the British Columbia-Alberta border that were sampled in 1972 (Hitchon et al., 1993). The samples correspond to formation waters from Devonian or pre-Devonian oil and gas fields. One of the wells (UWI 00/D-031-A/094-I-14/0; coordinates 58.781348°N, 121.004693°W), was sampled at two intervals. The interval corresponding to the Presqu'ile Formation (time equivalent to the upper portion of the Pine Point Formation) contained 54 mg/l of Li, exceeding the RET for Li. There is not enough Li data for statistical evaluation.

Table 4. Lithium concentrations in formation waters in BC

UWI	Lithium (mg/l)	Formation
00/C-061-C/094-P-07/0	42	Beaverhill Lake
00/D-031-A/094-I-14/0	54	Presqu'ile
00/D-031-A/094-I-14/0	26	Beaverhill Lake
00/C-100-I/094-H-03/0	46	Doig
02/D-088-L/094-J-09/0	34	Slave Point
00/B-076-G/094-J-10/0	35	No data

Fig. 3. Lithium-ion polymer battery

Geographic distribution

Maps showing the British Columbia portion of the Western Canada Sedimentary Basin and location of wells with produced water analyses were created to determine the geographic distribution of selected constituents and highlight clusters of analyses with high elemental concentrations. The results for Ca, K, Mg, Br, I, and B are shown below.

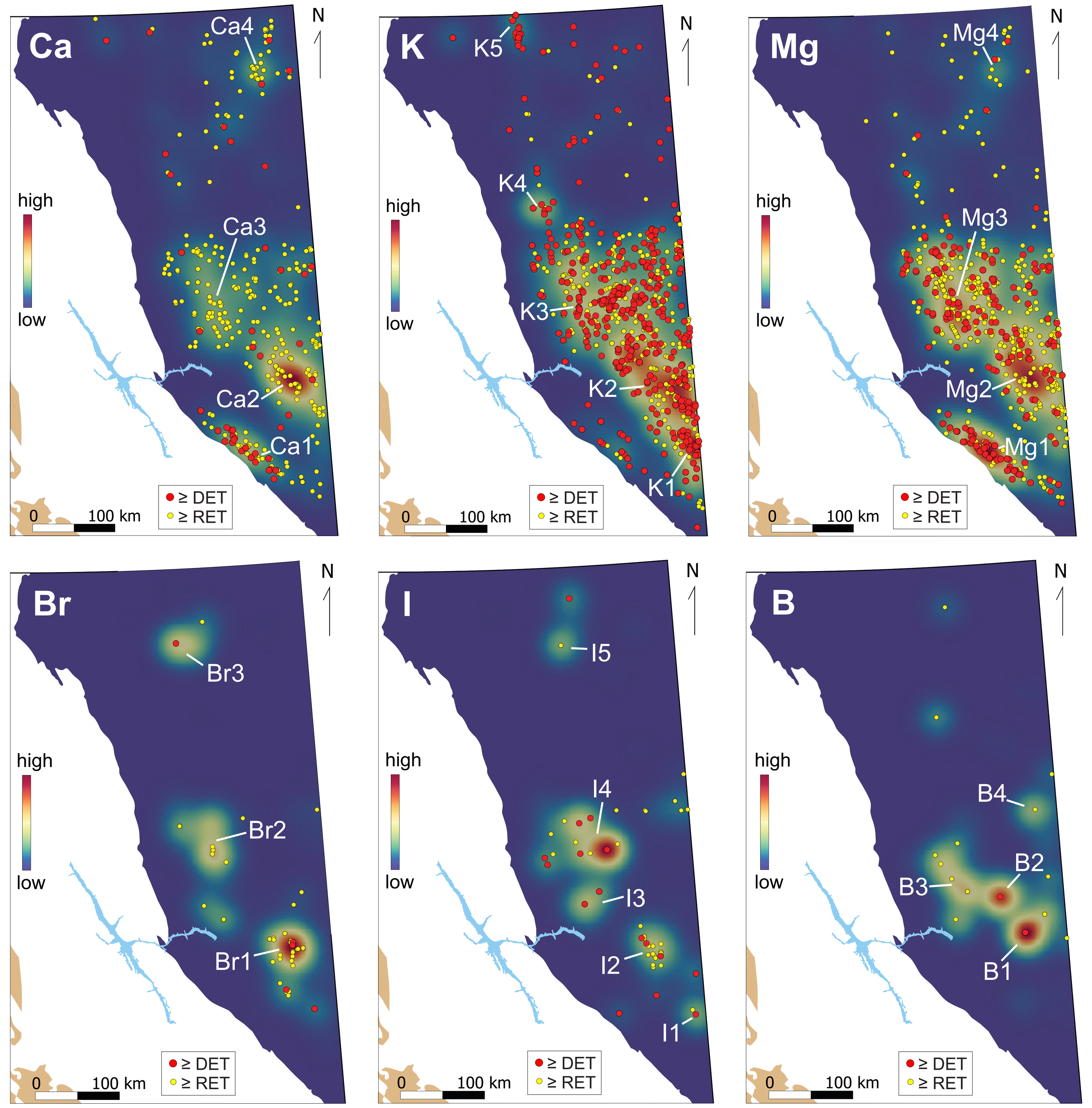

Fig. 4. British Columbia portion of the Western Canada Sedimentary Basin showing concentrations of Ca, K, Mg, Br, I, and B in wells. Only wells with reported values exceeding the regional exploration threshold (RET) and detailed exploration threshold (DET) are shown. Clusters of analyses with high elemental concentration are highlighted by background shading generated by the weighted kernel density estimation (KDE) module (TBF Tools) for Manifold System applied to the complete dataset using Gaussian kernel type, 20,000 m radius, 100 m cell size, and weighted by element concentrations. Clusters are identified by their respective element symbol followed by a numeral.

Data 'culling'

Routine culling of produced water data (Hitchon and Brulotte, 1994) practiced by hydrogeologists working in the oil and gas industry to classify waters or to remove nonrepresentative data for regional hydrogeological studies eliminates more than 44% of data entries in the AccuMap database, commonly because one or more constituent is not reported. This is too restrictive for exploration because it risks removing true anomalies as well as false. To test the effects of a more moderate culling approach on the AccuMap database, a method proposed by the USGS National Produced Waters Geochemical Database v2.3 (Blondes et al., 2017) was applied based on five flagging parameters: 1) pH outside the range of 4.5–10.5; 2) Mg > Ca; 3) K > Cl; 4) K > 5Na; and 5) charge balance error (CBE) greater than 15%

$$CBE_{(\%)} = \frac{\Sigma z \times m_c - \Sigma z \times m_a}{\Sigma z \times m_c + \Sigma z \times m_a} \times 100\%$$

where z is the absolute value of the ion charge and m_c is the molality of cation species and m_a is the molality of anion species (Jensen et al., 2013).

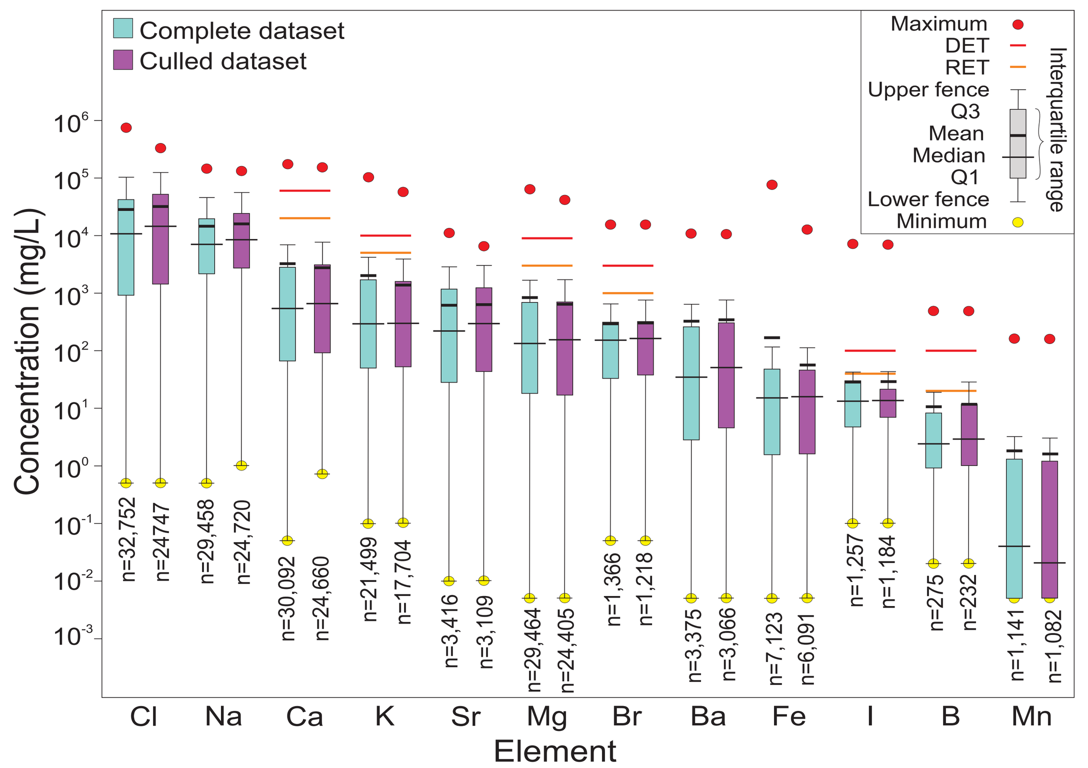

Fig. 5. Concentrations of elements in produced waters in British Columbia from the AccuMap database before culling (blue) and after culling (purple) according to the parameters set out by Blondes et al. (2017). This approach eliminates approximately 25% of data entries and does not significantly impact the mean, median, 1st and 3rd quartiles, and upper and lower fences. Regional exploration threshold (RET) and detailed exploration threshold (DET) as established by Hitchon et al. (1995); RET and DET values for B were established based on the range of concentrations in British Columbia.

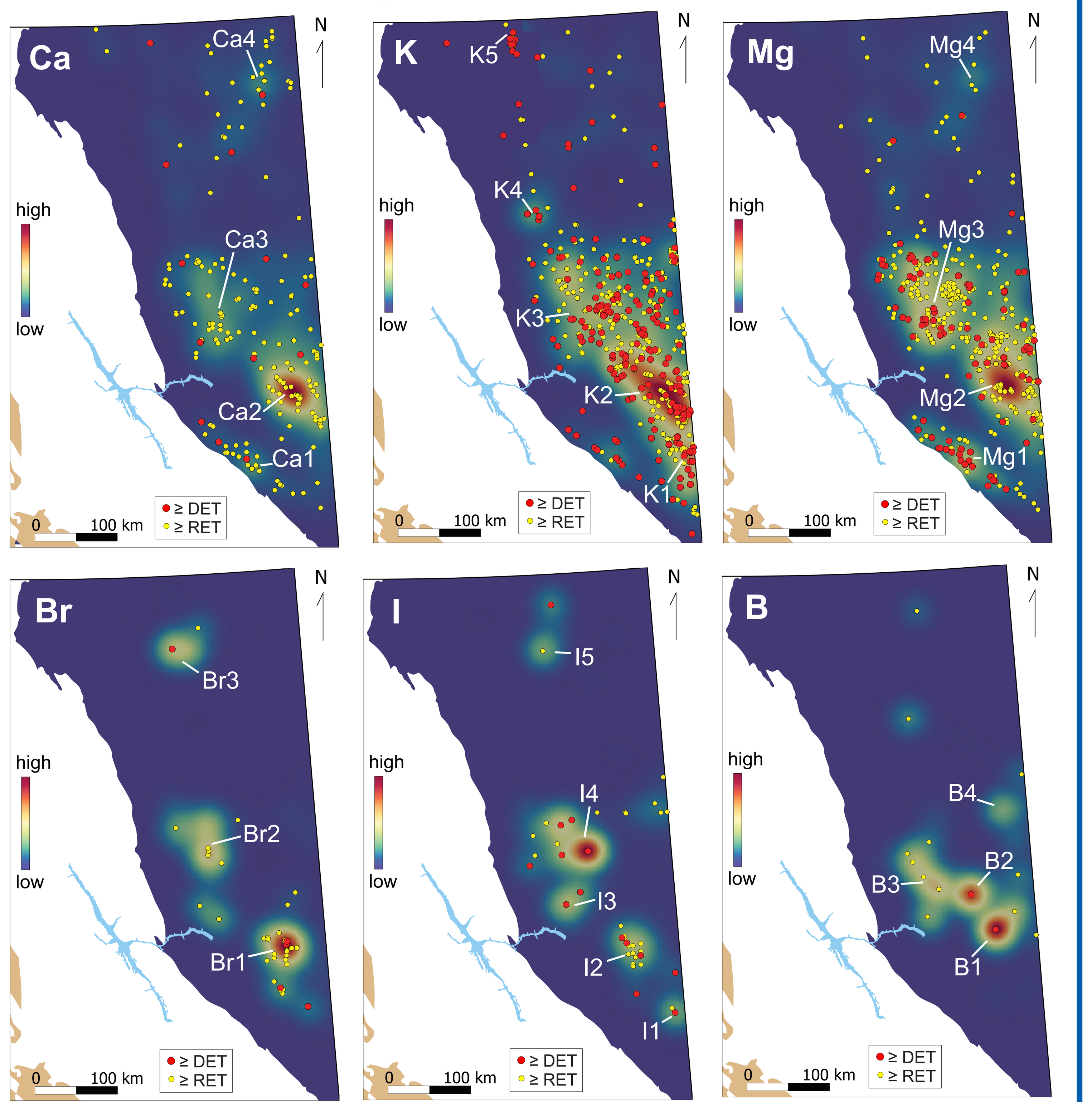

Fig. 6. British Columbia portion of the Western Canada Sedimentary Basin showing concentrations of Ca, K, Mg, Br, I, and B **after culling according to Blondes et al. (2017)**. Only wells with reported values exceeding the regional exploration threshold (RET) and detailed exploration threshold (DET) are shown. Clusters of analyses with high elemental concentrations are highlighted by background shading generated by the weighted kernel density estimation (KDE) module (TBF Tools) for Manifold System applied to the culled dataset using Gaussian kernel type, 20,000 m radius, 100 m cell size, and weighted by element concentrations. Clusters are identified by their respective element symbol and a numeral.

Summary

1) Produced waters are co-products of hydrocarbon extraction from conventional and unconventional fields. The treatment and disposal of these waters present significant cost to the oil and gas industry. However, these waters may contain significant concentrations of Cl, Na, Ca, K, Sr, Mg, Br, Ba, Fe, I, B, Mn, Li, and possibly other elements for which concentrations are not currently analyzed.

2) Most of the elements discussed in this study are considered specialty metals (e.g., Li and Mg), industrial minerals (e.g., B, Br, I), or starting materials for 'synthetic' industrial minerals (e.g., precipitated calcium carbonate).

3) Lithium exploration and development projects worldwide currently benefit from a bullish outlook for the battery-grade portion of the Li market. Virtually every site in the Alberta portion of the Western Canada Sedimentary Basin with reported Li concentrations equal or higher than 50 mg/l (RET) has been claimed. The British Columbia portion of the basin lacks equivalent Li data.

4) Automated data culling is probably beneficial for treatment of Ca, K, and Mg data because it can eliminate data entries for samples contaminated by mud filtrate KCl, completion fluids, or corrosion inhibitors, or data entries with sampling and analytical problems. However, culling also eliminates valuable Br, I, and B data, which may not be affected by contaminants.

5) This study is a first step toward locating anomalous areas for detailed follow-up studies and determining if any of these elements can be successfully extracted and marketed in BC to offset the costs of treatment and disposal of produced water. For detailed discussion see Simandl et al. (2018).

Acknowledgements:

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