The use of bromide and chloride mass ratios to differentiate salt-dissolution and formation brines in shallow groundwaters of the Western Canadian Sedimentary Basin

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Abstract In the Western Canadian Sedimentary Basin, the petroleum industry handles two geochemically distinctive brines that are traceable in the environment: formation brines extracted along with hydrocarbons from the basin, and salt-dissolution brines, produced by dissolving deep halite formations to create caverns for petroleum product storage. The concentrations of the conservative ions chloride (Cl) and bromide (Br) in many formation brines plot closely to the seawater evaporation trajectory of previous studies. These brines contain Cl/Br mass ratios of around 300, while salt-dissolution brines are relatively Br depleted, having Cl/Br mass ratios in excess of 20,000. An oilfield site in central Alberta had experienced nearby releases of both salt-dissolution and formation brines. Geochemical mixing trends were defined by theoretically mixing samples of local salt-dissolution and formation brine sources with background shallow groundwater. Most site monitoring wells and local surface water samples plotted directly on a salt-dissolution brine dilution trend, while results from four monitoring wells, all located directly downgradient of formation brine spills, suggested the mixing of formation brines into shallow groundwater. This work indicates that there is a large-scale salt-dissolution brine plume beneath the site and reinforces the use of Cl and Br concentrations and mass ratios as environmental tracers.

Résumé Sur le bassin sédimentaire de l'Ouest canadien, l'industrie pétrolière manipule deux solutions salines géochimiquement distinctes, qui sont traçables dans l'environnement: les saumures de formation extraites conjointement aux hydrocarbures du bassin, et les solutions salines de dissolution de sel qui sont issues de la dissolution des formations d'halite dans le but de créer des cavités de stockage des produits pétroliers. Dans plusieures solutions salines de formations, les concentrations des ions conservatifs de chlorure (Cl) et bromure (Br) sont étroitement corrélees à la trajectoire d'évaporation d'eau de mer tracée lors détudes antérieures. Ces solutions salines contiennent des rapports massiques Cl^-/Br^- proches de 300, tandis que les solutions salines de dissolution sont appauvries en Br, avec des rapports massiques de plus que 20,000. Ces deux types de solutions salines, de formation et de dissolution, ont été déversées à proximité d'un champ pétrolifère au centre de l'Alberta. Les trajectoires de mélange ont été calculées de manière théorique à partir d'échantillons de solutions salines locales de dissolution et de formation locales, mélangés à l'eau souterraine peu profonde. La plupart des échantillons prélevés dans les piézomètres et les eaux de surfaces suivent la trajectoire de dilution des solutions salines de dissolution, tandis que les résultats de quatre piézomètres situés enaval des déversements de solutions salines de formation suggère leurs mélange avec de-l'eau souterraines peu profonde. Ce travail indique la présence à grande échelle d'un panache de solution saline de dissolution sous le site, et étaye l'utilisation des concentrations en Cl et Br et leurs rapports massiques comme traceurs environnementaux.

Resumen En la Cuenca Sedimentaria Occidental Canadiense, la industria de petróleo maneja dos salmueras geoquímicamente distintas que son identificables en el ambiente: las salmueras de formación, extraídas junto con los hidrocarburos de la cuenca, y salmueras por disolución salina, producidas al disolver las formaciones profundas de halita, para crear cavernas para el almacenamiento de productos del petróleo. Las concentraciones de iones conservadores cloruro (Cl) y bromuro (Br) en muchas salmueras de formación, caen en la gráfica estrechamente en la trayectoria de evaporación del agua de mar de estudios anteriores. Estas salmueras contienen proporciones de masa Cl/Br alrededor de 300, mientras las salmueras por disolución salina son relativamente carentes de Br, haciendo proporciones de masa Cl/Br mayores de 20,000. Un sitio en un campo petrolífero en Alberta central había experimentado vertimientos cercanos tanto de salmueras por disolución salina, como de salmueras de formación. Las tendencias de mezcla geoquímica fueron definidas por medio de muestras teóricamente mezcladas, tanto de fuentes de salmueras de

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disolución salina local, como también de fuentes de salmuera de formación, con agua subterránea poco profunda de los alrededores. La mayoría de las muestras de los pozos de monitoreo en este sitio, lo mismo que del agua superficial local, al ser graficadas quedaron directamente en una tendencia de dilución de salmuera de disolución salina, mientras que los resultados obtenidos de cuatro pozos de monitoreo, todos localizados directamente gradiente abajo de derrames de salmuera de formación, sugieren la mezcla de salmueras de formación dentro del agua subterránea poco profunda. Este trabajo indica, que hay una pluma de salmuera de disolución salina, de gran tamaño, bajo el sitio y confirma el uso de las concentraciones de Cl y de Br y de sus proporciones de masa como trazadores medioambientales.

Keywords Hydrochemistry · Canada · Salinization · Brine · Seawater evaporation

Introduction

Ions of bromine and chlorine have long been recognized as reasonably conservative tracers in natural waters. This characteristic has led to the use of bromide (Br) concentrations and chloride (Cl)/Br mass ratios to infer the geochemical provenance of different groundwaters. Recent papers by Davis et al. (1998, 2004) have summarized many of these applications, and provide guidance to hydrologists in the interpretation of natural Br concentrations and Cl/Br mass ratios in the hydrosphere.

Br concentrations and Cl/Br mass ratios can also be used to delineate the impacts of man's activities on water resources. These activities have often resulted in subsurface contamination. A number of authors have used Cl/Br mass ratios and other geochemical relationships to distinguish between waters containing brine contamination. The use of Cl/Br mass ratios has been shown to be particularly effective when one of the sources derives from the dissolution of halite, as the resulting water has a disproportionately high Cl concentration relative to Br. Examples of common halite solutions affecting shallow groundwater include discharges of household water softeners, groundwater contamination by road salt and intrusion of (natural) halite dissolution brines into aquifers undergoing pumping. Several authors have outlined the use of Br/Cl mass ratios in delineating salt-dissolution brine sources in the environment and have provided case studies of the application of these techniques (e.g. Knuth et al. 1990; Richter et al. 1993; Whittemore 1995; Panno et al. 2006).

In western Canada, it can be argued that there are at least two fundamentally different types of brines that are handled in large quantities within the extensive oilfield production, storage and transportation infrastructure that has been built up over the past 60 years in the Western Canadian Sedimentary Basin (the WCSB). These include:

- Natural formation waters that are extracted with the oil and gas from geological formations within the WCSB. Most of these brines are geochemically related to, and bear the signature of, natural processes such as the mixing of well-known geochemical end member waters and sediment-formation water interactions over geological time.
- "Man-made" or salt-dissolution brines that are manufactured during the construction of underground storage caverns. These brines are manufactured by taking an available source of water at or near the ground surface and using it to dissolve salts in Devonian-aged salt bearing formations. The hydrogeochemical characteristics of these waters are distinct from those of natural WCSB brines.

This report presents an overview of the use of Cl/Br mass ratios to delineate various water sources in western Canada, both natural and man-made. In addition, a case study is presented from a site where both formation and salt-dissolution brines have been released to demonstrate the use of these methods.

Cl and Br in natural groundwaters

Precipitation and shallow groundwater

Previous studies have shown that concentrations of Cl in natural precipitation vary between less than 0.5 to more than 100 mg/L in North America. Typically Cl concentrations are highest near continental coastlines and decrease rapidly inland. Br concentrations are much lower-typically around 0.003 to 0.06 mg/L in natural precipitation (Davis et al. 1998, 2004). In conjunction with these values, Davis et al. (2004) noted a systematic distribution of Cl/Br mass ratios in potable groundwaters across North America. They found that the highest values of Cl/Br occurred on the Gulf and Pacific coasts, with mass ratios in excess of 200, while the lowest Cl/Br mass ratios occurred in the Interior Plains regions, with Cl/Br mass ratios around 50.

To characterize natural Cl and Br concentrations in Alberta, Canada, samples were taken from several shallow (<20 m depth), background groundwater sources as part of the present study. These, and the other sample results processed in 2005, were analyzed using ion chromatography (IC), with a high capacity column coupled with ultraviolet detection. This method provided lower-than-usual Br detection limits and overcame disruption of the IC baseline by the high Cl concentrations contained in some of the study samples. Analytical detection limits for Br analysis using this method were 0.003 mg/L, with a measurement uncertainty of approximately 20%. Standard Cl detection was used, with an analytical detection limit of 0.5 mg/L and a measurement uncertainty of 10% at 95% confidence levels.

Measured Cl/Br mass ratios from the shallow background groundwaters (<10 mg/L) ranged from 80 to 100 in southwestern Alberta to 87 to 167 in central Alberta (shown as sites 1 to 4 on Fig. 1; data given in Table 1 and illustrated on Fig. 2). These results fall within the ranges given by Davis et al. (2004).

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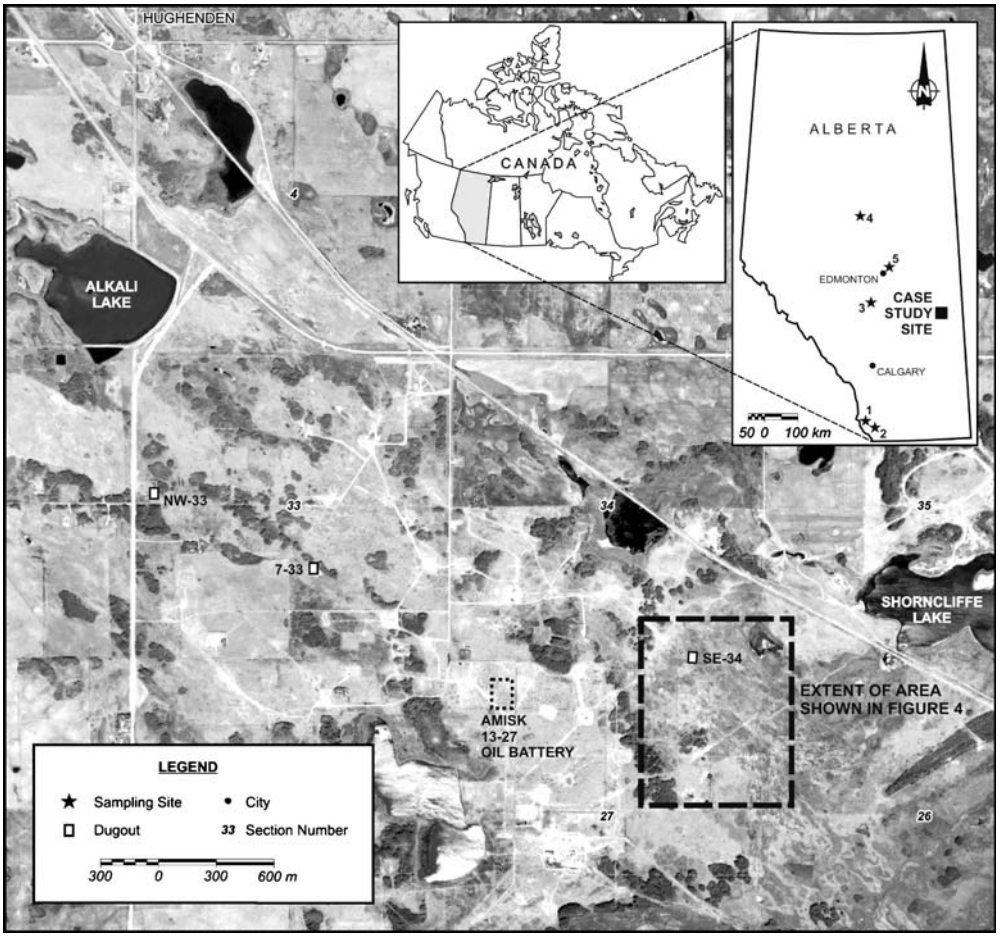


Fig. 1 Alberta (province *shaded in grey*) and case study site location map

Western Canadian Sedimentary Basin (WCSB) brines

As the author has been involved in a compendium of Cl and Br concentrations in brines from the WCSB which is intended to be published separately, a comprehensive evaluation of these data is not attempted in this study. However, several relevant points about the Br and Cl geochemistry of brines in sedimentary basins will be mentioned here:

- A "seawater evaporation trajectory" (S-E-T) has been defined as an index for formation waters in sedimentary basins worldwide using cross plots of Cl and Br concentrations (Carpenter 1978). The S-E-T is shown on Fig. 2. On the S-E-T, the ratio of Cl to Br remains constant (about 300) as seawater evaporates and becomes increasingly enriched, until the resulting brine becomes gypsum-saturated, at which point the Cl/Br mass ratio drops slightly to 270. Halite precipitation occurs at Cl≈180,000 mg/L and Br≈1,000 mg/L, and the Cl/Br mass ratio in the residual water decreases sharply as Cl is incorporated into halite. Finally, when the Br concentration of the residual solution reaches 224,000 mg/L, the Cl/Br mass ratio increases slightly as the precipitation of potassium salts occurs (Carpenter 1978).
- Brines from most formations in the WCSB plot on, or close to the S-E-T. Based on an analysis of Cl/Br mass ratios, it was interpreted that most brines in the WCSB were formed by the evaporative concentration of seawater, or by the mixing of these brines with fresh waters. The most concentrated brines in the WCSB, from Saskatchewan salt formations, show evidence of having undergone halite precipitation, but it is suggested that there are very few brines in the rest of the WCSB that have geochemical evidence of halite dissolution (J.T. Freeman, Matrix Solutions Inc. and K. Rakhit, Rakhit Petroleum Consulting Ltd., unpublished data, 2005). This finding is in contrast to other sedimentary basins in which natural salt-dissolution brines are more common (e.g. Richter et al. 1993; Whittemore 1995).

Salt-dissolution brines in western Canada

Since the 1950s, it has been a common practice in the WCSB to store petroleum products in underground storage caverns, constructed in salt-rich geological formations. In Alberta, salt units within the Middle Devonian-aged Elk Point Group are often used for these storage caverns. The constructing of these caverns is typically initiated by locating a source of water for the cavern construction, or "washing", process (Fig. 3a). Fresh sur-

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Table 1 Bromide and chloride concentrations in all samples

Site	Sample Point	Sample Depth (m)	Sample Date	Cl mg/L	Br mg/L	Cl/Br Mass ratio
Site 1	Spring	Surface	3-Oct-05	0.6	0.006	100
Site 2	Shallow farm well	3.8–9.2	10-Oct-05	4.7	0.059	80
Site 3	Shallow monitoring well	18.4–19.8	12-Oct-05	6.6	0.076	87
Site 4	Shallow monitoring well	6.0–7.5	13-Oct-05	4.5	0.027	167
Site 5	Recovery trench	3–4	10-Oct-05	43,000	5	8,600
	North pond	Surface	10-Oct-05	152,000	6.2	24,500
	South pond	Surface	10-Oct-05	161,000	2.2	73,200
Case study site (monitoring wells unless otherwise indicated)	02-1a	1.5–4.5	8-Nov-05	3,880	0.83	4,675
	02-1b	7.5–9.0	8-Nov-05	3,830	0.825	4,642
	02-2	2.2–5.2	8-Nov-05	7,170	1.85	3,876
	02-3	1.5–3.0	8-Nov-05	672	0.19	3,500
	02-4	2.0–5.0	8-Nov-05	919	2.6	353
	03-1	12.0–15.0	8-Nov-05	244	0.277	881
	03-2	12.5–15.5	8-Nov-05	3,250	2.81	1,157
	03-3	10.8–13.8	8-Nov-05	2,820	0.61	4,623
	03-4	1.6–3.1	8-Nov-05	4,510	0.74	6,095
	03-5	1.6–3.1	8-Nov-05	483	0.116	4,164
	03-6	7.9–10.9	8-Nov-05	4,720	0.98	4,816
	03-7	1.5–6.0	8-Nov-05	422	0.292	1,445
	SE-34 dugout	Surface	12-Feb-04	5,190	1.12	4,634
	SE-34 dugout	Surface	8-Nov-05	1,800	0.34	5,373
	Shorncliffe Lake	Surface	8-Nov-05	1,420	0.325	4,369
	Alkali Lake	Surface	8-Nov-05	15,200	3.2	4,750
	Amisk 13-27 oil battery	Separator	21-Oct-03	51,200	188	272

face water is often used for washing. The fresh water is pumped into the salt formation using an injection well. This water dissolves the salt and is removed to be replaced by fresher water, thus progressively forming a (typical 40,000–50,000 m^3) cavern in the formation. Once the cavern has been constructed, the saline wash water is often retained on the ground surface and used to displace the stored hydrocarbons as these products are removed for sale, and pumped back to the ground surface as the petroleum products are injected into the caverns. This can be performed using two wells, as shown on Fig. 3b, or the injection/extraction of the liquids can be conducted within a single well bore containing different-sized casing strings (L. Stringer, KEYERA Energy, personal communication, 2005). The brines that result from washing out the salt caverns are essentially salt-dissolution brines.

Due to the fact that the salt-dissolution brines are typically made by the dissolution of halite into relatively fresh water, these brines are characterized by very high Cl and very low Br concentrations. Composite pond samples from a cavern storage facility in central Alberta (site 5; Fig. 1) constructed into the Elk Point Group contained Cl concentrations above 130,000 mg/L (Table 1). In addition, the concentration of Br in these waters was low relative to the S-E-T, resulting in elevated Cl/Br mass ratios, in excess of 20,000 (Fig. 2; Table 1).

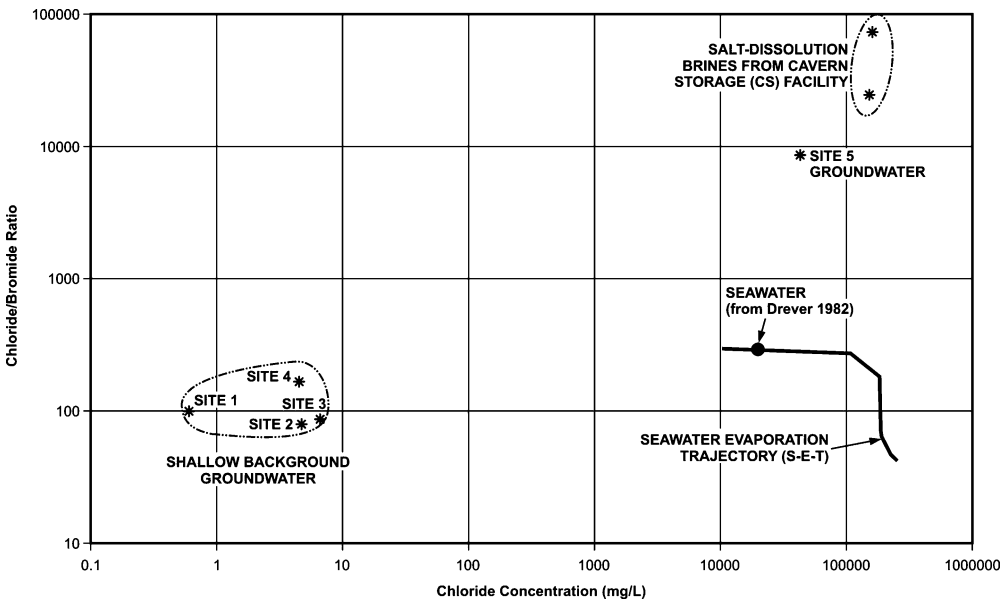


Fig. 2 Cl/Br ratio vs. Cl concentrations, from seawater, the background groundwaters (sites 1–4) and the cavern facility (site 5) samples shown relative to the seawater evaporation trajectory (S-E-T) of Carpenter (1978). The seawater point is from Drever (1982)

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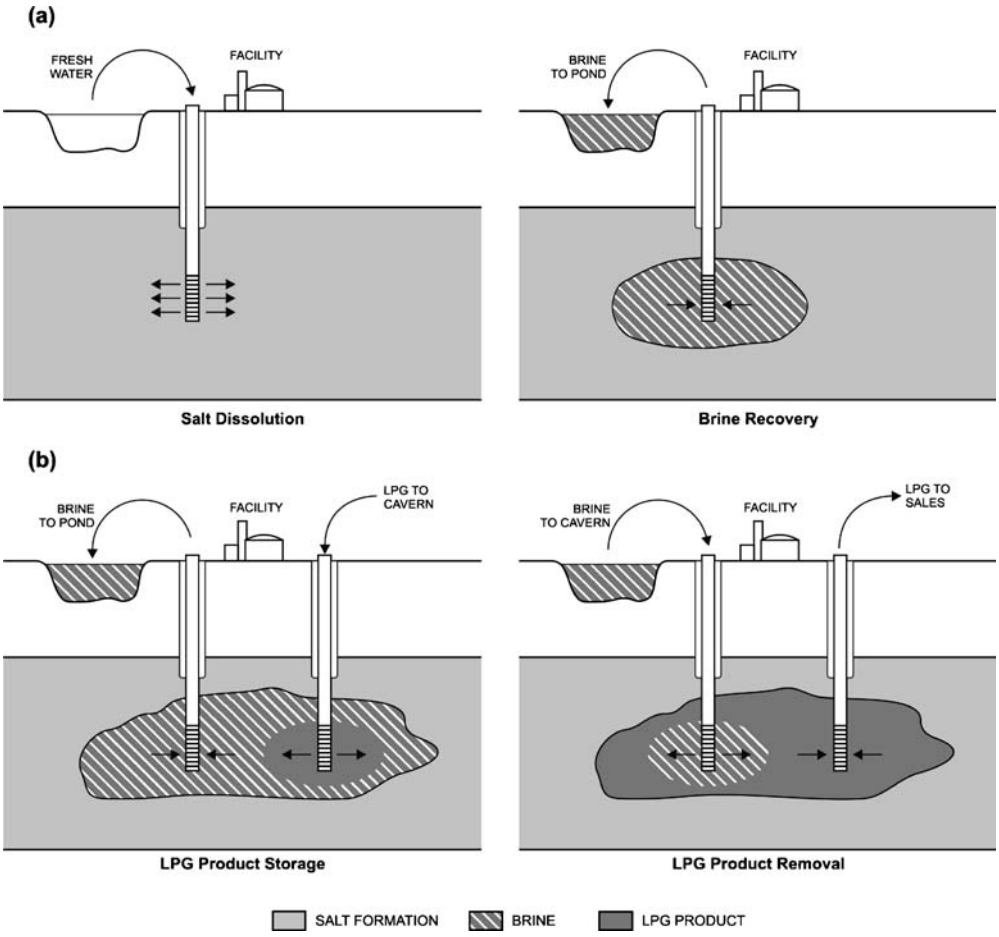


Fig. 3 Schematic of **a** salt cavern washing process, and **b** product storage operations. *LPG* liquefied petroleum gas

Cavern storage facility operations in western Canada are now closely regulated and modern environmental guidelines prescribe that cavern-washing brines are stored in constructed ponds with engineered liner systems. However, this was not always the case. Historical cavern storage facilities often stored brines in unlined ponds or even nearby natural sloughs. At site 5 (Fig. 1), shallow groundwater beneath the brine ponds was impacted by the cavern brines prior to the installation of an engineered liner system. Currently there is an active groundwater recovery trench installed in the shallow subsurface downgradient of the pond. A sample from the trench indicated a dilute pond brine, with a Cl concentration of 43,000 mg/L, and a Cl/Br mass ratio of 8,600 (Table 1).

The apparent reduction of the Cl/Br mass ratio with dilution from the stored brine into shallow groundwater may be due to the introduction of Br from organic matter in the soil. Cl/Br mass ratios are very low in organic material and Br can be preferentially released into groundwater (Davis et al. 1998). However, the Cl/Br mass ratios of both the stored salt-dissolution brines and the impacted shallow groundwater at site 5 are much higher than seawater and the associated S-E-T. Due to the relatively conservative nature of both Cl and Br, analysis of the ionic concentrations and determination of Cl/Br mass ratios have the potential to become important tools for determining the origin of spilled brines in the WSCB.

Case study: pipeline spills near a historical cavern storage facility

Background

From the late 1950s to the mid 1980s, a cavern storage facility was operated in central Alberta. The oldest wells at this site (1958) were licensed as liquefied petroleum gas (LPG) storage wells and were used to construct several caverns into the Prairie Evaporite Formation within the Elk Point Group. In this area, the Prairie Evaporite Formation is predominantly halite (Mossop and Shetsen 1994; Bachu et al. 1993). The caverns were constructed with fresh water taken from Shorncliffe Lake and the wash water was pumped into a natural slough called Alkali Lake. Both water bodies are located near the facility, as shown on an aerial photograph of the case study site (Fig. 1).

Despite the wash water having been placed in Alkali Lake several decades previously, Cl concentrations in the slough were still extremely high (>15,000 mg/L) when measured in the early 2000s, suggesting that it still contained a significant proportion of wash water from the original cavern washing process. Geophysical and hydrogeological studies previously conducted in the area (Beneteau et al. 2003) had indicated that a highly saline, dense plume had entered the shallow groundwater system from the slough and migrated in a shallow, coarse-grained

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glaciofluvial channel at least 2.4 km to the southeast, in the direction of groundwater flow. However, these studies also concluded that a low-permeability barrier to plume migration existed, which limited the lateral movement of salts in the groundwater. Nevertheless, sampling data from an Alberta Lakewatch program (McEachern 2000) had detected unusually high (around 1,000 mg/L) Cl concentrations in Shorncliffe Lake. There are no natural brine springs in this region of Alberta.

In the same area, there is a large amount of conventional heavy oil production. This production is focused on pools located within the Upper Cretaceous-aged Mannville Group. A substantial amount of formation water is produced with the oil, with the average "water cut" for wells in the vicinity of the case study site at more than 98.9% (Alberta Energy Utilities Board data for June 2003). This water is separated from the oil at centralized oil battery facilities and is injected back into the producing zones. Thus, a large volume of brines originating from the Mannville Group are handled on a continuous basis by the local oil industry in pipelines, at batteries and through injection wells. Some of this brine has been lost into the environment due to pipeline breaks and other spills.

One of the local oil producing companies had had several documented pipeline breaks in the area. In early 2002, a livestock producer located near two of these spills (occurring in 1992 and 1998; indicated on Fig. 4, an illustration showing a portion of the case study site) reported a salinity problem in a dugout (the SE-34 dugout). This dugout contained total dissolved solids (TDS) concentrations of 8,000 mg/L, which was well in excess of the Canadian livestock watering guideline of 3,000 mg/L (Canadian Council of Ministers of the Environment (CCME) 2002). The predominant ions in the livestock dugout were sodium (Na) and Cl, suggesting a brine source (Table 2). Cl concentrations in the dugout had fluctuated with rainfall conditions, ranging from 1,800 mg/L in November 2005 to 5,190 mg/L in February 2004. The oil company was asked by a provincial regulatory body, Alberta Environment, to investigate the salinity issue in the SE-34 dugout on behalf of the landowner.

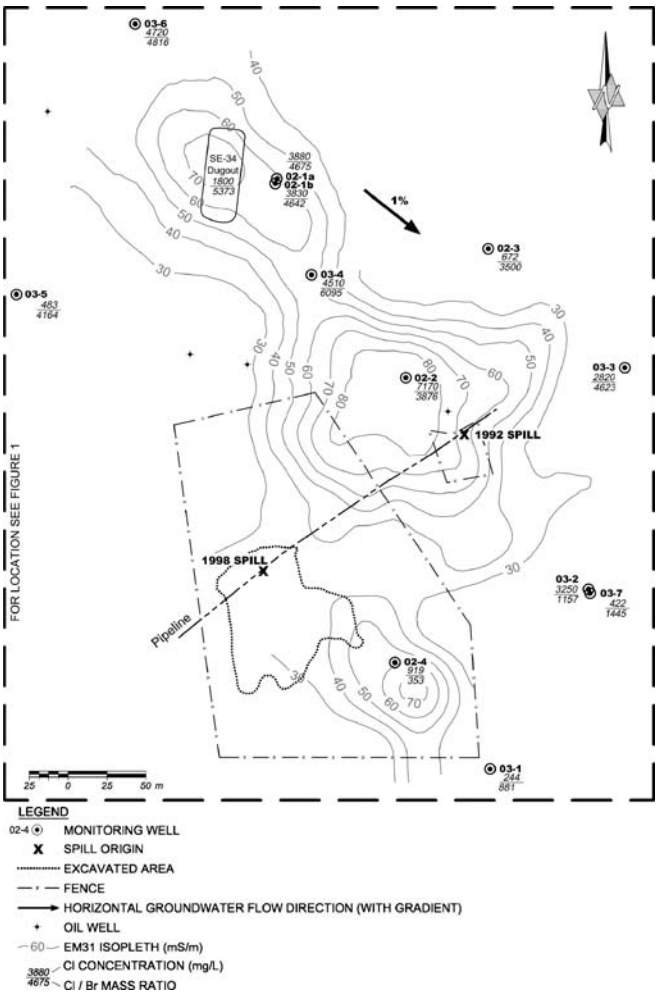


Fig. 4 Electromagnetic (EM31), Cl and Br results for the case study site

Field investigation

An electromagnetic (EM) survey was conducted across the known pipeline spills and the dugout area using a Geonics EM31 ground conductivity meter. The EM31 survey identified conductivity anomalies in the vicinity of the known 1998 pipeline spill, but there were also two anomalies northwest of the 1992 spill, including one in the vicinity of the SE-34 dugout (Fig. 4). Based on the results of the EM survey, twelve monitoring wells were installed in August 2002 and October 2003. The drilling program encountered relatively permeable glaciofluvial sands interbedded with clays and silty clays in the upper 5–15 m depth, with measured hydraulic conductivity values between 4×10^{-8} m/s (well 02-1b) and 5×10^{-5} m/s (well 02-1a). Contoured groundwater elevations indicated that groundwater flowed toward the southeast with a horizontal hydraulic gradient of 0.01 (Fig. 4). The horizontal groundwater flow direction indicated that the SE-34 dugout (and associated EM anomaly) was hydraulically upgradient of the pipeline spills.

Groundwater samples were collected and analyzed from the site monitoring wells and a number of local surface water bodies (Table 1). Notable was the fact that the minimum Cl concentration found at the site was near 200 mg/L (03-1) while the rest of the wells, including wells upgradient of the SE-34 dugout, had Cl concentrations in excess of 1,500 mg/L (Fig. 4). The expected background Cl concentration for overburden groundwater would be well below 50 mg/L, based on the author's experience in the area.

It was decided to examine the differences between Cl/Br mass ratios in order to explain the elevated Cl concentrations in the surface water bodies and monitoring wells. The extremely high Cl concentrations in the groundwater were considered unlikely to be the result of evaporative concentration alone, and the fact that there were both formation water and salt-dissolution brine

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Table 2 Routine potability analysis at SE-34 dugout

Parameter	Units	Value	Guideline	Source of guideline
Laboratory pH	pH units	7.93	6.5–8.5[(ao)]	[a]
Laboratory EC	µS/cm	12,700	–	NS
Na	mg/L	1,860[e]	200[(ao)]	[a]
K	mg/L	78.2	–	NS
Ca	mg/L	297	1,000	[b]
Mg	mg/L	545	–	NS
SAR	Ratio	14.81[e]	4/9[f]	[d]
Fe	mg/L	0.22	5	[c]
Mn	mg/L	0.22[e]	0.2[(ao)]	[c]
Cl	mg/L	4,370[e]	100–700	[c]
CO_3	mg/L	<0.5	–	NS
HCO_3	mg/L	369	–	NS
SO_4	mg/L	702	1,000	[b]
NO_2+NO_3–N	mg/L	0.038	100	[b]
TDS	mg/L	8,030[e]	3,000	[b]

Notes:

NS not specified; *ao* aesthetic objective; *SAR* sodium adsorption ratio

[a] Summary of Guidelines for Canadian Drinking Water Quality (Health Canada 2004)

[b] Livestock water guideline, Canadian Water Quality Guidelines for the Protection of Agricultural Uses (Canadian Council of Ministers of the Environment (CCME) 2002)

[c] Irrigation water guideline, Canadian Water Quality Guidelines for the Protection of Agricultural Uses (Canadian Council of Ministers of the Environment (CCME) 2002)

[d] Irrigation guideline from American Society of Civil Engineers (ASCE) 1996

[e] Exceeds guideline

[f] *4* limited; *9* unacceptable

sources in the area was thought to provide the most likely explanation for this phenomenon.

Br and Cl concentrations were measured for the monitoring wells, the dugout and a sample of "produced" water from a nearby oil battery (Amisk 13–27). The produced water, from the McMurray Formation within the Mannville Group, had a Cl concentration of 51,200 mg/L and a Cl/Br mass ratio of 272 (Table 1). Since this is similar to the Cl/Br mass ratio of seawater (292), the sample plots virtually on the S-E-T ("Mannville Brine", Fig. 5). This result is typical of the 370 Mannville Group samples that were compiled in the Rakhit study (J.T. Freeman, Matrix Solutions Inc. and K. Rakhit, Rakhit Petroleum Consulting Ltd., unpublished data, 2005).

The chemistry of the original cavern wash water is unknown, but a sample taken from the wash water disposal slough located near the cavern storage facility (Alkali Lake; Fig. 1) indicated a Cl/Br mass ratio of 4,750. While less than the Cl/Br mass ratios observed at site 5, the other cavern facility in central Alberta, this water still plotted well above the S-E-T (Alkali Lake; Fig. 5).

In order to highlight a discussion about the site groundwater samples, several theoretical mixing lines were estimated by calculating Cl and Br concentrations, from 100 to 0% mixtures of each end member considered. For the mixing lines shown on Fig. 5, three different end members were used:

A. Produced water from the Mannville Group (Mannville Brine)
B. The slough containing the cavern wash water (Alkali Lake)
C. A shallow background groundwater sample from central Alberta (site 4)

In addition, mixing zones were defined, around each mixing line, in order to represent some of the uncertainty associated with mixing calculations. Specific mixing zones were estimated by using the extremes of the stated uncertainty ranges for the analytical methods, as well as the highest and lowest values from the range of concentrations in two sample populations: the shallow background groundwater samples and the cavern storage (CS) waters from site 5.

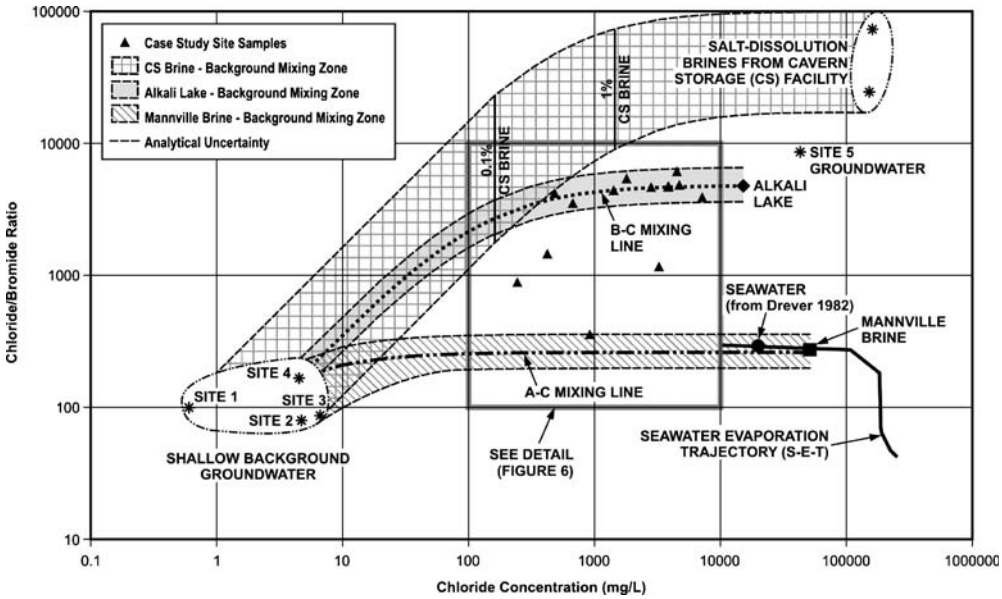
A theoretical mixing zone between the CS brines and the shallow background groundwater is shown as a checkered pattern on Fig. 5. This mixing zone is clearly distinct from the mixing zone estimated by the theoretical mixing of Mannville brine (A) and that of the background shallow groundwater samples, shown as a hatched area around the A-C mixing line on Fig. 5. The A-C mixing zone should illustrate the dilution of Mannville brine into a central Alberta background groundwater. The trajectory of this mixing line is similar to the S-E-T (Fig. 5).

If one plots a mixing line between Alkali Lake water (B), and a single background water sample (C), the resulting trajectory represents the dilution trend of the Alkali Lake salt-dissolution brine into fresh groundwater. This mixing zone (shaded on Fig. 5), does not correspond to the CS brine-background mixing zone, deviating from it at about the 0.1% CS brine concentration isopleth (Fig. 5). The Alkali Lake sample, like the site 5 groundwater sample, is Br-enriched relative to the CS brine samples from site 5 and would form a separate mixing zone when mixed with background groundwater. Like the CS brine-background mixing zone, the B–C mixing zone is divergent from the Mannville brine-background groundwater (A–C) mixing zone.

Data from most of the monitoring wells and surface water bodies in the case study site plot close to the Alkali Lake-background groundwater (B–C) trajectory as shown on Fig. 6, an enlargement of the center portion of Fig. 5. Monitoring wells such as 03–5 and 03–6, which are upgradient of the SE-34 dugout, and several of the other wells, particularly those with Cl/Br mass ratios in excess of 3,000, plot directly within the B–C mixing zone, indicating that the elevated Cl concentrations in the site groundwater resulted from mixing of fresh groundwater and water that has migrated from a salt-dissolution brine source.

Points falling in the region in between the A–C and B–C mixing zones on Fig. 6 are interpreted to have been contaminated by the salt-dissolution brine, and would have originally plotted near the B–C mixing zone, but were subsequently impacted by formation water, which caused

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these waters to plot closer to the A–C mixing zone. On Fig. 6, the relative proportions of mixing between water on a salt-dissolution dilution trend and formation waters have been indicated by theoretically mixing Mannville brine (A) with different points along the B–C trajectory and then contouring these data. Monitoring wells 02-4 and 03-2 are directly downgradient of the known pipeline spills (Fig. 4) and are interpreted to contain more than 1% Mannville brine. Monitoring wells 02-2, 03-2 and 03-7 are also interpreted as having been potentially impacted by the formation water, although these samples are believed to contain less than 0.3% Mannville brine (Fig. 6).

The SE-34 dugout and Shorncliffe Lake samples also plot very close to the salt-dissolution brine dilution trend

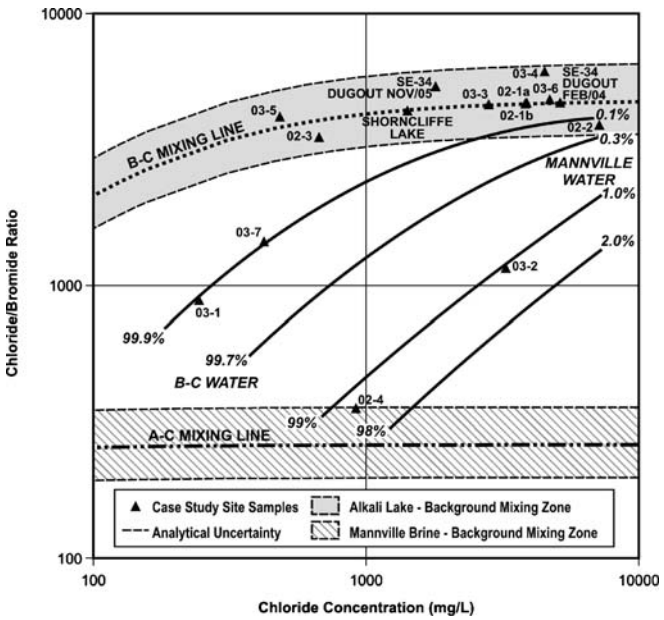


Fig. 6 Enlargement of the Cl/Br ratio vs. Cl concentration cross plot shown on Fig. 5. Data for dugout SE-34 were acquired during February 2004 and November 2005

(B–C mixing line) with the majority of the monitoring wells (Fig. 6). It is interpreted that monitoring wells 02-1a/b and 02-2 and the SE-34 dugout are located in a local groundwater discharge area, where salt constituents sourced from Alkali Lake are near the ground surface. The SE-34 dugout may act as a groundwater sink within this discharge area. Shorncliffe Lake is also believed to have received discharge from this regional salt-dissolution groundwater plume. Thus, the Cl and Br concentrations and Cl/Br mass ratios suggest that there is a large body of surface water and groundwater in the area that has been affected by salt constituents originating from Alkali Lake, which was used for disposal of the salt-dissolution brine used for cavern washing.

Theoretically, because the evaporative-transpirative potential in this portion of Alberta is relatively high, it is possible that the variation in Cl concentrations could derive from the evaporation of water at the case study site. In areas of western Canada and elsewhere where salts are concentrated through evaporation, sulphate (SO_4) and Cl concentrations typically increase proportionally, at least to the point of gypsum saturation (e.g. Whittemore 1995). In these wells however, the SO_4 concentrations of the groundwaters tended to be similar, with a decrease in SO_4/Cl mass ratios noted as the Cl concentration of the groundwaters increased (Table 1).

Conclusions

Across North America, Cl concentrations and Cl/Br mass ratio relationships can be used to characterize the origins of various groundwaters. In precipitation and shallow groundwaters in Alberta, concentrations of both ions are low and the expected Cl/Br mass ratio is around 100, whereas formation waters produced from the WCSB are predominantly Na-Cl waters and can be extremely saline, with Cl concentrations greater than 10,000 mg/L. As

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shown in the Rakhit study (J.T. Freeman, Matrix Solutions Inc. and K. Rakhit, Rakhit Petroleum Consulting Ltd., unpublished data, 2005), many of the formation brines in the basin have Cl and Br concentrations that fall close to the S-E-T defined by Carpenter (1978) and have Cl/Br mass ratios of about 300.

The underground storage of petroleum products in man-made salt caverns has resulted in production of geochemically distinct salt-dissolution brines in the WCSB. These brines are made by using relatively fresh water to dissolve halite salts in deep geological formations, typically within the Devonian-aged Elk Point Group. The resulting brines also have high Cl concentrations, but have very low Br concentrations and Cl/Br mass ratios in excess of 20,000.

In cases where salt constituents in groundwater may have come from either a formation or salt-dissolution brine source, Cl/Br mass ratios and cross-plots can help to determine the origin of these ions. This approach has been previously presented in the literature by several authors, who have discussed the delineation of salt-dissolution brines from sources other than cavern-washing such as road salt, water softeners or formation waters that have undergone salt dissolution (e.g. Richter et al. 1993; Whittemore 1995).

At the case study site, located in central Alberta, Canada, a dugout contained elevated Cl concentrations that could have potentially derived from either an upgradient slough that was used for historical disposal of a cavern wash water (a salt-dissolution brine) or nearby pipeline spills involving formation brine from the Mannville Group. Several of the monitoring wells downgradient of the spills showed evidence of a formation brine dilution influence (up to about 1%), but given that the Cl/Br mass ratio of the dugouts and the monitoring wells upgradient of the pipeline spills were typically 3,000 or higher and also plotted directly on a salt-dissolution brine dilution trend, it can be concluded that salt constituents in the dugouts were sourced from the cavern wash water disposal slough rather than the pipeline spills or evaporative concentration. Unusually high Cl concentrations (>1,000 mg/L) in Shorncliffe Lake, located about 900 m east of the site, also appear to be geochemically indicative of a salt-dissolution brine source, which suggested that a widespread area has been contaminated by brine constituents from the cavern wash water disposal slough.

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