Groundwater nitrate and chloride trends in an agriculture-intensive area in southern Alberta, Canada
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ABSTRACT
The potential effect of manure management from livestock production on groundwater quality is an issue of concern. Groundwater sampling from a regional transect in southern Alberta, Canada, was conducted to determine changes in groundwater quality with time. The study area has extensive irrigation and a high density of confined feeding operations. Nitrate-N (NO₃⁻/N) and chloride (Cl⁻) concentration data from 23 groundwater-study wells were evaluated from 1994 to 2014. Twelve of these wells were water-table wells and 11 were piezometers. Of the 23 wells, 14 had significant temporal trends (increasing or decreasing) for NO₃⁻-N and/or Cl⁻ concentrations. On a regional basis, NO₃⁻-N increased slightly with time while Cl⁻ changed very little, suggesting that the effects of agricultural activities on regional groundwater quality have generally remained constant. However, concentration changes occurred on a smaller scale. Shallow groundwater in coarse-textured soils is at a relatively higher risk of contamination than groundwater in fine-textured soils, especially in locations where intensive agricultural activities occur.

Key words | agriculture, chloride, confined feeding operations, groundwater quality, spatial and temporal trends, nitrate

INTRODUCTION
Groundwater contamination and associated water quality remains a concern worldwide for environmental and human health issues (Olson et al. 2005; McCallum et al. 2008; Kaown et al. 2012). Sources of anthropogenic nitrate (NO₃⁻) and chloride (Cl⁻) are typically found at or near the land surface, with concentrations typically greater near the top of the water table and decreasing with depth. In agriculture-intensive areas, contamination of shallow groundwater by manure sources may occur as a result of manure collection and storage areas and manure spreading in fields (Rodvang & Simpkins 2001; McCallum et al. 2008).

Nitrate and Cl⁻ are highly mobile anionic species, and when elevated concentrations of these parameters occur in groundwater as the result of agricultural activities, their concentrations are typically correlated with the magnitude and extent of manure use and soil infiltration. Therefore, NO₃⁻ and Cl⁻ are often used as indicators of manure contamination in groundwater (Maulé & Fonstad 2000; Lorenz et al. 2014). Although NO₃⁻ has been used as an indicator of groundwater contamination by manure, NO₃⁻ is non-conservative because it can be attenuated during groundwater transport, e.g., by denitrification processes in the presence of appropriate bacteria and restricted O₂ availability.

Nitrate-N (NO₃⁻-N) generally occurs naturally at low concentrations in groundwater, and concentrations > 3 mg L⁻¹ are considered to be derived from anthropogenic sources (Madison & Brunett 1985). However, naturally high concentrations of NO₃⁻ in groundwater, i.e., geologic NO₃⁻, can be found in oxidized till and fine lacustrine sediments in southern Alberta (Hendry et al. 1984; Rodvang &
Simpkins 2001; Rodvang et al. 2002). Irrespective of the source, the maximum acceptable concentration for NO$_3$-N in drinking water is 10 mg L$^{-1}$, as established by the Federal-Provincial-Territorial Committee on Drinking Water (Health Canada 2014), to be protective of the health of the most vulnerable consumers, who are infants under 6 months of age or adults with abnormal stomach enzymes, from developing methemoglobinemia.

Chloride, which typically does not undergo biological transformations or sorb to soil, and travels at the same rate as groundwater (Wang et al. 2000), has widely been used as a conservative tracer to indicate potential groundwater contamination by manure (Maulé & Fonstad 2000; Rodvang et al. 2004; Olson et al. 2005; McCallum et al. 2008). Shallow groundwater with Cl$^-$ concentrations >10–20 mg L$^{-1}$ has generally been considered contaminated by anthropogenic sources in Alberta (Forrest et al. 2006; Lorenz et al. 2014).

Correlations between NO$_3$-N and Cl$^-$ concentrations suggest that concentrations in water may be potentially derived from the same source. Normally, when both parameters are increasing, it could be assumed that manure is a source. If Cl$^-$ increases but NO$_3$-N does not increase, manure could be a potential source assuming that attenuation (e.g., denitrification) is occurring or that equilibrium in the system has been reached for NO$_3$-N.

Rodvang et al. (2004) reported high concentrations of NO$_3$-N and Cl$^-$ in shallow groundwater in an area of intensive irrigation and a high density of confined feeding operations (CFOs) in southern Alberta. The study was carried out in the 1990s and early 2000s, and based on isotope analysis and land-use practices, it was concluded the NO$_3$-N originated from geologic and agricultural sources. The presence of relatively high Cl$^-$ in some locations suggested the origin of contamination was from manure. For sites located near highly intensive agricultural land use in the study area, Rodvang et al. (2004) observed an increase in NO$_3$-N and Cl$^-$ concentrations with time in coarse-textured fluvial and lacustrine sediments. They found that average NO$_3$-N and Cl$^-$ concentrations increased from 12.5 to 17.4 mg L$^{-1}$ and from 19.4 to 34.4 mg L$^{-1}$ during the 6-year period, respectively. In the areas of low-intensity agriculture (i.e., pasture or native range), they found lower average concentrations of both parameters in the shallow groundwater, with no significant change with time, although concentrations did significantly increase in some individual wells.

The current study re-activated groundwater monitoring in the same area previously studied as per recommendations for long-term monitoring of groundwater quality to document potential changes with time (Rodvang et al. 1998). The objective of this study was to provide 6 years of additional data to further evaluate spatial-temporal trends of NO$_3$-N and Cl$^-$ concentrations in groundwater in this agriculture-intensive area in southern Alberta. Land-use practices related to manure production and application have likely decreased in the past 10 years in Alberta because of reduced cattle numbers, so it was hypothesized that groundwater quality may have improved during the 20-year span of the historical and current monitoring periods, from 1994 to 2014.

**METHODS**

**Study area**

The study area was located near Picture Butte, Alberta, Canada, in the eastern portion of the Lethbridge Northern Irrigation District, referred to as the Battersea area (Figure 1). The Battersea area has the highest density of livestock in Alberta and 82% of the land base is irrigated (Rodvang et al. 2004). The study area has previously been described by Rodvang et al. (2002, 2004). The stratigraphy of the Battersea area can be divided into two physiographic regions: (1) a bedrock high in the northwest and (2) a lacustrine basin in the southeast. The bedrock is overlain by glacial till, which in turn is overlain by fine- to coarse-grained glaciolacustrine deposits, which can consist of up to 15 m thick homogenous silty clay material at lower elevations (Rodvang et al. 2002, 2004). The study area is in the Mixedgrass Natural Subregion, and soils in the area are Orthic Dark Brown Chernozem (Typic Haploboroll) soils. The fine-textured glaciolacustrine sediments are overlain by fine- and medium-textured lacustrine sand deposits along the western and northern portions of the study area, and by coarse- to fine-grained lacustrine and fluvial sand in the eastern portion of the study area. The coarse-grained
surficial sand deposit increases in thickness towards the eastern portion of the study area, constituting an unconfined aquifer, which has been used as a water supply in the area since 1920 (Rodvarg et al. 2002).

The general climate at the study area is represented by 30-year mean monthly temperatures that range from 18.2°C (July) to −6.0°C (January) (Environment Canada 2015). The mean annual precipitation is approximately 400 mm, with 225 mm occurring during the growing season from May through August (ARD 2014). Additional water for crops in the area is provided by an extensive irrigation system.

The ground-surface elevation at the wells ranged from 948 to 854 m above sea level (masl). Mean water-table measurements ranged from approximately 1 (LB7-2) to 7 m (LB19-2) below ground surface (mbgs) throughout the study area, corresponding to approximate mean elevations of 865 masl and 853 masl, respectively. Based on previous hydraulic head measurements for groundwater levels at the wells, groundwater flow direction was determined to be from the northwest to southeast in the study area, towards the Oldman and Little Bow Rivers (Lorenz et al. 2014).

A regional groundwater monitoring transect of 115 wells (water-table wells and piezometers) was installed in 1993 and 1994 and sampled from 1994 to 2001 by Rodvarg et al. (1998, 2002). Installation details of these wells have been previously reported by Rodvarg et al. (1998, 2002). The transect was initially selected to represent a cross-section of geologic, hydrogeologic, and anthropogenic conditions within the area. Individual groundwater wells were located next to farms, cultivated fields, CFOs, and pastureland.

From 2009 to 2014, 44 of the original wells were reactivated, and 23 were selected for statistical trend analysis in the current study. Well selection was based on location within the Battersea area and the availability of historical (1994–2001) and current (2009–2014) data (Table 1). One of these 23 wells was damaged and was re-installed in 2010.

The 23 wells were located at 12 sites (Figure 1), where at each site either a single water-table well was used or a water-table well plus one or three piezometers were used (Table 1). The wells were arranged along a west–east transect, and the furthest west well (LB2-1) was approximately 17 km from the furthest east well (LB19-2).

The groundwater wells in the Battersea area were installed and categorized into three main geologic groups: till and fine lacustrine, medium lacustrine, and shallow
coarse lacustrine textured deposits. In this paper, ‘coarse’ refers to all shallow coarse-textured lacustrine deposits, ‘medium’ refers to the medium-textured deposits, and ‘fine’ refers to the till and fine lacustrine deposits.

Twelve of the 23 wells were water-table wells, with 3 m long screened intervals and ranged in depth from 2.29 to 7.25 mbgs. Eleven of the 23 wells were piezometers with variable screen (from 0.5 to 1 m) and sand pack lengths (Table 1). The total depth of piezometers ranged from 1.77 to 18.94 mbgs.

Land use on well property is summarized in Table 1. Livestock were only in CFOs, and the vast majority of the land was used for crop production. Up-gradient land use may also impact groundwater quality, and it has been included in Table 1.

### Groundwater sampling and analysis

A total of 583 groundwater samples, collected from the 23 wells, were used for statistical analysis. Groundwater
samples were collected from each well either once or twice per year from 1994 to 2001 (Rodvang et al. 2004) and monthly to three times per year from 2009 to 2014. Sampling occurred in the spring pre-irrigation, in the summer during irrigation, and in the fall after irrigation was done for the season. Purging and sampling of wells from 1994 to 2001 has previously been described (Rodvang et al. 2002, 2004). From 2009 to 2014, wells were purged prior to sample collection by removing at least three well volumes using an inertial pump or polyethylene bailer. Once wells recharged, samples were collected, stored at volumes using an inertial pump or polyethylene bailer.

For concentrations of NO$_3$-N (quantitative determination of nitrate and nitrite by air-segmented continuous flow-analysis; APHA et al. 1995) and Cl$^-$ (quantitative determination of chloride based on potentiometric titration of H$_2$O$_2$; APHA et al. 1995). Samples were analyzed by the Alberta Agriculture and Forestry (AF) lab, and quality control/quality assurance protocols were followed for each batch of analysis (APHA et al. 1995). More than 90% of recovery for certified standards and non-matrix match spiked sample was guaranteed. Laboratory analytical methods for NO$_3$-N and Cl$^-$ were different between the two periods (i.e., 1994–2001 vs. 2009–2014); however, appropriate quality control procedures were carried out to compare methods and ensure data were comparable. A three-step validation process was performed when the new method was adopted (APHA et al. 1995). In addition, the lab used at least 100 samples to run one parameter with two different methods or instruments (regression and Lin’s agreement test) (Lin 1989) before switching to the new method.

**Statistical analyses**

Often it is difficult to assess the presence and significance of trends because of sampling frequency, data gaps, length of monitoring period, and the presence of uncontrolled variables (Stuart et al. 2007). Long-term NO$_3$-N and Cl$^-$ concentration trends were therefore investigated at individual wells using the Mann–Kendall trend test (Time Trends software v3.3, https://www.niwa.co.nz; Ian Jowett, NIWA, New Zealand; Mann 1945; Kendall 1975; Gilbert 1987). The Mann–Kendall trend test is widely used to assess trends in environmental studies, such as concentrations of dissolved chemicals in surface waters and groundwater (e.g., Helsen & Frans 2006; Wassenaar et al. 2006). This non-parametric test evaluates whether variable values tend to increase or decrease with time and does not require an assumption of normality. A non-significant trend may result because there are no trends or because observable trends have opposite directions, i.e., cancelling one another. The magnitude of the trend was estimated using the Sen’s slope estimator (median annual change in concentration, i.e., mg L$^{-1}$ yr$^{-1}$). The trend slopes were also expressed as a percent of the median concentration by dividing the slope by the median and multiplying by 100 (relative trend slopes). Trends were considered significant or not significant only when the data-set for a given well contained nine or more data points. Sample values below the detection limits of the laboratory methods were given a value of zero. Increasing or decreasing trends from 1994 to 2014 were considered significant when $P < 0.05$. Median values for each season were used (four seasons per year: Jan–Mar, Apr–Jun, Jul–Sep, Oct–Dec) for the statistical trend analyses to reduce potential serial autocorrelation. Thus, the influence of autocorrelation and also seasonality was minimal in the trend analyses.

Qualitative assessments were also performed to determine if there were associations between temporal trends in concentration (increasing, decreasing, or no trend) and (1) well concentration being above or below the anthropogenic thresholds (5 mg L$^{-1}$ for NO$_3$-N, 20 mg L$^{-1}$ for Cl$^-$); (2) above or below certain depths (8.3 mbgs for NO$_3$-N, 8.4 mbgs for Cl$^-$); and (3) soil texture (coarse, medium, fine). The 8.3 mbgs for NO$_3$-N and 8.4 mbgs for Cl$^-$ were chosen because below these two depths, NO$_3$-N and Cl$^-$ did not exceed the 3 and 20 mg L$^{-1}$ anthropogenic thresholds, respectively.

Additionally, a principal component analysis (PCA) was carried out to explore potential factors that could explain the variation observed for NO$_3$-N and Cl$^-$ in our study (Pearson 1901) for those wells with a significant trend. In general, PCA can be used to select those variables that...
RESULTS AND DISCUSSION

Median concentrations and spatial distribution

The concentration of NO₃-N for all 583 groundwater samples ranged from less than detection limit (0.05 mg L⁻¹) to a maximum of 127.7 mg L⁻¹ (LB9-7, August 2014), with an overall mean of 18 mg L⁻¹. Median NO₃-N concentrations for individual wells ranged from 0.05 to 74.6 mg L⁻¹ (Table 2). The NO₃-N concentration was greater than the anthropogenic threshold of 3 mg L⁻¹ in 64% of all the samples (n = 374), and 83% of these (n = 310) corresponded with coarse-textured deposits. The median NO₃-N concentration was also greater than 3 mg L⁻¹ in 12 wells (Table 2).

The concentration of Cl⁻ for all samples for the 20-year period ranged from less than the detection limit (5 mg L⁻¹) to about 730 mg L⁻¹ (LB7-2, June 1997), with an overall mean of 58 mg L⁻¹. Median concentrations for the wells ranged from 5 to 232 mg L⁻¹ (Table 2). The Cl⁻ concentrations were greater than the anthropogenic threshold of 20 mg L⁻¹ in 52% of samples (n = 305), and 70% of these (n = 212) corresponded to coarse-textured deposits. Median Cl⁻ concentrations were greater than 20 mg L⁻¹ in nine wells.

Spatial distributions of the medians were explored using ArcGIS 10.1 software. In this study, the highest median concentrations of NO₃-N and Cl⁻ were generally observed in the central part of the study area. Lower NO₃-N concentrations were generally observed in the western portion of the area, with the exception of LB2-1, which had the highest median concentration of NO₃-N (74.6 mg L⁻¹), as well as the highest median concentration of Cl⁻ (231.9 mg L⁻¹) (Figure 2(a)). Previous work suggested that the elevated NO₃-N concentration in LB2-1 was likely of geologic origin, as tritium was not detected (Rodvang et al. 1998).

Relatively low Cl⁻ concentrations were observed in the eastern portion of the study area (Figure 2(b)). Elevated NO₃-N and Cl⁻ concentrations were observed at LB9-2 and LB13-3, characterized by coarse-grained, shallow sediments, and high δ¹⁸O values (greater than −18‰; Turchenek 2004), suggesting relatively younger groundwater with potential effects from manure.

The sensitivity of groundwater contamination to land use has typically been observed to decrease with depth, with studies finding higher concentrations of NO₃-N in shallow wells compared to deeper wells (Forrest et al. 2006). In this study, NO₃-N concentrations were greatest and most variable in relatively shallow wells, screened near the top of the water table, with concentrations and variability decreasing with depth. Elevated NO₃-N concentrations (i.e., >3 mg L⁻¹) were detected in samples collected from depths ≤8 mbgs (Figure 3).

Data from 2010 to 2014 had similar ranges in concentration as previously reported from 1994–2001. The previous work in this area suggested that high NO₃-N and Cl⁻ concentrations were due to agricultural activity, which included a high density of CFOs and manure production and irrigated crops (Rodvang et al. 2004; McCallum et al. 2008; Turchenek 2014). There was also evidence of high NO₃-N concentrations caused by geologic sources (Rodvang et al. 2004). McCallum et al. (2008) also showed that elevated NO₃-N in shallow, young groundwater, as a result of manure application, underwent denitrification when the younger water mixed with deeper, older, and more reduced groundwater.

Temporal changes in concentration

Of the 23 wells, statistical analysis showed that significant temporal trends were observed for concentrations in 10 of the wells for NO₃-N, in 10 of the wells for Cl⁻, and in six of the wells for both parameters. No significant trends were observed in 13 of the wells for NO₃-N (six piezometers and seven water-table wells), 13 of the wells for Cl⁻ (seven piezometers and six water-table wells), and in nine of the wells for both parameters (Table 2). Significant increases in concentration with time were observed in 35% of the wells for NO₃-N (six piezometers and two water-table wells) and in 26% of the wells for Cl⁻ (three piezometers...
Table 2 | Summarized statistics for NO$_3^-$-N and Cl$^-$ concentrations (1994–2014)

<table>
<thead>
<tr>
<th>Texture</th>
<th>Well ID</th>
<th>Well type</th>
<th>Well ID</th>
<th>Well depth (mbgs)</th>
<th>N</th>
<th>1994–2014 mean (mg L$^{-1}$)</th>
<th>1994–2014 median (mg L$^{-1}$)</th>
<th>Overall trend</th>
<th>Sen’s slope (mg L$^{-1}$ yr$^{-1}$)</th>
<th>Relative slope (% yr$^{-1}$)</th>
<th>1994–2014 mean (mg L$^{-1}$)</th>
<th>1994–2014 median (mg L$^{-1}$)</th>
<th>Overall trend</th>
<th>Sen’s slope (mg L$^{-1}$ yr$^{-1}$)</th>
<th>Relative slope (% yr$^{-1}$)</th>
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<td>Fine</td>
<td>LB2-1</td>
<td>WT</td>
<td>5.72</td>
<td>33</td>
<td>70.4</td>
<td>74.55</td>
<td>decrease</td>
<td>–2.09</td>
<td>–2.8</td>
<td>227.8</td>
<td>231.92</td>
<td>decrease</td>
<td>–3.87</td>
<td>–1.7</td>
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<tr>
<td></td>
<td>LB6-6x</td>
<td>WT</td>
<td>4</td>
<td>18</td>
<td>4.70</td>
<td>1.93</td>
<td>ns</td>
<td>–</td>
<td>–</td>
<td>30.8</td>
<td>14.18</td>
<td>decrease</td>
<td>–3.13</td>
<td>–22.1</td>
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<tr>
<td></td>
<td>LB7-2</td>
<td>WT</td>
<td>2.29</td>
<td>35</td>
<td>2.20</td>
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<td>ns</td>
<td>–</td>
<td>–</td>
<td>150.2</td>
<td>74.45</td>
<td>decrease</td>
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<tr>
<td></td>
<td>LB7-3</td>
<td>P</td>
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<td>13</td>
<td>4.38</td>
<td>5.07</td>
<td>increase</td>
<td>0.37</td>
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<td>79.9</td>
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<td>LB13-2</td>
<td>P</td>
<td>11.04</td>
<td>17</td>
<td>0.10</td>
<td>0.05</td>
<td>ns</td>
<td>–</td>
<td>–</td>
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<td>8</td>
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<td>–</td>
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<td>7.83</td>
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<td>–</td>
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<td>4.96</td>
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<td>10</td>
<td>0.04</td>
<td>0.05</td>
<td>ns</td>
<td>–</td>
<td>–</td>
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<td>13</td>
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<td>0.68</td>
<td>ns</td>
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<td>38</td>
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<td>44</td>
<td>6.30</td>
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<td>increase</td>
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<td>3.4</td>
<td>23.9</td>
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<td>50</td>
<td>24.8</td>
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<td>–7.9</td>
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<td>10.78</td>
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<td>LB22-3</td>
<td>WT</td>
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<td>48</td>
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<td>–</td>
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<td>4.2</td>
<td>21</td>
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<td>0.13</td>
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<td>ns</td>
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<td>–</td>
<td>44.9</td>
<td>46.09</td>
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<td>4.72</td>
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<td>LB13-3</td>
<td>P</td>
<td>4.58</td>
<td>50</td>
<td>37.7</td>
<td>34.72</td>
<td>increase</td>
<td>1.97</td>
<td>5.7</td>
<td>53.0</td>
<td>60.27</td>
<td>increase</td>
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<td>3.8</td>
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<td>P</td>
<td>18.94</td>
<td>21</td>
<td>0.20</td>
<td>0.23</td>
<td>increase</td>
<td>0.02</td>
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<td>P</td>
<td>8.26</td>
<td>16</td>
<td>1.20</td>
<td>0.77</td>
<td>increase</td>
<td>0.17</td>
<td>22.1</td>
<td>9.80</td>
<td>10.64</td>
<td>ns</td>
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WT, water-table well; P, piezometer; n, number of the samples; ns, not significant.

*Decreasing and increasing trends were significant at P ≤ 0.05.
Concentrations significantly decreased with time in 9% of the wells for NO₃⁻N (two water-table wells) and in 17% of the wells for Cl⁻ (one piezometer and three water-table wells).

LB2-1, at the western extent of the area, was the only well that had a decreasing trend for both parameters.

Results from the study generally indicated increasing trends for NO₃⁻N and Cl⁻ concentrations in the central and eastern portions of the study area. Three wells (LB9-7, LB11-4, and LB13-3) that displayed increasing trends for NO₃⁻N and Cl⁻ were in the center of the region, where soil texture is relatively coarse and there are potential sources of NO₃⁻. One of these wells was a water-table well and two were piezometers, though all were near the top of the water table (within 4.58 mbgs). In four wells, NO₃⁻N concentrations increased with time and Cl⁻ concentrations remained constant. Stable Cl⁻ concentrations, with increasing NO₃⁻N concentrations, suggests that equilibrium was approached for Cl⁻ or the source has remained the same with time. The trend of increasing NO₃⁻N concentration may indicate that conditions were less favorable for denitrification, as dissolved oxygen concentrations at these wells were higher than the threshold of 0.2 mg L⁻¹ required for denitrification (Rodvang et al. 2002).
Decreasing NO$_3$-N concentration trends may have been caused by reduced source contributions (e.g., reduced manure spreading) or increased denitrification. Wells with observed decreasing trends for both parameters (NO$_3$-N and Cl$^-$) were likely the result of the land-use practices related to manure production and application; a reduction in source contributions, such as less manure application in the area. The opposite is likely for wells with increasing trends for both parameters or for Cl$^-$, suggesting an increase in source contributions or that the effect of residual influences from many years of manure application sustained the level of contamination during the study period.

For wells with observed significant trends, Sen’s slope values, which indicate trend direction and strength, for NO$_3$-N ranged from $-2.09$ mg L$^{-1}$ yr$^{-1}$ (LB2-1) to $3.59$ mg L$^{-1}$ yr$^{-1}$ (LB9-7) (Table 2), with a mean of $0.33$ mg L$^{-1}$ yr$^{-1}$. For Cl$^-$, Sen’s slopes ranged from $-13.5$ mg L$^{-1}$ (LB7-2) to $8.31$ mg L$^{-1}$ yr$^{-1}$ (LB9-7), with a mean of $-0.01$ mg L$^{-1}$ yr$^{-1}$. This suggests that on a regional basis, the NO$_3$-N concentration has increased slightly with time and the Cl$^-$ concentration has changed very little from 1994 to 2014.

The largest positive Sen’s slope values for NO$_3$-N and Cl$^-$ were calculated for LB9-7. This well also had the highest mean NO$_3$-N and Cl$^-$ concentrations in the last sampling year (2014) compared to other wells, with values of $112$ mg L$^{-1}$ and $202$ mg L$^{-1}$, respectively. The largest negative Sen’s slope was calculated for LB2-1 for NO$_3$-N and for LB7-2 for Cl$^-$, Both of these wells were water-table wells in fine-textured material.

Although the Sen’s slope values provide an indication of change with time, care needs to be taken not to use this statistic to extrapolate into the future, as statistical trend extrapolation is not a definitive forecasting tool (Aguilar et al. 2007).

Relative trend slopes for each well ranged from $-7.9$ to $22.1$% yr$^{-1}$ for NO$_3$-N and from $-10.3$ to $22.1$% yr$^{-1}$ for Cl$^-$ (Table 2). LB22-2 had the greatest positive relative slope (22.1% yr$^{-1}$) for NO$_3$-N; however, the median concentration for the 1994–2014 period was relatively low (0.77 mg L$^{-1}$) (Table 2). LB15-1 had the greatest positive relative slope (10.3% yr$^{-1}$) for Cl$^-$. LB15-4 had the most negative relative slope for NO$_3$-N ($-7.9$% yr$^{-1}$) and LB6-6x had the most negative relative slope for Cl$^-$ ($-22.1$% yr$^{-1}$).

Spatial distributions of the trends (relative slopes) were explored using ArcGIS 10.1 software (Figure 4). There were generally more intensive livestock operations and cropping in the central part of the study area, and more rangeland/grazing in the east, therefore most of the trends were expected.

Qualitative assessment showed no consistent relationship between temporal concentration trends and total well depth (Table 3). Significant changes in concentrations of NO$_3$-N and/or Cl$^-$ with time were observed in the shallowest (LB11-4; 1.77 m) and the deepest (LB21-1; 18.94 m) wells (Table 2). As expected, at some nests with multiple wells (LB7 and LB13), significant changes in concentration (increase or decrease) were observed in the shallow wells but not in the deeper wells. In contrast, at nests LB21 and LB22, there was no significant change in NO$_3$-N and Cl$^-$ concentrations with time in the shallowest wells but a significant increase in NO$_3$-N concentration with time in the deepest well at both nests.

For the wells that had significant trends, either increasing or decreasing, more wells had significant trends when the median NO$_3$-N concentration was greater than $3$ mg L$^{-1}$ or when median Cl$^-$ concentration was greater than $20$ mg L$^{-1}$, compared to those wells with a concentration less than these two threshold values. Eight wells for NO$_3$-N and Cl$^-$ had significant trends in concentration with time when median concentrations were greater than the two threshold values, compared to only three wells for NO$_3$-N and two wells for Cl$^-$ when median concentrations were less than the threshold values (Table 3). This suggests that groundwater in wells with high concentrations of NO$_3$-N (i.e., $>3$ mg L$^{-1}$) and/or Cl$^-$ (i.e., $>20$ mg L$^{-1}$) – presumably caused by agricultural activities – had a greater likelihood of changes in concentration with time, either increasing or decreasing, with the former more predominant than the latter. In these cases, where groundwater quality has likely been affected by agricultural activities, increasing and decreasing trends in concentration may be responses to changes in activities such as manure production, for example.

Of the 14 wells screened in coarse-textured deposits, four wells had no significant trend for NO$_3$-N and Cl$^-$, seven wells had an increasing trend for NO$_3$-N, and six wells had an increasing trend for Cl$^-$ (Table 2). All of the
wells screened in medium-textured lacustrine deposits had no trend detected for NO$_3$-N or Cl$^-$ (Table 3). Three of the five wells screened in till and fine-textured lacustrine deposits were water-table wells and had decreasing trends in Cl$^-$ concentrations and one had a decreasing trend in NO$_3$-N. The results are consistent with a previous study in this area by Rodvang et al. (2002, 2004), who reported no significant temporal trends or decreasing trends for NO$_3$-N and Cl$^-$ in the till and lacustrine deposits.

As indicated above, on a regional basis, NO$_3$-N concentration increased slightly and Cl$^-$ concentration changed very little from 1994 to 2014. The significant trends in concentrations observed in shallow groundwater for individual wells, however, may have been the result of local changes to manure and crop management. On the other hand, several wells (about 40%) had no significant temporal changes in NO$_3$-N and Cl$^-$ concentrations. Rodvang et al. (2002) found that annual mean concentrations reached a state of equilibrium at some wells in the high agricultural-intensity portion of this aquifer. Rodvang et al. (2004) went on to speculate that if agricultural activity remained constant, concentrations will fluctuate seasonally, but mean annual concentrations will reach a steady state throughout the aquifer.

The Battersea region has been an area of intensive agriculture for several decades with the highest density of CFOs in Alberta and irrigation-based crop production on much of the cultivated land. In a small-plot, manure-rate study in this area, Olson et al. (2009) showed that on a loamy sand soil, NO$_3$-N from beef manure leached readily through the soil profile and into the shallow (about 2–2.5 mbsgs) groundwater on an annual basis. However, on a loam soil, they reported that NO$_3$-N accumulated from the highest manure application rate (120 Mg ha$^{-1}$ yr$^{-1}$, wet weight) took 8 years to reach the water table. Considering that livestock production, and hence manure production, has been present in this area for much longer, it is very likely that much of the shallow groundwater is in steady state in terms of NO$_3$-N and Cl$^-$ contributions from agricultural activities.
For the Battersea area and for other areas with intensive livestock activity and vulnerable groundwater, contamination of groundwater by NO$_3$-N from manure will eventually reach steady-state conditions, and concentrations should not change provided agricultural intensity and practices remain constant. To reduce NO$_3$-N concentration in contaminated groundwater, a reduction in the application rates and frequency of manure application on crop land is likely required.

After the discovery of bovine spongiform encephalopathy in Alberta in 2003, the cattle population in Alberta was reduced substantially and has not fully recovered. The annual number of total cattle in Alberta in 2002 was 5,825,000, total cattle in 2003 was 5,310,000, and in 2015 was 4,900,000 (Statistics Canada 2015). Given fewer cattle and less manure production during the study period, it was hypothesized that contamination to groundwater may have been reduced. However, the trend analysis on the data from 1994 to 2014 in this study does not support this hypothesis. Possibly, residual influences from many years of manure application sustained the level of contamination during the study period.

### PCA analysis

A PCA was performed to explore potential relationships between the relative slope of the trend for each well and their characteristics including depth, texture type (coarse vs. fine), and land use up-gradient of the well property (crop-land vs. manure-related activities) that may have impacted the groundwater quality.

In the PCA plots (Figure 5), potential relationships between variables were shown as vectors with the same direction. We reduced the amount of variation to two principal components. For NO$_3$-N, the proportion of variation explained by the first and second principal component of the PCA was 44% and 30%, respectively, which means that two components contain 74% of the variation of the four original variables; a large covariance in the first component of the relative trend slope with well depth and land use up-gradient of the well property occurred. For Cl$^-$, the proportion of variation explained by the first and second principal component of the PCA was 48% and 35%, respectively, and these two components contain 83% of the variation; wells with significant increasing temporal trend seem to be related with coarse texture.

### SUMMARY AND CONCLUSIONS

This study was conducted to determine if changes in groundwater quality occurred with time in the Battersea area, a region with extensive irrigation, a high density of CFOs, and historical groundwater data. Concentrations of NO$_3$-N and Cl$^-$ in shallow groundwater were analyzed in monitoring wells from 1994 to 2014 to evaluate the spatial and temporal variations of groundwater quality. A Mann–Kendall test was applied to identify temporal trends in NO$_3$-N and Cl$^-$ and indicated no significant trends in NO$_3$-N and Cl$^-$.
Cl\(^-\) concentrations in 57\% of the wells; as opposed to some wells where significant changes occurred. Concentrations significantly increased with time in 35\% of the wells for NO\(_3\)\(-\)N and in 26\% of the wells for Cl\(^-\). Concentration significantly decreased with time in 9\% of the wells for NO\(_3\)\(-\)N and in 17\% of the wells for Cl\(^-\). Increasing trends for NO\(_3\)\(-\)N concentrations were observed at LB9-7, LB13-3, and LB11-4, wells located in the center of the study area where soil texture is relatively coarse. This suggests that the soil texture may play a significant role in the potential risk to impacts on groundwater in the area.

Although an appreciable overall trend for NO\(_3\)\(-\)N and Cl\(^-\) concentrations in the region was not observed, increasing trends were observed at specific wells and on a regional basis, NO\(_3\)\(-\)N increased slightly with time while Cl\(^-\) changed very little. Concentrations of NO\(_3\)\(-\)N and Cl\(^-\) greater than 3 mg L\(^{-1}\) and 20 mg L\(^{-1}\), respectively, suggest contamination by anthropogenic sources for slightly more than half of the wells. Decreasing trends were most observed at wells screened in fine-textured soils including well LB2-1, which had the highest mean concentration of NO\(_3\)\(-\)N (geologic origin) and Cl\(^-\).

By applying PCA, three factors were identified with the trends: well depth, land use up-gradient of the well property for nitrate, and texture for chloride.

The current study is consistent with previous findings suggesting that agricultural activities and the subsurface geology continued to influence groundwater quality in the study area. These findings indicated that shallow groundwater in coarse-textured soils are at a relatively higher risk to contamination, especially in locations where intensive activities occur. Our results may suggest that the effects of land-use practices and management in the study area appear to have a greater effect at the local scale as opposed to the entire region. Further study on the local controls and practices at individual locations, as well as potential cumulative effects, should be investigated.

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