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Use of major ion and stable isotope geochemistry to delineate natural and anthropogenic sources of nitrate and sulfate in the Kettle River Basin, British Columbia, Canada



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ABSTRACT

The Kettle River Basin in South central British Columbia (Canada) is under increasing anthropogenic pressures affecting both water quantity and quality of surface waters and aquifers. We investigated water quality and sources and processes influencing NO_3^- and SO_4^{2-} in the Kettle River Basin using a combination of chemical and isotopic techniques. The dominant water type in the Kettle River Basin is Ca-HCO_3 with surface waters having total dissolved solids (TDS) concentrations of < 115 mg/L and groundwaters having TDS values of up to 572 mg/L. Based on $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values and concentration data, NO_3^- in surface waters originates primarily from natural soil nitrification processes, with additional influences from anthropogenic activities, such as waste water effluents at sampling locations downstream from population centres. The source of NO_3^- in groundwater was predominantly nitrification of soil organic matter, although nitrate in a few groundwater samples originated from anthropogenic sources, including manure or septic systems. The dominant source of SO_4^{2-} in surface water and groundwater samples was the natural oxidation of sulfide minerals. With increasing distance downstream, surface water $\delta^{18}\text{O}_{\text{SO}_4}$ values increase beyond the range of oxidation of sulfide minerals and into the range of soil and atmospheric-derived SO_4^{2-} that is in part derived from anthropogenic emissions. Hence, we conclude that recent anthropogenic impacts have affected water quality only marginally at only few sites in the Kettle River Basin. The presented data will serve as an excellent baseline against which future impacts can be assessed.

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1. Introduction

Increased industrial, agricultural and urban development has increased nitrogen, phosphate and sulphate fluxes in many watersheds worldwide [e.g., (IEAE, 2013)]. Increased nutrient fluxes can negatively impact water quality in aquatic systems; adverse effects to ecosystems

include eutrophication, hypoxia and acidification, all of which subsequently lead to a loss of biodiversity (Vitousek et al., 1997). NO_3^- has been found in increasing concentrations in surface waters and in groundwaters in many different locations worldwide (Kendall et al., 2007; Vitousek et al., 1997; Xue et al., 2009). Isotopic studies of nitrate in surface water and groundwater can be used to discriminate between sources of nitrate, as nitrate originating from different sources has characteristic $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values (e.g., Kendall, 1998; Mayer et al., 2002). In addition, the process of denitrification preferentially

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metabolizes the light isotopes ^{14}N and ^{16}O thereby enriching ^{15}N and ^{18}O in the remaining nitrate (Böttcher et al., 1990). This leads to characteristic trends of increasing $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values as nitrate concentrations decrease suggesting that denitrification occurs. Whether this process is coupled with oxidation of organic matter or with pyrite oxidation can be further revealed by isotope analyses on sulfate, since sulfide oxidation typically yields significantly increased concentrations of sulfate in the aquifer with low $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the sulfate (McCallum et al., 2008). Other sources of SO_4^{2-} with distinct isotopic compositions in aqueous systems include the atmosphere, pedosphere and lithosphere (Mayer, 2005), as well as anthropogenic activities. Lithospheric sources of SO_4^{2-} include evaporites, and sulfide minerals in igneous, metamorphic and sedimentary rocks that oxidize to SO_4^{2-} . Atmospheric SO_4^{2-} can be derived from both natural and anthropogenic sources; however, in industrial countries, the majority of atmospheric SO_4^{2-} has been identified to be of anthropogenic origin (Aravena and Mayer, 2010; Benkovitz et al., 1996; Mayer, 2005). Natural sources of atmospheric SO_4^{2-} include volcanic emissions, sulfur emissions from wetlands and seaspray (Mayer, 2005), while anthropogenic activities contribute precursors of SO_4^{2-} (e.g., SO_2) to the atmosphere through burning of fossil fuels (Clark and Fritz, 1997). Soaps, detergents and fertilizers can also contribute anthropogenic SO_4^{2-} to aqueous systems (Mayer, 2005). Therefore, the dual isotope approach for nitrate and sulfate ($\delta^{15}\text{N}\text{-NO}_3^-$, $\delta^{18}\text{O}\text{-NO}_3^-$, $\delta^{34}\text{S}\text{-SO}_4^{2-}$, and $\delta^{18}\text{O}\text{-SO}_4^{2-}$) is often effective in identifying the contaminant sources and the processes leading to nitrate and sulfate contamination of surface water and groundwater (Otero et al., 2009; Rock and Mayer, 2002). However, this approach has not been widely used to assess contamination sources for aquatic ecosystems in western Canada, including British Columbia.

The Kettle River Basin is located in South central British Columbia (BC), Canada, between the Monashee Mountains in the west, the Okanagan Highlands in the east and the US border in the south. The originally rather pristine watershed is drained by the Kettle and the West Kettle River and has recently been exposed to increasing anthropogenic pressures. The high number of surface water applications and licenses has resulted recently in lower flows than previously recorded (Outdoor Recreation Council of BC, 2011) and there are concerns that the quality of surface water and groundwater may deteriorate due to expanding anthropogenic land use. In a recent water quality report published by Environment Canada and the BC Ministry of Environment (2007), the water quality of the Kettle River at the sampling station Midway was ranked only as “fair” based on seasonal guideline exceedances of phosphorous and fluoride and other parameters associated with high turbidity during high flows and the Outdoor Recreation Council of BC ranked the Kettle River as the most endangered river in BC in 2011.

Previous water quantity and quality monitoring in the Kettle River Basin has focused on surface water systems. A water quality monitoring network began collecting data bi-weekly on the Kettle River at the Midway station at the outlet of the basin in 1972 (Environment Canada, 2003). Results and recommendations from the Water Quality assessment

published by Dessouki (2009) state that aquatic life standards were seasonally exceeded by total aluminium, total chromium, fecal coliform, dissolved fluoride and total iron. This report recommended monitoring to be continued on the Kettle River to assess the impact of various land uses in the Kettle River Basin, to assess its potential as a source of drinking and irrigation water, and to monitor trans-boundary effects between British Columbia and Washington State (Dessouki, 2009). Aqueous chemistry of groundwater has not been previously systematically investigated in the Kettle River basin and there are only limited reports assessing surface water quantity and quality. As a consequence, the current impact of changing land use in the watershed on groundwater on surface water chemistry is unknown. The objective of this study was to delineate natural and anthropogenic sources and processes affecting NO_3^- and SO_4^{2-} in surface waters and groundwater in the Kettle River Basin. A combination of hydrological, geochemical and isotopic approaches was used to achieve this goal.

2. Study area

The Kettle River Basin is located in South central British Columbia, Canada. The study area extended from the headwaters of the Kettle River and the West Kettle River, beyond their confluence to the Canadian–US border, south of the town of Midway (Fig. 1a). The Kettle River originates in the Monashee Mountains at an elevation of 1350 m above sea level (asl) and the headwaters of the West Kettle River are located in the Okanagan Highlands at 1250 m asl (Dessouki, 2009). The Kettle and West Kettle rivers flow south from their respective headwaters for circa 160 km and 105 km, respectively towards their confluence. Downstream of the confluence the river continues as the Kettle River, until the town of Rock Creek (BC), where the river turns east towards the town of Midway (BC). Beyond Midway, the Kettle River flows south into the United States at an elevation of 572 m asl. Beyond the confluence, the Kettle River flows for an additional 50 km before crossing the Canada–United States border.

2.1. Hydrology and hydrogeology

Historical average annual temperatures recorded between 1981 and 2010 vary from 5.0 °C at the Beaverdell North climate station to 10.4 °C at the Osoyoos climate station (Environment Canada, 2014). Average annual precipitation determined at the Beaverdell North and Osoyoos climate stations ranged from 323 mm to 485 mm between 1981 and 2010 (Environment Canada, 2014). This shows that the southern portion of the watershed between Rock Creek and Midway is characterized by higher temperatures and lower amounts of precipitation compared to the more northern areas within the basin.

Hydrometric stations located on the Kettle and West Kettle Rivers, prior to their confluence, indicate that the Kettle River contributes more to flow beyond the confluence. In 2009 and 2010, the daily maximum flow rates along the Kettle River prior to the confluence were 197 m³/s and 205 m³/s, respectively; the daily minimum flow rates were 1.4 m³/s and 1.6 m³/s in 2009 and 2010 (Environment

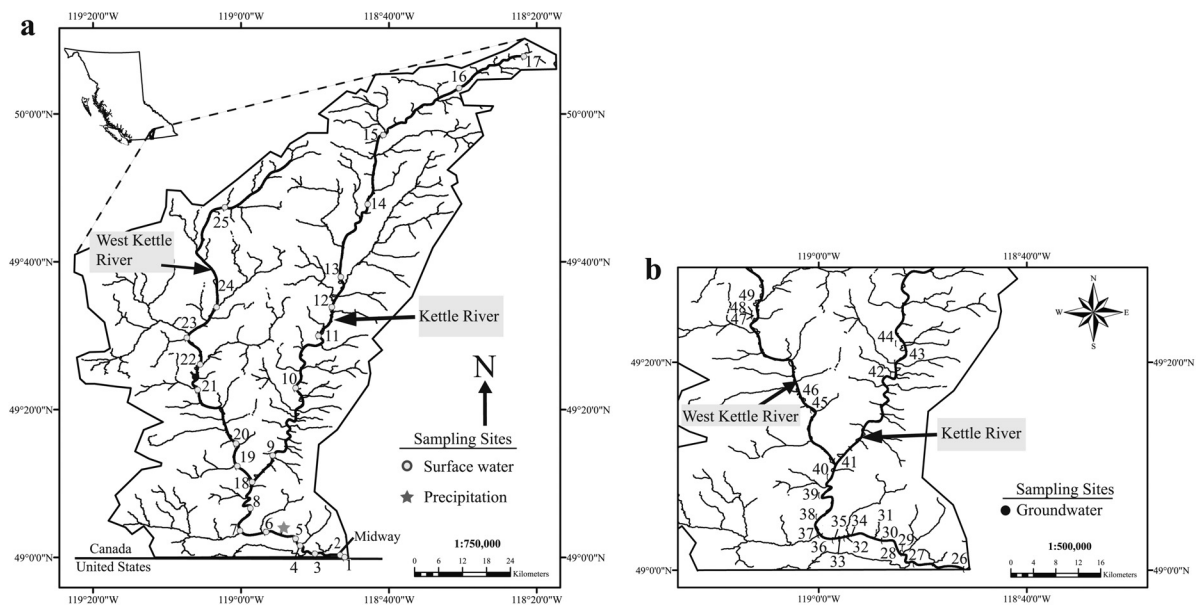


Fig. 1. Location of the Kettle River Basin, and surface water (a) and groundwater (b) sampling stations.

Canada, 2014). Daily maximum flow rates along the West Kettle River prior to the confluence were $57 \text{ m}^3/\text{s}$ and $92 \text{ m}^3/\text{s}$ in 2009 and 2010, respectively, whereas the daily minimum flow rates were $0.5 \text{ m}^3/\text{s}$ in 2009 and $0.7 \text{ m}^3/\text{s}$ in 2010. The US Geological Survey (USGS) maintains a hydrometric station south of the US border at Ferry, Washington, that reported daily annual average discharge rates in 2009 of $30 \text{ m}^3/\text{s}$ and in 2010 of $37 \text{ m}^3/\text{s}$, compared to the average value between 1929 and 2013 of $43 \text{ m}^3/\text{s}$, indicating overall lower flow rates in 2009 and 2010 (USGS, 2014).

The BC Ministry of Environment Observation Well #306 located near Beaverdell, BC has recorded groundwater levels since 1989 (BC Ministry of Environment, 2014). The average groundwater levels measured in 2009 were 5.71 m below ground surface (mbgs) and in 2010 5.57 mbgs, compared to the daily annual average between 1990 and 2008 of 5.47 mbgs, indicating groundwater levels were lower in 2009 and 2010 compared to historical average levels. Observed decreases in surface water discharge rates and groundwater levels may be due to climatic conditions or anthropogenic surface water and groundwater use. There was not sufficient climate or anthropogenic water use data available to determine the reason for the decline.

2.2. Geology and topography

The Kettle River Basin is located within the Omineca belt in the Canadian Cordillera and is underlain by parts of the Kootenay and Quesnel terranes (Gabrielse and Yorath, 1991; Monger et al., 1982). The bedrock is composed of chert, volcanics, volcanoclastics, mudstones, siltstones and greenschist metamorphic rocks (BC Geological Survey, 2005). The topography in the Kettle and West Kettle River Basin is characterized by flat valley bottoms surrounded by steep bedrock hills. Advance and retreat of Pleistocene glaciers (Clague and James, 2002) lead to deposition of

thick sequences of glacial and fluvial materials in valley bottoms. There is no information available on the origin of glacial materials in the Kettle River Basin and because of the size of the Cordilleran ice sheet, it is not possible to hypothesize on the provenance of these materials. The uppermost sections of the valley bottoms are comprised of fluvial materials, deposited by the Kettle and West Kettle Rivers, the provenance of which is likely derived from within the basin. Unconsolidated materials of either glacial or fluvial origin are composed of sand, gravel, silt and clay (Wei et al., 1993, 2010).

2.3. Anthropogenic activity

Anthropogenic activity within the basin began in the 1850s initially due to mineral exploration, which led to development of several mines. The largest of these was the Highland Bell Mine, which was a silver-lead-zinc mine in continuous production between 1913 and 1991 (BC Ministry of Energy and Mines, 2011). Currently, there are several sites of active exploration (BC Ministry of Energy and Mines, 2011). Other types of anthropogenic activity include logging since much of the basin is forested (BC Ministry of Environment, 1997) and agriculture and ranching activities (Sprout and Kelly, 1964). Population in the basin is concentrated in the small towns of Midway, Rock Creek, Beaverdell, Westbridge and Bridesville and rural areas surrounding these towns. The 2011 census reported 674 people living in Midway; a population was not reported for other towns or rural areas (BC Stats, 2014).

3. Methods

3.1. Sampling campaigns and sampling locations

Surface water and groundwater samples were collected during three sampling campaigns in 2009 and 2010 on the

following sampling dates: October 30–November 1, 2009, June 17–June 21, 2010 and October 15–18, 2010. Surface water samples were collected at various sites between the headwaters of the two rivers and their confluence, and between the confluence and the southernmost location on the river before it crosses the Canadian–US border. During each sampling campaign, between 22 and 25 surface water samples were collected. Groundwater samples were collected in 2010 from residential groundwater wells. In June of 2010, 23 groundwater samples were collected and in October of 2010, 25 groundwater samples were collected. The location of surface water and groundwater sampling stations are summarized in Table S1 and shown in Fig. 1a and b. In addition to surface water and groundwater samples, a total of four precipitation samples were collected between June 8 and June 18, 2010 from one location near Rock Creek, BC (49.061°N and –118.905°W).

3.2. Field methods

Surface water samples were collected from the river where the water was fast flowing and well mixed. During sample collection, a YSI probe was used to measure field parameters including temperature, pH, electrical conductivity and dissolved oxygen. Surface water and groundwater samples were collected for analysis of major anions (alkalinity, Cl^- , SO_4^{2-} and NO_3^-) and cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+), silica and stable isotope abundance ratios of hydrogen ($\delta^2\text{H}_{\text{H}_2\text{O}}$), oxygen ($\delta^{18}\text{O}_{\text{H}_2\text{O}}$), NO_3^- ($\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$) and SO_4^{2-} ($\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$). All water samples were filtered through a 45- μm Millipore filter, except those for alkalinity analysis and transported and stored either refrigerated or frozen. Sample water for major cation and anion analysis was collected in 125 mL plastic high-density polyethylene (HDPE) bottles. For cation analysis, HNO_3^- was added until the pH of sample water was less than 2.0. Sample water for stable isotope analysis of NO_3^- was also collected using 125 mL HDPE bottles and was preserved by freezing. Sample water for $\delta^2\text{H}$ and $\delta^{18}\text{O}$ analysis was collected in 10 mL vacuum-sealed containers.

Precipitation samples were collected during rain events. Sample bottles were opened during rain events and subsequently closed after the rain event. Precipitation samples were analyzed for major anion and cation concentrations, and $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values.

3.3. Laboratory methods

All laboratory analysis was completed at the University of Calgary, either in the Applied Geochemistry Group Laboratory or in the Isotope Science Laboratory.

3.3.1. Anions and cations

Major anions including SO_4^{2-} and NO_3^- concentrations were analysed by Ion Chromatography (IC) (Dionex ICS-2000). When measured more than once, the average of the measurements was reported. Concentrations of major cations were determined by Atomic Absorption Spectrometry (PerkinElmer AAnalyst 100) and alkalinity was measured by titration with 0.1 N sulfuric acid. The

reported uncertainty associated with each of these methods was less than 5%. Charge balance was calculated using major anion and cation concentrations and was usually better than 3% for surface water samples and the average charge balance of groundwater samples was 0.7% (Table S1).

3.3.2. Stable isotope analyses

Hydrogen ($^2\text{H}/^1\text{H}$) and oxygen isotope ratios of water ($^{18}\text{O}/^{16}\text{O}$) were measured using a Los Gatos Research “DLT-100” laser spectroscopy instrument. The measurement uncertainty of $\delta^{18}\text{O}$ is $\pm 0.2\text{‰}$ and for $\delta^2\text{H}$ is $\pm 1.0\text{‰}$. Measured $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values are reported relative to Vienna Standard Mean Ocean Water (V-SMOW).

The stable isotope composition of dissolved NO_3^- ($^{15}\text{N}/^{14}\text{N}$ and $^{18}\text{O}/^{16}\text{O}$) was determined using the “denitrifier method”, which reduces NO_3^- to the measurement gas N_2O using denitrifying bacteria (Casciotti et al., 2002; Sigman et al., 2001). $\delta^{15}\text{N}$ values of nitrate were determined with a measurement uncertainty of $\pm 0.5\text{‰}$ and for $\delta^{18}\text{O}$ values of nitrate with an uncertainty of $\pm 1.0\text{‰}$. The obtained $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values were calibrated and normalized against N_2 (air) and V-SMOW using international reference materials.

The stable isotope composition of dissolved SO_4^{2-} ($^{34}\text{S}/^{32}\text{S}$, $^{18}\text{O}/^{16}\text{O}$) was determined by first producing a pure BaSO_4 precipitate by addition of BaCl_2 solution. Subsequently, the dried BaSO_4 was thermally decomposed in an elemental analyser to SO_2 and in a pyrolysis reactor to CO for subsequent sulfur and oxygen isotope ratio measurements, respectively, that were normalized with several international reference materials. $\delta^{34}\text{S}_{\text{SO}_4}$ values are reported relative to Vienna Canyon Diablo Troilite (V-CDT) with a measurement uncertainty of $\pm 0.3\text{‰}$. $\delta^{18}\text{O}$ values of dissolved sulphate are reported with respect to V-SMOW with a measurement uncertainty of $\pm 0.5\text{‰}$.

4. Results and discussion

4.1. $\delta^2\text{H}$ and $\delta^{18}\text{O}$

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation, surface water and groundwater samples in the Kettle River Basin were used to assess the temporal and spatial variations of source water, and processes, such as evaporation. Precipitation in the southern interior of British Columbia is dominantly derived from weather systems that originate from the Pacific Ocean that experience successive rainout of the heavy isotopes ^2H and ^{18}O causing $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of atmospheric moisture and subsequent precipitation to become increasingly more negative with increasing distance from the coast (Yonge et al., 1989). In the summer months, precipitation can be partially augmented by local water vapour sources due to convective activity caused by evaporation and transpiration due to high rates of insolation and cool unstable air (Athanasopoulos, 2009; Wassenaar et al., 2011). A local meteoric water line has been established for the Okanagan Basin (OMWL) which borders the Kettle River Basin, to the west with a relation of $\delta^2\text{H} = 6.6 \times \delta^{18}\text{O} - 22.7$ based on 106 precipitation samples

collected between April 2006 and June 2010 (Wassenaar et al., 2011). The Global Meteoric Water Line (GMWL) follows the relationship $\delta^2\text{H} = 8 \times \delta^{18}\text{O} + 10$ (Craig, 1961). The few $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of precipitation water collected near Rock Creek plot either along the OMWL or between the OMWL and the GMWL and had average $\delta^{18}\text{O}$ values of $-15.2 \pm 1.7\text{‰}$ ($n=4$) and $\delta^2\text{H}$ values of $-117 \pm 13\text{‰}$ ($n=4$). $\delta^{18}\text{O}$ values ranged from -17.7 to -13.8‰ and $\delta^2\text{H}$ values ranged from -134 to -103‰ .

Isotopic compositions of surface water samples plot within a narrow range of values between the GMWL and the OMWL (Fig. 2). The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of surface water samples were $-17.0 \pm 0.4\text{‰}$ and $-129 \pm 3\text{‰}$ ($n=72$), respectively. $\delta^{18}\text{O}$ values ranged from -17.9 to -16.4‰ and $\delta^2\text{H}$ values ranged from -137 to -125‰ . Only slight variations in isotopic compositions beyond the measurement uncertainty were observed along the flow paths of the Kettle River and along the West Kettle River. This indicates that surface water is of meteoric origin and has not undergone significant evaporation.

The $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater samples plot between the GMWL and the OMWL, and most samples fall within the range of precipitation samples (Fig. 2). The average $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values of groundwater samples were $-16.9 \pm 0.5\text{‰}$ and $-129 \pm 5\text{‰}$ ($n=48$), respectively. $\delta^{18}\text{O}$ values ranged from -18.3 to -15.7‰ and $\delta^2\text{H}$ values ranged from -143 to -122‰ . Groundwater and surface water samples have very similar ranges in $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values (Fig. 2), suggesting that surface waters are primarily derived from groundwaters originating from unconsolidated valley aquifers. Groundwater samples from two locations were found to have more negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values compared to other groundwater samples and precipitation (circled in Fig. 2). Based on the location of these samples, this water is likely representative of bedrock aquifers.

4.2. Major ion chemistry

A summary of average concentrations of major anions, cations and total dissolved solids (TDS) for surface water samples collected before and after the confluence of the Kettle and West Kettle Rivers and for groundwater is provided in Table 1. Surface water and groundwater samples were dominantly Ca-HCO₃ water type with only two groundwater samples with Na-HCO₃ water type. These two samples were also characterized by more negative $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values compared to other groundwater samples and precipitation, suggesting that these two groundwater samples originate from bedrock aquifers.

Concentrations of dissolved constituents in surface water were generally lower in the high run-off season in June and higher during base flow in October. Bicarbonate was the dominant anion ranging from average concentrations of 19 to 80 mg/L, followed by SO₄²⁻ (1.3 to 6.6 mg/L), while average Cl⁻ and NO₃⁻ concentrations were < 4 and < 0.25 mg/L, respectively. Average cation concentrations in surface water samples were dominated by Ca²⁺ ranging from 5.9 to 21 mg/L, followed by silica concentrations varying between 3.5 and 6.6 mg/L, while average concentrations of other cations were consistently < 4 mg/L. TDS of surface waters ranged from 36 mg/L at high flow to 124 mg/L at base flow. The dominant anion in groundwater was bicarbonate with an average concentration of 193 mg/L, followed by SO₄²⁻ (28 mg/L), NO₃⁻ (17 mg/L) and Cl⁻ (11 mg/L). Ca²⁺ was the cation measured in highest concentrations in groundwater (49 mg/L), followed by Na⁺ (23 mg/L) while the average concentrations of other cations (Mg²⁺, K⁺ and Si⁴⁺) were less than 10 mg/L. Groundwater TDS ranged from 145.7 to 571.5 mg/L with an average value of 336 mg/L and exhibited little variation between June and October at the re-sampled groundwater wells.

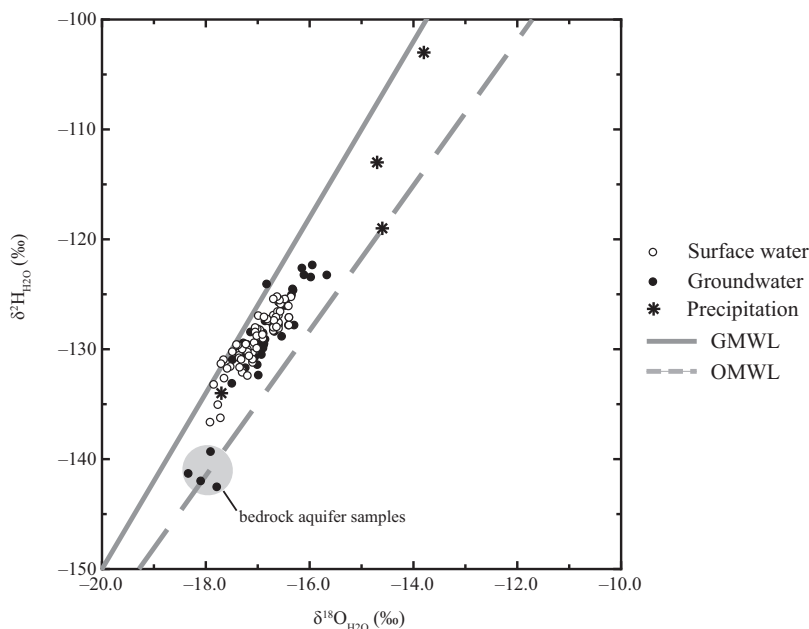


Fig. 2. $\delta^{18}\text{H}_2\text{O}$ and $\delta^2\text{H}_2\text{O}$ values of precipitation water, surface water and groundwater. Samples are shown in relation to the Global Meteoric Water Line (GMWL) and the Okanagan Meteoric Water Line (OMWL; Wassenaar et al. (2011)).

Table 1

Average major anion and cation concentrations in the Kettle and West Kettle Rivers, and in groundwater.

Sampling event	Location and type of sample	HCO ₃ ⁻ (mg/L)	NO ₃ ⁻ (mg/L)	Cl ⁻ (mg/L)	SO ₄ ²⁻ (mg/L)	Ca ²⁺ (mg/L)	Mg ²⁺ (mg/L)	Na ⁺	K ⁺	Si ⁴⁺ (mg/L)	TDS (mg/L)
Oct. 2009 and 2010	Kettle before confluence	64	0.09	0.7	4.1	18	1.7	1.7	0.59	4.6	96
	West Kettle before confluence	63	0.10	3.7	5.2	17	2.9	3.5	0.93	6.6	101
June 2010	Kettle after confluence	80	0.20	2.1	6.6	21	3.4	3.7	0.95	5.8	124
	Kettle before confluence	30	–	0.31	2.2	10	0.76	0.70	0.36	3.5	48
	West Kettle before confluence	19	–	1.1	1.3	5.9	1.0	1.5	0.46	5.1	36
	Kettle after confluence	26	–	0.63	1.8	8.2	1.1	1.3	0.48	4.7	45
Oct. 2009 & 2010	Groundwater	190	28	11	29	49	9.2	22	2.4	8.3	341
June 2010	Groundwater	196	6.3	11	28	48	9.8	23	2.0	8.3	330

4.3. Occurrence and sources of nitrate

High concentrations of NO₃⁻ in aqueous systems can negatively influence ecosystems and human health. The maximum allowable concentration of NO₃⁻ in drinking water in Canada is 45 mg/L (Health Canada, 2010) since elevated NO₃⁻ concentrations in drinking water can potentially cause methemoglobinemia, gastric cancer and non-Hodgkin's lymphoma (Babiker et al., 2004). In the Grand Forks area east of the study area, elevated NO₃⁻ concentrations in groundwater have been previously reported and were thought to be associated with agricultural practices, although the specific source has not been identified (Wei et al., 2010). In the agricultural areas surrounding Osoyoos, to the west of the Kettle River Basin, elevated NO₃⁻ concentrations have also been detected in groundwater which is thought to originate from synthetic fertilizers associated with agricultural practices (Athanasopoulos, 2009). Therefore, we evaluated the occurrence of nitrate in surface waters and groundwaters of the study area and attempted to determine the nitrate sources.

4.3.1. NO₃⁻ concentrations

NO₃⁻ was not detected in surface water samples collected in June 2010, whereas in October 2010, NO₃⁻ concentrations of surface waters sampled were generally less than 0.5 mg/L, with the exception of one sample with a concentration of 1.7 mg/L, but NO₃⁻ contributes on average only 0.1% of TDS. NO₃⁻ concentrations in groundwater samples from the Kettle River Basin varied from “not detected” to 41.3 mg/L, approaching the maximum allowable concentration for drinking water (Health Canada, 2010). The average concentration of detectable NO₃⁻ in groundwater was 27.7 ± 8.5 mg/L in June (*n* = 18) and 6.3 ± 5.7 mg/L in October (*n* = 16) indicating significant nitrate pollution of some aquifers constituting on average 5.8% of TDS. The NO₃⁻ concentrations of precipitation samples ranged from 0.92 to 2.06 mg/L with an average NO₃⁻ concentration of 1.4 ± 0.6 mg/L (*n* = 3).

4.3.2. δ¹⁵N_{NO₃} and δ¹⁸O_{NO₃} values

It was only possible to determine δ¹⁵N and δ¹⁸O values for one surface water sample from June and six samples from October of 2010, due to low NO₃⁻ concentrations.

δ¹⁵N values of surface water nitrate ranged from 3.0 to 7.2‰ and δ¹⁸O values ranged from -0.6 to 8.1‰. The average δ¹⁵N value of surface water nitrate was 5.1 ± 1.8‰ (*n* = 7) and the average δ¹⁸O value of NO₃⁻ was 3.2 ± 3.0‰ (*n* = 7). δ¹⁵N values for groundwater nitrate ranged from 2.5 to 18.9‰ and δ¹⁸O values of nitrate ranged from -8.7 to 5.5‰. The average δ¹⁵N value of groundwater nitrate was 7.2 ± 3.9‰ (*n* = 38) and the average δ¹⁸O value of NO₃⁻ was -3.7 ± 3.2‰ (*n* = 38).

4.3.3. Identification of nitrate sources

Natural sources of NO₃⁻ in watersheds include predominantly nitrification of soil organic matter and to a much smaller extent biogenic soil emissions. Anthropogenic sources include synthetic fertilizers, animal manure, septic systems, wastewater treatment effluents, and anthropogenic N sources contributing to atmospheric N deposition (Kendall et al., 2007). Denitrification, a redox reaction that occurs under anoxic conditions, is a key process with the potential to decrease NO₃⁻ concentrations in groundwater and surface waters (Aravena and Robertson, 1998; Mayer et al., 2002; Seitzinger et al., 2002).

Sources of NO₃⁻ can often be differentiated using a dual isotope approach based on the stable isotope ratios of N (¹⁵N and ¹⁴N) and O (¹⁸O and ¹⁶O), as different sources of NO₃⁻ often have unique combinations of δ¹⁵N_{NO₃} and δ¹⁸O_{NO₃} values (e.g., Mayer, 2005; Kendall et al., 2007; Xue et al., 2009). Plotting δ¹⁵N versus δ¹⁸O values in relation to the isotopic compositions of different NO₃⁻ sources from the literature reveals that nitrate in surface water and groundwater of our study area is mainly derived from soil nitrification, sewage and/or manure (Fig. 3a). Surface water and groundwater samples plot within the range of soil nitrification and within the overlap between soil nitrification and sewage/manure. This suggests that NO₃⁻ is derived from soil nitrification, effluents from wastewater treatment or septic systems, manure or is a mixture of these sources. The spatial distribution of δ¹⁵N values of groundwater samples was investigated to determine whether the groundwater NO₃⁻ derived from sewage/manure originates from several point sources or a non-point source. Anthropogenically influenced groundwaters, as indicated by δ¹⁵N values greater than 8.0‰, are distributed throughout the Kettle River Basin, indicating

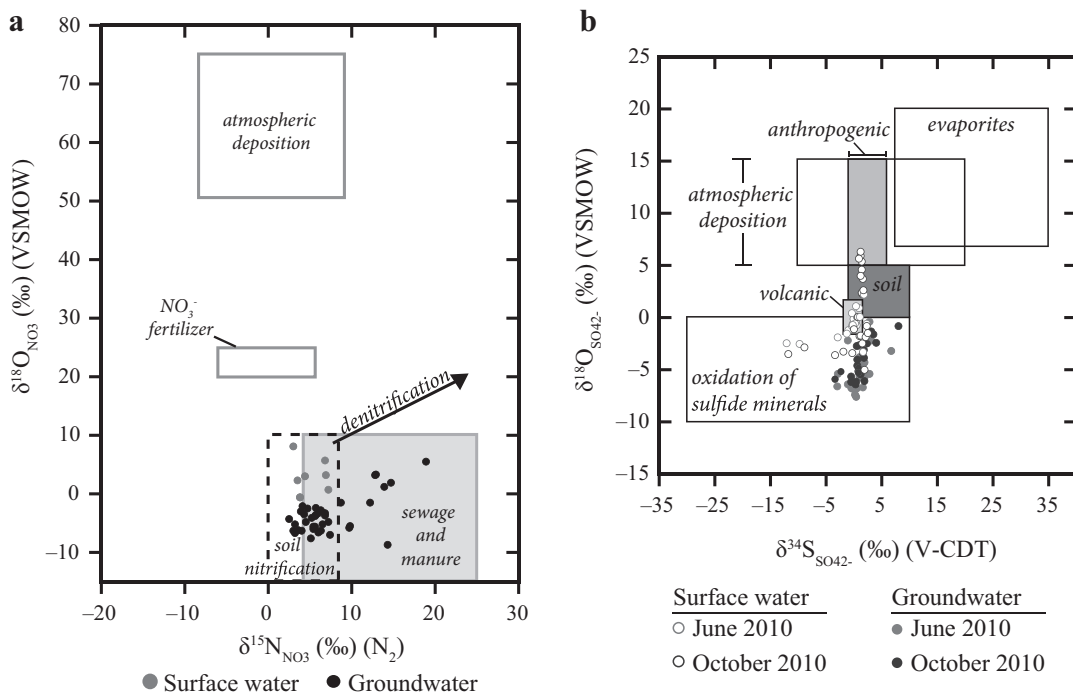


Fig. 3. Surface water and groundwater $\delta^{15}\text{N}$ and $\delta^{18}\text{O}$ values of NO_3^- in relation to isotopic compositions of potential NO_3^- sources (a: after Mayer, 2005 and Kendall et al., 2007) and surface water and groundwater $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values in relation to isotopic compositions of potential SO_4^{2-} sources (b: after Mayer, 2005).

the contamination originates from various point source locations.

A combination of concentration and isotopic data can be used to assess mixing between NO_3^- from soil nitrification and sewage/manure, or to indicate whether or not denitrification is an active process attenuating NO_3^- concentrations (Mayer et al., 2002). If mixing of nitrate from two different sources is occurring, NO_3^- concentrations and $\delta^{15}\text{N}$ values typically increase. In contrast, if denitrification is occurring NO_3^- concentrations decrease and $\delta^{15}\text{N}$ values increase. NO_3^- concentrations of surface water and groundwater samples are plotted versus $\delta^{15}\text{N}$ values in Fig. 4, and expected mixing and denitrification trends are indicated with arrows. Surface water nitrate concentrations are very low; however, there are three samples (circled in Fig. 4a) that, based on elevated $\delta^{15}\text{N}_{\text{NO}_3}$ values compared to the other surface water samples, may have NO_3^- derived from a mixture of soil nitrification and nitrate from effluents of waste waters, septic systems or manure. All three of these samples were collected from locations downstream of population centers; two were collected downstream of Rock Creek and one was collected downstream of Beavertell. Hence, the $\delta^{15}\text{N}_{\text{NO}_3}$ values of these three samples suggest a slight anthropogenic NO_3^- influence on surface waters downstream of population centres most likely from wastewater effluents.

As shown in Fig. 4b, groundwater samples had higher NO_3^- concentrations in June compared to October. The higher NO_3^- concentrations in June could be due to recharge during snowmelt delivering NO_3^- from soil nitrification, septic systems or manure to the groundwater.

In order to identify possible mixing or denitrification trends, the $\delta^{15}\text{N}_{\text{NO}_3}$ values and concentrations of NO_3^- of samples collected in June and October from the same well were connected (Fig. 4b). In most locations, the $\delta^{15}\text{N}$ values did not vary significantly despite decreasing nitrate concentration indicating that the source of NO_3^- did not change temporally. Only at one groundwater sampling site did $\delta^{15}\text{N}_{\text{NO}_3}$ values increase and concentrations decrease between June and October suggesting that denitrification may have occurred in this aquifer. Because dissolved oxygen concentrations of groundwater samples collected from this well were 10.6 mg/L in June 2010 and 6.3 mg/L in October of 2010, denitrification is likely not an active process in the aquifer and instead the source of NO_3^- appears to change temporally.

Considering concentration and stable isotope data for NO_3^- , only three surface water samples were identified to have slight anthropogenic influence and 6 of 25 groundwater samples are likely to have NO_3^- originating from either waste water effluents from septic systems or manure. Denitrification does not appear to be an active process attenuating NO_3^- concentrations in groundwater accessed by the sampled wells in the Kettle River Basin.

4.4. Occurrence and sources of sulfate

Since no SO_4^{2-} concentration data have been reported for groundwater in the Kettle River Basin and its proximal areas, we evaluated the occurrence and sources of sulfate in surface waters and groundwaters of the study area and the potential connection to nitrate contamination.

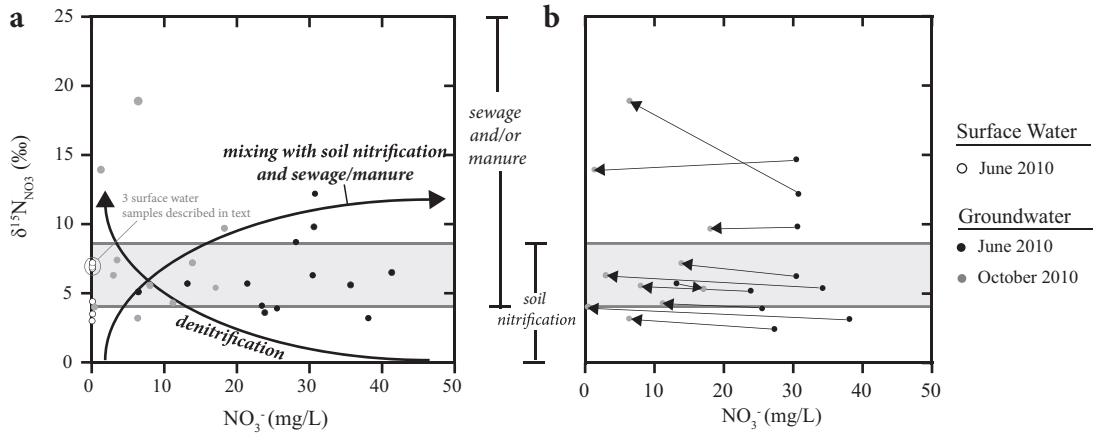


Fig. 4. Surface water and groundwater $\delta^{15}\text{N}_{\text{NO}_3}$ values versus NO_3^- concentrations. Ranges of $\delta^{15}\text{N}_{\text{NO}_3}$ of sewage and/or manure and soil nitrification are indicated. Mixing and denitrification trends are indicated with arrows in (a). Samples collected from the same sampling stations or wells in June and October are connected with lines in (b).

4.4.1. SO_4^{2-} concentrations

Surface water SO_4^{2-} concentrations ranged from 0.7 to 8.3 mg/L and the average concentration of all surface water samples was 4.0 ± 2.3 mg/L ($n = 72$). Fig. 5a depicts surface water SO_4^{2-} concentrations with increasing distance downstream. On average, SO_4^{2-} in surface water constituted 4.5% of TDS. Groundwater SO_4^{2-} concentrations ranged from 4.3 to 145.6 mg/L and the average SO_4^{2-} concentration of groundwater samples was 28.4 ± 32.1 mg/L ($n = 48$) comprising 7.6% of TDS.

4.4.2. $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values

$\delta^{34}\text{S}$ values of surface water SO_4^{2-} ranged from -12.1 to 2.5 ‰ and the average $\delta^{34}\text{S}$ value of SO_4^{2-} in surface waters samples was -0.3 ± 3.4 ‰ ($n = 47$). $\delta^{18}\text{O}$ values in surface

water sulfate ranged from -5.0 to 6.3 ‰ (Fig. 5b) and the average $\delta^{18}\text{O}$ value of SO_4^{2-} was 0.0 ± 2.8 ‰ ($n = 47$). The range of groundwater $\delta^{34}\text{S}_{\text{SO}_4}$ values was -3.4 to 8.0 ‰ and the range in $\delta^{18}\text{O}_{\text{SO}_4}$ values was -7.6 to 0.1 ‰ (Fig. 5b). The average $\delta^{34}\text{S}$ value of SO_4^{2-} was 1.2 ± 2.1 ‰ ($n = 48$) and the average $\delta^{18}\text{O}$ value of SO_4^{2-} was -4.3 ± 1.9 ‰ ($n = 48$).

4.4.3. Identification of sulfate sources

The $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values of the various sources of SO_4^{2-} have been extensively studied and documented (e.g., Claypool et al., 1980; Mayer, 2005; Seal, 2006) revealing the following: sulfate from evaporite dissolution is characterized by elevated $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values; sulfate from sulfide mineral oxidation is often characterized by low $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values; sulfate from atmospheric deposition in industrialized countries has typically $\delta^{34}\text{S}$ values from 0 to 6‰ and $\delta^{18}\text{O}$ often > 5 ‰, whereas sulfate derived from mineralization of soil organic sulfur has a similar range of $\delta^{34}\text{S}$ values, but lower $\delta^{18}\text{O}$ values than sulfate from atmospheric deposition.

Plotting $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values for surface water SO_4^{2-} from the Kettle River Basin (Fig. 3b) indicates that the sources of surface water SO_4^{2-} are sulfide oxidation in bedrock or Quaternary deposits, with possible contributions from mineralization in soils and/or atmospheric SO_4^{2-} deposition. Surface water samples collected from the two sampling sites closest to the headwaters of the Kettle River have more negative $\delta^{34}\text{S}_{\text{SO}_4}$ values (-12.1 to -8.9 ‰) compared to other surface water (-3.4 to 1.9 ‰) and groundwater samples. These $\delta^{34}\text{S}_{\text{SO}_4}$ values combined with low $\delta^{18}\text{O}$ values of sulfate are indicative of oxidation of sulfide minerals in the sedimentary and volcanic lithologies. Lithological differences underlying the sampling sites is a potential reason for the more negative $\delta^{34}\text{S}$ values at the headwaters of the Kettle River, as sedimentary units contain sulfide minerals that often have more negative $\delta^{34}\text{S}$ values than sulfides in volcanic lithologies (Seal, 2006).

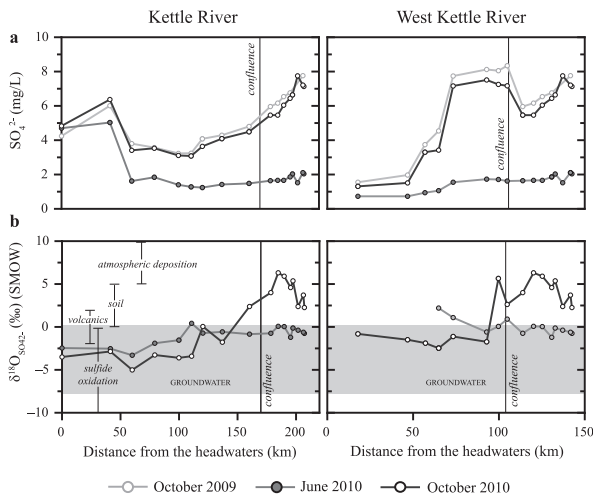


Fig. 5. Surface water SO_4^{2-} concentrations (a) and $\delta^{18}\text{O}_{\text{SO}_4}$ values (b) with distance downstream along the Kettle and West Kettle Rivers, in relation to the ranges of $\delta^{18}\text{O}_{\text{SO}_4}$ values of groundwater samples and sources of sulphate.

$\delta^{18}\text{O}$ values of SO_4^{2-} in surface water samples indicate that additional sources of SO_4^{2-} may also be influencing surface water samples. Fig. 5b shows $\delta^{18}\text{O}_{\text{SO}_4}$ values in surface water samples plotted against distance downstream, in relation to the ranges of $\delta^{18}\text{O}$ values of respective SO_4^{2-} sources. Upstream of the confluence of the Kettle and West Kettle Rivers, $\delta^{18}\text{O}$ values of SO_4^{2-} are within the range of SO_4^{2-} from sulfide oxidation and mineralization of soil organic sulfur, however downstream of the confluence, a few samples fall within the range of $\delta^{18}\text{O}_{\text{SO}_4}$ values of SO_4^{2-} derived from atmospheric deposition or mineralization of organic soil sulfur. Sulfate from atmospheric deposition that has cycled through the pedosphere, or potentially sulfate from local anthropogenic impacts may be responsible for the increasing $\delta^{18}\text{O}$ values of surface waters in the more populated area after the confluence of West Kettle and Kettle Rivers (Fig. 5b).

As shown in Fig. 5b, the dominant source of groundwater SO_4^{2-} appears to be oxidation of sulfide minerals but we found no evidence that sulfide oxidation is linked to denitrification. The isotopic composition of a few SO_4^{2-} samples that are close to the soil SO_4^{2-} range suggest that this may be an additional source of SO_4^{2-} to groundwater.

5. Conclusions

We investigated the geochemical compositions of surface water and groundwater and identified the natural and anthropogenic sources and processes influencing NO_3^- and SO_4^{2-} in the Kettle River Basin. Interpretation of $\delta^{15}\text{N}_{\text{NO}_3}$ and $\delta^{18}\text{O}_{\text{NO}_3}$ values and NO_3^- concentration data suggest that NO_3^- in surface water and groundwater is predominantly derived from natural sources, with some evidence of additional contributions from anthropogenically derived NO_3^- , in both surface water and groundwater samples. Possible anthropogenic influence on surface water samples was confined to three samples collected directly downstream of population centres suggesting that waste water effluent is the likely nitrate source. Groundwater samples identified to contain anthropogenic NO_3^- were confined to point source locations and manure or septic systems were identified as the likely nitrate sources. Based on $\delta^{34}\text{S}_{\text{SO}_4}$ and $\delta^{18}\text{O}_{\text{SO}_4}$ values of surface water and groundwater samples, the source of SO_4^{2-} appears to be primarily from natural processes, including oxidation of sulfide minerals and mineralization of soil sulfur compounds, although the latter are in part derived from anthropogenically impacted atmospheric SO_4^{2-} deposition. The obtained data provide a solid baseline against which impacts of future anthropogenic activities on quantity and quality of groundwater and surface water in the watershed can be assessed.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.crte.2015.04.002>.

References

- Aravena, R., Robertson, W.D., 1998. Use of multiple isotope tracers to evaluate denitrification in groundwater: study of nitrate from a large septic system plume. *Groundwater* 36 (6), 975–982.
- Aravena, R., Mayer, B., 2010. Isotopes and processes in the nitrogen and sulfur cycles. In: Aelion, C.M., Höhener, P., Hunkeler, D., Aravena, R. (Eds.), *Isotopes in biodegradation and bioremediation*. CRC Press, New York, pp. 203–246.
- Athanasopoulos, P., 2009. Using stable isotopes to develop a regional hydrogeological model and characterize nitrate sources in groundwater (MSc. Thesis). Department of Geological Sciences, University of Saskatchewan, Saskatoon, Saskatchewan.
- Babiker, I.S., Mohamed, M.A.A., Terao, H., Kat, K., Ohta, K., 2004. Assessment of groundwater contamination by nitrate leaching from intensive vegetable cultivation using geographical information system. *Environ. Int.* 29 (6), 1009–1017.
- BC Geological Survey, 2005. Digital Geology Maps. <http://www.empr.gov.bc.ca/Mining/Geoscience/PublicationsCatalogue/DigitalGeologyMaps/Pages/default.aspx>, [accessed 15 Feb 2011].
- BC Ministry of Energy and Mines, 2011. Minfile Mineral Inventory. <http://minfile.gov.bc.ca/>, [accessed 8 July 2011].
- Ministry of Environment, 1997. Kootenay Air and Water Quality Study Phase 1–Water Quality in Region 9 The Kettle River Basin. www.env.gov.bc.ca/wat/wq/kootenay/kootenay19.pdf, [accessed 16 September 2010].
- Ministry of Environment, 2014. Observation Well Network. http://www.env.gov.bc.ca/wsd/data_searches/wells/index/html, [accessed 16 November 2014].
- BC Stats, 2014. 2011 British Columbia Municipal Census of Population and Housing. <http://www.bcstats.gov.bc.ca/StatisticsBySubject/Census/2011Census/PopulationHousing.aspx>, [accessed 16 November 2014].
- Benkovitz, C.M., Schotlz, M.T., Pacyna, J., Tarrason, L., Dignon, J., Voldner, E.C., Spiro, P.A., Logan, J.A., Graedel, T.E., 1996. Global gridded inventories of anthropogenic emissions of sulfur and nitrogen. *J. Geophys. Res.* 101 (29), 253.
- Böttcher, J., Strebler, O., Voerkellius, S., Schmidt, H.L., 1990. Using isotope fractionation of nitrate-nitrogen and nitrate-oxygen for evaluation of microbial denitrification in a sandy aquifer. *J. Hydrol.* 114 (3–4), 413–424.
- Casciotti, K.L., Sigman, D.M., Hastings, M.G., Böhlke, J.K., Hilkert, A., 2002. Measurement of the oxygen isotopic composition of nitrate in seawater and freshwater using the denitrifier method. *Anal. Chem.* 74, 4905–4912.
- Clague, J.J., James, T.S., 2002. History and isostatic effects of the last ice sheet in southern British Columbia. *Quat. Sci. Rev.* 21, 71–87.
- Clark, I., Fritz, P., 1997. *Environmental isotopes in hydrogeology*. CRC Press, New York.
- Claypool, G.E., Hoser, W.T., Kaplan, I.R., Sakai, H., Zak, I., 1980. The age curves of sulphur and oxygen isotopes in marine sulphate and their mutual interpretation. *Chem. Geol.* 28, 199–260.
- Craig, H., 1961. Isotopic variations in meteoric waters. *Science* 133, 1702–1703.
- Dessouki, T.C.E., 2009. Canada–British Columbia Water Quality Monitoring Agreement: Water Quality Assessment of the Kettle River at Midway and Carson (1990–2007). Prepared for the Ministry of Environment. www.env.gov.bc.ca/wat/wq/quality/kettle_midway/kettle_midway07.pdf, [accessed 27 November 2009].
- Environment Canada, 2003. Kettle River at Midway, Federal-Provincial Monitoring Station. <http://waterquality.ec.gc.ca/waterqualityweb/stationOverview.aspx?stationId=BC08NN0011>, [accessed 22 November 2009].
- Environment Canada, 2014. Canadian Climate Normals or Averages 1971–2000. http://www.climate.weatheroffice.gc.ca/climate_normals/index_e.html, [accessed 16 November 2014].
- Environment Canada, B.C., Ministry of Environment, 2007. Canada–British Columbia. Water Quality Agreement. Annual Report 2006–2007. <http://www.waterquality.ec.gc.ca/web/Environment~Canada/Water~Quality~Web/assets/PDFs/Reports/>

- ANNUAL%20REPORT%2006-07%20-%20Final.doc, [accessed 27 November 2009].
- Gabrielse, H., Yorath, C.J., 1991. Chapter 1: introduction. In: Gabrielse, H., Yorath, C.J. (Eds.), *Geology of the Cordilleran Orogen in Canada*. Geological Survey of Canada, Ottawa, pp. 3–11.
- Health Canada, 2010. Guidelines for Canadian Drinking Water Quality—Summary Table. Environmental and Workplace Health. http://www.hc-sc.gc.ca/ewh-semt/pubs/water-eau/2010-sum_guide-res_recom/index-eng.php, [accessed 10 November 2011].
- IEAE, 2013. Application of isotope techniques for assessing nutrient dynamics in River Basins, IAEA-TECDOC-1695. International Atomic Energy Agency (published May 2013, ISBC 978-92-0-138810-0).
- Kendall, C., 1998. Tracing nitrogen sources and cycling in catchments. In: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier (521 p.).
- Kendall, C., Elliott, E.M., Wankel, S.D., 2007. Chapter 12 – tracing anthropogenic inputs of nitrogen to ecosystems. In: Michener, R.H., Lajtha, K. (Eds.), *Stable Isotopes in Ecology and Environmental Science*. 2nd edition. Blackwell Publishing, pp. 375–449.
- Mayer, B., Boyer, E.W., Goodale, C., Jaworski, N.A., van Breemen, N., Howarth, R.W., Seitzinger, S., Billen, G., Lajtha, K., Nadelhoffer, K., van Dam, D., Hetling, L.J., Nosal, M., Paustian, K., 2002. Sources of nitrate in rivers draining sixteen watersheds in northeastern US: isotopic constraints. *Biogeochem.* 57–58, 171–197.
- Mayer, B., 2005. Chapter 6 – assessing sources and transformations of sulfate and nitrate in the hydrosphere using isotope techniques. In: Aggarwal, P.K., Gat, J.R., Froehlich, K.F.O. (Eds.), *Isotopes in the Water Cycle*. Springer, Netherlands.
- McCallum, J.E., Ryan, M.C., Mayer, B., Rodvang, S.J., 2008. Mixing-induced groundwater denitrification beneath a manured field in southern Alberta, Canada. *Appl. Geochem.* 23 (8), 2146–2155.
- Monger, J.W.H., Price, R.A., Tempelman-Kluit, D.J., 1982. Tectonic accretion and the origin of the two major metamorphic and plutonic belts in the Canadian Cordillera. *Geol.* 10 (2), 70–75.
- Outdoor Recreation Council of BC, 2011. The Endangered Rivers List. http://www.orcbc.ca/pro_endangered.htm, [accessed 12 December 2011].
- Otero, N., Torrentó, C., Soler, A., Menció, A., Pla-Mas, J., 2009. Monitoring groundwater nitrate attenuation in a regional system coupling hydrogeology with multi-isotopic methods: The case of Pana de Vic (Osona, Spain). *Agric. Ecosyst. Environ.* 133 (1–2), 103–113.
- Rock, L., Mayer, B., 2002. Isotopic assessment of sources and processes affecting sulphate and nitrate in surface water and groundwater of Luxembourg. *Isotopes Environm. Health Stud.* 38 (4), 191–206.
- Seal, R.R., 2006. Sulfur isotope geochemistry of sulfide minerals. *Rev. Mineral Geochem.* 61, 633–677.
- Sigman, D.M., Casciotti, K.L., Andreani, M., Barford, C., Galanter, C., Böhlke, J.K., 2001. A bacterial method for nitrogen isotopic analysis of nitrate in seawater and freshwater. *Anal. Chem.* 74, 4905–4912.
- Seitzinger, S.P., Styles, R.V., Boyer, E.W., Alexander, R.B., Billen, G., Howarth, R.W., Mayer, B., van Breemen, N., 2002. Nitrogen retention in rivers: model development and application to watersheds in northeastern USA. *Biogeochem.* 57/58, 199–237.
- Sprout, P.N., Kelly, C.C., 1964. Soil Survey of the Kettle River Valley in the Boundary District of British Columbia—Report No. 9 of the British Columbia Soil Survey. BC Department of Agriculture, Kelowna, BC and Research Branch, Canada Department of Agriculture <http://sis.agr.gc.ca/cansis/publications/bc/bc9/intro.html>, [accessed 7 July 2011].
- United States Geologic Survey (USGS), 2014. USGS Real-Time Data for USGS 12401500 Kettle River Near Ferry, WA. <http://waterdata.usgs.gov/nwis/uv?12401500>, [accessed 16 November 2014].
- Vitousek, P.M., Aber, J.D., Howarth, R.W., Likens, G.E., Matson, P.A., Schindler, D.W., Schlesinger, W.H., Tilman, D.G., 1997. Human alteration of the global nitrogen cycle: sources and consequences. *Ecol. Appl.* 7 (3), 737–750.
- Wassenaar, L.L., Athanopoulos, P., Hendry, M.J., 2011. Isotope hydrology of precipitation, surface and ground waters in the Okanagan Valley, British Columbia, Canada. *J. Hydrol.* 411, 37–48.
- Wei, M., Kohut, A.P., Kalyn, D., Chwojka, F., 1993. Occurrence of nitrate in groundwater, Grand Forks, British Columbia. *Quat. Internat.* 20, 39–49.
- Wei, M., Allen, D.M., Carmichael, V., Ronneseth, K., 2010. State of Understanding of the Hydrogeology of the Grand Forks Aquifer. Ministry of Environment, Simon Fraser University.
- Yonge, C., Goldenberg, L., Krouse, H.R., 1989. An isotope study of water bodies along a traverse of southwestern Canada. *J. Hydrol.* 106, 245–255.
- Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Talyer, P., van Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotopes methods for nitrate source identification in surface- and groundwater. *Water Res.* 43, 1159–1170.