



Application of the stable isotope composition of SO₄ to tracing anomalous TDS in Nose Creek, southern Alberta, Canada

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Abstract—Nose Creek, a tributary of the Bow River, has a TDS load that is significantly higher than the Bow River or its other tributaries. Chemical and stable isotope analyses were used to elucidate the sources of TDS in Nose Creek. Oxygen and H isotopes indicate that water is added to Nose Creek by leaky municipal pipes, via groundwater infiltration, as the creek flows through the cities of Airdrie and Calgary. Upstream of Airdrie, the high $\delta^{34}\text{S}$ of dissolved SO₄ (+17‰), is consistent with derivation from the local sour gas industry. The SO₄ concentration of Nose Creek doubles as the creek flows through agricultural land between Airdrie and Calgary, while the $\delta^{34}\text{S}$ composition remains a consistent 5‰. This is indicative of S derived from local soils. Within Calgary, SO₄ is derived from oxidation of reduced forms of S in the till, related to the influx of municipal groundwater. © 1997 Elsevier Science Ltd

INTRODUCTION

Chemical analyses alone are often not sufficient to elucidate the sources of, and controls on, the inorganic chemistry of surface water. Stable isotope analyses offer the potential to distinguish sources of dissolved inorganics in surface water, particularly SO₄. In southern Alberta, stable isotopes of SO₄ have been used to trace both natural and anthropogenic inputs of S into the environment (e.g. Krouse and Grinenko, 1991; Hendry *et al.*, 1986; Norman and Krouse, 1992; Fennell, 1994; Fennell *et al.*, 1994; van Donkelaar *et al.*, 1995; Eden, 1996). These studies have focused on tracing industrial emissions into the atmosphere, lakes, groundwater, soils and vegetation. A number of workers have also used S isotopes to trace non-point source inputs into river systems (e.g. Hitchon and Krouse, 1972; Rabinovich and Grinenko, 1979; Ivanov, 1983; Longinelli and Edmond, 1983; Trembaczowski and Halas, 1993). These investigations served to identify natural sources of SO₄, such as dissolution of evaporites or oxidation of sulphide minerals. Sulfate is a major component of the dissolved load in a river, so by gaining a better understanding of the source and controls on SO₄, we may gain a better understanding of riverine chemistry as a whole. In this work, the stable isotope composition of SO₄ is used to determine the controls on the inorganic chemistry of Nose Creek in southern Alberta.

Nose Creek was examined as part of a larger study of the Bow River Basin (Fig. 1). It was chosen for a

more detailed study because the total dissolved solids (TDS) load is significantly higher than the Bow River or the other tributaries of the Bow (Table 1). These high concentrations must be the result of either natural phenomena or anthropogenic activity in the basin. This study combines both chemical and stable isotope analysis to determine the origin of the high dissolved load in Nose Creek.

STUDY AREA

Nose Creek is located in southern Alberta, Canada (Fig. 1a), in an area dominated by prairie grassland. The basin has a dry-subhumid climate, with annual precipitation of 400 mm, and potential evapotranspiration of 530 mm (Ozoray and Barnes, 1977). Precipitation is concentrated in the spring and summer, with a dry fall and winter (Fig. 2). Nose Creek extends 45 km from its confluence with the Bow River to its head waters N of the town of Crossfield (Fig. 1b, c). The creek drains a 986 km² area, and has an average annual flow of 0.73 m³/s (Environment Canada, 1990). The creek has one main tributary (West Nose Creek) and several ephemeral tributaries. The basin lies outside of any of the Bow River irrigation districts, so groundwater and precipitation are the only sources of water in the creek. Discharge in the creek is relatively high during spring and early summer, and low in the fall and winter.

The Nose Creek basin is underlain by up to 15 m of a silty to sandy Balzac Till, with abundant blocks of

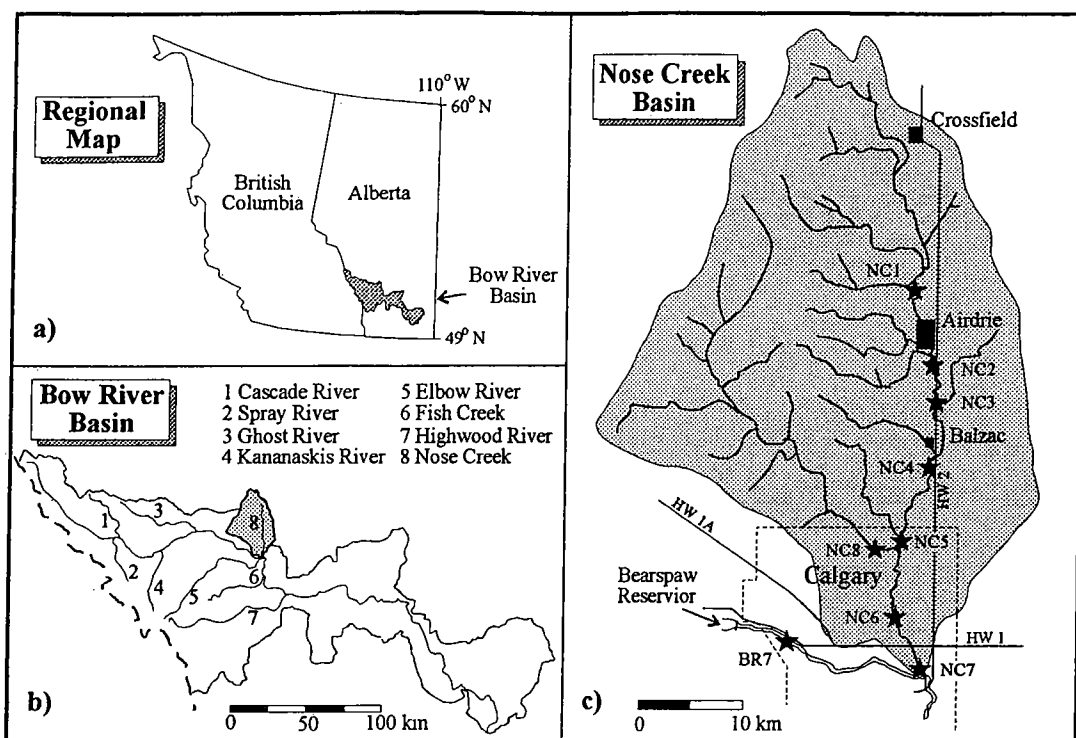


Fig. 1. (a) Regional map showing location of the Bow Basin; (b) Bow Basin, showing major tributaries to the Bow River; and (c) the Nose Creek basin, showing sample locations and the Bears paw Reservoir.

Table 1. Chemical Data for Nose Creek (NC), the Bow River (BR), and tributaries to the Bow River (BT)

Sample	Location	t°C	pH	Ca meq/l	Mg meq/l	Na meq/l	K meq/l	Alk meq/l	SO ₄ meq/l	Cl meq/l	SiO ₂ mg/l
Nose Creek – Fall											
NC1-0893	north of Airdrie	3.4	8.1	4.55	5.96	9.10	0.43	10.69	6.04	2.71	6.16
NC2-0893	Airdrie	4.7	8.6	2.99	4.27	6.48	0.28	6.58	5.21	1.75	0.41
NC3-0893	north crossing	4.2	8.3	3.32	4.60	7.53	0.28	7.10	6.46	2.68	0.79
NC4-0893	south crossing	4.3	8.4	3.38	5.04	9.22	0.30	7.65	7.50	2.80	0.47
NC5-0893	Country Hills	1.4	8.6	3.91	5.86	9.83	0.31	7.90	9.69	2.60	0.17
NC6-0893	32nd Ave. NW	4.7	8.6	4.35	5.23	4.30	0.16	7.42	5.54	1.13	4.77
NC7-0893	Calgary Zoo	2.3	8.5	4.57	5.42	4.92	0.17	7.84	5.73	1.36	4.30
NC8-0893	Centre Street	5.3	8.2	4.28	5.26	4.88	0.16	8.03	4.79	0.90	3.98
Nose Creek – Spring											
NC1-0696	north of Airdrie	15.0	8.4	3.88	5.20	7.57	0.34	734.6	4.19	1.18	6.29
NC2-0696	Airdrie	17.1	8.5	3.12	4.06	6.26	0.31	658.3	1.15	1.26	2.31
NC3-0696	north crossing	16.6	8.6	3.14	4.37	6.48	0.32	674.5	2.22	1.31	0.47
NC4-0696	south crossing	16.6	8.6	3.06	3.99	6.48	0.31	10.46	2.29	1.35	0.51
NC5-0696	Country Hills	18.4	8.7	3.11	3.55	6.35	0.20	9.26	2.74	1.47	1.41
NC6-0696	32nd Ave. NW	18.2	8.5	3.03	3.51	4.27	0.21	7.43	2.62	1.14	1.24
NC7-0696	Calgary Zoo	19.1	8.2	3.05	3.37	4.61	0.19	7.17	2.65	1.75	1.5
NC8-0696	Centre Street	16.8	8.5	3.90	4.31	4.08	0.18	9.21	2.39	0.86	1.97
Bow River and tributaries											
BR7-0893	Bowness	9.1	7.9	2.49	1.12	0.12	0.02	2.82	0.67	0.01	3.72
BT1-0893	Spray River	4.6	8.1	2.75	1.23	0.04	0.01	2.94	1.06	0.01	3.83
BT2-0893	Kananaskis River	9.7	7.6	2.47	0.99	0.05	0.01	2.85	0.57	0.03	3.59
BT3-0893	Ghost River	9.1	8.2	2.55	1.09	0.09	0.02	3.64	0.48	0.00	5.46
BT4-0893	Jumping Pound	3.6	8.9	3.22	1.29	0.30	0.03	4.56	0.16	0.07	7.19
BT5-0893	Elbow River	11.1	8.2	3.09	1.21	0.16	0.02	3.21	0.75	0.08	4.28
BT6-0893	Fish Creek	8.1	8.5	3.78	1.79	0.73	0.05	5.49	0.38	0.23	6.29
BT7-0893	Highwood River	4.2	8.2	3.26	1.29	0.31	0.03	4.56	0.77	0.04	4.13

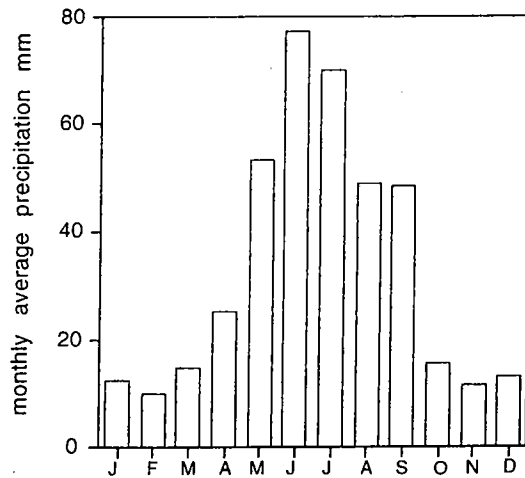


Fig. 2. Monthly average precipitation for the Calgary area (from Klivokiotis and Thomson, 1986)

limestone and quartzite, and rare blocks of granite and gneiss (Moran, 1986). The Porcupine Hills Formation, a non-marine, fine grained, calcareous, cherty sandstone, forms the bedrock of the basin (Green, 1972). The dominant land use in the north part of the basin is agricultural (mostly cereal grains and canola crops). In addition, there are two natural gas processing facilities that remove S, one at Crossfield and one at Balzac. The southernmost part of the basin lies within the NE section of the City of Calgary. This section of the city is dominated by residential housing, the Calgary International Airport and some light industry.

Sample stations along Nose Creek have the prefix NC and those on the Bow River, the prefix BR (Fig. 1, Tables 1 and 2). An important feature to note is that

although station NC5 lies within the City of Calgary, the surrounding area is undeveloped agricultural land. Stations NC6 and 7 lie within the developed part of the city.

METHODOLOGY

Samples from Nose Creek representing two flow regimes, fall base flow conditions and spring/summer high discharge, were collected. The fall samples were collected along Nose Creek over a 2 day period (October 30 to 31, 1993). Spring samples were collected on June 5, 1996. For each set, 7 samples were collected along Nose Creek, and 1 from West Nose Creek (Fig. 1c). Additional samples were collected from major tributaries of the Bow River, and the Bow River itself (Fig. 1b). Sample bottles were cleaned following procedures defined by Environment Canada (1983). Unstable parameters (pH, temperature, and dissolved O₂) were measured *in-situ*. For the remaining analyses, samples were collected in the middle of the creek, 10 cm below the surface. The water was passed through a 0.45 mm filter. Samples for cation analysis were acidified to pH < 2 with ultrapure HNO₃. Samples for anion analysis were untreated and stored at 4°C. For stable isotope analysis, dissolved SO₄ was precipitated in the field as BaSO₄, by the addition of BaCl₂. The water was then acidified to pH < 2 in order to dissolve any BaCO₃. Chemical and stable isotope analyses were conducted at the University of Calgary. Alkalinity was determined using an Orion 960 auto-titrator within 24 h of sample collection. Anions were measured by ion liquid chromatography and cation concentrations were measured by atomic absorption. Analytical error was estimated to be less than 2%.

Stable isotope compositions (¹⁸O, D, ³⁴S) are expressed using the usual δ notation:

$$\delta(\text{‰}) = [(R_{\text{sample}} - R_{\text{standard}})/R_{\text{standard}}] \times 10^3 \quad (1)$$

where R is the ratio of heavy to light isotopes. The standards used are V-SMOW for O and H, and Cañon Diablo Troilite (CDT) for S. For δ³⁴S analyses, SO₂ was prepared using the method of Yanagisawa and Sakai (1983); δ¹⁸O_{(SO₂) was measured with CO₂ prepared by graphite reduction of}

Table 2. Isotope Data

Sample	Location	δ ¹⁸ O _(H₂O) SMOW	δD _(H₂O) SMOW	δ ³⁴ S _(SO₂) CDT	δ ¹⁸ O _(SO₂) SMOW
Nose Creek – Fall 1993					
NC1-0893	north Airdrie	-12.51	-105.9	16.66	7.02
NC2-0893	Airdrie	-13.70	-120.3	7.88	3.97
NC3-0893	North crossing	-14.00	-125.9	5.53	3.33
NC4-0893	South Crossing	-15.18	-123.0	6.15	3.40
NC5-0893	Country Hills	-15.05	-122.2	4.61	0.63
NC6-0893	32nd Ave. NW	-17.50	-139.5	-5.89	-7.03
NC7-0893	Calgary Zoo	-18.19	-140.6	-6.25	-2.29
NC8-0893	Centre Street	-19.02	-141.1	-7.44	-3.66
Nose Creek – Spring 1996					
NC1-0696	north Airdrie	-15.20	-121.9	lost	3.90
NC2-0696	Airdrie	-15.40	-121.5	12.56	1.41
NC3-0696	North crossing	-15.40	-124.2	10.82	4.39
NC4-0696	South Crossing	-15.50	-124.6	9.68	4.30
NC5-0696	Country Hills	-15.10	-120.3	7.21	1.08
NC6-0696	32nd Ave. NW	-15.20	-115.4	0.33	2.40
NC7-0696	Calgary Zoo	-15.30	-120.9	-1.02	0.37
NC8-0696	Centre Street	-17.80	-131.9	-0.83	0.68
Below Bears paw Reservoir					
BR7-0893	Bowness	-18.80	-146.0	10.48	—

BaSO₄ (Shakur, 1982); $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ was measured by isotopic equilibration of CO₂ with H₂O (Epstein and Mayeda, 1953); and δD was measured using H₂ produced by the Zn-reduction method of Coleman *et al.* (1982). Combined sampling and analytical errors for isotope data were estimated to be 0.2‰ for $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ and $\delta^{34}\text{S}$, and 1‰ for δD and $\delta^{18}\text{O}_{(\text{SO}_4)}$ ‰.

RESULTS AND DISCUSSION

Source of Nose Creek water

For the fall samples, precipitation and surface runoff can be eliminated as major contributors to Nose Creek, as only 9 mm of precipitation were recorded in the 2 months preceding sampling. The only water that municipalities pipe directly into Nose Creek is storm water runoff, and all of the storm sewers observed during sampling were dry. Therefore, groundwater must be the primary source of water in Nose Creek in the fall. This is consistent with Ozoray and Barnes (1977) who indicate that in the fall, groundwater is the principal source of surface water in large parts of southern Alberta. In contrast, during spring sampling storm sewers draining paved streets were observed discharging into Nose Creek. Environment Canada recorded 78 mm of precipitation in the 2 months preceding the spring sampling.

Inorganic chemistry of Nose Creek water

Chemical data for Nose Creek and other tributaries of the Bow River are presented in Table 1. Two features distinguish Nose Creek water from the other tributaries: (1) concentrations of inorganic ions are anomalously high, and (2) the dominant ions in Nose Creek are Na-SO₄-HCO₃, whereas all other tributaries to the Bow River are Ca-HCO₃ waters (Fig. 3). Precipitation cannot be a major source of the dissolved load because it is relatively dilute (north Calgary precipitation has an average TDS of 4 mg/l). Therefore, the high TDS load of Nose Creek can only be explained by either natural controls (e.g. weathering of till and/or bedrock, evaporation, etc.), or anthropogenic activity in the basin.

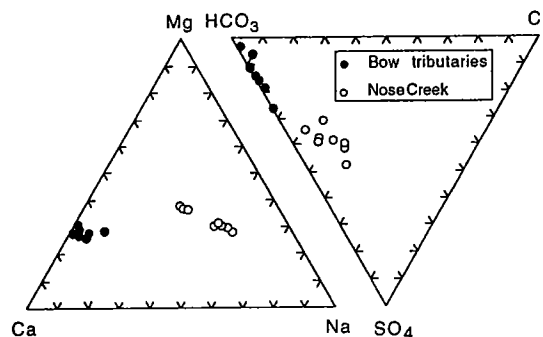


Fig. 3. Ternary plot of major ions for Nose Creek (open circles) and other tributaries to the Bow River (closed circles).

Figure 4 illustrates the variation in major ion concentrations along the length of Nose Creek for spring and fall. For the spring samples, the most important features to note are that: 1) upstream of Airdrie, in the headwaters of Nose Creek, concentrations are high compared to other tributaries of the Bow River, and 2) Nose Creek is diluted where the creek flows through the cities of Airdrie and Calgary. For the fall samples, concentrations of Na and SO₄ are generally higher, the cities of Airdrie and Calgary cause more significant dilution, and concentrations of major ions (particularly Na and SO₄) increase steadily as the creek flows through agricultural land between Airdrie and Calgary. These spatial relations imply that municipalities act as point source inputs of relatively dilute water, and that in the fall either a dispersed source, or a physico/chemical process, significantly increases the TDS of Nose Creek within the agricultural areas of the basin. In the spring, the major ion chemistry is relatively consistent along the creek, although the concentration of SO₄ does increase through the agricultural area.

Of the dissolved solids, Cl is the easiest to account for because of its conservative nature and limited numbers of potential sources. There are no natural sources of Cl in the Nose Creek Basin, the concentration of Cl in precipitation is low (0.165 mg/l), and neither the bedrock nor the till in the basin contain evaporites. This implies that Cl is derived from an anthropogenic source. The most likely source of the Cl is road salt used to melt winter ice on Highway (HW) 2 and other secondary roads (Fig. 1). Road salt used by Alberta Transportation is typically 95% NaCl, with the remainder being K, Ca, and Mg chlorides. Accepting that road salt is the major source of Cl, it only accounts for 10–20% of the cations in Nose Creek, and does not account for the significant levels of SO₄. The steady increase in major ion concentrations along the length of Nose Creek between Airdrie and Calgary, particularly in the fall (Fig. 4), makes it difficult to define a source based on chemistry alone. It is unlikely that in-stream evaporation could account for the observed increase. Thus, there must be addition from non point-source(s) along the length of the creek. Stable isotopes of water and SO₄ were used to trace the source(s).

Oxygen and hydrogen isotope compositions of Nose Creek water

Stable isotope data for Nose Creek are presented in Table 2. On a plot of δD vs $\delta^{18}\text{O}$ (Fig. 5), the data for the spring samples plot in a relatively tight cluster, with δD of -120 to 125‰ and $\delta^{18}\text{O}$ of -15‰. The data falls just off the local meteoric water line (LMWL), suggesting precipitation is the dominant source of creek water. This is consistent with the bulk of precipitation occurring during the spring (Fig. 2). If groundwater is being added to the creek, the consis-

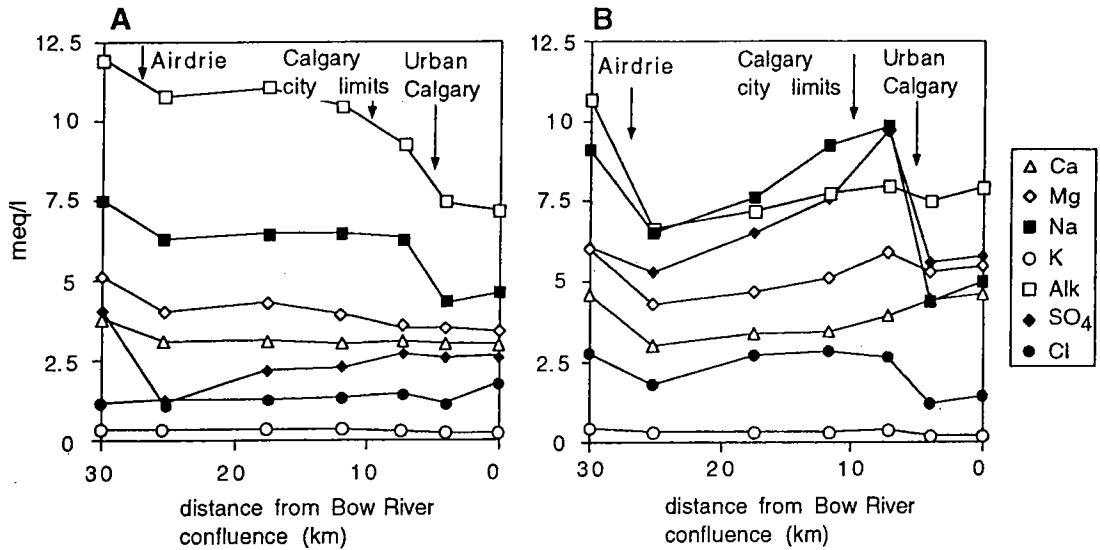


Fig. 4. Variation in major dissolved ions along the length of Nose Creek for (a) spring, and (b) fall runoff. Note that the land between the Calgary City Limits and 'urban Calgary' is undeveloped agricultural land.

tency of the isotope composition along the creek suggests that the proportion of groundwater to rain water is nearly constant.

In the fall, Nose Creek water becomes relatively depleted in the heavy isotopes of O and H in the downstream direction, $\delta^{18}\text{O}$ decreases from -12.5 to -19.0‰ . On a plot of δD vs $\delta^{18}\text{O}$ (Fig. 5), the fall samples define a best fit line with a slope of 5.4 ($r^2=0.92$), as compared to a slope of 8 for the local meteoric water line (LMWL). Data defining a slope lower than the LMWL represents either evaporation or mixing. In a small creek, evaporation along the flow path would be unlikely. If it did occur, the δD and

$\delta^{18}\text{O}$ values would progressively increase downstream, opposite to what is observed. The progressive downstream decrease in δD and $\delta^{18}\text{O}$ in the fall sample set can only be explained by addition of water relatively depleted in D and ^{18}O .

The isotope data for the fall samples in Fig. 5 plot in 3 clusters, with each cluster representing a separate reach of Nose Creek: (1) upstream of Airdrie, (2) between Calgary and Airdrie, and (3) within Calgary. The higher $\delta^{18}\text{O}$ values upstream of Airdrie (relative to the LMWL) are consistent with groundwater being the principal source of the head waters of Nose Creek (Ozoray and Barnes, 1977). The best fit line defined by

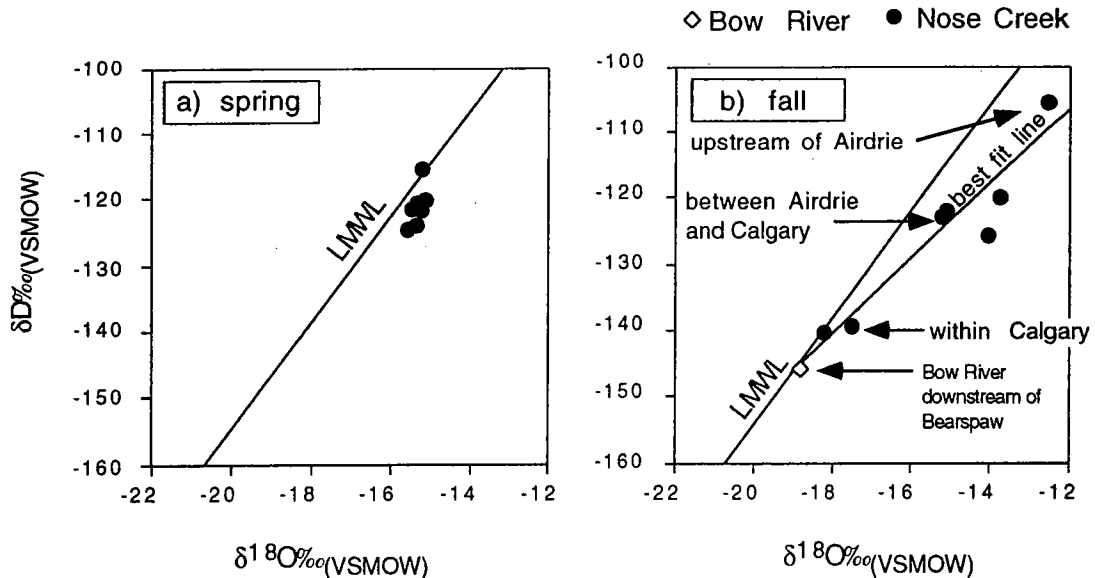


Fig. 5. Plot of δD versus $\delta^{18}\text{O}$ for (a) spring and (b) fall, and the Bow River below the Bears paw Reservoir (square). The local meteoric water line ($\delta\text{D} = 8\delta^{18}\text{O} + 6$) is given for reference.

Nose Creek water passes through Bow River water sampled downstream of the Bears paw Reservoir (Figs. 1 and 5; Bowness sample in Tables 1 and 2). Normally, such a relationship would be interpreted as mixing between two end members (i.e. the head waters of Nose Creek and the Bow River). Because Nose Creek is a tributary of the Bow River, it seems impossible that Nose Creek water is mixing with Bow River water along the length of Nose Creek. However, it is important to note that the stable isotope composition of Nose Creek water only changes as it flows through the two cities (Airdrie and Calgary). This suggests that the cities are adding significant amounts of water to the creek, consistent with the observed dilution (Fig. 4). Cities can add water to a creek directly via storm sewer discharge and sewage outlets, or indirectly from leaking pipes via groundwater (current estimates by the City of Calgary put water loss from Calgary pipes at 15%). Although lawn watering can add additional water, it is minor relative to water loss from pipes. There was no storm sewer discharge observed during sampling, and residential or industrial sewage is not discharged into Nose Creek. Therefore, the water being added to the creek by Airdrie and Calgary must be derived from groundwater. Both Airdrie and north Calgary draw their water supply from the same source, the Bears paw Reservoir on the Bow River, consistent with the mixing relationship observed in Fig. 5. Thus, the observed dilution and increased flow of Nose Creek is a result of addition of municipal water, derived from the Bears paw Reservoir, and added to Nose Creek via groundwater infiltration.

Assuming the relationship in Fig. 5 represents perfect mixing, an isotope balance approach can be used to calculate the amount of Bears paw Reservoir water being added to Nose Creek at Airdrie and Calgary in the fall. These calculations suggest that the flow of Nose Creek increases by a factor of 1.6 as it flows through Airdrie and 3.8 as it flows through Calgary. There are limited stream flow data to compare with these results. Environment Canada operated two gauging stations on Nose Creek from 1980 to 1986, one below the confluence with West Nose Creek, just S of station NC5, and one at the same location as station NC7 (Table 3). Excluding the high

flow year of 1986, the flow between the two stations increases an average of 4.5 times ($n=4$), in good agreement with the 3.8 fold increase in flow calculated from the isotope data. Given the average flow for October of $0.33 \text{ m}^3/\text{s}$, a 3.8 fold increase in flow implies Calgary is adding approximately 22 Ml/day to Nose Creek, or 10% of the 220 Ml/day that are piped into north Calgary from the Bears paw reservoir. This is reasonable when compared to the estimated 15% water loss through leaky pipes in Calgary.

In summary, δD and $\delta^{18}\text{O}$ data indicate that in a dry climate, municipalities can add significant amounts of water to local water bodies. During base flow conditions, water from the head waters of Nose Creek is mixed with two pulses of 'Bow River' water added via leaky pipes in the cities of Airdrie and Calgary, increasing the creek discharge approximately 4 fold. It should be noted that the town of Balzac apparently does not alter the isotope composition of Nose Creek water. The small population of Balzac (250), as compared to Calgary (700,000) and Airdrie (25,000), would not introduce as much municipal water into the basin. The volume of water added to the creek by spring rains (3 times baseflow conditions) appears to overwhelm any isotope signature of municipal water being added to the creek. Municipal water use in the city is relatively constant, summer consumption is 10–15% greater than winter (Engineering and Environmental Services, The City of Calgary). Thus, we can assume the addition of municipal water calculated for October (22Ml/day), is consistent through the year. Taking the Environment Canada (1990) average discharge for Nose Creek of 11,500 Ml, from May to October, municipal water accounts for 35% of discharge during this time. Whereas during low flow in October, municipal water accounts for 77% of discharge. Flow data is not available for winter months, however flow conditions would be similar to, if not less than, October.

Sources of Sulfate

Evaporation cannot account for the observed increases in major ion concentrations between Airdrie and Calgary. This implies that a dispersed source(s) adds inorganic solutes along this reach. The S and O stable isotope compositions of SO_4 can serve to identify these source(s). Dissolved SO_4 can be derived from the dissolution of SO_4 minerals, the oxidation of pyrite and other forms of reduced S, and anthropogenic inputs (e.g. fertilizer, industrial emissions from natural gas facilities that process S, etc.). Given the typical concentration of SO_4 in Calgary rain (1.5 mg/l), atmospheric SO_4 cannot be a major contributor of SO_4 to Nose Creek. Soils in southern Alberta generally have sufficient S content for most crop plants, so that S-based fertilizer is not commonly used (Hendry *et al.*, 1986). Even where used in parts of

Table 3. Environment Canada flow data for Nose Creek

Year	Flow data south of NC5 ¹ (m^3/s)	Flow data at NC7 ² (m^3/s)	Increase in flow (X)
1980	0.047	0.203	4.3
1981	0.054	0.234	4.3
1982	0.034	0.191	5.6
1983	0.021	—	—
1984	0.044	0.176	4.0
1985	0.107	—	—
1986	0.567	0.904	1.6

Environment Canada stations ¹05BH003 and ²05BH901.

the eastern Bow Basin, Hendry *et al.* (1986) noted that the application of S-based fertilizer did not affect the groundwater chemistry. The only plausible origin(s) of SO_4 in Nose Creek are (1) weathering of till and/or bedrock, or (2) anthropogenic input. The O isotope composition of SO_4 was used to determine if the SO_4 was derived from a primary source (e.g. SO_4 minerals), or the oxidation of reduced S.

The $\delta^{18}\text{O}$ of SO_4 and water are plotted in Fig. 6. The fall samples have a relatively wide distribution with $\delta^{18}\text{O}_{(\text{SO}_4)}$ ranging from +7 to -7‰, and a positive correlation with $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$. In contrast the spring samples only have a 5‰ variation in $\delta^{18}\text{O}_{(\text{SO}_4)}$, and $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ is constant. Overall, the $\delta^{18}\text{O}_{(\text{SO}_4)}$ values of all samples are depleted compared to evaporite minerals; the $\delta^{18}\text{O}_{(\text{SO}_4)}$ compositions of evaporites range from +10 to +16‰ (Claypool *et al.*, 1980). Exchange reactions between water and SO_4 cannot be invoked to explain the depleted $\delta^{18}\text{O}_{(\text{SO}_4)}$ because the $\text{SO}_4\text{-H}_2\text{O}$ exchange is extremely slow at temperature and pH conditions comparable to Nose Creek (Lloyd, 1968). However, when reduced S is oxidized, 50 to 100% of the O is derived from water (Van Stempvoort and Krouse, 1994). Therefore, the positive correlation between $\delta^{18}\text{O}_{(\text{SO}_4)}$ and $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ in the fall samples suggests SO_4 is derived from oxidation of a reduced S source. The uniform $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ in the spring samples makes a correlation impossible. The spring rains would likely be washing out soluble salts built up in the soil, so a correlation between $\delta^{18}\text{O}_{(\text{SO}_4)}$ and $\delta^{18}\text{O}_{(\text{H}_2\text{O})}$ would not even be expected. However, as in the fall, the depleted $\delta^{18}\text{O}_{(\text{SO}_4)}$ values suggest at least some of the SO_4 was derived from a reduced S source.

The stable isotope composition of S in SO_4 was examined in an attempt to identify the source(s) of S. The $\delta^{34}\text{S}$ values are plotted against SO_4 concentrations in Fig. 7. For the fall samples, these data plot in

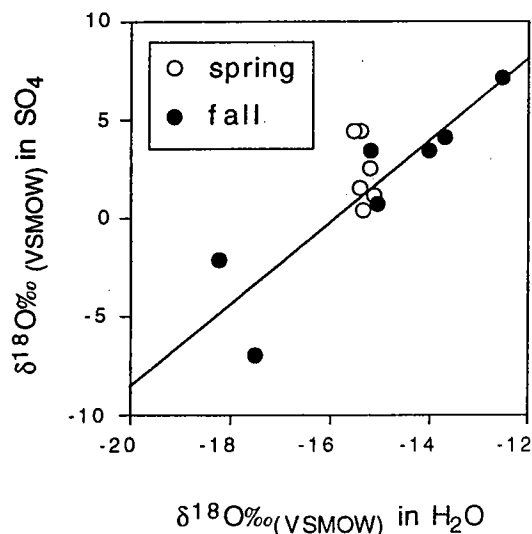


Fig. 6. $\delta^{18}\text{O}$ in SO_4 versus $\delta^{18}\text{O}$ of water for spring (open circles) and fall (closed circles).

clusters as in Fig. 5, representing the 3 reaches of Nose Creek: (1) upstream of Airdrie, (2) between Airdrie and Calgary, and (3) within Calgary. Unlike Fig. 5, these data do not define a mixing line, but rather, each reach of the creek has a different source of SO_4 . There is only one data point upstream of Airdrie so it is difficult to say if it represents a unique source. However, the $\delta^{34}\text{S}$ composition of +17‰ is well above values typical of surface water in southern Alberta, but consistent with SO_2 emissions during processing of sour gas. Emissions from the Crossfield gas plant have $\delta^{34}\text{S}$ values near +25‰ (Norman and Krouse, 1992). Between Airdrie and urban Calgary, the SO_4 concentration increases almost linearly with distance, however the $\delta^{34}\text{S}_{(\text{SO}_4)}$ remains relatively constant at +5‰. This indicates that a single, but uniformly dispersed source of SO_4 , is being added between the two cities during the fall. This source is likely related to the dominant land use, agriculture. Fertilizer application can be ruled out because it is not common, and the $\delta^{34}\text{S}$ value of S-based fertilizer sold in this area was determined to be +14‰, higher than that observed. One possible source is oxidation of organic S in soils. Samples were collected in the last part of October, near the end of the local harvest. During this time soils are loose and uncovered, making them susceptible to wind erosion. The high suspended solid load and brown colour of Nose Creek are consistent with large amounts of particulates being added. Fennell (1994) examined an area 25 km NW of the Nose Creek basin that is underlain by the Balzac Till. In this area A-horizon soils typically have $\delta^{34}\text{S}$ values in the range of +3 to +10‰. The $\delta^{34}\text{S}$ of the SO_4 added to Nose Creek between Airdrie and Calgary (+5‰) falls within this range.

In the fall, the $\delta^{34}\text{S}$ value of SO_4 in Nose Creek is -7.7‰ in Calgary. Using the calculated increase in volume of Nose Creek as it flows through Calgary, a combined mass and isotope balance can be used to calculate the $\delta^{34}\text{S}$ composition of the SO_4 source within Calgary needed to cause the observed change in the $\delta^{34}\text{S}_{(\text{SO}_4)}$ of Nose Creek. These calculations yield a $\delta^{34}\text{S}$ value of -14.6‰ and a SO_4 concentration of 4.3 meq/l for water being added from Calgary. The calculated concentration of SO_4 is significantly higher than that of the Bow River (Table 1). The excess SO_4 must be derived from the till and/or bedrock that the groundwater flows through. The calculated value of the SO_4 (-14‰) is consistent with the average $\delta^{34}\text{S}$ value of -12.5‰ ($n = 10$) for total S (pyrite + organic S) in the Balzac till (Fennell, 1994). This implies that the large flux of water being added by the City of Calgary is oxidizing reduced forms of S in the till, which is then mobilized as SO_4 and transported into Nose Creek via groundwater flow. This is also observed by Hendry *et al.* (1986, 1989) in the eastern Bow River Basin, where groundwater in oxidized tills has anomalously high SO_4 concentrations relative to unoxidized tills, and has $\delta^{34}\text{S}$ values of -9.2‰. Hendry *et al.* (1986, 1989)

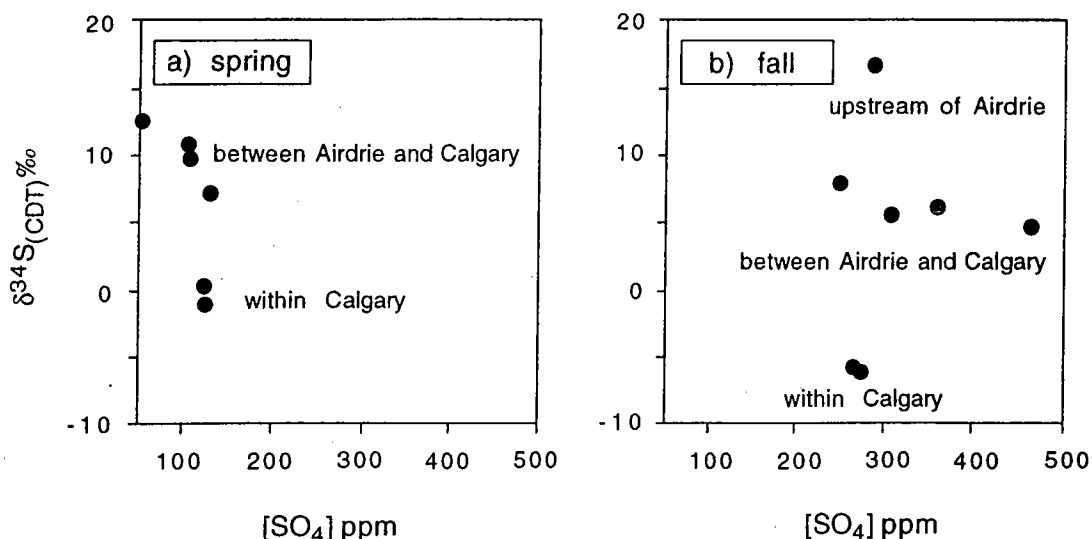


Fig. 7. $\delta^{34}\text{S}$ versus SO_4 concentration for (a) spring and (b) fall.

demonstrated that in this area, the high SO_4 concentrations are related to oxidation of organic matter in the till.

The spring samples show a simpler relationship between SO_4 concentration and $\delta^{34}\text{S}$. The sample for $\delta^{34}\text{S}_{(\text{SO}_4)}$ upstream of Airdrie was lost, so only the trend down stream of Airdrie can be analysed. There is a progressive decrease in the $\delta^{34}\text{S}$ value of dissolved SO_4 between Airdrie and Calgary, with a concurrent increase in SO_4 concentration (Fig. 7). This appears to be a simple mixing relation between a source with $\delta^{34}\text{S} > +12\text{‰}$ (possibly emissions from the Crossfield natural gas processing facility) and a relatively depleted source. The $\delta^{34}\text{S}$ value of dissolved SO_4 approaches $+5\text{‰}$ as the creek reaches Calgary, similar to the fall samples. This may reflect soluble SO_4 being leached from soils by spring rains. The $\delta^{34}\text{S}_{(\text{SO}_4)}$ drops 5‰ where Nose Creek enters urban Calgary. This observed shift in the $\delta^{34}\text{S}$ is likely the result of mixing of 3 sources: (1) SO_4 in the creek before it reaches the city, (2) SO_4 in storm water, and (3) oxidized S from tills in the Calgary area as observed in the fall samples. The $\delta^{34}\text{S}_{(\text{SO}_4)}$ measured from storm sewer discharge is $+13\text{‰}$. There was no storm water discharge in the fall, so the addition in the spring of SO_4 in storm sewer discharge, with a relatively enriched isotope composition, would explain why the drop in $\delta^{34}\text{S}_{(\text{SO}_4)}$ at Calgary is less significant than in the fall.

CONCLUSIONS

This study shows that in a dry climate, municipalities can add significant amounts of water to local aquifers. During base flow conditions 2 pulses of Bow River water (the municipal water supply) are added to Nose Creek via leaky pipes in the cities of Airdrie and

Calgary. This water increases discharge in the creek 4 fold during base flow, diluting the dissolved inorganics, and thus enhancing water quality in Nose Creek. Municipal water accounts for 35% of spring and summer discharge, and up to 77% of fall and winter discharge in Nose Creek. In terms of basin scale water budgets, water from leaky pipes has been recorded as lost from the river system, however this study illustrates that at least two thirds of this 'lost water' is eventually returned to the Bow River via Nose Creek.

The more positive $\delta^{34}\text{S}$ values above Airdrie suggests that the processing facility that removes S from natural gas near Crossfield may be a major source of dissolved SO_4 in the headwaters of the creek. Significant loading of inorganic constituents occurs in the agricultural area between Airdrie and Calgary. Stable isotope evidence suggests that oxidation of organic matter in soils is the primary source of SO_4 . Sulfate relatively depleted in ^{34}S is added within Calgary through oxidation of reduced forms of S (pyrite + organic-S) in tills, by the anthropogenically increased groundwater recharge.

This study illustrates how a combined chemical and stable isotope study can help elucidate processes controlling surface water chemistry. However, this work would have been further enhanced by measuring discharge at sample sites, thus allowing for more accurate mass balance calculations.

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REFERENCES

- Claypool G. E., Holser W. T., Kaplan I. R., Sakai M. and Zak I. (1980) The age curves of sulfur and oxygen isotopes in marine sulfate and their mutual interpretation. *Chemical Geology* **28**, 199–260.
- Coleman M. L., Cheperd T. J., Durham J. J., Rouse J. D. and Moore G. R. (1982) Reduction of water with zinc for hydrogen isotopes analysis. *Analytical Chemistry* **54**, 993–995.
- Eden G. F. (1996) Sources of sulphur in post-industrial sediments of Waterton Reservoir, S.W. Alberta. M.Sc. thesis, University of Calgary, Canada, 147 pp.
- Environment Canada (1983) Sampling for water quality. Inland Waters Directorate, Water Resources Branch, Water Survey of Canada, Ottawa, Canada, 55 pp.
- Environment Canada (1990) Historical Streamflow Summary Alberta. Inland Waters Directorate, Water Resources Branch, Water Survey of Canada, Ottawa, Canada, 629 pp.
- Epstein S. and Mayeda T. K. (1953) Variation of ^{18}O content of waters from natural sources. *Geochimica Cosmochimica Acta* **4**, 213–224.
- Fennell J. W. (1994) Source and distribution of sulfate and associated organics at a sour gas plant in southern Alberta. M.Sc. thesis, University of Calgary, Canada, 192 pp.
- Fennell J. W., Bentley L. R., Lyness L. S. and Anderson P. (1994) Source and distribution of sulphate in groundwater near a sour gas plant in southern Alberta. 4th Annual Conference on groundwater and soil remediation, Sept. 21–23, Calgary, 529–543.
- Green R. (1972) Geological map of Alberta. Scale 1:267,000, Alberta Geological Survey, Natural Resources Division.
- Hendry M. J., Cherry J. A. and Wallick E. I. (1986) Origin and distribution of sulfate in a fractured till in southern Alberta, Canada. *Water Resources Research* **22**(1), 45–61.
- Hendry M. J., Krouse H. R. and Shakur M. A. (1989) Interpretation of oxygen and sulfur isotopes from dissolved sulphates in tills of southern Alberta, Canada. *Water Resources Research* **25**(3), 567–572.
- Hitchon B. and Krouse H. R. (1972) Hydrogeochemistry of the surface waters of the MacKenzie River drainage basin, Canada, stable isotopes of oxygen, carbon and sulphur. *Geochimica Cosmochimica Acta* **36**, 1337–1357.
- Ivanov M. V. (1983) The sulphur cycle in continental reservoirs. In *The Global biogeochemical sulphur cycle*, SCOPE Report 19, (eds M. V. Ivanov and J. R. Freney), pp. 331–356, Wiley, New York.
- Klivokiotis P. and Thomson R. B. (1986) The climate of Calgary, Climatological Studies No. 38, The climate of Canadian cities No. 3, Environment Canada, Atmospheric Environment Service, Ottawa, Canada, 52 pp.
- Krouse H. R. and Grinenko V. A. (1991) Stable isotopes: Natural and anthropogenic sulphur in the environment. SCOPE Report 43, John Wiley and Sons, New York, 440 pp.
- Lloyd R. M. (1968) Oxygen isotope behavior in the sulfate water system. *Journal of Geophysical Research* **73**, 6099–6110.
- Longinelli A. and Edmond J. M. (1983) Isotope geochemistry of the Amazon Basin: A reconnaissance. *Journal of Geophysical Research* **88**, 3707–3717.
- Moran S. R. (1986) Surficial geology of the Calgary urban area. Alberta Research Council, Terrain Sciences Department.
- Norman A. and Krouse H. R. (1992) Stable isotope studies of atmospheric sulphur: comparison of Calgary, Canada and Bermuda. In *Critical issues in the global environment*, vol. 2, Atmospheric Chemistry, Air and waste management association, Pittsburgh.
- Ozoray G. F. and Barnes R. (1977) Hydrology of the Calgary-Golden area, Alberta. Alberta Research Council Report 77-2, 38 pp.
- Rabinovich A. L. and Grinenko V. A. (1979) Sulfate sulfur isotope ratios for USSR river water. *Geokhimiya* **3**, 441–454.
- Shakur A. (1982) ^{34}S and ^{18}O variations in terrestrial sulphates. Ph.D. thesis, University of Calgary, Canada, 229 pp.
- Trembacowski A. and Halas S. (1993) Sulphur isotopes in sulphates in natural waters: (1) surface waters of relatively unpolluted terrains. *Isotopenpraxis* **28**, 215–228.
- van Donkelaar C., Hutcheon I. E. and Krouse H. R. (1995) $\delta^{34}\text{S}$, $\delta^{18}\text{O}$, δD in shallow groundwater: tracing anthropogenic sulfate and accompanying groundwater/rock interactions. *Water, Air and Soil Pollution* **79**, 279–298.
- Van Stempvoort D. R. and Krouse H. R. (1994) Controls of $\delta^{18}\text{O}$ in sulfate: Review of experimental data and application to specific environments. In *Environmental geochemistry of sulfide oxidation*, (eds C. N. Alpers and D. W. Blowes), pp. 446–480, ACS Symposium Series 550.
- Yanagisawa F. and Sakai H. (1983) Precipitation of SO_2 for sulphur isotope ratio measurements by thermal decomposition of $\text{BaSO}_4\text{-V}_2\text{O}_5\text{-SiO}_2$ mixtures. *Analytical Chemistry* **55**, 985–987.