

THE UNIVERSITY OF CALGARY

Sources of Sulphur in Post-Industrial Sediments of Waterton Reservoir, S.W.

Alberta

by

George Francis Eden

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THE UNIVERSITY OF CALGARY  
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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled "Sources of Sulphur in Post-Industrial Sediments of Waterton Reservoir, S.W. Alberta" submitted by George Francis Eden in partial fulfilment of the requirements for the degree of Master of Science.



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## ABSTRACT

The man-made Waterton Reservoir, initially flooded in 1965 and characterized by over 40cm of recent sediment fill, was investigated to evaluate if a record of technogenic sulphur emitted by two upwind sour gas processing plants is preserved in the accumulating sediments. Stable sulphur isotope ratio determinations were used to constrain sulphur sources. Active erosion of the reservoir shoreface by wind-driven waves supplies locally-derived sediment. Total sediment sulphur concentration is remarkably low, less than 30 $\mu$ mole/g, and is similar to reported local soil sulphur concentration measurements. Although rapid throughput of water provides an essentially unlimited aqueous sulphate supply, diagenetic sulphur addition via dissimilatory sulphate reduction is of minor importance. Consequently, spatial and temporal variations in total sediment sulphur concentration and total sediment  $\delta^{34}\text{S}$  reflect technogenic sulphur sources, possibly introduced as elemental sulphur dust, or as organic detritus which had previously incorporated technogenic sulphate via assimilation.

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## CHAPTER 1 - INTRODUCTION

### BACKGROUND

Increased environmental awareness and government policy predicate that benign energy sources satisfy our growing energy demands. In the near term, natural gas appears to be the fossil fuel of choice. Natural gas is a mixture of light hydrocarbon gases, predominantly methane, which releases a comparatively small amount of carbon dioxide to the environment per unit of energy produced. Utilization of natural gas therefore minimizes the potential environmental impact with respect to greenhouse emissions. While this is desirable, other potential environmental problems associated with the production and processing of natural gas must be considered.

A significant proportion of the natural gas produced in Western Canada is known as sour gas because it contains varying amounts of hydrogen sulphide. Interaction between the deeply buried carbonate reservoir rocks in which the gas has accumulated, and the hydrocarbon fluids themselves, is considered to be responsible for the generation of the H<sub>2</sub>S component of the natural gas (Krouse et al, 1988). As H<sub>2</sub>S is a poisonous and corrosive gas, it must be removed from the natural gas prior to delivery to consumers.

Separation of the H<sub>2</sub>S from sour gas, and its recovery as elemental sulphur, is the basis of Alberta's by-product sulphur industry and has made Canada one of the leading sulphur exporters in the world. The process to recover the elemental sulphur in general use by the sour gas industry results in the emission of contaminant sulphur dioxide to the atmosphere, and its subsequent dispersal throughout the environment as "acid rain", a term which includes wet and dry deposition of acidic components. Since the 1950's, concern over the cumulative effects of acid precipitation on the environment has stimulated an enormous body of research. It also has fostered changes in regulatory requirements, resulting in a progressive reduction in SO<sub>2</sub> emissions since about 1975.

Lakes accumulate materials introduced to their catchment basins, and are potentially sensitive indicators of environmental change. The continuous historical record preserved in lake sediments, in principle, offers the opportunity to compare the pre-industrial background to present conditions in lakes exposed to technogenic emissions.

During the last 15 years, investigations of pristine, technogenically influenced, and experimentally-modified lakes have elucidated aspects of the biogeochemical cycling of sulphur in lakes. A state-of-the-art overview is presented by Cook and Kelly (1992). Anoxic habitats which contain both sulphate and organic matter are sites of dissimilatory sulphate reduction ("DSR", Figure 1.1), a process of fundamental importance to the accumulation of sulphur in lake sediments. Anoxic conditions are a prerequisite, however such conditions can occur within a few centimeters below the sediment-water interface (Kelly and Rudd, 1984). Dissimilatory sulphate reduction is potentially areally widespread in the sediments of subaqueous settings, and is not restricted to lakes having anoxic bottom water.

The dissimilatory sulphate reduction pathway is used by certain genera of bacteria during metabolism, with sulphur being the electron acceptor for oxidation of organic matter in much the same manner as oxygen is used by aerobic organisms (Jørgenson, 1983). The end-product of the metabolism is hydrogen sulphide, which is excreted by the cells (Zinder and Brock, 1978). Reaction of the product hydrogen sulphide with metal ions to form metal sulphides, such as pyrite, establishes a mechanism by which the total sulphur concentration of lake sediments can be increased. Elevated lake water sulphate concentration owing to acid precipitation may result in increases in the rate of dissimilatory reduction (Kelly and Rudd, 1984), however the concomitant production of alkalinity may diminish the rate of lake acidification.

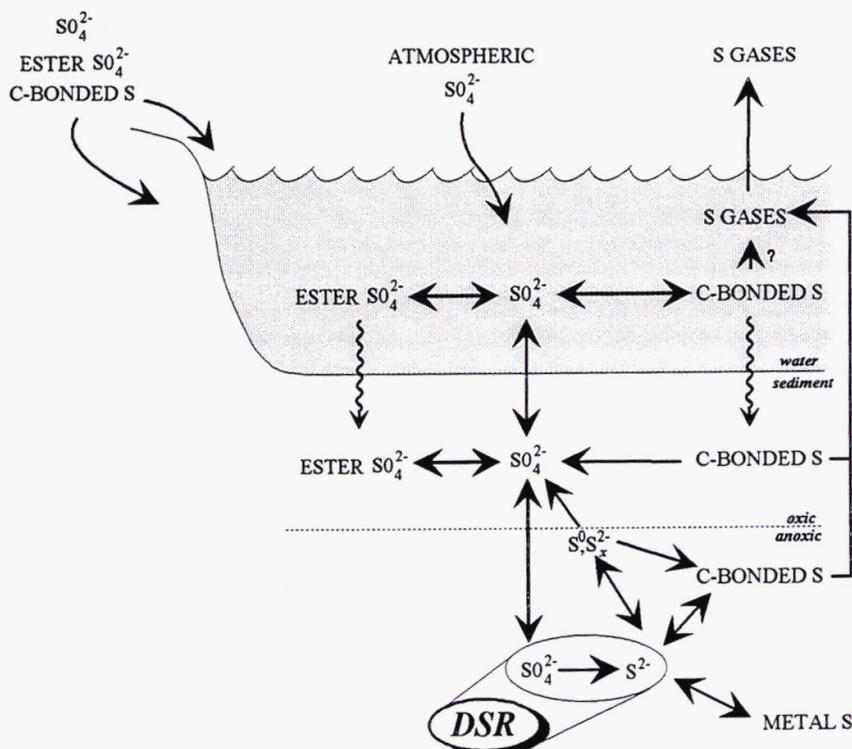


Figure 1.1 Schematic diagram of the lacustrine sulphur cycle. Ester  $\text{SO}_4^{2-}$  and C-bonded S are categories of sulphur-containing organic compounds. After Cook and Kelly (1992) and David and Mitchell (1985).

In Alberta, the sour gas industry has unwittingly provided an ideal natural laboratory for studies of sulphur cycling in the environment. This is a consequence of the stable sulphur isotopic composition of sulphur recovered and emitted by the sour gas industry differing significantly from that of ambient environmental sulphur. In effect, a labelling experiment has been conducted ever since the processing of sour gas began at Turner Valley in 1925. Twenty-five years of research utilizing measurement of stable sulphur isotope ratios has elucidated mechanisms by which the technogenic sulphur interacts with vegetation, soils and groundwater in Alberta (e.g. Krouse 1980; Krouse 1991). Such studies have demonstrated that in addition to that dispersed as  $\text{SO}_2$  emissions, technogenic sulphur can enter the environment as wind-transported elemental sulphur dust, and aqueous sulphate derived from the oxidation of  $\text{SO}_2$  or elemental sulphur. All living organism require sulphur as a minor nutrient (Howarth and Stewart, 1992); consequently, "labelled" technogenic sulphur can be incorporated into the biosphere.

In the synoptic discussion which follows, the stable sulphur isotope methodology and notation are introduced, and the principal results of applications of the technique are illustrated by examples from sediment sulphur studies of lakes in northeastern North America. Finally, the objectives and methods of the thesis research are presented, and important contrasts with prior lake sediment sulphur studies are emphasized.

## STABLE ISOTOPE NOTATION

The isotopes of a given element differ in mass, a manifestation of the number of neutrons present in the atomic nucleus. In the case of sulphur, there are 4 stable and 6 radioactive isotopes. Stable sulphur isotopes having mass 32, 33, 34 and 36 have natural abundances of 95.02, 0.75, 4.21 and 0.02%, respectively (Holdren et al, 1983). Stable sulphur isotope relative abundance determinations are generally restricted to  $^{32}\text{S}$  and  $^{34}\text{S}$  because they are the most abundant.

By convention, stable isotope relative abundances are reported using the  $\delta$  (del) notation and are expressed in parts per thousand (‰ or “per mil”). Using the example of sulphur:

$$\delta^{34}\text{S} (\text{‰}) = \left[ \frac{(^{34}\text{S}/^{32}\text{S})_{\text{sample}}}{(^{34}\text{S}/^{32}\text{S})_{\text{standard}}} - 1 \right] \times 10^3$$

The internationally accepted standard is troilite (FeS) from the Cañon Diablo meteorite (abbreviated CDT), which has a value of 0‰. Owing to small variations in the isotopic composition of this standard, a V-CDT scale has been introduced by the International Atomic Energy Agency, Vienna. The zero on the V-CDT scale is defined by a standard IAEA-S-1, having a value of -0.30‰ (IAEA, 1995). A relative scale is used because relative abundances can be measured with high precision. Positive and negative  $\delta^{34}\text{S}$  values mean a sample is “enriched” and “depleted” in  $^{34}\text{S}$ , respectively.

The chemical properties of each isotope are identical, however the mass differences influence the rates of their participation in chemical and physical processes. This gives rise to an alteration of the stable isotope abundances known as isotope fractionation. In the case of stable sulphur isotopes, the only known process by which large fractionations occur under terrestrial conditions is dissimilatory sulphate reduction. The anaerobic sulphate-reducing bacteria consume “light”  $^{32}\text{SO}_4^{2-}$  in preference to “heavy”  $^{34}\text{SO}_4^{2-}$  (Thode et al, 1951). Sulphide produced by the reduction of the sulphate is characteristically depleted in  $^{34}\text{S}$  and the remaining unreacted sulphate enriched in  $^{34}\text{S}$ . In contrast, assimilatory reduction of sulphate (i.e. synthesis of amino acids, etc.) is minimally isotopically selective from the view point of sulphur.

#### TECHNOGENIC SULPHUR ACCUMULATION IN SEDIMENTS OF LAKES

Prior studies of lake sediments in eastern North America and Europe have suggested that technogenic sulphate loading is reflected in the historical sedimentary record, as demonstrated by profiles of total sediment sulphur concentration and stable isotope ratios obtained from analysis of undisturbed, vertical sediment cores (e.g. Nriagu and Coker, 1983). Increased total sulphur concentration in the surficial sediment layer, and depth-coincident depletion of total sediment  $^{34}\text{S}$  is the hallmark signature of technogenic sulphate loading (Figure 1.2) as demonstrated by studies of numerous lakes in eastern North America and northern Europe. This is commonly present in only the uppermost few centimeters of unconsolidated sediments, perhaps representing the record of several decades of sedimentation. Origin of such profiles is attributed to stimulation of activity of sulphate-reducing bacteria owing to an increase in sulphate availability (Thode et al, 1987), commonly termed “sulphate fertilization” (Fry, 1988).

## McFARLANE LAKE

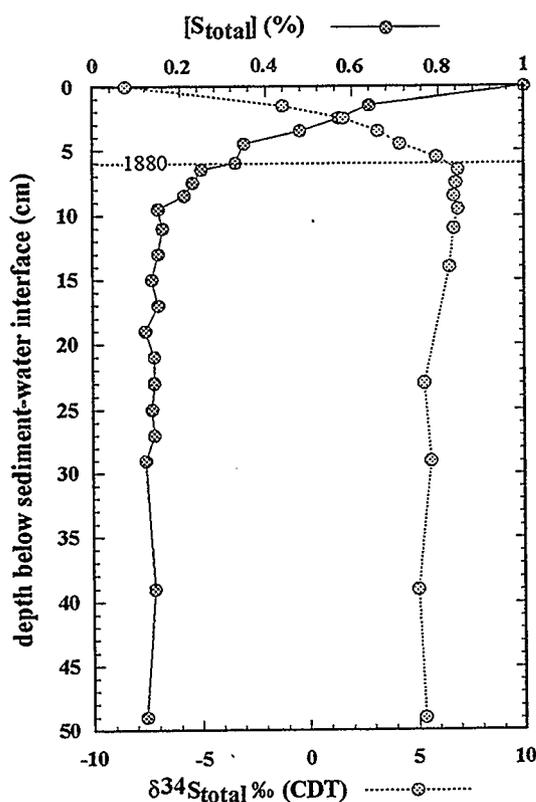


Figure 1.2 Profiles of total sulphur concentration and  $\delta^{34}S$  for sediments from a lake in the vicinity of Sudbury, Ontario. The dramatic increase in sulphur concentration, and the depth-coincident depletion in  $^{34}S$  were attributed to the beginning of smelting of copper-nickel ores in Sudbury, starting in about 1890. The broken horizontal line represents 1880 as determined by  $^{210}Pb$  dating. Data from Nriagu and Coker (1983).

Three components to the sulphur isotope stratigraphy of lake sediment cores were identified by Fry (1990), applicable to settings where the isotopic composition of technogenic sulphur differs from that of the ambient environment, and where dissimilatory sulphate reduction is limited by sulphate availability:

- a uniform pre-industrial baseline reflecting sources of sulphur in precipitation, soils and watersheds, preserved in the sediments below 20 to 40 cm below the sediment-water interface;

- sedimentation of materials incorporating technogenic sulphur, resulting in a shift of the sulphur isotopic composition of the post-industrial sediments towards that of the industrial source (Krouse, 1980);
- dissimilatory sulphate reduction, adding sulphur strongly depleted in  $^{34}\text{S}$  owing to the isotope selectivity characteristic of the process.

The latter component is a dynamic, diagenetic process superimposed on the record comprising the accumulation of sulphur-bearing materials, which has the potential to obscure the recognition of technogenic sulphur. The strict temporal significance of the sulphur concentration and stable isotope profiles is also potentially clouded by artifacts arising from post-depositional processes such as sediment reworking, and diffusion of reactants and products during dissimilatory sulphate reduction (e.g. Holdren et al, 1984; Carignan and Nriagu, 1985).

It is emphasized that the sulphur cycle in lakes comprises inorganic and organic forms of sulphur as sources of sulphur to the sediments, and as products of reactions occurring in the sediments (Figure 1.1). Clearly, a comprehensive understanding of sulphur storage in lake sediments requires apportioning of the total sulphur pool.

Unfortunately, at present no standard technique for the assay of the components of the total sulphur pool exists, clouding intercomparison of studies. Drying of sediments prior to analysis can lead to significant and variable losses of organic sulphur (Amaral et al, 1989). Furthermore, wet chemical extractions, often performed in sequence, may yield different results depending on the order in which performed (Amaral et al, 1993).

## TRACING TECHNOGENIC SULPHUR IN ALBERTA

The stable sulphur isotopic composition of both the elemental sulphur recovered at sour gas plants and the  $\text{SO}_2$  emitted during the sulphur recovery process differs from that of the

ambient environment throughout much of Alberta. The average  $\delta^{34}\text{S}$  of sour gas industry-related emissions in Alberta is +22‰ (Krouse, 1989); that of soils and vegetation in unaffected areas is approximately 0‰ or lower (Krouse, 1980). As long as subsequent stable isotope fractionation is not significant, in principle technogenic sulphur can be recognized in the environment by its characteristic sulphur isotope composition. The application of stable sulphur isotope methods for recognition of technogenic sulphur is reviewed in Krouse (1980) and Krouse (1991). More recent Alberta groundwater examples include van Donkelaar (1993), van Donkelaar et al (1995), and Fennell (1994).

## OBJECTIVES AND METHODS

The objective of this research was to determine if a record of technogenic sulphur emitted by the sour gas industry is preserved in the sediments of lakes situated downwind from these facilities.

The man-made Waterton Reservoir, initially flooded in 1965 and characterized by over 40cm of recent sediment fill, was investigated to evaluate the impact of two sour gas processing plants located upwind of the study area. The Shell Waterton Complex and the Gulf Pincher Creek Plant together have recovered over 22 million tonnes of elemental sulphur to year end 1992. In the process, approximately 573 253 tonnes of sulphur have been emitted to the environment since sulphur recovery operations began in late 1956. Prior mapping of the  $\text{SO}_2$  dispersal plume from these facilities (Twin Butte Task Force, 1984; Thimm and Weleschuk, 1990) demonstrates that portions of the catchment area have been subjected to anthropogenic sulphur deposition. Changes in regulatory requirements, and the closing of one of the local sour gas plants have resulted in a dramatic decline in local technogenic sulphur emissions in the study area.

The reservoir is over 40m deep and a considerable area is below wave base, reducing the loss of historical record which could result from physical mixing of the sediments.

Furthermore, large annual fluctuations in reservoir water level preclude establishment of aquatic communities in the littoral zone, limiting bioproductivity, and in turn minimizing the disruption of sediments through bioturbation. Southern Alberta experienced ashfall from the May, 1980 eruption of Mount St. Helens, potentially providing a geochronologic marker to constrain dating of sediments accumulating in Waterton Reservoir.

Commencement of sour gas processing operations in the study area pre-dates the beginning of sediment accumulation in Waterton Reservoir. Consequently, a nearby natural lake (Beauvais Lake), from an "upwind" setting was investigated in an effort to characterize the pre-industrial background.

Two vertical sediment cores from Waterton Reservoir and one from Beauvais lake were obtained and analysed to provide information on the spatial and temporal variability of total sediment sulphur concentration and total sediment sulphur isotopic composition. Porewaters from the Waterton Reservoir cores were analysed, and the sulphur isotopic composition of porewater sulphate was determined to provide insights to diagenetic processes occurring within the accumulating sediments. Water suites, comprising samples collected from locations in the catchment area over the course of a single day, provide an instantaneous "snapshot" of the chemical and isotopic composition of waters entering and leaving Waterton Reservoir.

To obtain the required large volume, undisturbed samples for chemical and stable isotope characterization of sediments and porewaters, a piston coring device of original design was constructed. Equipment and protocol for sediment subsampling in an oxygen-free environment, and for recovering and preserving representative porewaters for geochemical and stable isotopic characterization were established.

The present study differs from those of northeastern North America in several important respects. The entire history of sediment accumulation in Waterton Reservoir spans only

three decades. Isotope systematics, the high sedimentation rate and a constrained history of declining emissions from local industrial sources provide an unprecedented temporal resolution for investigation of sulphur storage mechanisms. The stable sulphur isotopic composition of sulphate from dilute porewaters provides important information about diagenetic processes and sulphur sources to the sediments of Waterton Reservoir. Long-distance transport of sulphur, including that of volcanic derivation, must be considered in studies of sulphur accumulation in lake sediments.

## CHAPTER 2 - SETTING

### LOCATION AND PHYSIOGRAPHY

The study area is situated in the extreme southwest corner of Alberta, immediately to the north of Waterton Lakes National Park, and approximately 250km south of Calgary (Figure 2.1). In deference to prior studies, and because a community of the same name lies near the geographic centre of the study, it will be referred to as the Twin Butte area. The principal lake investigated, the man-made Waterton Reservoir, is situated approximately 12.5km east of Twin Butte, and Beauvais Lake is located approximately 25km to the northwest of the community.

The region is one of marked geographic contrasts. The Front Ranges of the Rocky Mountains rise abruptly to elevations as high as 3200m from the more subdued, hummocky topography of Rolling Plains Embayment situated to the east. Rivers and creeks are deeply incised, creating steep-walled valleys commonly with relief of greater than 30m. Timberline is at approximately 2100m elevation. Montane and Aspen Parkland vegetation of the mountain valleys and foreslopes gives way to fescue grasslands in the hummocky terrain to the east of the hamlet of Twin Butte. Ranching and cattle grazing are the principal land uses in the area. Further east, between the valleys of the Waterton and Belly rivers, irrigation has encouraged greater agricultural diversity. Here, forage and cereal crops are grown to support the local dairy industry.

The study area includes the entire catchment basin of Drywood Creek, one of the major tributaries of the Waterton River, in turn, a tributary of the Oldman River. Both of the sulphur recovery plants in the area are situated adjacent to Drywood Creek (Figure 2.2), and small impoundments were constructed near each to facilitate withdrawal of water from Drywood Creek for industrial use.

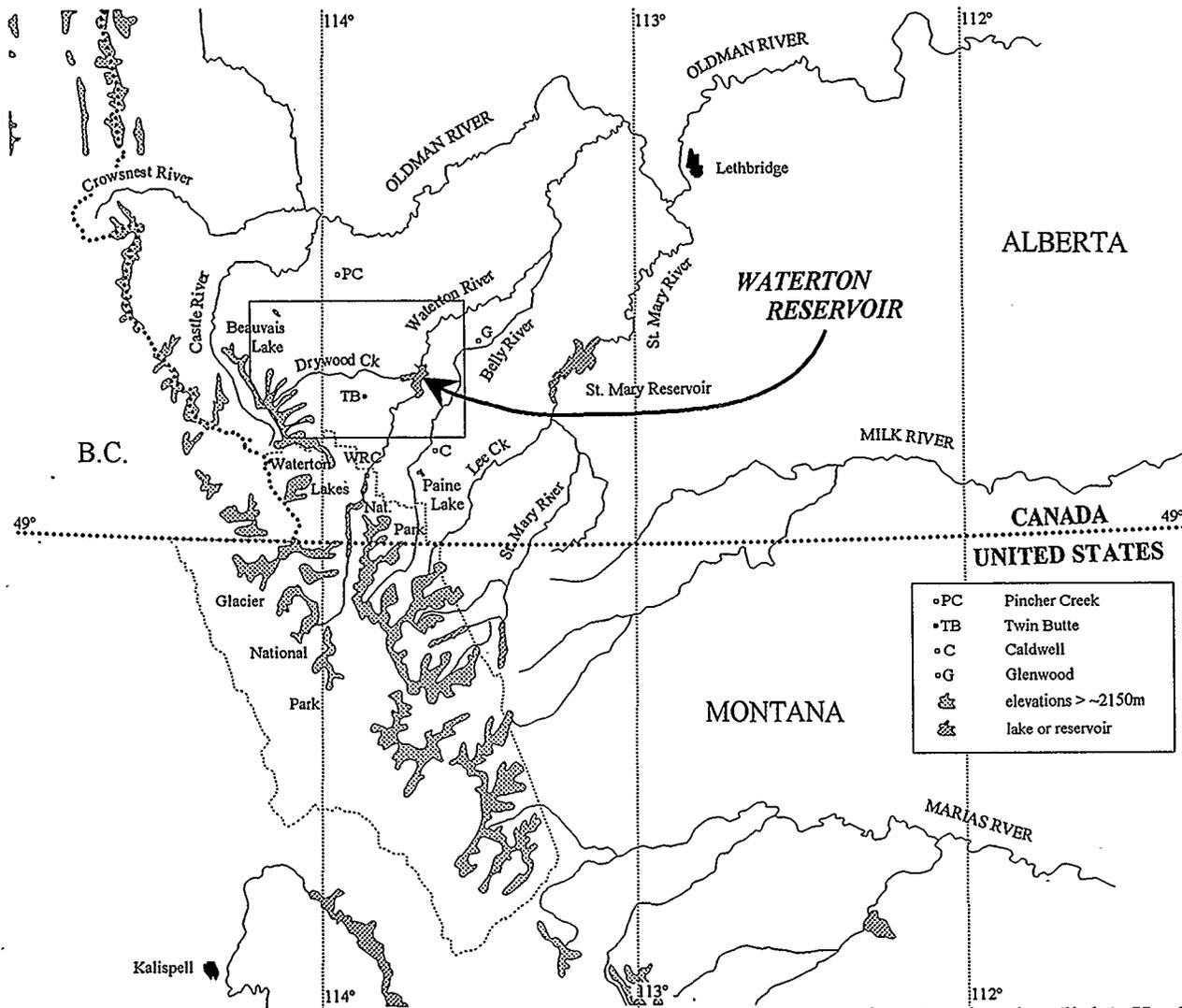


Figure 2.1 Location of study area. Patterns represent lakes (dark), and mountainous areas in excess of 2150m elevation (light). Headwater region of the Waterton River is in an alpine setting, with areas of permanent ice.

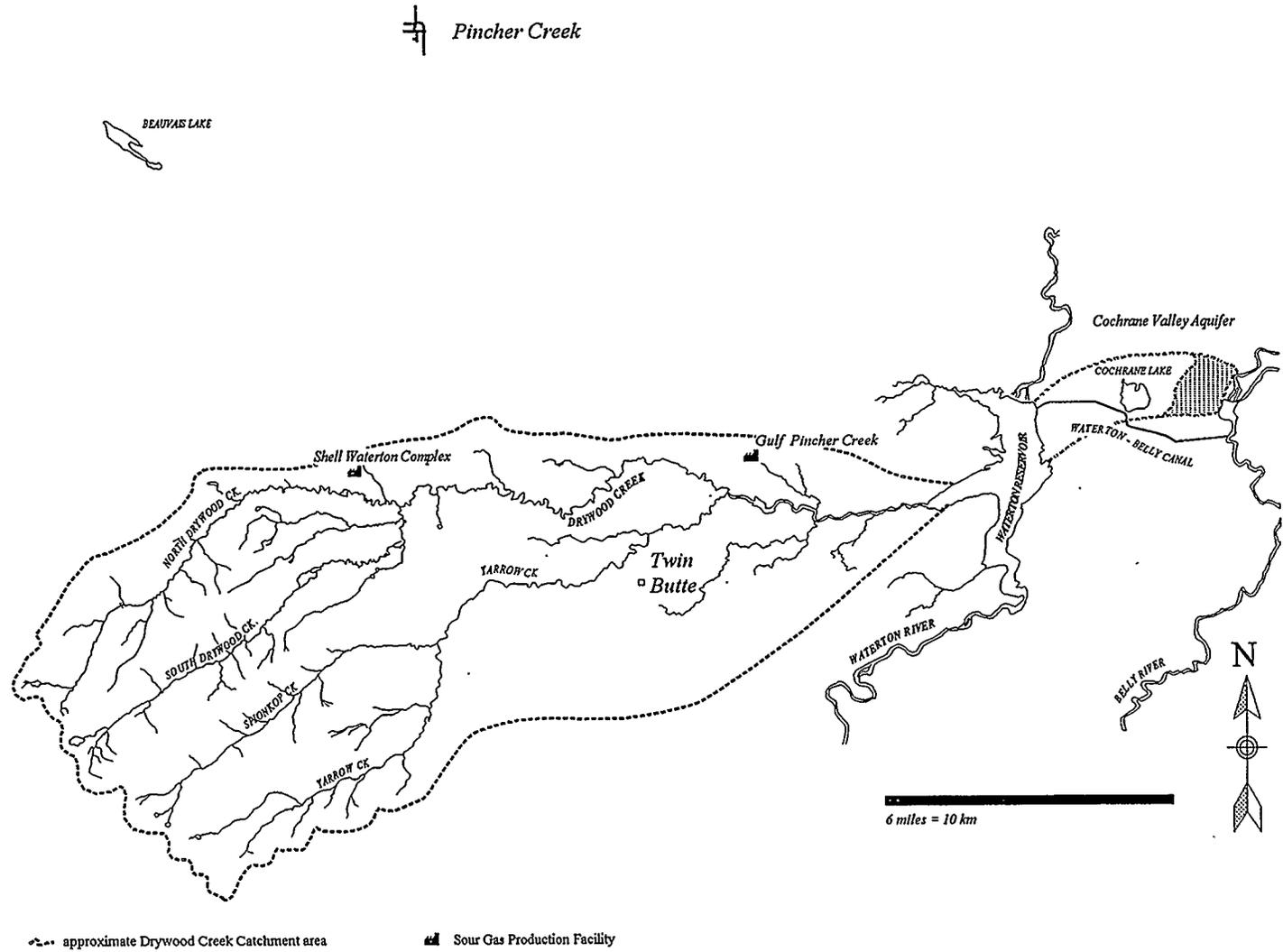


Figure 2.2 Drywood Creek catchment area. The patterned area represents the interstratified facies of the subsurface Cochrane Valley Aquifer (refer to text for discussion).

Construction of a large earthfill dam in the gorge of the Waterton River downstream of the confluence of Drywood Creek created Waterton Reservoir. The reservoir attains a maximum depth in excess of 40m at the toe of the dam. At full supply level (1185.672m), Waterton Reservoir has an area of about  $10.9 \times 10^6 \text{m}^2$  and contains approximately  $176 \times 10^6 \text{m}^3$  of water. The reservoir has serviced the needs of the United Irrigation District since it was initially filled in 1965, however it's principal role is to supply water to the St. Mary Reservoir, located about 30km to the east. Water is diverted from Waterton Reservoir via the Waterton-Belly Diversion Canal and the Belly-St. Mary Diversion Canal. Throughput of water is rapid; the mean residence time is approximately 60 days. Large annual fluctuations in water level preclude development of shoreline-stabilizing aquatic plants. As a result, the shoreline of the reservoir is actively eroded by wind-driven waves.

In contrast, Beauvais Lake is a small lake, having a surface area of  $0.9 \text{km}^2$  and a catchment area of approximately  $7 \text{km}^2$ . Maximum water depth is approximately 10.7m, and the residence time of water in the lake is approximately 4 years. Inflow to Beauvais Lake is primarily from diffuse surface run-off and precipitation; two intermittent streams provide a small proportion of the water. Aquatic plants flourish to a depth of 3.5m, and approximately 18% of the lake area is shallower than this. Beauvais Lake is a mesotrophic lake, and becomes weakly thermally stratified during the summer. Anoxic conditions may develop in the bottom waters during stratification, and dissolved oxygen concentration falls to zero in deep areas during the winter (Crosby, 1990b).

## CLIMATE

The climate of the area is characterized by contrasts, and is profoundly influenced by the physiographic setting. The mean annual temperature is approximately  $4.5^\circ\text{C}$ . Precipitation is highest in the mountainous areas to the west, and decreases dramatically to the east, where agriculture is tenuous in the absence of irrigation. May and June tend to be the wettest months in the plains area (e.g. Caldwell and Pincher Creek), with about 25% of

the annual precipitation happening during these months. This is a consequence of orographic precipitation occurring when moist maritime air masses carried by southeasterly winds impinge on the extreme topography of the Front Range. Severe rainstorms associated with such weather conditions have been identified as the principal cause of flooding of the Waterton River subbasin and the Oldman River basin in 1908, 1964, 1975 (Warner, 1973; Phinney, 1982). Similar conditions were associated with flooding of Drywood Creek basin in 1995, when more than 300mm of rain fell in a 24 hour period at the Shell Waterton Plant site (Norris Graham, pers. com. 1995).

In the mountainous areas, precipitation is more uniformly distributed throughout the year and approximately 50% of the precipitation falls as snow, with heaviest accumulations occurring above the treeline. Orographic effects described above result in the snowpack having a higher moisture content at the end of the winter season than does snowpack in the vicinity of Lake Louise (Warner, 1973), approximately 300km further north. Although snowmelt contributes a large proportion of annual runoff, it is not the cause of any known summer floods in the region (*ibid.*). Snowmelt is generally complete by the end of May in the mountains, and about one month earlier in the plains.

Annual evaporation has been estimated for Paine Lake (Crosby, 1990a) and Beauvais Lake (Crosby, 1990b). At these lakes, and in the surrounding areas, annual average evaporation exceeds precipitation (Table 2.1).

Table 2.1: Annual Precipitation and Evaporation Data - Paine and Beauvais Lakes

	mean annual precipitation	mean annual lake evaporation	mean annual sunshine
Paine Lake	687mm	729mm	2370 hours
Beauvais Lake	602mm	715mm	2370 hours

Annual precipitation and evaporation summaries for two lakes in study area. Lakes are identified on Figure 2.1. Data are from Crosby (1990a,b). Annual evaporative loss exceeds precipitation at these locations.

Melting and sublimation of snow cover in the foreslopes and plains during frequent winter chinooks contributes to the moisture deficit. The Waterton region is characterized by an average of 50 chinook-days per year (Yackel, 1995). Accumulating moisture deficits have lead to periodic drought conditions in the area. Since 1950, years identified as drought years are 1961, 1977, 1984, 1988 and 1990, the latter two being categorized as “wheat droughts” (W. Nemanishen, pers. com. 1995).

The Waterton region is famous for its strong winds. Local folklore abounds with characters who developed a westward lean and would fall flat if transported to other climates (Stenson, 1985). In the vicinity of the St. Mary Reservoir, it is calm only 2% of the time. The wind blows almost continuously from the west at an average speed of 33 kph and with gusts reported in excess of 170 kph (Crosby, 1990c). The strong winds and periodic drought conditions contribute to soil deflation in the region, and may contribute to the high sedimentation rate observed in Waterton Reservoir. The winds also provide a mechanism by which elemental sulphur recovered at the two local sour gas plants can be broadcast over a wider area.

## GEOLOGIC SETTING

### Bedrock geology

In contrast to other regions of Alberta, the Front Ranges of the Rocky Mountains in the Waterton area are characterized by rocks of Precambrian age. The eastern edge of the Front Ranges geologic subprovince in the Waterton region is delineated by the Lewis Thrust, which has carried west-dipping units comprising the Middle Proterozoic Purcell Supergroup over complexly folded and thrust faulted upper Cretaceous sands and shales of the Belly River Formation. The headwater area of the north branch of the Drywood Creek watershed comprises almost continuous exposure of the lower part of the Purcell Supergroup (Tippett et al, 1991). In westward progression from the Lewis Thrust, red and green argillites of the Apekunny Formation are overlain by red argillites and white

quartzites of the Grinnell Formation. These in turn are overlain by a complete section of Siyeh Formation dolomites, quartzites and algal limestones. Resistant ledges of the overlying Purcell Lava (Nichol Creek Formation) cropping out along the valley floor have formed pools and waterfalls in Drywood Creek. Dolomites and argillites of the overlying Sheppard and Kintla Formations of the Upper Purcell Supergroup crop out intermittently further upstream along Drywood Creek. Paleozoic units comprise only a small proportion of the bedrock, restricted to exposures on high peaks. A similar bedrock geology floors the headwaters of the South Drywood, Spionkop and Yarrow Creek drainage basins.

The subdued topography of the foreslopes and plains masks the geologic complexity of bedrock which underlies the area. Westward-dipping imbricate panels of Upper Cretaceous sands and shales typical of the Foothills geologic subprovince crop out along valley walls, and tightly folded Cretaceous bedrock is exposed in the gorge of the Waterton River immediately downstream of Waterton Dam. Waterton Reservoir is floored largely by siliciclastic rocks of the Belly River and to a lesser extent, Bearpaw Formations (Douglas, 1951). A recent synthesis of surface and subsurface geologic data demonstrates that bedrock is structurally deformed for a considerable distance to the east of the study area (Heibert, 1992). Subsurface anticlinal culminations, cored by thrust-faulted Paleozoic carbonates, form the prolific sour natural gas reservoirs which have been commercially exploited since 1956.

#### Surficial geology

Consolidated bedrock in the region is unconformably overlain by local pre-glacial, and more widespread glacial and post-glacial unconsolidated deposits. Development of the local pre-glacial topographic surface has been described by Stalker (1960). Northeasterly flowing ancestral rivers systems cut down through a slowly rising topographic surface. Migrating river courses abandoned remnant gravels on high ground.

Pleistocene glaciation modified and disrupted pre-glacial drainage and associated deposits. Tills of both Laurentide and Cordilleran derivation mantle the study area (Stalker and Harrison, 1977). Glacial erratics assigned to the Foothills erratics train area found on the Blood Indian Reserve, east of the Belly River, at elevations between 1067m and 1189m. Here, Stalker (1963) described the occurrence of two Cordilleran and several Laurentide tills. The foreslopes of the Front Range area are characterized by hummocky moraine topography having slopes of 16 to 30% and with gray luvisol soils (Shields and Lindsay, 1986). Numerous ephemeral ponds occur in topographic depressions. East of Twin Butte, the terrain is more subdued (10 to 15% slopes) and soils are predominantly black chernozems (*ibid.*).

Gravel-filled pre-glacial channels are exposed along the Oldman River at Lethbridge and Medicine Hat. Elsewhere in the region, similar paleovalleys exhumed by the present topographic surface are a commercial source of aggregate materials (Shetsen, 1981), and where buried in the shallow subsurface, may be important aquifers. Aquifers of this type occur in the vicinity of Cochrane Lake, at the Gulf Pincher Creek gas plant (Twin Butte Task Force, 1984), and at the Shell Waterton gas plant (van Donkelaar, 1993). Drift thicknesses reach approximately 30m in the paleovalleys.

## HYDROLOGIC SETTING

### Surface waters

Environment Canada hydrometric gauging stations (located on Drywood Creek, Waterton-Belly Diversion Canal and locations on the Waterton River upstream and downstream of Waterton Dam) permit quantification of the principal inlets to, and outlets from, Waterton Reservoir. Discharge data are reported on a daily basis. The daily water level of Waterton Reservoir is also reported. Analyses of water samples collected approximately monthly by Environment Canada from the Waterton River near Waterton

National Park provide data on seasonal trends in water chemistry. Historical chemical data for this station are available from the mid 1970's to the present.

Long term discharge records for the relevant hydrometric stations illustrate the strong seasonal variability in discharge rates. During the period from late summer through winter, flow rates tend to diminish and reach a minimum in late winter. Peak discharge occurs from mid-May through to the end of June (Figure 2.3). Chemistry of the Waterton River also varies with river stage; highest total dissolved solids concentrations occur immediately after low flow conditions. The mean total dissolved solids concentration of the Waterton River is 91.2 mg/L (n=317, S.D.=15.9).

The Waterton River is the principal source of water to Waterton Reservoir, providing on a monthly average basis approximately 82 to 88.5% of the measured inflow. Mean daily flow rate of the Waterton River during the flood of 1964 was of the order of 7 times higher than mean peak flow rates. The reservoir water level fluctuates largely in accordance to the balance between inflow and outflow, with a mean annual range of 8.6m. Water level is drawn down in the autumn to accommodate runoff during the following spring. The extreme annual water level fluctuation precludes growth of aquatic plants in the littoral zone and the maximum annual range of greater than 15m occurred in 1969.

The morphometry of the reservoir was established prior to dam construction by a detailed topographic survey, permitting area and capacity to be calculated, in turn permitting estimation of water volume for a given reservoir level. Knowledge of water volume and outflow rates permits estimation of the residence time of water in Waterton Reservoir using the relationship:

$$\text{Residence time} = \text{lake volume} / \text{outflow rate} \quad (1)$$

Residence times calculated from mean monthly discharge and level data are of the order of 275 days during the low flow period, and 20 days during peak discharge in June.

### Waterton Reservoir Catchment - mean daily discharge rate

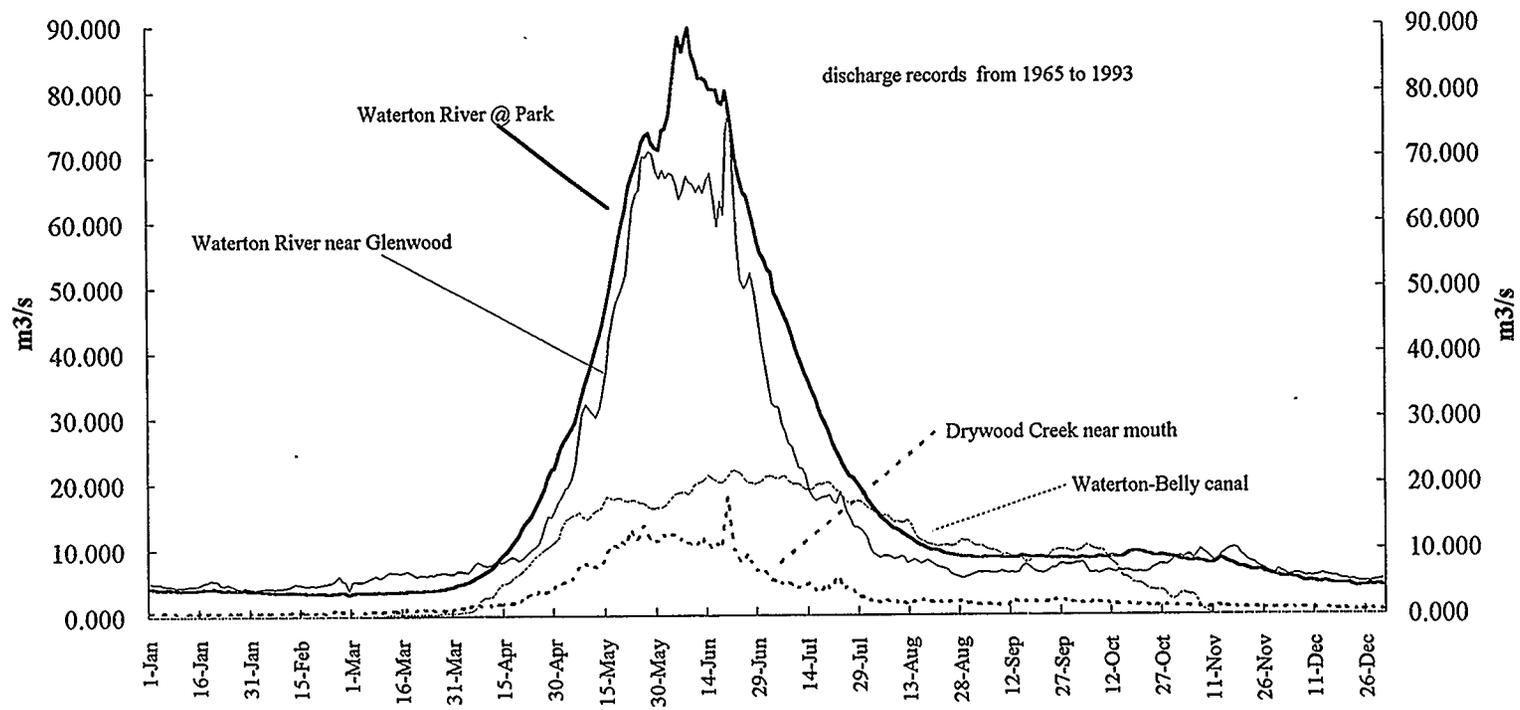


Figure 2.3 Hydrologic balance of Waterton Reservoir. Mean daily discharge data from Environment Canada records, from 1965 to 1993.

Water samples collected and analysed in 1983 during the investigations of the Twin Butte Soils and Water Evaluation Task Force provide information on the chemical composition of waters from creeks, lakes and ephemeral ponds in the area. Surface water compositional ranges are summarized as Table 2.2. The high concentrations exhibited suggest that evaporative processes can influence the surface waters of the area. This interpretation was reinforced by stable oxygen and hydrogen isotope data (Wallick et al, 1984).

Table 2.2. Surface water and groundwater concentration ranges, Twin Butte Area

	Surface Waters		Groundwaters	
	Low	High	Low	High
Calcium (ppm)	14.4	168.0	0.3	395.0
Magnesium (ppm)	10.0	208.0	<0.1	118.0
Sodium (ppm)	1.7	292.0	2.0	700.0
Potassium (ppm)	0.35	53.0	0.39	7.5
Sulphate (ppm)	<0.10	865.0	5.27	1505.0
Chloride (ppm)	0.2	29.3	0.4	46.0
Nitrate (ppm as N)	<0.003	0.32	<0.003	28.3
Silica (ppm)	0.56	25.0	0.32	14.8
Fluoride (ppm)	0.09	0.41	0.07	0.50
Iron (ppm)	<0.01	0.22	<0.1	0.79
Manganese (ppm)	<0.004	0.404	<0.004	1.29
Total Organic C (ppm)	0.4	61.0	2.4	34.7
Total Inorganic C (ppm)	16.0	132.0	26.0	132.0
Bicarbonate (ppm)	7.3	689.0	145.0	673.0

Ranges of constituent concentrations of surface and groundwaters collected in September and October 1983, by the Twin Butte Soils and Water Evaluation Task Force. Data are from Wallick (1984).

Using the mean of the annual evaporation values of Beauvais and Paine Lakes, and considering the mean Waterton Reservoir water level (and corresponding area), annual evaporation from Waterton Reservoir is estimated to be of the order of  $6.74 \times 10^6 \text{m}^3$ . This corresponds to about 5.5% of the volume of Waterton Reservoir at mean water level. Similarly, estimated annual precipitation is  $5.96 \times 10^6 \text{m}^3$ , corresponding to 4.9% of the reservoir volume at mean water level.

### Groundwaters

Water for domestic and livestock purposes is obtained from both bedrock fractures and surficial deposits in the area. Ranges of analyses of samples collected during the 1983 investigations of the Twin Butte Soils and Water Evaluation Task Force are summarized in Table 2.2. Water well records did not permit differentiation between bedrock aquifer and surficial aquifer waters. The general similarity in compositional ranges suggests effective communication between surface waters and groundwaters.

A noteworthy hydrogeologic feature of the study area is the Cochrane Valley Aquifer, a buried gravel aquifer occupying a paleovalley extending from the northeastern shore of Waterton Reservoir, beneath Cochrane Lake, and towards the valley of the Belly River (Figure 2.2). Gravels and sands comprising the aquifer were deposited to a maximum proven thickness of 29m, and form an apparently continuous hydraulic unit extending approximately 4km from the Waterton Reservoir (Vanden Berg and Geiger, 1973). Hydraulic properties apparently deteriorate beyond this to the east, and the aquifer is interpreted to be interstratified with impermeable materials over the remaining 1.5km of preserved aquifer length. The aquifer discharges into the valley of the Belly River at a spring on the property of Jacob Lenz (*ibid.*).

Prior to the filling of Waterton Reservoir, the aquifer was unsaturated throughout much of the gravel thickness, with a free water table at an elevation of 1148.5m, about 2.75m higher than the elevation of the Waterton River. Recognizing the potential effects on the aquifer of filling of the Waterton Reservoir, a co-operative investigation by the Alberta Government and the federal Prairie Farm Rehabilitation Administration (PFRA) was launched. Data are summarized in Vanden Berg and Geiger (1973). Five piezometer nests were installed to monitor water table levels and to measure hydraulic pressure in the Cochrane Valley Aquifer during, and after filling of the reservoir. The piezometers and several domestic wells experienced virtually instantaneous response during reservoir filling when the reservoir water level exceeded the height of the former free water table, proving

efficient hydraulic connection between the reservoir and the aquifer. The casing of one farm well was forced out of the ground resulting in an uncontrolled flow, and a spring developed in the middle of a small slough. To preclude additional problems, the PFRA installed a number of pressure relief wells designed to accommodate high flow rates, and the Government of Alberta installed two piezometers specifically for determination of aquifer parameters. Discharge from the pressure relief wells averages  $0.409\text{m}^3/\text{s}$  (Vanden Berg and Geiger, 1973). Seepage from Waterton Reservoir to the Cochrane Valley Aquifer was estimated to be of the order of  $0.26\text{m}^3/\text{s}$  (ibid.) Recharge of waters from the surrounding tills apparently supplies the difference.

## CHAPTER 3 - LOCAL SOUR GAS INDUSTRY EMISSIONS

A brief overview of sour gas processing provides useful background for understanding the sources and quantities of technogenic sulphur emissions which result from these activities. Statistics illustrating the magnitude of the industry, and a synoptic overview of relevant gas processing topics follow. A conservative emissions estimate for the local sour gas industry is developed.

### BACKGROUND

As energy demand increased rapidly in the late 1950's, Canadian production and exports of natural gas increased proportionately (as did the number of gas producing facilities). According to the ERCB, 40.56% of net cumulative production of marketable gas to year end 1992 was from sour gas pools (ERCB, 1993), and a forecast by the same agency suggests that about 44% of the  $4.2 \times 10^9 \text{ m}^3$  gas remaining to be discovered will be sour (ERCB, 1992a).

The recovery of elemental sulphur as a by-product of sour gas processing is the basis for Alberta's large sulphur industry. At present, approximately 60 sulphur recovery plants have been built in Alberta. By-product sulphur accounted for 87.6% of Canada's total sulphur production of 6.5 million tonnes in 1992 (Prud'homme, 1993). Canada was, in 1992, the world's largest exporter of this commodity (Doyle, 1993).

A vast sulphur inventory accumulated during the 1970's in response to a decade of global oversupply. By 1978, more than 20 million tonnes were stockpiled in elemental S blocks in Alberta (6 million tonnes in a sulphur block 3.2 km long at the Ram River plant). Approximately 16 million tons of the inventory was sold between 1979 and 1992 at an

average price of about \$75 per tonne, generating over 1 billion dollars to the industry (Hyne, 1993).

## PROCESSING OF SOUR GAS

Prior to delivery to users, undesirable components of natural gas must be removed. Sour gas conditioning typically comprises processes for removal of liquids (water and hydrocarbon liquids), acid gas separation, and sulphur recovery. This results in a consistent dry, sweet gas suitable for consumer use. The following process synopses are largely based on descriptions from gas processing and sulphur recovery sections of the Kirk-Othmar Encyclopedia of Chemical Technology (Hillard, 1978 and West, 1978).

The  $\text{CO}_2$ ,  $\text{H}_2\text{S}$  and other sulphur compounds in natural gases are collectively termed acid gases. These are typically removed from the raw gas stream at a sour gas processing facility through use of chemical or physical solvents in a countercurrent absorber. The impurities react with the solvent to form a complex which later is decomposed in a regeneration still by application of heat using steam. MEA (monoethanolamine) is the oldest and most widely used of the chemical solvents, however trace compounds in the raw gas stream such as COS and  $\text{CS}_2$  cause excessive solvent degradation.  $\text{CO}_2$  in the feed gas also reacts to form heat stable salts which accumulate in the solution and must periodically be removed. DEA (diethanolamine) was later introduced as degradation-resistant alternative, compatible with existing MEA equipment.

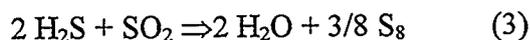
A more recently used solvent, Sulfinol, comprises a mixture of a physical solvent, sulpholane (tetrahydrothiophene dioxide) and a chemical solvent, diisopropanolamine. It was introduced by Shell to avoid the degradation losses associated with  $\text{CS}_2$  and COS in inlet gases. Greater gas treating capacity, lower heat requirements and lower circulating rates are among the energy-saving advantages realized by facilities using this solvent.

Chief among the disadvantages is the tendency for Sulfinol to absorb heavy hydrocarbons from the inlet gas.

The concentrated acid gases comprise the feed for a sulphur recovery plant. The modified Claus process is the most widely used process for conversion of H<sub>2</sub>S to elemental sulphur. Briefly, acid gases are combined with a stoichiometric quantity of air to burn 1/3 of the total H<sub>2</sub>S to SO<sub>2</sub>:



The sulphur dioxide and remaining hydrogen sulphide react over a bauxite catalyst forming elemental sulphur:



The resulting sulphur vapour is condensed during passage through a series of condensers and heaters, and the elemental sulphur collected as a liquid for recovery.

Theoretical recovery efficiency for the Claus process is greater than 99.5% (Clark et al 1994) however practical recovery is commonly up to 2% less. Fluctuations in feed gas composition, and carry-over of hydrocarbon and solvent from sour absorption facilities result in side reactions or deactivation of catalysts. These cause operational upsets and plant shut-downs, increasing emissions (ERCB, 1982).

A typical tail gas exiting a Claus facility contains 2% H<sub>2</sub>S, 1% SO<sub>2</sub>, entrained liquid S, S vapour and reduced S compounds such as COS and CS<sub>2</sub> (Legge, 1982). Combustion at temperatures in the range of 580°C with excess air and CH<sub>4</sub> in tall incinerator stacks is intended to oxidize these components to SO<sub>2</sub> prior to dispersal to the atmosphere. Water vapour is also produced by the reactions of the Claus process (reactions 2 and 3, above).

## SOURCES OF EMISSIONS

Incinerator stack emissions are the principal source of technogenic sulphur to the environment surrounding sour gas processing facilities. Despite the high efficiency of the sulphur recovery process, the huge quantities produced results in large quantities of SO<sub>2</sub> emissions. Considering capacities as of January, 1992 (ERCB, 1992b), the total recovery capability of the 52 active sulphur recovery plants in Alberta was 26084 tonnes S/d with a licensed emission limit of 609 tonnes S/d (about 1218 tonnes expressed as SO<sub>2</sub>). Of this total, 70% of the S production capability and 55% of the potential emissions were from only 5 sour gas plants.

Of secondary importance are gases diverted to and incinerated in smaller flare stacks during gas plant operational upsets. Legge (1982) illustrates the relative importance of flare stack emissions over a 7 year period. Significantly, during an upset the flare stack can contribute more S emissions on a daily basis than does the incinerator stack under normal operating conditions. Sulphur gases measured in flare stack emissions include SO<sub>2</sub>, H<sub>2</sub>S, CS<sub>2</sub> and COS (Stroscher, 1984).

Technogenic sulphur may also be introduced to the local environment from the elemental S produced at these facilities. H<sub>2</sub>S (g) and H<sub>2</sub>S<sub>x</sub> (g) entrained with product sulphur may escape when liquid S is loaded for shipment, formed as slates or other solids, or poured to block. These contaminants may also be trapped in solid elemental S, and may be subsequently released during remelting or transportation. The more recent practice of degassing of liquid S has diminished the concentration of these impurities.

The friability of solid elemental sulphur has resulted in S dust problems in the vicinity of sulphur recovery plants. Friability in part originates as a consequence of the decrease in volume of solid sulphur accompanying polymorphic transformation with cooling. Interestingly, reduction in H<sub>2</sub>S and H<sub>2</sub>S<sub>x</sub> content of product S may result in increased

friability (Clark et al, 1994). Dust associated with S block ablation by wind, or from disaggregation by explosive or mechanical means may be carried by the wind for considerable distances. Generation of sulfuric acid by ubiquitous sulphur oxidizing soil microbes in dust-affected soils is a possible mechanism by which technogenic sulphur may be introduced to soil solutions and ultimately to groundwater. Water misting to control dust may also contribute to the formation of acidic solutions.

Surface run-off from the sulphur storage and handling areas is typically retained in evaporation ponds at the plant sites. Seepage of sulphate-rich waters from these ponds may also introduce technogenic sulphur to the environment. Retention of run-off in the ponds permits water treatment prior to disposal via evaporation, irrigation or injection into deep wells. In some cases, effluent water is discharged to watersheds after treatment to meet regulatory standards.

Blow outs of sour gas wells during drilling or work-over operations, leaks in sour gas pipelines, and SO<sub>2</sub> emitted from sulphur block fires during remelting may also contribute to the technogenic S burden in the vicinity.

Of the sources mentioned, incinerator stack and flare stack emissions are the most readily quantified. Data submitted by gas plant operators to regulatory agencies includes inlet gas volumes and compositions, sulphur production, incinerator stack gas composition, and volumes of gas flared. Incinerator stack operating conditions are continuously monitored and data reported to regulatory agencies.

Continuous ambient atmospheric monitoring of H<sub>2</sub>S and SO<sub>2</sub> concentrations from trailer-mounted units in the vicinity of gas plants is also reported to regulatory agencies. In addition, sulphur recovery plants are required to maintain dustfall cylinders and a network of sulphation stations which permit quantification of ground level SO<sub>2</sub> and H<sub>2</sub>S exposure on a monthly average basis.

## REGULATORY BACKGROUND

H<sub>2</sub>S is acutely toxic in small quantities, consequently it is not surprising that industrial activities which involve handling of this compound are regulated. An overview of the regulatory environment under which the industry has operated follows. Profound decreases in SO<sub>2</sub> emissions from the industry have been the direct result of regulatory pressures.

Sulphur recovery from sour gas processing in Alberta began in 1952 with small plants capable of producing about 30 tonnes S/d at both Jumping Pound and Turner Valley fields. Prior to this, H<sub>2</sub>S removed from sour gas was simply vented to the atmosphere (Stenson, 1985). During 1960, in an time of public complaint and fearing proliferation of gas processing facilities, the Air Pollution Branch of the Alberta Department of Health was formed. Guidelines requiring as much sulphur recovery as economically feasible were the flavour of the era. These requirements seemed appropriate at a time when gas plants such as the Pincher Creek plant were coping with frequent operational upsets and in doing so were essentially “writing the book” on sour gas processing. At this time, the industry on average recovered about 89% of the sulphur from the inlet gas (ERCB, 1982). In 1961 regulations required that all sulphur not recovered be incinerated to SO<sub>2</sub>, and maximum ground level SO<sub>2</sub> concentration criteria were established in the vicinity of sour gas plants.

A review of emissions from the sour gas industry in the late 1960's lead to strict new regulations introduced with the Clean Air Act of 1971. A minimum sulphur recovery efficiency of 95.9% for sulphur recovery plants was stipulated, and gas plants producing between 1016 and 4064 tonnes S/day were required to recover 98% to 99% by the compliance date, January 1st, 1975 (ERCB, 1971).

Increasingly strict regulations were introduced in 1980 following an 8-fold increase in marketable gas between 1960 and 1979. During the same period, annual SO<sub>2</sub> emissions

from the industry increased from about  $55 \times 10^3$  tonnes (expressed as S equivalent) to  $170 \times 10^3$  tonnes (S), reaching a zenith of almost  $290 \times 10^3$  tonnes (S) in 1972 (ERCB, 1982).

Regulations were again revised in 1988, the principal change being introduction of minimum sulphur recovery guidelines for plants processing gas having 1 to 10 tonnes S/d in the inlet gas stream (ERCB-AE, 1988). Under these regulations, large facilities in the 2000 tonnes S /d (raw gas) category were required to recover 99.8% of the sulphur.

## LOCAL SOUR GAS INDUSTRY HISTORY

The exploitation history of sour gas accumulations in the area are summarized in the following section to provide a framework for estimation of emissions from the local sour gas industry.

### Gulf Pincher Creek Plant

The Pincher Creek gas field was discovered in 1948 by the drilling of B.A. Pincher Creek #1 (15-24-3-29W4M) after extensive seismic refraction and gravity surveys. Subsequent delineation drilling indicated that the porous Mississippian carbonate reservoir was potentially gas-bearing for a strike length of about 19 km and, in 1953, marketable gas reserves were estimated by B.A. to be  $65 \times 10^9$  m<sup>3</sup> (2.3 TCF) (Gordy and Frey, 1977). On the basis of these vast reserves and a growing export demand for natural gas, the decision to build a sour gas processing plant was made. The high acid gas content (10.78% H<sub>2</sub>S and 6.16% CO<sub>2</sub>; OGJ, 1958) demanded a facility unlike any built before by the industry.

Sour gas processing operations in the area began December 31<sup>st</sup>, 1956 when gas began to flow into the B.A. Pincher Creek plant. Initially, natural gas liquids were extracted, elemental S produced and the sweetened, dry gas re-injected to the reservoir. Acid gases from the inlet stream were absorbed using MEA, and sulphur recovered in a Claus plant. Capacity was increased to accompany the arrival of the Trans-Canada pipeline in October

of 1958, when sales of gas from the plant began. Sulphur production capacity was increased from 228.6 tonnes S/d from  $1.69 \times 10^6$  m<sup>3</sup>/d raw inlet gas to 685.8 tonnes S/d from  $5.10 \times 10^6$  m<sup>3</sup>/d raw inlet gas (bid).

In many respects the Pincher Creek plant was a technologic proving ground for the sulphur recovery industry. Stenson (1985) describes the early days of plant operation as a dangerous circus. Operational upsets were common, requiring emergency plant turn-down and gas flaring. Many upsets were caused by MEA foaming, resulting in carry-over of solvent and hydrocarbon to the Claus plant, in turn causing degradation of the bauxite catalyst and affecting Claus reaction equilibria.

In the early '60's a process change to acid gas absorption by DEA was predicated by excessive solvent loss from COS and CS<sub>2</sub> in the inlet gas stream (Stenson, 1985). Production of elemental S peaked at 175931 tonnes/year (~ 482 tonnes/day) in 1962, and plant throughput declined with unexpected rapidity shortly afterwards. Production decline associated with water encroachment in the Pincher Creek field was blamed (Gordy and Frey, 1977), and reservoir performance-based estimates of marketable gas plummeted to  $10.7 \times 10^9$  m<sup>3</sup> (0.38 TCF) (ERCB, 1993). To offset diminishing productivity, processing of sour gas from the nearby Lookout Butte field began in 1967.

Compliance with increasingly rigorous emissions regulations proved difficult for operators of a plant of this vintage. The plant was the first in Alberta requiring incineration of effluent gases from the Claus reactor (Stenson, 1985). Modifications and frequent replacement of catalyst beds in the Claus plant permitted sulphur recovery efficiency of 94% "for reasonable periods of time" (Gulf, 1972). As raw gas deliverability declined, voluntary reductions in plant capacity achieved further reductions in emissions (Gulf, 1972; Gulf, 1975). The Pincher Creek plant was shut-down on April 4<sup>th</sup>, 1983, and remaining raw gas from Pincher Creek and Lookout Butte fields transferred by pipeline to the nearby Shell Waterton Complex for processing. Site reclamation studies accompanying

the decommissioning of the gas plant prompted the environmental investigations of the Twin Butte Soils and Water Evaluation Task Force in the autumn of 1983 (Twin Butte, 1984).

### Shell Waterton Complex

One of Canada's largest gas accumulations was discovered by Shell in 1957 with the drilling and completion of Shell Waterton #1 (4-21-4-1W5M). The Waterton field comprises several west-dipping, imbricated panels of Paleozoic carbonate reservoirs, with fracture systems locally providing communication between discrete reservoirs of Mississippian and upper Devonian age. Marketable gas reserves are estimated at  $73.75 \times 10^9 \text{ m}^3$  (2.6 TCF) (ERCB, 1993) and total recoverable sulphur is estimated to be in the order of 15.2 million tonnes (Gordy and Frey, 1977). The huge reserves, high potential gaswell deliverability and high  $\text{H}_2\text{S}$  content of the raw gas (up to 34.85%  $\text{H}_2\text{S}$ ; Shell, 1973) predicated construction of a second sour gas plant in the region.

Gas processing at the Shell Waterton plant began in January of 1962. Initial design capacity of the plant was 1453 tonnes S/day and  $3.4 \times 10^6 \text{ m}^3/\text{day}$  sales gas. To optimize acid gas recovery, the yet-to-be proven Low Temperature Flash (LTF) process was used to remove about 85% of the acid gas component prior to sweetening using a MEA absorber (Stenson, 1985). Sulphur was recovered in a 3-stage Claus plant. The gas plant was expanded in 1966 to a capacity of 1673 tonnes S/day and  $4.8 \times 10^6 \text{ m}^3/\text{day}$  sales gas. Accompanying expansion was a conversion to Sulfinol sweetening to reduce solvent degradation. Demand for further increases in gas processing capacity prompted Shell to build a second, similar gas plant on the site. Shell Waterton Plant II came on stream in December of 1972, resulting in a combined capacity of 3014 tonnes S/day and  $8.9 \times 10^6 \text{ m}^3/\text{day}$  sales gas (Shell, 1973). Since 1972, process improvements to the Shell Waterton Complex have increased capacities slightly. Notably, elemental sulphur production has been increased incrementally by sulphur recovery from the tail gas exiting the Claus plants, beginning in 1976. Only recently has the Shell Waterton Complex been demoted by one

from its rank as the 3<sup>rd</sup> largest sulphur recovery plant (by sulphur production capacity) in Alberta.

Motivated by the Clean Air Act of 1971, Shell designed and a SCOT (Shell Claus Off-gas Treatment) plant to minimize the sulphur concentration of a significant proportion of gases being fed to the incinerator stack. Briefly, SO<sub>2</sub> in Claus effluent gas is reduced to H<sub>2</sub>S, and COS and CS<sub>2</sub> are hydrolysed. After cooling, the gas comprising H<sub>2</sub>S, CO<sub>2</sub>, N<sub>2</sub> and H<sub>2</sub>O(v) is compressed and fed to a countercurrent amine absorber, where H<sub>2</sub>S is selectively absorbed in a diisopropanolamine (DIPA) solution. Effluent gas from the SCOT plant is incinerated to produce SO<sub>2</sub>, and H<sub>2</sub>S liberated by heat from the pregnant DIPA solution is fed to the front end of the Claus plant for sulphur recovery. Conversion of up to 99.8% of inlet gas S to elemental sulphur is possible in Claus-SCOT facilities (West, 1978). Water recovered by the SCOT plant (about 1300 m<sup>3</sup>/day) is utilized elsewhere in the sour gas facility (Norris Graham, pers. com. 1995).

#### TWIN BUTTE AREA SULPHUR PRODUCTION SUMMARY

The preceding discussion is intended to give a sense of the scale of the local sour gas industry. The annual sulphur production from the two sour gas processing facilities from 1957 to 1992 is summarized as Figure 3.1. Data are based on monthly summary statistics submitted by the plant operators to the Energy Resources Conservation Board. ERCB ST-3 gas plant records provided data prior to 1971; subsequent data are from ERCB S13-A reports. Cumulative production of elemental sulphur from the Pincher Creek and Waterton gas plants to year end 1992 was approximately  $22 \times 10^6$  tonnes.

Readily apparent from Figure 3.1 is the dramatic contrast in capacity of the Shell and Gulf plants. Plant expansions described earlier are also observed, as is the decline in elemental S production from the Pincher Creek plant as gas reserves in the Pincher Creek field were rapidly depleted

## Twin Butte area - annual S production

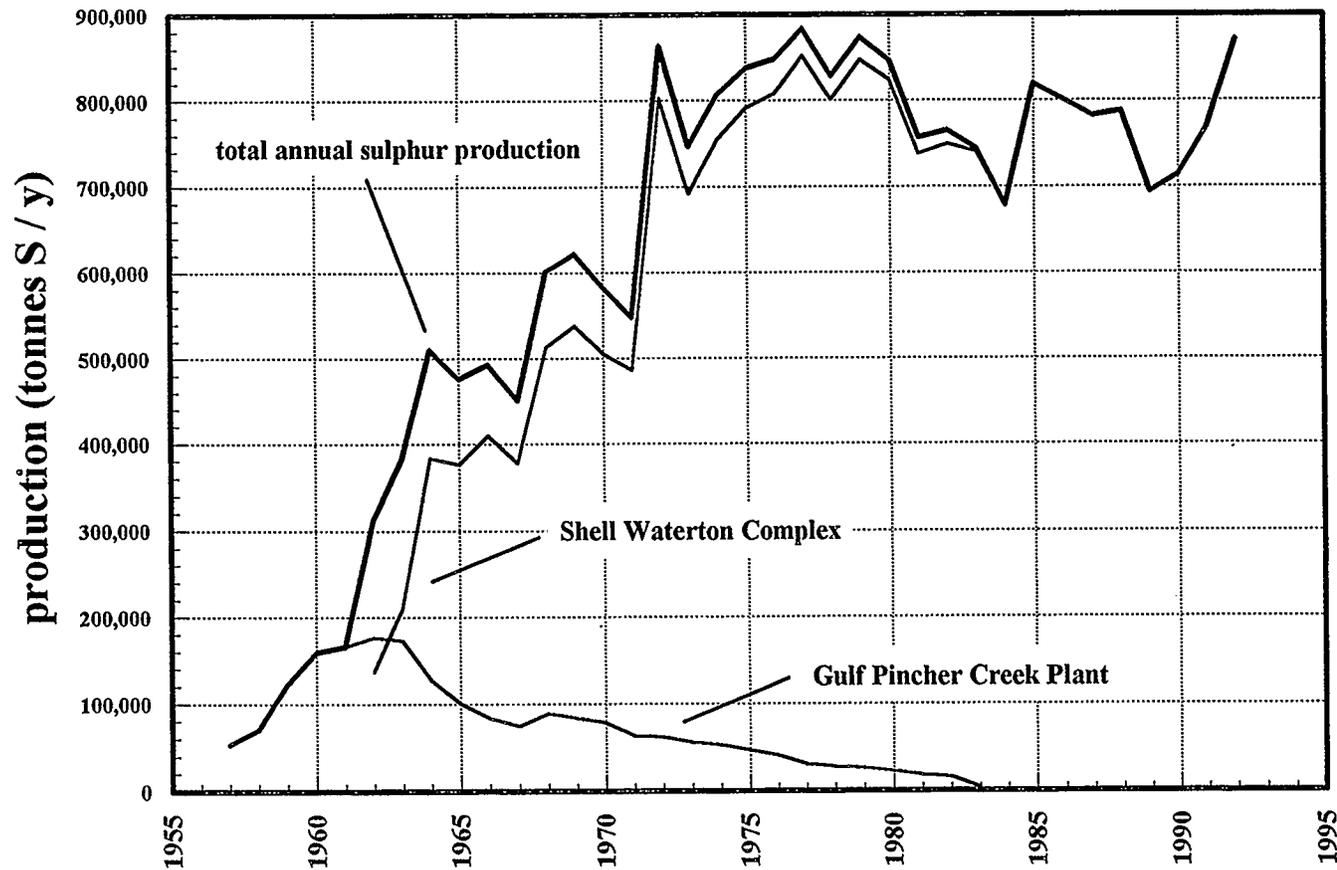


Figure 3.1 Twin Butte area annual sulphur production. Data are from ERCB monthly production records.

## ESTIMATE OF TWIN BUTTE AREA TECHNOGENIC SULPHUR EMISSIONS

A comprehensive historical evaluation of the deposition of technogenic sulphur in the Twin Butte area is beyond the scope of this research. An estimate of the local sour gas industry emissions history based on incinerator stack emissions data is illustrated as Figure 3.2. Monitoring and reporting requirements have evolved with time and not all information could be obtained from regulatory agencies, necessitating certain simplifying assumptions. In the absence of summary information, the estimate for the Gulf Pincher Creek facility relies exclusively on sulphur production data. In calculating sulphur emissions, a sulphur recovery efficiency of 94% was assumed throughout the operating history of the plant. This value is consistent with sulphur recovery efficiency reported by Gulf in submissions to regulatory agencies (e.g. Gulf, 1972).

The better-constrained estimate for Shell Waterton Complex uses actual monthly incinerator stack emissions submitted by the operator to Alberta Environment and its antecedent agencies. As data for 1962 and 1963 could not be retrieved, emissions for these years are estimated using an assumed 93.5% recovery efficiency (Shell, 1961).

Comparison of Figures 3.1 and 3.2 reveals the dramatic drop in emissions resulting from compliance with regulations introduced with the Clean Air Act. Emissions decreased to about 40% of prior levels following the start-up of the SCOT plant at Shell Waterton Complex as sulphur production remained essentially constant.

The local emissions scenario presented is conservative as only incinerator stack emissions are considered. Intermittent data submitted to Alberta Environment for Shell Waterton Complex indicates that the flare stack on average generates about 2.36% of total annual emissions (data for 19 years, S.D.=1.71). More frequent operational upsets early in local sulphur recovery industry history probably contributed a greater proportion than this. As will be discussed later, discharge of liquid effluent from the Shell Waterton Complex

## Twin Butte area - incinerator stack emissions

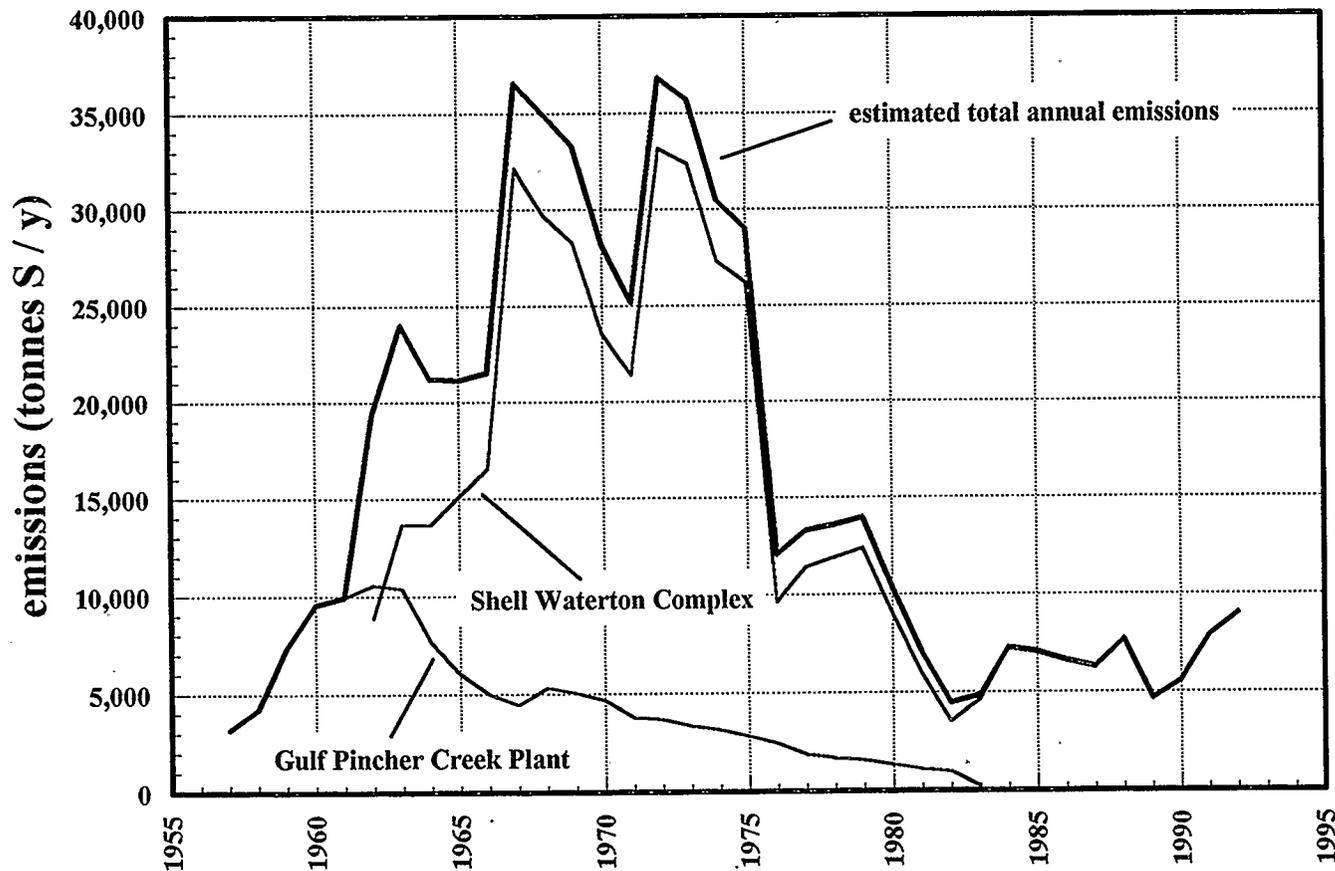


Figure 3.2 Twin Butte area annual incinerator stack emissions. Assumes 94% sulphur recovery for Gulf Pincher Creek Plant. Estimate for Shell Waterton Complex based on monthly incinerator stack data submitted by Shell to Alberta Environment.

contributes approximately 144 tonnes/yr S to Drywood Creek, an amount equivalent to about 2.5% of the annual incinerator stack emissions (at levels representative of the period from 1982 to the present, Figure 3.2). During the decommissioning of the Gulf Pincher Creek plant the latter half of 1983, over 75000 tonnes of elemental S were mechanically disaggregated and bulk hauled to Shell Waterton Complex. Sulphur dust generated from these operations contributed to an overall elemental S increase in the soil in the vicinity of the Pincher Creek plant (Gulf, 1983).

On the basis of the estimate presented as Figure 3.2, cumulative incinerator stack emissions from both facilities total approximately 576620 tonnes S to year end 1992, of which about 81% have occurred since Waterton Reservoir was flooded in 1965. About 66781 tonnes (as S) have been emitted by Shell Waterton Complex since the Pincher Creek plant ceased operations.

#### ISOTOPIC COMPOSITION OF LOCAL TECHNOGENIC SULPHUR

The sulphur isotopic composition of the raw inlet gas and the elemental sulphur recovered at each of the local sour gas plants was determined during the investigations of the Twin Butte Soils and Water Evaluation Task Force, and is summarized in Table 3.1.

The sulphur isotopic composition of the H<sub>2</sub>S in the raw gas and the by-product elemental sulphur are similar, and both are enriched with respect to sulphur in Alberta soils (range of  $\delta^{34}\text{S}$ : +5‰ to -30‰; Krouse, 1991).

Table 3.1.  $\delta^{34}\text{S}$  of elemental sulphur and inlet  $\text{H}_2\text{S}$  from local sour gas plants.

	Shell Waterton Complex	Gulf Pincher Creek
Raw Inlet Gas ( $\text{H}_2\text{S}$ )	+16.3‰, +16.4‰	+17.3‰
By-product Sulphur	+17.0‰	+18.1‰
	+17.1‰	+18.2‰
		+18.3‰

The two values of inlet gas for Shell represent gases from different fault-segregated pools within the gas field. Sour gas formerly processed at the Pincher Creek Plant is now processed at Shell Waterton Complex. Data are from Twin Butte Soils and Water Evaluation Task Force (Twin Butte, 1984). Sulphur isotope analyses were performed at the Stable Isotope Laboratory, Department of Physics and Astronomy, The University of Calgary, under the direction of Dr. H.R. Krouse.

## CHAPTER 4 - FIELD PROCEDURES

### SEDIMENT AND INTERSTITIAL WATER SAMPLING AND PRESERVATION

Cores of reservoir bottom sediment were collected to assess whether changes in the relative contribution of technogenic sulphur are manifest in the accumulating sediments. Two cores of Waterton Reservoir sediments were obtained. Locations selected were from deep water settings to avoid sediment reworking by wind-driven currents or bioturbation, which would complicate the interpretation of geochemical profiles. Core SE22 was collected September 22, 1993 from a location near the mouth of the Drywood Creek arm of the reservoir (Figure 4.1). Water depth on this day at the sample location was 28 m, and a core 42.5 cm long was recovered from this site. On January 21, 1994 a 40 cm long core was retrieved through ice cover from a location near the Waterton Dam, in water 28.5 m deep (core JA21, Figure 4.1).

Sediments of Waterton Reservoir began accumulating about eight years after start-up of local sour gas processing operations and a nearby lake was cored in an effort to characterize the pre-industrial record. Core MY27 was obtained May 27, 1994 from a water depth of 10 m in Beauvais Lake, located about 30 km west-northwest of Waterton Reservoir and upwind of both local sour gas processing facilities (Figure 4.2). A sediment core 52.5 cm long was recovered.

Superimposed on the physical sedimentary record is a more subtle record of dynamic diagenetic change having biological or physico-chemical origin. To investigate the nature of diagenetic processes affecting the sediments and resulting in the observed geochemical record, interstitial water samples for solute chemical and stable isotopic characterization were obtained. The two sediment cores from Waterton Reservoir were segmented at 2.5 cm increments and representative pore waters were expressed and

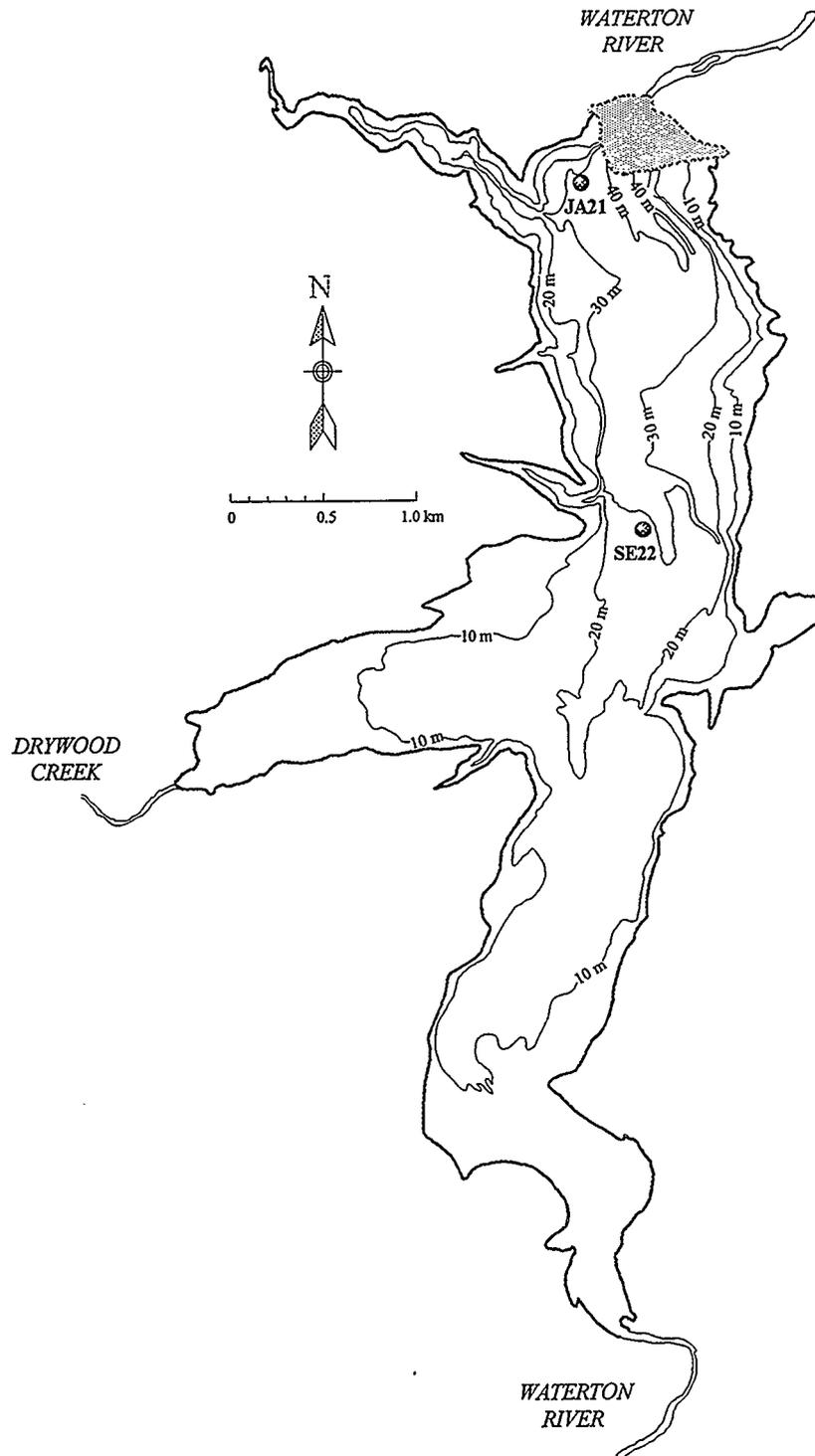


Figure 4.1 Bathymetry of Waterton Reservoir. Depths are referenced to full supply level at 1185.672m amsl. Based on a detailed topographic survey undertaken in 1957 for the Prairie Farm Rehabilitation Administration. Spherical symbols identify approximate core locations.

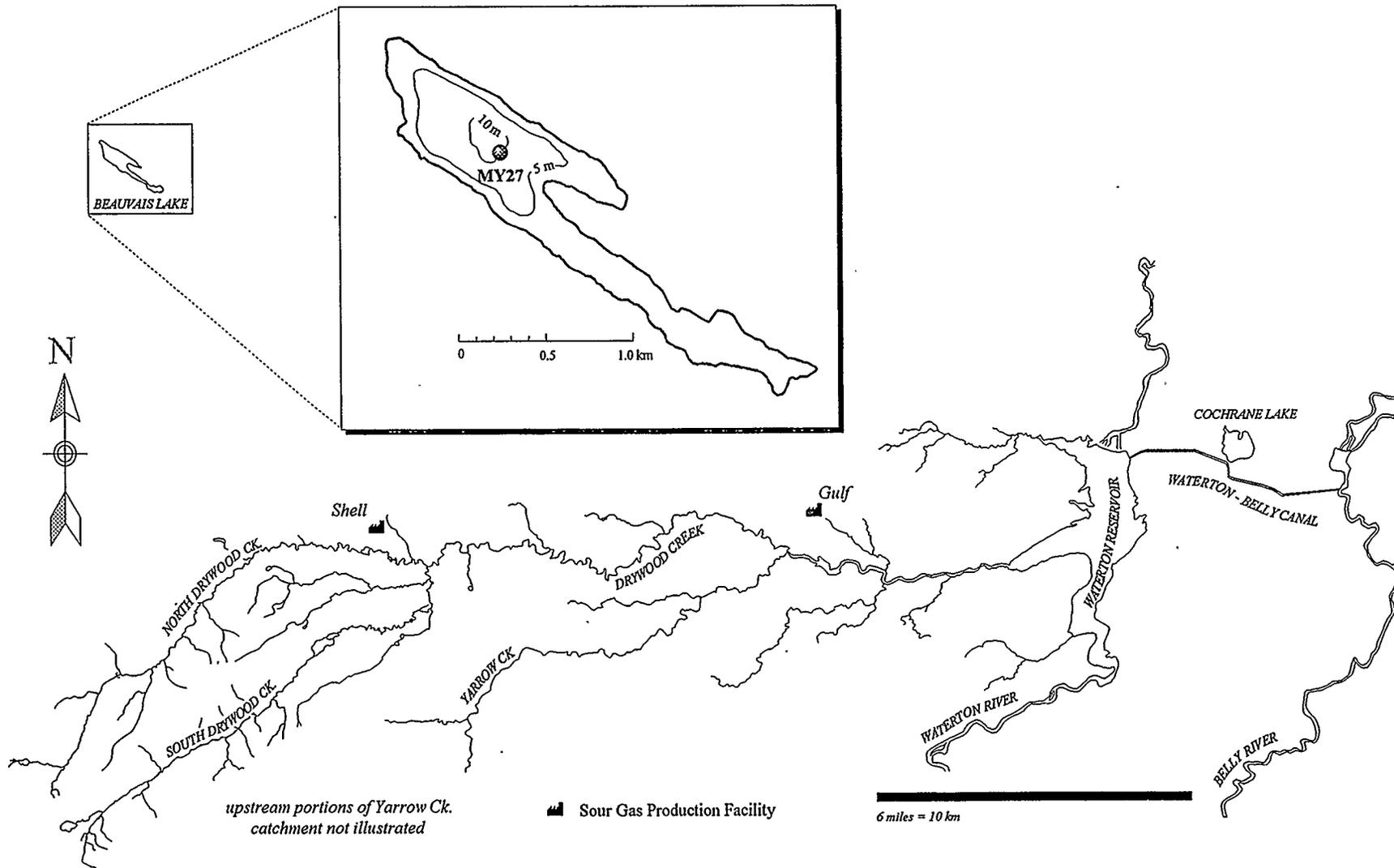


Figure 4.2 Bathymetry of Beauvais Lake, and location of core MY27. Bathymetry after Crosby (1990b).

preserved. Logistics prohibited identical treatment of the Beauvais Lake core, consequently no pore waters were obtained.

#### Constraints on equipment suitability

Analysis of porewaters squeezed from reconnaissance sediment samples obtained using an Eckman dredge indicated that interstitial waters are dilute, characterized by total dissolved solids of about 250 mg/L, and having low aqueous sulphate concentration. As conventional stable sulphur isotope ratio determinations require at least 1 milligram of sulphur equivalent (Krouse and Weiser, 1992), maintenance of fine temporal resolution demands that the sediment sample have considerable surface area in order that sufficient analyte be obtained. Furthermore, as sediments and their porewaters commonly are anoxic several centimeters below the sediment-water interface, precautions must be taken to minimize artifacts arising from sample handling. Notably, a vertical orientation must be maintained to prevent mixing, and samples must be manipulated promptly, and under an inert atmosphere (Adams, 1991).

These requirements predicated the design and construction of a large diameter coring device, the Eden-Lopez Large Volume Interface Sampler (ELVIS) and associated core extrusion, subsampling and porewater extraction equipment. Protocol was established to recover minimally-disturbed sediment core, segment the core at uniform vertical increments and transfer representative samples to storage containers in the field, with little or no exposure to ambient atmosphere. Interstitial waters were subsequently expressed from sediment samples, beginning within hours of coring and after transport from the field to the laboratory.

#### Design and operational synopsis of ELVIS

The coring device is capable of recovering a sediment core having a diameter of 11.35 cm and up to 62 cm long, as presently configured. The transparent acrylic core tube permits prompt inspection of recovered sediment. Threaded connections between the principal

components of ELVIS facilitate the required changes in configuration during coring and extrusion operations. Two operators can readily deploy and retrieve ELVIS with minimal equipment, and field testing has confirmed suitability for boat or ice-supported use in water as deep as 40 m.

An undisturbed sediment core is a prerequisite to obtaining representative porewaters. Sources of sediment disruption and corer design philosophy are discussed in Mudroch and MacKnight (1991). Gravity and percussion-type corer designs were rejected because they require internal sprung “fingers” to retain the core, and because sediment can be lost owing to shock waves arising from corer deployment. A piston-type corer having an obstruction-free interior, and using partial vacuum from an internal piston to retain the sediment, was considered to be the most appropriate design. The limited free-fall distance characteristic of piston corers further reduces the potential for sediment disturbance.

In principle, ELVIS and other piston corers work by penetration of the sediment by a core tube descending past a stationary internal piston. The piston creates a partial vacuum, facilitating sample entry, reducing core compaction and promoting sample retention (*ibid.*). Depth of penetration of the core tube into the sediment is in part dependent on sediment properties, mass of the coring device and the length of the core tube. The total mass of ELVIS is 13 kg, comprising the coring device and the trigger weight. A collar allows further addition of weight to the corer head.

Deployment of ELVIS and pertinent information are summarized in Figure 4.3. Operation requires two lines; one to lower and recover, and a second thinner line to trigger deployment of ELVIS. “Static” climbing rope (rappelling line) is used in both applications to minimize stretch. The hoisting line must be taut during all phases of deployment. After being lowered to the sediment-water interface, a rapid pull on the trigger line causes an eccentric catch to pivot about a horizontal axis. This releases the

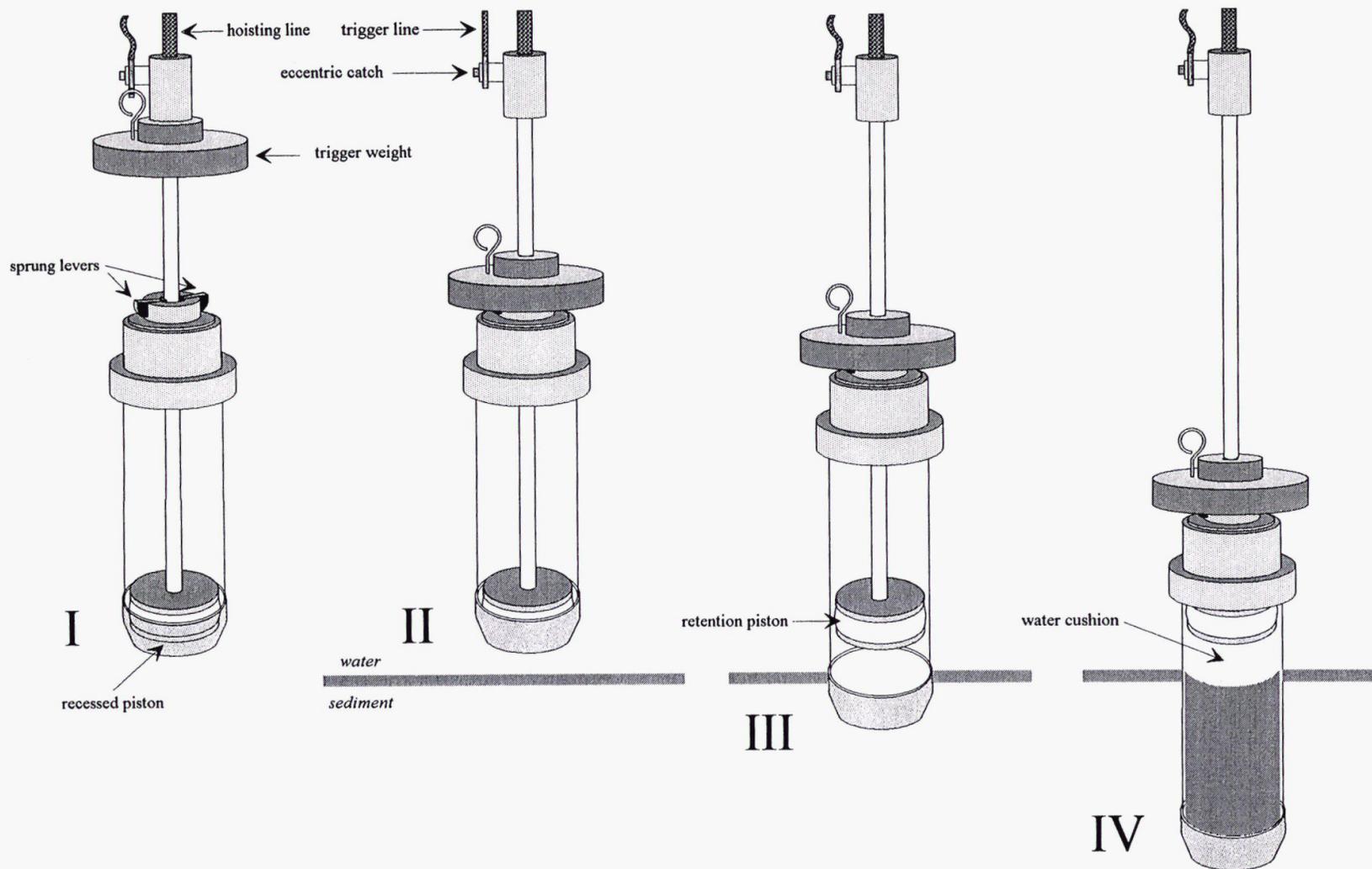


Figure 4.3 Schematic illustrating sequence of events during deployment of ELVIS. I) Configuration while being lowered through water column. II) Immediately after release of trigger weight. III) Initial penetration of sediment. IV) Complete sediment penetration. Water cushion minimizes disruption of sediment-water interface.

4.75 kg trigger weight, permitting it to free-fall about 40 cm down the piston rod where it impacts the elevated outer edges of two sprung levers, in turn releasing the stainless steel rod and allowing descent of the core tube into the sediments.

Water in the core tube above the retention piston is permitted to escape during deployment through vents in the corer head. Tautness of the hoisting line maintains the vertical orientation of ELVIS and restricts motion of the retention piston relative to the sediment-water interface. A short interval of time is permitted to elapse to permit sediment penetration prior to recovery. Pulling sharply on the hoisting line frees ELVIS from the sediment. Care must be taken to ensure slow and smooth retrieval to the surface to prevent sediment loss through cavitation from the open nose of the corer.

A novel feature of ELVIS is the use of a “water cushion” to minimize disruption of the sediment-water interface during coring. The retention piston is recessed 6.2 cm into the nose of the core tube prior to deployment. The resultant confined water volume resists displacement of the interface as the surrounding core tube penetrates the sediment. The presence of clear water overlying sediment upon recovery of ELVIS demonstrates the efficacy of this design.

Prior to removal of ELVIS from the water, an end cap consisting of an expandable piston and an annular perimeter is fitted on the bottom of the coring device to ensure core retention. This piston is subsequently used to extrude sediment from the core barrel. After temporarily unscrewing the corer head from the core tube, removal of a slotted cylindrical spacer placed between the inside surface of the corer head and the upper surface of the retention piston frees up a corresponding length of travel, permitting complete insertion of the expandable extrusion piston into the bottom of the coring device. The corer head is re-installed, and the core is confined by pistons at either end during transport to shore. The vertical orientation of the sediment-filled corer during transport is maintained by use of a robust retort stand equipped with “Varigrip” column clamps.

### Extrusion and subsampling of sediment

Objectives of the present project require representative samples for both sediment characterization and interstitial water studies. To preclude artifacts arising from accidental mixing of the core during transport, subdivision of the core was undertaken in the field. Sediment was extruded under an inert atmosphere by upward displacement of the extrusion piston at the base of the sediment column relative to the stationary core tube (procedural description below). This approach was intended to minimize disruption of uncompacted surficial material. The core was segmented at uniform vertical increments and a small aliquot was reserved for water content determination. All remaining sediment was made available for extraction of interstitial water by sediment squeezing after transport to the laboratory.

Two sample containers are required for each sediment increment. A 5 ml LDPE (low-density polyethylene) vial was used for the small aliquot used for water content determination, and Rubbermaid "Servin' saver" polypropylene tubs (400 ml capacity) were utilized for storage of the remaining sediment. The latter containers were selected because their diameter coincides closely with the internal diameter of both ELVIS and the sediment squeezing equipment, reducing sample manipulation. The base of each of the 400 ml tubs was pierced with a slender needle, and the resulting pinhole covered with a flap of tape (folded over at one end to facilitate subsequent removal).

Prior to use, all sample containers were cleaned by filling with ~1 N HCl and soaking for approximately 15 minutes, followed by triple rinses using distilled water. Containers were then filled and soaked with ~1 N HNO<sub>3</sub>, rinsed six times with distilled water and oven dried. All containers were labelled, and vials for water content determination were preweighed. A short time prior to coring, sample containers were transferred to a large inflatable glove bag where they were filled with N<sub>2</sub>, and transferred to and sealed in ziploc

plastic bags. The N<sub>2</sub>-charged glove bag was used for transport of the sample containers to the field.

After removal of the corer head, the retention piston is removed by pushing the extrusion piston from below while pulling on the retention piston. The water cushion overlying the sediment remains in place to minimize disturbance, and to reduce contact with air during this brief (several seconds) exposure. An N<sub>2</sub>-charged glove bag, preloaded with the required equipment and an appropriate number of sample containers, is placed over the open end of the core tube, and cut to permit entry of the core tube. A positive pressure provided by flow from a pressurized N<sub>2</sub> cylinder reduces atmospheric infiltration, and duct tape is wrapped around the joint to provide a seal. All subsequent handling of sediments occurs in an inert atmosphere.

The water cushion is carefully removed using a 60cc syringe, and transferred to a plastic bottle for containment. The core is pushed upwards until the sediment surface is flush with the top of the core tube, and a length of inexpensive, thin-walled ABS tubing<sup>1</sup> is cut to fit the length between the base of the extrusion piston and the nose of the corer. Subsequent repeated insertion of purpose-built 2.5 cm thick disks into the nose of the corer permits extrusion of sediment slices of consistent thickness. A robust jack stand is used to facilitate extrusion of the sediment from ELVIS.

A representative sediment sample is taken with a spatula and placed in a preweighed, numbered, N<sub>2</sub>-charged 5 ml vial for subsequent determination of water content. The larger sample tub is opened and the pinhole in the base revealed by partial removal of the tape flap. This container is inverted and placed over the top of the core tube. Slow insertion of an extrusion disk by raising the jackstand forces sediment into the container (the pin hole permits trapped N<sub>2</sub> to escape, allowing entry of the sediment). The sediment slice is decapitated using a broad stainless steel blade, and the sample container righted, sealed

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<sup>1</sup> tubing intended for domestic built-in vacuum applications is appropriate

and placed into a ziplock bag. Tools are cleaned by wiping with paper towels and rinsing with a small volume of distilled water. The procedure is repeated until the entire core has been extruded and subdivided, after which the N<sub>2</sub>-charged ziplock bags containing the sample tubs and vials are transferred to coolers for transport to the laboratory.

#### Porewater extraction by sediment squeezing

Interstitial waters were expressed from moist sediments through use of large diameter squeezers loosely patterned after those illustrated by Patterson et al (1978). A piston pushes down upon the moist sediment in a confined volume, forcing interstitial waters through filters supported by perforated plastic disks located at the base of the assembly, and out of the bottom of the squeezer body. Force is gradually applied using a 4 ton hydraulic jack in a purpose-built rack.

To economize, the squeezers were machined from ABS plastic, and the cylindrical sediment cavity was lined with a stainless steel sleeve for durability and to ensure a good seal with the dual O-rings on the piston. Squeezers used in the present study were 11.4 cm in diameter, to facilitate sediment loading and to provide a large surface area to accelerate the porewater extraction process. Contact time of porewaters with air and the stainless steel squeezer liner was thus minimized, reducing potential for artifacts related to squeezing. Six sediment squeezers and support racks were constructed to expedite porewater extraction and preservation, as it is prudent to preserve interstitial waters as rapidly as possible. Porewaters were expressed and preserved within about 36 hours of coring.

Porewaters were filtered as they were expressed from the squeezers by passing sequentially (from base of mud down) through Whatman # 1 paper supported by a Millipore mesh spacer on a perforated machined plastic disk, and a 0.22  $\mu\text{m}$  Millipore membrane supported by a Millipore mesh spacer on a second perforated machined disk

(Figure 4.4). Grooves and channels on the underside of the perforated disks permit passage of filtered water to an exit hole in the base of the squeezer.

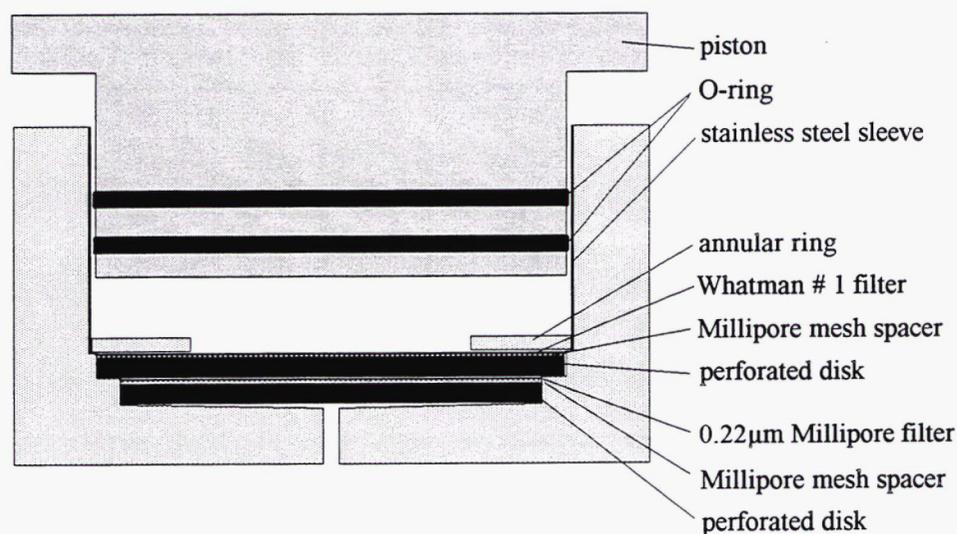


Figure 4.4 Schematic cross-section of sediment squeezers illustrating arrangement of porewater filtration elements.

Expressed waters flowed directly through a 3/16" polypropylene barbed male fitting and a short length of 1/8" ID Tygon tubing before being collected in a 60 cc syringe. In this manner, oxidation and exchange with ambient atmosphere is avoided. The initial few milliliters of expressed waters were not collected, to eliminate artifacts resulting from exposure to air trapped in the squeezer body and tubing. In practice, about 120 ml of interstitial water could be collected in about 1.5 hours of squeezing, reducing the wet sediment to a moist cake about 0.5 cm thick. Subsequent calculations indicate that volume of water expressed is equivalent to about 47 weight percent of the initial porewater in the 2.5 cm sediment slice.

The moist sediment cake and piston are readily removed from the squeezer by careful introduction of pressurized N<sub>2</sub> through a tube connected to the barbed fitting, after removal of the squeezer from the jack stand. The sediment cake is placed in a ziplock bag for interim storage in a refrigerator.

#### Preservation of interstitial waters

Expressed interstitial waters were refiltered through 0.45 µm syringe tip filters prior to preparing separate aliquots for chemical and stable isotopic characterization. Owing to the relatively small volume of interstitial water available, appropriately small containers were utilized. The protocol described earlier for cleaning of plasticware prior to use was obeyed.

Analyses of porewaters from core SE22 were by intent more comprehensive than those for core JA21 and preservation methods for SE22 are described. Protocols are based on those established by Lico et al (1982).

A 10 ml aliquot of porewater for alkalinity measurement was promptly dispensed in a small disposable plastic beaker, permitting determination of this parameter as squeezing progressed. Temperature and pH of this aliquot were also measured.

Approximately 30 ml of filtered water was carefully introduced to a 30 ml capacity, opaque, wide-mouth HDPE (high-density polyethylene) bottle, to which a few ml of acidified cadmium acetate solution had been added to preserve aqueous sulphide as CdS for stable sulphur isotope ratio determination. The solution was made up in advance by adding 6.25 g of reagent grade cadmium acetate to 50 ml of 17 N acetic acid and diluting with 200 ml distilled water. Headspace was eliminated by filling completely prior to capping tightly.

In an effort to preserve for aqueous sulphide concentration determination by ion-selective electrode, a filtered aliquot was carefully introduced to a 30 ml capacity, opaque, wide-mouth HDPE bottle to which an equal volume of sulphide anti-oxidant buffer (SAOB II) solution (Orion Research, 1980) had been added. Headspace was eliminated as before.

A third 30 ml aliquot was introduced to a 30 ml capacity, clear, wide-mouth HDPE bottle, to which a few ml of 0.1 N  $\text{BaCl}_2$  solution had been added to preserve aqueous sulphate as  $\text{BaSO}_4$  for stable isotopic characterization. Owing to small sample volume and suspected low sulphate concentrations, the sample was not acidified to inhibit coprecipitation of  $\text{BaCO}_3$ , as  $\text{BaSO}_4$  has a slight but measurable solubility in acidic solutions (Greenberg et al, 1985).

Approximately 10 ml of filtered water was introduced by hypodermic needle to a sterile, evacuated serum vial ("vacutainer") for stable oxygen and stable hydrogen isotopic ratio measurements.

A filtered aliquot for principal anion concentration determination was dispensed in a 4 dram glass vial and capped with a teflon-lined septum. To preserve for main cation abundance determination, a similar volume of filtered water was introduced to a second 4 dram glass vial and a drop of concentrated HCl was added to reduce pH to approximately 2.5 to inhibit loss through precipitation and colloid formation.

Any remaining filtered interstitial water was transferred to an evacuated serum vial and refrigerated for future use as required. With the exception of bottles containing precipitates for stable sulphur isotope ratio determinations, all filled sample containers were stored under refrigerated conditions.

## WATER SAMPLE SUITES

Suites of surface and spring waters were collected with the aim of providing an instantaneous characterization of water chemistry and isotopic composition of the principal inputs to, and outlets from Waterton Reservoir. Included were samples from settings upstream of the Waterton gas plant, from a location near the headwaters of North Drywood Creek. Samples comprising each of the suites were collected over the course of one day, and were promptly preserved. Suites 94MR13 and 95MR13 (March 13, 1994 and 1995, respectively) typify a late winter hydrologic regime, probably representing baseflow conditions modified by a small proportion of snow and ice melt-derived water. On each of these dates, an open water lead separated ice from the shoreline of Waterton Reservoir and rivers and creeks were essentially free of shore ice, with traces of mobile ice fragments carried by flowing water.

Samples collected 95AP27 (April 27, 1995) represent late spring hydrologic conditions. Refrozen snow from a late season storm was present at elevations above ~1400 m, that is, in the vicinity of Shell Waterton Complex (Figure 2.2). By this time of year, all ice on Waterton Reservoir had disappeared, and snow patches remained only on north-facing slopes in alpine settings.

The small suite of samples collected 95AU03 (August 3, 1995) for supplementary stable isotope characterization probably reflect typical summer conditions in the mountains and foothills. Although the Waterton Park - Pincher Creek region experienced flooding in early June of 1995, antecedent weather conditions are not unusual for the region. High rates of orographic precipitation are associated with collision of maritime air masses with the severe topography of the mountain front in southwestern Alberta (Warner, 1973). Roads leading to gasfield production facilities have since been reconstructed, although evidence of flooding is apparent. Relatively high-gradient reaches of North Drywood Creek were swept of surficial sediment, resulting in water flowing directly over bedrock.

Stream beds of tributaries which flow down subalpine slopes of this catchment basin are characterized by recent boulder and cobble-sized debris.

Surface waters were collected by submerging a 4 quart food-grade polyethelene jug in ambient water and filling and rinsing at least three times prior to collection of the sample aliquot. River and creek samples were obtained by reaching or wading into rapidly flowing water taking precautions to avoid induced turbidity. Gas plant effluent was collected where it flowed from a large-diameter galvanized conduit into North Drywood Creek. Spring waters were obtained by pressing the open jug against the tufa deposits and permitting water to trickle in slowly. Reservoir waters were obtained by drilling through ice with an ice auger (94MR13 suite), wading into thigh-deep water (95MR13 suite) or by reaching into surface water from the dock near the Waterton dam (95AP27 and 95AU03 suites). Water from the Cochrane Valley Aquifer was obtained from flowing relief wells located on the south-facing peninsula on the north shore of Cochrane Lake. The high rate of discharge from these continuously flowing wells (typically > 1500 L/min) ensures that representative waters were acquired.

#### Field Measurements on Water Suites

To facilitate rapid collection of samples over a large geographic area, measurement of field parameters was minimized. Temperature and pH were determined on a 50 ml aliquot of raw water immediately after sampling. An Orion 290A pH meter, calibrated with pH buffers spanning a range from pH 4 to pH 10 and using an Orion Triode pH-ATC electrode was utilized to determine these parameters.

#### Sample Preservation

Prior to use, all sample bottles were cleaned following protocols described earlier. An aliquot of raw water was dispensed into a pre-cleaned 125 ml nalgene bottle for alkalinity determination. All visible bubbles were removed by tapping and agitation, and head space

minimized by filling completely. The bottle was capped tightly and stored in a cooler prior to analysis.

Approximately 500 ml of sample were dispensed into a distilled water-rinsed Nalgene polysulphone filter holder. Suction was applied with a hand-operated pump and samples were filtered through 0.45  $\mu\text{m}$  cellulose acetate membranes. Separate 125 ml aliquots were collected for main anions ( $\text{Cl}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{PO}_4^{2-}$ ,  $\text{SO}_4^{2-}$ ) and major cations ( $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Li}^+$ ,  $\text{Mn}^{2+}$ , and  $\text{Fe}^{3+}$ ). Samples for major cation determinations were preserved by acidification to approximately pH 2.5 by addition of concentrated HCl. Filtered aliquots of sample for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of water were decanted into a clean disposable beaker and drawn through a sterile needle into evacuated, stoppered glass cylinders (vacutainers) for storage prior to analysis.

The remaining raw water was transferred to pre-cleaned 2 L PETE carbonated beverage bottles and placed in a cooler for transportation back to the laboratory. Upon return to the laboratory, this aliquot was promptly filtered through a 0.45  $\mu\text{m}$  cellulose acetate membrane and  $\text{BaCl}_2$  was added to precipitate aqueous sulphate as barium sulphate for stable sulphur isotope ratio determinations. Samples from suites 95MR13, 95AP27 and 95AU03 were acidified with HCl to inhibit co-precipitation of  $\text{BaCO}_3$ , permitting stable oxygen isotope determinations on aliquots of resultant barium sulphate.

#### OTHER SURFACE WATER SAMPLES

In addition to the water samples collected as the suites described, representative specimens were also collected as an adjunct to coring operations. Using a 2.2 L capacity acrylic Kemmerer bottle, waters were collected from near surface (approximately 2 m water depth) and near bottom (approximately 2 m off bottom) settings during acquisition of core MY27. Similarly, water was collected through ice cover on January 26, 1994 from a location in close proximity to the location of core JA21.

Measurement of parameters in the field, and preservation protocol for these specimens was the same as described for surface water suites.

#### GEOLOGIC MATERIALS COLLECTED

A suite of 4 soil samples for stable sulphur isotopic characterization was collected on January 26, 1994 from a recently exposed soil profile on the shore of Waterton Reservoir. Wave action accompanying high water level of the reservoir during the summer of 1993 lead to pronounced shoreface erosion and exposure of profiles of approximately 0.5 m vertical extent. Soil samples JA26-1 through 4 represent a transect (from base up) through a single location on the northwest shore of the reservoir near the public campground.

Two specimens of bedrock (samples WOC 1 and 2) for whole-rock stable sulphur isotope ratio determinations were collected from the gorge of the Waterton River immediately downstream of Waterton Dam. Complexly folded and thrust-faulted upper Cretaceous sedimentary rocks crop out along the western wall of the gorge, and stratigraphically equivalent units floor the reservoir and occur along reaches of Drywood Creek and Waterton River, upstream of the reservoir (Douglas, 1951).

## CHAPTER 5 - LABORATORY METHODS

Analytical procedures used to determine concentration and stable isotope ratios of samples collected are described. Except as noted, chemical analyses were performed using equipment and facilities of the Department of Geology, the University of Calgary. Stable isotope analyses were performed at the Stable Isotope Laboratory, the Department of Physics and Astronomy, The University of Calgary under the direction of Dr. H.R. Krouse.

### SEDIMENT ANALYSES

#### Water content

Water content of sediments was determined by comparison of wet sediment and dry sediment masses. Sediments were air dried for about 5 days in a loosely covered container (to inhibit atmospheric contamination), followed by dessication in a closed vessel for approximately 2 more days. Although relatively slow, air drying of sediments is appropriate because sulphur may be lost from lake sediments, particularly those which have been freeze-dried or oven-dried at elevated temperatures (Amaral et al, 1989). Dry mass measurements were recorded and the sediments returned to the dessicator. Dry mass measurements were repeated and recorded several times over several days to ensure complete porewater evaporation.

Water content was calculated using the relationship

$$\%_{\text{water}} = 100 \cdot [(M_{\text{total}} - M_{\text{sediment}}) / M_{\text{total}}] \quad (4)$$

where  $M_{\text{total}}$  and  $M_{\text{sediment}}$  are wet and dry masses, respectively. This form of relationship yields water contents close to 0 for rock and 100% for pure water, and is preferred for sediment studies (Håkanson and Jansson, 1983).

### Total sulphur in sediments and other geologic samples

Total sediment sulphur was determined on the air-dried sediment aliquot remaining after water content determination. The sediments were powdered and homogenized by grinding with a mortar and pestle, and  $[S_{\text{total}}]$  was determined using a Leco SC32 induction furnace at the inorganic geochemistry laboratory of Geological Survey of Canada - Calgary (subsequently abbreviated GSC-Calgary). In this method, the sample is rapidly combusted in a stream of purified  $O_2$  at about  $1500^\circ\text{C}$ , and  $SO_2$  produced is measured by a solid-state infrared detector (Tabatabai and Bremner, 1991). Certified coal standards having  $0.45 \pm 0.02$  wt% S and  $0.72 \pm 0.02$  wt% S were used to calibrate the instrument. Owing to low sulphur concentrations, the ceramic crucibles (which had never been used previously) were pre-conditioned by heating in the furnace prior to use. After permitting the crucibles to cool, 0.2 g to 0.3 g aliquots were loaded and analysed. Analyses were generally performed in triplicate and mean values were reported. Air dried soils, and powdered and homogenized bedrock specimens were also analysed using the Leco SC32 instrument.

Sulphur analyses by independent methods were performed on a small number of samples to confirm the values obtained with the Leco SC32 instrument. Analyses of several reservoir sediment samples from core SE22 were performed by XRF using a Phillips PW1410 instrument. Dried and powdered samples were prepared as fused glass disks using 4.5 g lithium tetraborate and 0.5 g lithium metaborate per gram of oven-dried ( $110^\circ\text{C}$ ) sample. NIST concrete reference standards 1884 and 1887 were utilized for instrument standardization.

Three sediment samples from core SE22 were also analysed by an ion chromatographic method described by Tabatabai et al (1988). In this method, ignition of samples mixed with  $NaHCO_3$  and  $Ag_2O$  at  $550^\circ\text{C}$  precedes their digestion in 1 M acetic acid. Reactions with the flux during heating converts sulphur present in the sample to sulphate. Resultant  $SO_4^{2-}$  concentration is determined by ion chromatography from diluted and filtered acetic acid solutions. Solutions were analysed at the GSC-Calgary using a Dionex 500 liquid

chromatograph system with a ED40 electrochemical detector and Dionex Anion Self-regenerating Suppressor ASRS-I at a current setting of 100 ma. Anions were separated using a Dionex IONPAC AS4A-SC 4 mm column with a sodium carbonate/bicarbonate eluent at a flow rate of 2.0 ml per minute. Sample volume was 20  $\mu$ L, and system calibration used standard solutions in the range of 5 ppm to 75 ppm (by weight).

To assess the utility of the method in samples containing reduced sulphur species, standards were prepared using powdered pyrite, marcasite and elemental sulphur mixed with a kaolinite XRD standard (Kga-1, available from the Source Clay Minerals Repository, The University of Missouri) to mimic a sediment matrix. Experimental results indicate that between 85.1 and 86.8 wt% of the pyrite, 91.4 and 92.7 wt% of the marcasite, and 85 wt% of the elemental S were recovered from the prepared mixtures using this method.

#### Total carbon

Total carbon was determined at the GSC-Calgary using a CEC 440 C-H-N Analyser operating at a combustion temperature of approximately 970°C and a reduction temperature of 700°C. Aliquots of air dried sediment weighing approximately 2 mg were analysed in duplicate, and the mean value reported.

#### Total organic carbon

Total organic carbon was determined in the organic geochemistry lab of the GSC-Calgary using a Delsi Rock-Eval II pyrolysis unit equipped with a total organic carbon module. Aliquots of air dried sediment (approximately 100 mg) were analysed in duplicate, and mean total organic carbon values determined and reported.

## WATER ANALYSES

Methods used for chemical and stable isotopic characterization of water samples varied on the basis of sample date as described below. Differences in analytical procedures used for stable sulphur isotope ratio and cation concentration determinations of interstitial waters predicated by the small sample size are also described.

### Anion concentration measurements

Liquid chromatographic methods were used to determine the principal anion concentrations of waters collected. Concentrations of  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{F}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{2-}$  were determined by either of 2 instruments. Miscellaneous waters G701-5 and CVA-1, and porewaters expressed from core SE22 were analysed using a Waters high pressure liquid chromatography system. Filtered samples were passed through a Waters Anion HC column and anions were detected using a Waters 430 conductivity detector linked with a Shimadzu CR4A Chromatopac data processor and chart recorder. 150  $\mu\text{L}$  samples were carried by a sodium borate-gluconate eluent at a flow rate of 2 ml per minute. The system was calibrated using standards in the 5 mg/L to 50 mg/L range, and analyses were performed in duplicate. Peak height ratios were utilized to calculate anion concentrations.

Anion abundances for all other waters were analysed at the GSC-Calgary using the Dionex 500 chromatography system described previously. Concentration values reported in all cases are the mean of two analyses, expressed as mg/L.

The use of buffered eluents in the analytical equipment described precludes determination of  $\text{HCO}_3^-$  and  $\text{CO}_3^{2-}$  concentrations with these instruments. Bicarbonate concentration was estimated from forward titration of filtered sample with  $\text{H}_2\text{SO}_4$  using an Orion 940 expandable ionAnalyser with an Orion 960 tower dispenser and a Ross pH electrode. Sample volumes were 10 ml for porewaters and 20 ml for water suites. Titrations continued until solution pH was less than 2.5 pH units. Porewater titrations were

conducted immediately as each sediment aliquot was squeezed; those of water suites were done upon return to the laboratory. Bicarbonate concentrations were calculated using the relationship

$$\text{HCO}_3^- = ((N_t \cdot V_t) / V_s) \cdot 61000 \quad (5)$$

where  $N_t$  is the normality of the  $\text{H}_2\text{SO}_4$  titrant,  $V_t$  is titrant volume (ml) to reach the inflection point, and  $V_s$  is the sample volume used. Calculated results are in units of mg/L (Lico et al 1982).

Measurement of  $\text{S}^{=}$  concentration of interstitial waters expressed from sediments of core SE22 was attempted using an ion specific electrode. Samples preserved with SAOB II were analysed after calibration using similarly preserved  $\text{S}^{=}$  standards of 5 and 50 mg/L concentration. SAOB II adjusts ionic strength, is preferentially oxidized, and converts  $\text{H}_2\text{S}$  and  $\text{HS}^-$  to  $\text{S}^{=}$  for measurement with a Silver / Sulphide electrode in conjunction with a double junction reference electrode (Orion Research, 1980). No aqueous sulphide was detected in the interstitial waters analysed with this method.

#### Cation concentration measurements

Abundance measurements of the cations  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{Fe}^{2+}$  were determined by atomic absorption spectrophotometry of filtered and acidified samples. Analyses were performed by direct aspiration into an air-acetylene flame with appropriate monochromators using a Perkin Elmer 5000 AA spectrophotometer. Data are reported as the mean of four measurements per sample aliquot.

Cation abundances for the small volume interstitial water samples expressed from sediments of core SE22 were analysed by liquid chromatography at the GSC-Calgary. Aliquots of filtered and acidified sample were analysed using a Dionex 500 liquid chromatograph system with a ED40 electrochemical detector and self-regenerating suppressor. Cations were separated on a Dionex IONPAC CS-12 4 mm column using a 4.0 mM methanesulfonic acid and 5 mM pyrophosphoric acid eluent at a flow rate of 1.0

ml per minute. Sample size was 25  $\mu\text{L}$ . Cations determined by this method are  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . The instrument was calibrated using standard solutions in the range of 0.1 to 25 mg/L.

## STABLE ISOTOPE MEASUREMENTS

### Measurement of $\delta^{34}\text{S}$ of sediments and geologic materials

Results of sulphur concentration and stable sulphur isotope determinations reported by Amaral et al (1989) emphasize that sulphur may be lost from lake sediments as a result of sample drying, and that  $\delta^{34}\text{S}$  determinations of dry and wet sediments may be different. Sulphur representative of total sediment sulphur was extracted from Waterton Reservoir and Beauvais Lake sediment samples using a modification of the nitric acid - bromine digestion of Krouse and Tabatabai (1986). This method permits extraction of sulphur from wet sediments, minimizing potential artifacts related to sample handling. Selection of this method was also favoured by the fact that sulphur isotope fractionation associated with oxidation of reduced sulphur is negligible (Mayer et al, 1992). Results are expressed relative to the VCDT standard.

Briefly, about 50 g of the damp sediment cake remaining after porewater squeezing was placed in a 600 ml pyrex beaker, and 25 ml concentrated  $\text{HNO}_3$  was added. The mixture was stirred with a clean teflon rod, and about 5 ml  $\text{Br}_2$  (l) was added. After covering with a watch glass and allowing to sit overnight, the contents of the beaker were gently heated to dryness in a sand bath to evolve  $\text{Br}_2$  (g). Approximately 25 ml of concentrated  $\text{HCl}$  was then added to wet the sediments, and the sample was again heated to dryness. A second aliquot of  $\text{HCl}$  was added, and the sediments again heated to dryness. A slurry was made by adding about 25 ml of 1 M  $\text{HCl}$ , and the slurry was carefully decanted into centrifuge bottles. After centrifugation for about 5 minutes at 5000 rpm, clear supernatant was decanted and filtered through a 0.45  $\mu\text{m}$  cellulose acetate membrane and diluted with

approximately 100 ml of distilled water. Several mg of  $\text{BaCl}_2$  (s) was then added to the solution, precipitating dissolved sulphate as  $\text{BaSO}_4$  (s). The  $\text{BaSO}_4$  precipitate was recovered by filtration through a 0.45  $\mu\text{m}$  membrane, thoroughly rinsed with distilled water and dried in a dessicator. Dry  $\text{BaSO}_4$  was removed from the filter by scraping with a clean stainless steel blade.

$\text{BaSO}_4$  was prepared for  $\delta^{34}\text{S}$  determination following the method of Ueda and Krouse (1986). In this method, a mixture of  $\text{V}_2\text{O}_5 + \text{SiO}_2 + \text{BaSO}_4$  sample (1:1:20) is homogenized with a mortar and pestle, decanted into a quartz tube and topped with quartz wool followed by copper turnings<sup>1</sup>. The loaded tube is heated for thirty minutes at 900°C, and the  $^{34}\text{S}/^{32}\text{S}$  abundance ratio of the evolved  $\text{SO}_2$  determined using a dual collector mass spectrometer built with V.G. Micromass 602 components, situated on-line. The hot copper reduces  $\text{SO}_3$  to  $\text{SO}_2$ , and  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (v) are removed from the evolved gas by use of  $\text{N}_2$  (l) + pentane, and dry ice traps, respectively.

#### $\delta^{34}\text{S}$ of aqueous sulphate

$\text{BaSO}_4$  precipitated from water suites was collected on 0.45  $\mu\text{m}$  filters, rinsed sequentially with 1 M HCl (to dissolve possible co-precipitated  $\text{BaCO}_3$ ) and distilled water, dessicated, and prepared for stable sulphur isotope ratio determinations using methods and instruments described above.

A comparison of two precipitation protocols was undertaken using water collected from Waterton Reservoir. Sample 95AU03-SW3A was prepared by direct precipitation from filtered water by addition of  $\text{BaCl}_2$  (s). The second aliquot (95AU03-SW3B) was filtered, and concentrated by heating (sample volume of 2 L reduced to approximately 100 ml) prior to addition of  $\text{BaCl}_2$  (s). Analysis of  $\text{BaSO}_4$  precipitates yielded  $\delta^{34}\text{S}$  of +4.73‰ and +4.71‰ for 95AU03-SWA and 95AU03-SWB, respectively. The close agreement indicates that sulphur isotope ratios of samples are not affected by fractionation resulting

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<sup>1</sup> respiratory protection and gloves should be used when handling the  $\text{V}_2\text{O}_5 + \text{SiO}_2$  mixture

from dissolution of BaSO<sub>4</sub> precipitate in the relatively large (~ 2 L) and dilute water samples collected as water suites.

The small volume of interstitial water samples predicated use of different analytical procedures. Following precipitation by addition of a few drops of 0.1 N BaCl<sub>2</sub> solution, BaSO<sub>4</sub> was recovered on 25 mm diameter 0.45 µm cellulose acetate membranes, rinsed thoroughly with distilled water and dried in a dessicator. To minimize the loss of BaSO<sub>4</sub> resulting from static generated during scraping, the filters then were ashed in covered ceramic crucibles at 850°C.

Measurement of stable sulphur isotope ratios using the equipment described earlier requires as a minimum approximately 1 mg (as S) owing to the volume of the stainless steel bellows used for pressure control (Krouse and Weiser, 1992). As samples of this quantity were unavailable, a recently developed analytical technique suitable for determination of δ<sup>34</sup>S of samples as small as a few micrograms was used for interstitial waters from cores SE22 and JA21, and for surface waters MY27S and MY27D. The method is described in detail by Giesemann et al (1994) and is summarized below.

The method comprises a gas flow combustion system coupled with ion integration mass spectrometry (GF-C-MS). Approximately 100 to 700 µg of BaSO<sub>4</sub> is combined with a small quantity of V<sub>2</sub>O<sub>5</sub> and loaded in a tin capsule. The sample and container are combusted with a pulse of O<sub>2</sub> at 1030°C in the oxidation-reduction furnace of a Carlo Erba NA1500 Elemental Analyser. Combustion gases are carried in a He stream through a reactor (containing tungstic anhydride, copper oxide and native copper) where SO<sub>3</sub> is reduced to SO<sub>2</sub> and excess O<sub>2</sub> is eliminated. Water vapour is removed in an anhydron trap, and SO<sub>2</sub> is separated from remaining combustion gases by a gas chromatography using a Propac QS column. A portion of the He and SO<sub>2</sub> stream is introduced to the mass spectrometer source. Isotope ratios of the sample gas and a gas standard are measured and compared. Using this method, δ<sup>34</sup>S measurements from samples as small as 0.9 µg (as S)

as determined by Dr. A.-L. Norman are reported. Analytical uncertainties are  $\pm 5\%$  for samples of less than  $2.5 \mu\text{g S}$ ,  $\pm 0.5\%$  for samples between  $7$  and  $15 \mu\text{g S}$  and  $\pm 0.25\%$  for samples larger than  $15 \mu\text{g S}$ .

#### $\delta^{34}\text{S}$ of aqueous sulphide

The intense yellow colour diagnostic of CdS was not visible on  $0.45 \mu\text{m}$  membranes after filtration of appropriately preserved sample aliquots from core SE22. The buff-coloured precipitate obtained resembles that from surface water samples preserved following the same protocol, and identified by XRD as CdCO<sub>3</sub> (otavite). No measurements of  $\delta^{34}\text{S}$  of aqueous sulphide were attempted.

#### $\delta^{18}\text{O}$ of water

Measurement of  $\delta^{18}\text{O}$  of porewaters expressed from core SE22 and of waters comprising the 95AP27 samples suite were determined using a modification of the CO<sub>2</sub> equilibration technique of Epstein and Mayeda (1953). A 5 ml aliquot of sample is equilibrated at ambient temperature by rocking overnight with a standard pure CO<sub>2</sub> gas introduced under pressure. The resulting CO<sub>2</sub> gas in the container headspace is directed into an on-line Micromass 903 mass spectrometer where the  $^{18}\text{O}/^{16}\text{O}$  abundance is measured. Results are expressed relative to Standard Mean Ocean Water (SMOW).

#### $\delta\text{D}$ of water

$\delta\text{D}$  of waters expressed from core SE22, and of waters comprising suite 95AP27 was determined by the method described by Coleman et al (1982). A  $5 \mu\text{L}$  aliquot is placed in a reaction chamber with approximately 250 mg of zinc metal shot. Following evacuation and heating to  $450^\circ\text{C}$  for approximately 30 minutes, H<sub>2</sub> liberated from the sample during oxidation of the zinc metal to ZnO is collected. The D/H abundance ratio of the gas is measured on a Micromass 602 mass spectrometer. Results are expressed relative to SMOW.

$\delta^{18}\text{O}$  of aqueous sulphate

The oxygen isotopic composition of several aqueous sulphate samples from suite 95AP27 was determined according to the method of Shakur (1982).  $\text{BaSO}_4$  precipitated from samples comprising this suite had previously been acidified to eliminate co-precipitated carbonate which could corrupt the measured oxygen isotope ratios. A mixture of  $\text{BaSO}_4$  and pure graphite (1:1 by mass) is reacted at  $1000^\circ\text{C}$  in an evacuated chamber for 30 to 45 minutes. The  $\text{CO}_2$  and  $\text{CO}$  produced is transferred to a second chamber where  $\text{CO}_2$  is trapped by freezing, and a voltage discharge across two pieces of platinum foil converts any remaining  $\text{CO}$  to  $\text{CO}_2$ . Thawing then liberates the  $\text{CO}_2$  for collection, and the  $^{18}\text{O}/^{16}\text{O}$  abundance ratio is determined on a Micromass 602 mass spectrometer. Results are expressed relative to SMOW.

## CHAPTER 6 - ANALYTICAL RESULTS

Results of measurements of chemical parameters and of stable isotope ratio determinations for sediments, porewaters, surface water suites and geologic materials analysed are presented. Emphasized in the text and accompanying illustrations are measurements of total sulphur and sulphate in sediments (and geologic materials) and waters. Concentration data for other aqueous species are summarized as tables.

### SEDIMENT DESCRIPTION

Sediments recovered from Waterton Reservoir are light yellowish gray, massive to indistinctly thinly-bedded, cohesive muds. Sediments of core JA21 were vaguely black flecked over the basal 25 cm. A fibrous organic object resembling a blade of grass occurred in a single sample from this core at a depth of approximately 36 cm below the sediment-water interface. No direct or trace evidence of a benthic fauna was observed in either of the cores collected from Waterton Reservoir.

During squeezing of porewaters from Waterton Reservoir sediments, it was observed that the sediments had developed a subtle, orange-hued mottling particularly where the sediments were in contact with the plastic of the sample containers.

The highly flocculent nature of the deep water sediments of Beauvais Lake made it difficult to determine the depth of the sediment-water interface, in turn complicating deployment of ELVIS. During retrieval, some sediment was lost out of the nose of the core barrel. The retention piston was observed to be contacting the sediment, suggesting that the water cushion had been displaced into the core, and that the core had possibly been stretched. These observations indicate that core MY27 is partially disturbed, confounding the interpretation of chemical and stable isotope profiles.

The uppermost 10 cm of core MY27 comprise yellowish gray, partly pelloidal sediments having a gel-like consistency. These overlie with sharp contact approximately 24 cm of massive, olive black soft mud. The basal portion of the core comprises approximately 18.5 cm of yellowish gray, cohesive muddy sediment characterized by contorted stratification and olive black mottling. The contact with the overlying sediments is gradational. Aquatic worms (*Oligochaetes*) and other benthic invertebrates (*Chironomids*) are the most common benthic organisms in Beauvais Lake (Crosby, 1990), and were observed in the core. Interestingly, dried and powdered sediments from Beauvais Lake are characterized by a "bovine" aroma.

#### TOTAL SULPHUR CONCENTRATION OF SEDIMENTS

Total sulphur concentration measurements (abbreviated  $[S]_{\text{total}}$ ) for sediments from Waterton Reservoir are illustrated as Figure 6.1.  $[S]_{\text{total}}$  for core SE22 averages 9.54  $\mu\text{mole/g}$  (S.D.= 1.77). The profile for this parameter with depth below the sediment-water interface for core SE22 is monotonous, and suggests that the sulphur concentration decreases from the base of the core to the top. Replicate sets of measurements using the same sample aliquot for several sediment intervals from this core are illustrated (open symbols on diagram). These data demonstrate the uncertainty associated with this analytical procedure at such low concentrations.

Data for core JA21 indicate that on average there is slightly higher  $[S]_{\text{total}}$  concentration (mean 16.5  $\mu\text{mole/g}$ , S.D. = 8.8) and that  $[S]_{\text{total}}$  decreases in a step-wise manner from the base of the core to the top 10 cm, where the lowest concentrations are observed (approximately 6  $\mu\text{mole/g}$ ). No visible change in sediment character is associated with the observed segments of the profile.

Figure 6.2 illustrates the same parameter for samples from core MY27. Significantly, the total sulphur concentration of Beauvais Lake sediments (mean = 254.5  $\mu\text{mole/g}$ , S.D. =

## WATERTON RESERVOIR total sediment S concentration

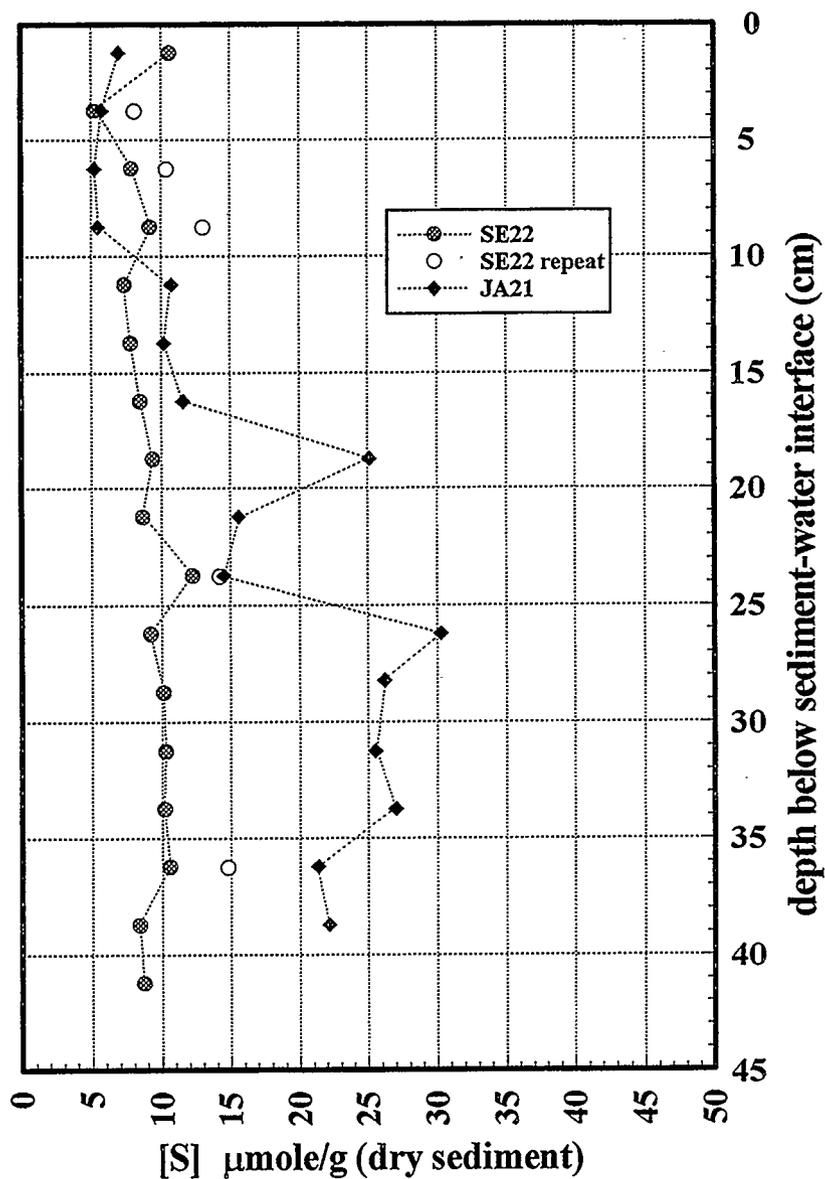


Figure 6.1 Total sulphur concentration of cores SE22 and JA21, Waterton Reservoir. Open symbols represent replicate set of measurements using same instrument on a different day, illustrating the uncertainty associated with the measurements at such low concentrations.

# BEAUVAIS LAKE

## total sediment S concentration

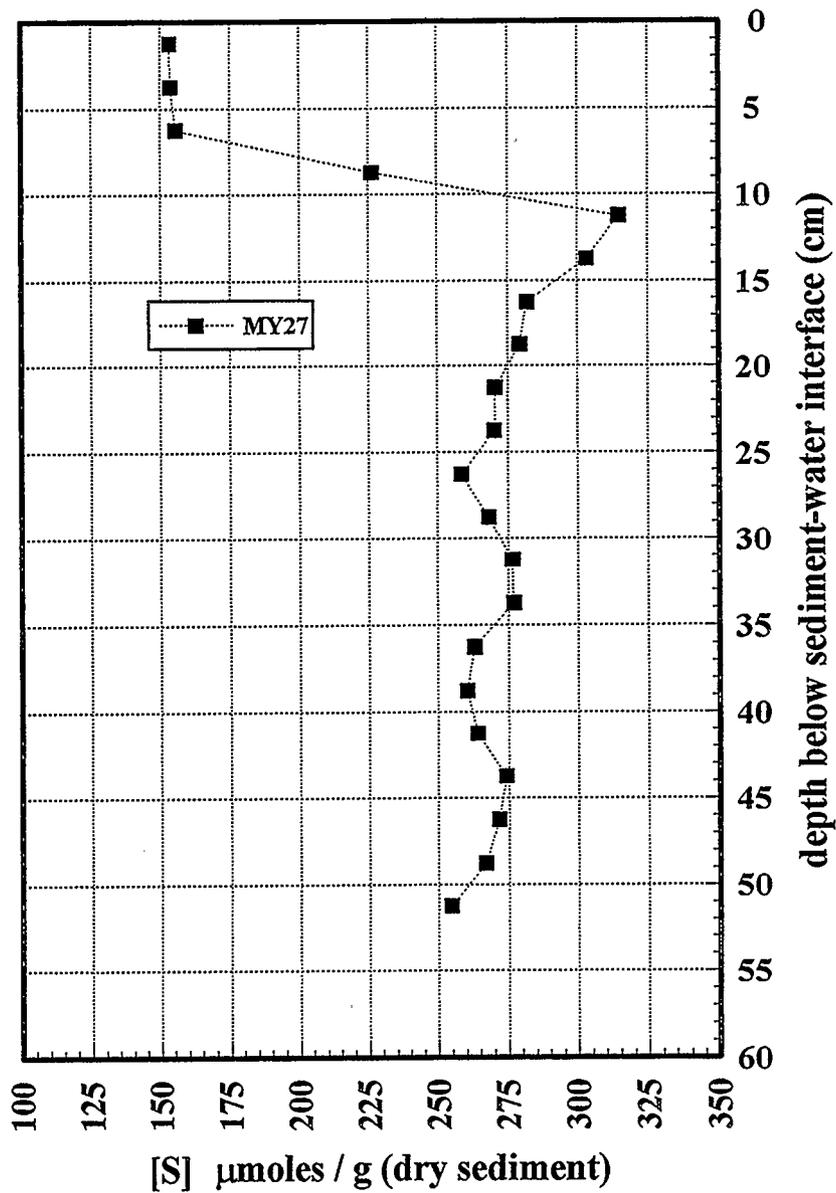


Figure 6.2 Total sulphur concentration of sediments from core MY27, Beauvais Lake.

45.3) is considerably higher than that of Waterton Reservoir.  $[S]_{total}$  increases from 250  $\mu\text{mole/g}$  at the base of the core to about 310  $\mu\text{mole/g}$  at a depth of 10 cm below the sediment-water interface. The uppermost 10 cm of core MY27 (corresponding to the yellowish-gray, gel-like sediments) is characterized by the lowest sulphur concentrations observed in this core (approximately 155  $\mu\text{mole/g}$ ).

#### INDEPENDENT DETERMINATIONS OF $[S]_{total}$

Owing to the low sulphur concentrations determined for reservoir sediment samples, verification of  $[S]_{total}$  was attempted by independent means. Data from analyses by XRF and an ion chromatographic technique (Tabatabai et al, 1988) for several sample aliquots of core SE22 are tabulated below.

Table 6.1. Comparison of total sediment sulphur concentration determinations using three different analytical methods.

sample	$[S]_{total}$ by XRF ( $\mu\text{mole/g}$ )	$[S]_{total}$ by ion chromatography ( $\mu\text{mole/g}$ )	$[S]_{total}$ by Leco SC32 ( $\mu\text{mole/g}$ )	$[S]_{total}$ by Leco SC32 repeat ( $\mu\text{mole/g}$ )
SE22-1		15.8	10.6	
SE22-2			5.2	8.1
SE22-3			7.9	10.3
SE22-4			9.2	13.0
SE22-5		12.5	7.4	
SE22-7	15.9		8.5	
SE22-8	15.0		9.4	
SE22-9	15.9	13.9	8.6	
SE22-10	12.8		13.2	14.2
SE22-11	13.1		9.2	
SE22-15			10.3	14.8
SE22-17			8.7	12.1

The [ $S_{total}$ ] concentrations determined using the Leco SC32 instrument are generally low in comparison with those determined by the other methods, and repeat sets of sulphur determinations vary by as much as 4.8  $\mu\text{mole/g}$ . Leco determinations are reported for internal consistency, and to permit comparison with other lake sediment studies reported in the literature.

### $\delta^{34}\text{S}$ OF SEDIMENTS

The stable isotopic ratios of sulphur representative of the total sediment sulphur pool (abbreviated  $\delta^{34}S_{total}$ ) for sediment subsamples of cores from Waterton Reservoir are presented as Figure 6.3. Both profiles exhibit an oscillatory character and share a common inflection at a depth of 16.25 cm below the sediment-water interface, however  $\delta^{34}S_{total}$  values for core SE22 are consistently more depleted than those of core JA21. Mean  $\delta^{34}S_{total}$  of cores SE22 and JA21 are -10.56‰ (S.D. = 4.07) and -2.74‰ (S.D. = 5.98), respectively. The relative uniformity of data in each core between 21.25 cm and 31.25 cm depths is noteworthy.

Figure 6.4 presents the results of determinations of  $\delta^{34}S_{total}$  for sediment samples from Beauvais Lake core MY27. The data demonstrate that the mean  $\delta^{34}S_{total}$  is -3.34‰ (S.D. = 3.52) and that  $\delta^{34}S_{total}$  values progressively become more enriched and are characterized by increased variability in younger sediments.

### SEDIMENT CARBON DATA

Results of analyses for total carbon and total organic carbon for core SE22, and total organic carbon for core MY27 are illustrated as Figure 6.5. Data for Waterton Reservoir sediments display little variability with depth and indicate that organic carbon comprises about 42% of the total carbon pool. Mean total carbon and total organic carbon values are 2.20 wt% (S.D. = 0.07) and 0.93 wt% (S.D. = 0.07), respectively.

## WATERTON RESERVOIR total sediment $\delta^{34}\text{S}$

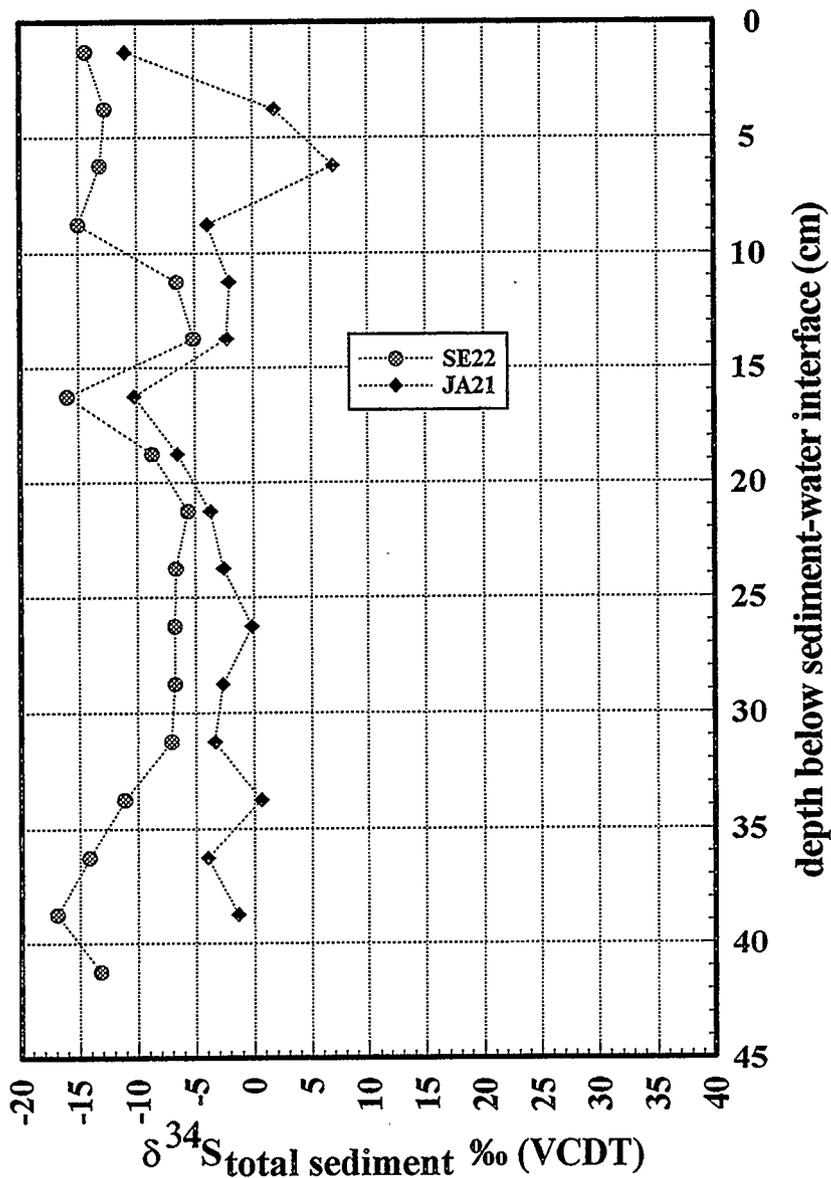


Figure 6.3  $\delta^{34}\text{S}$  of total sulphur for sediments of cores SE22 and JA21, Waterton Reservoir. Total sediment sulphur recovered as  $\text{BaSO}_4$  following  $\text{HNO}_3$ - $\text{Br}_2$  extractions performed on damp sediment sample aliquots after squeezing of porewaters.

# BEAUVAIS LAKE total sediment $\delta^{34}\text{S}$

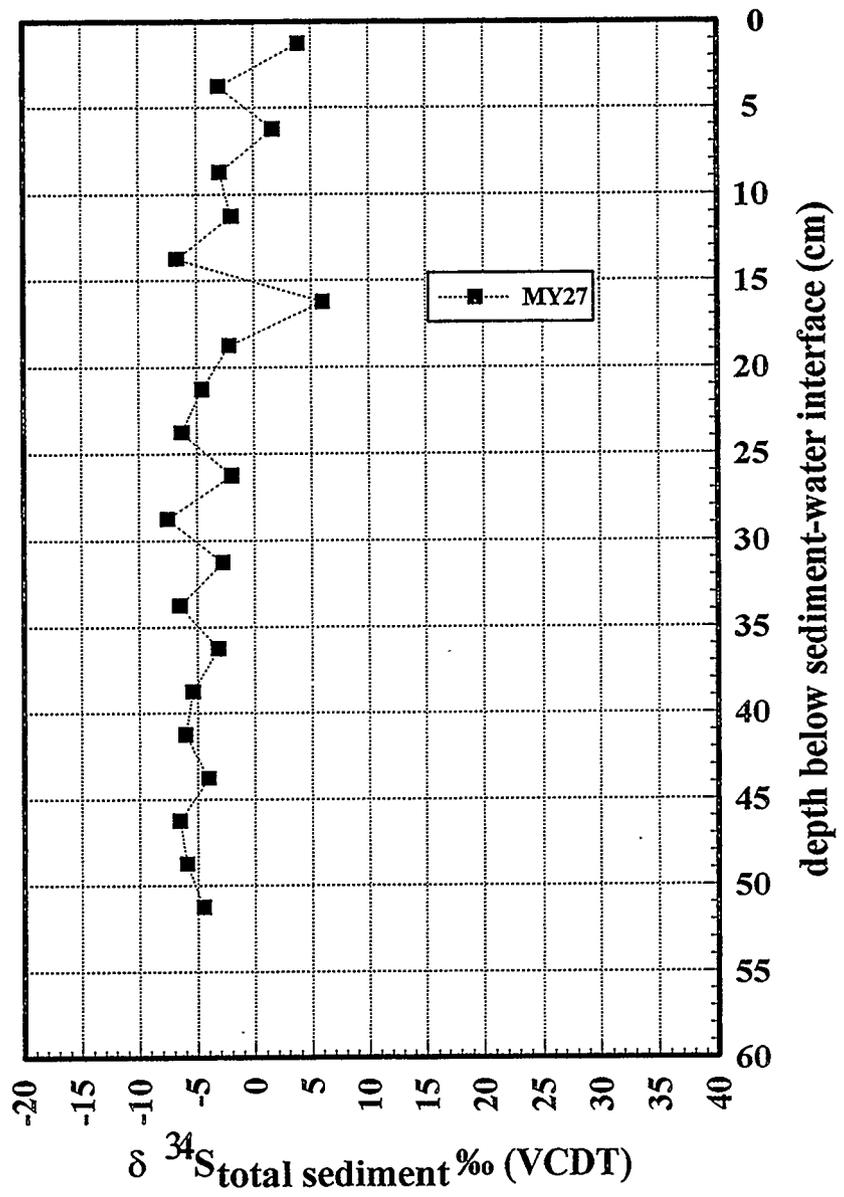


Figure 6.4  $\delta^{34}\text{S}$  of total sulphur for sediments of core MY27, Beauvais Lake. Total sediment sulphur recovered as  $\text{BaSO}_4$  following  $\text{HNO}_3$ - $\text{Br}_2$  extractions performed on damp sediment sample aliquots.

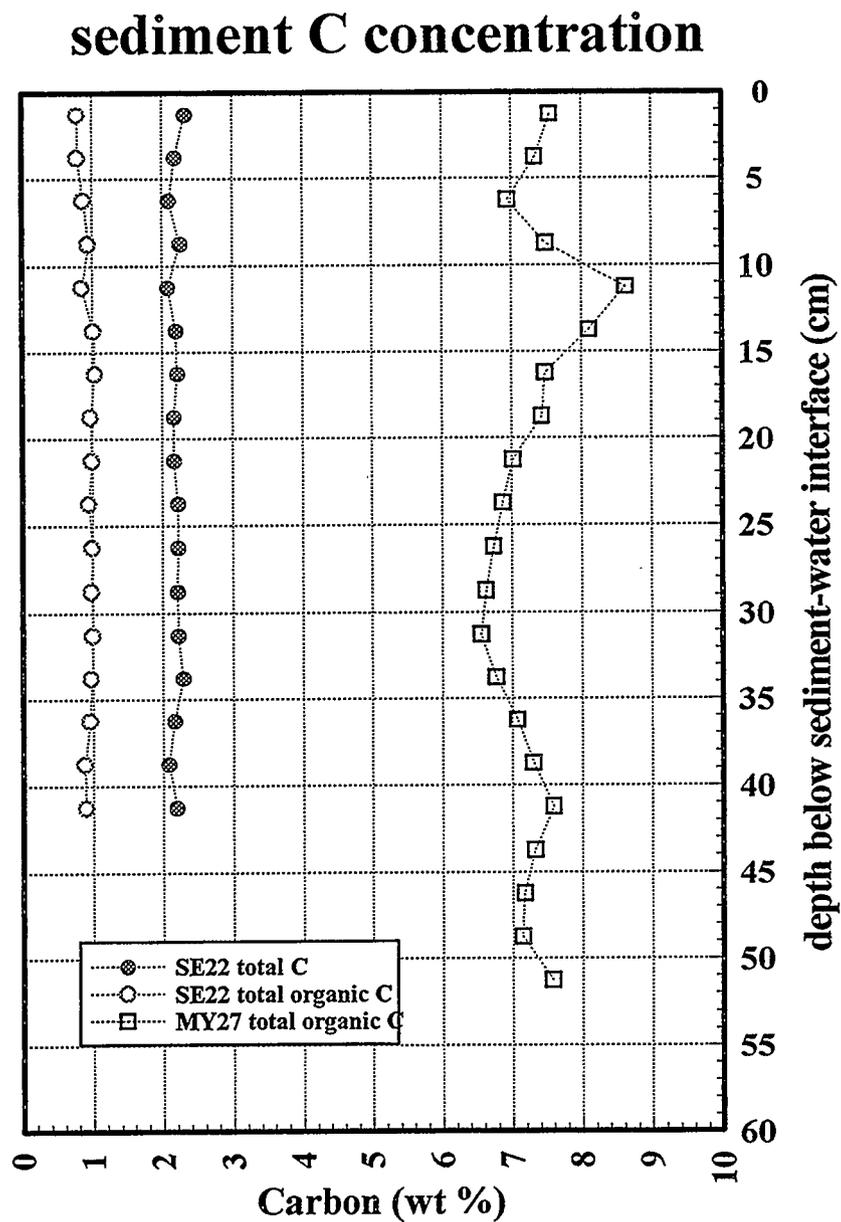


Figure 6.5 Sediment carbon measurements for core SE22 (Waterton Reservoir) and MY27 (Beauvais Lake).

The mean total organic carbon concentration of Beauvais Lake sediments (7.27 wt%, S.D. = 0.49) is higher than that of Waterton Reservoir, and displays greater variance. A decrease in total organic carbon concentration apparently corresponds to the change in sediment character in the uppermost 10 cm of the core, although more gradual decreases of similar magnitude occur elsewhere in the profile.

#### WATER CONTENT OF SEDIMENTS

The water contents of sediments from Waterton Reservoir are summarized as Figure 6.6. Mean water content for cores SE22 and JA21 are 40.4 wt% (S.D. = 1.9) and 42.7 wt% (S.D. = 2.2), respectively. Profiles generally suggest higher water content in younger, and presumably less compacted sediments. The difficulty in collecting a representative sample for water content determination of the surficial sediment layer is illustrated by opposite data trends in the top 5 cm of the cores.

#### POREWATER SULPHATE CONCENTRATION

Porewater sulphate concentration profiles for cores SE22 and JA21 are illustrated as Figure 6.7. Both profiles exhibit maximum sulphate concentrations in porewaters expressed from the surficial sediment layer, although high sulphate values persist to a slightly greater depth in porewaters of core SE22. Sulphate concentration in the surficial layer approaches that of Waterton Reservoir sulphate (range 11.0 mg/L to 17.2 mg/L, discussed later in chapter). Porewaters expressed from greater depths in each core are characterized by lower sulphate concentrations.

Sulphate concentrations (and those of all other anion species determined for that matter, Table 6.2) in porewaters from core SE22 are higher than those of JA21; whether this reflects reality or is an artifact of comparing data from different analytical equipment cannot be determined from the data available. Interestingly, subtleties in sulphate

## WATERTON RESERVOIR water content of sediments

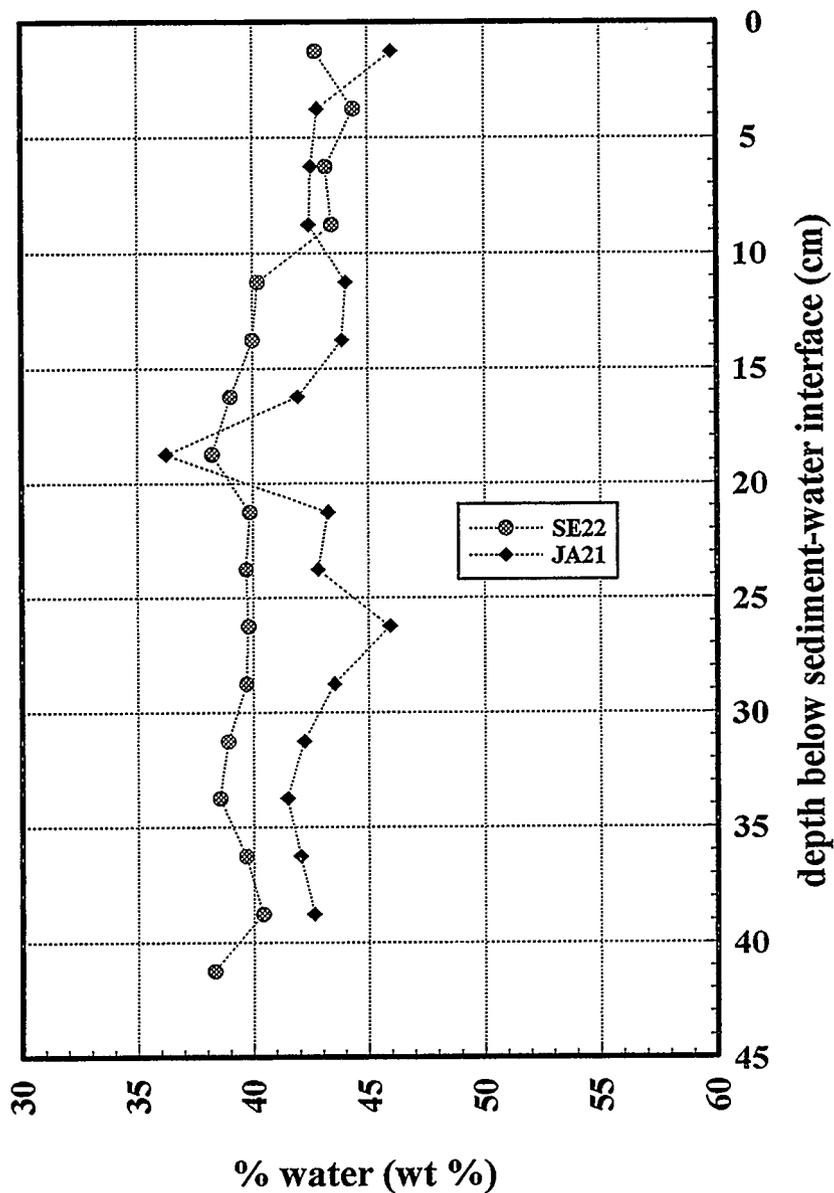


Figure 6.6 Sediment water content determinations for core SE22 and JA21 (Waterton Reservoir).

## WATERTON RESERVOIR

### porewater $\text{SO}_4^{2-}$ concentration

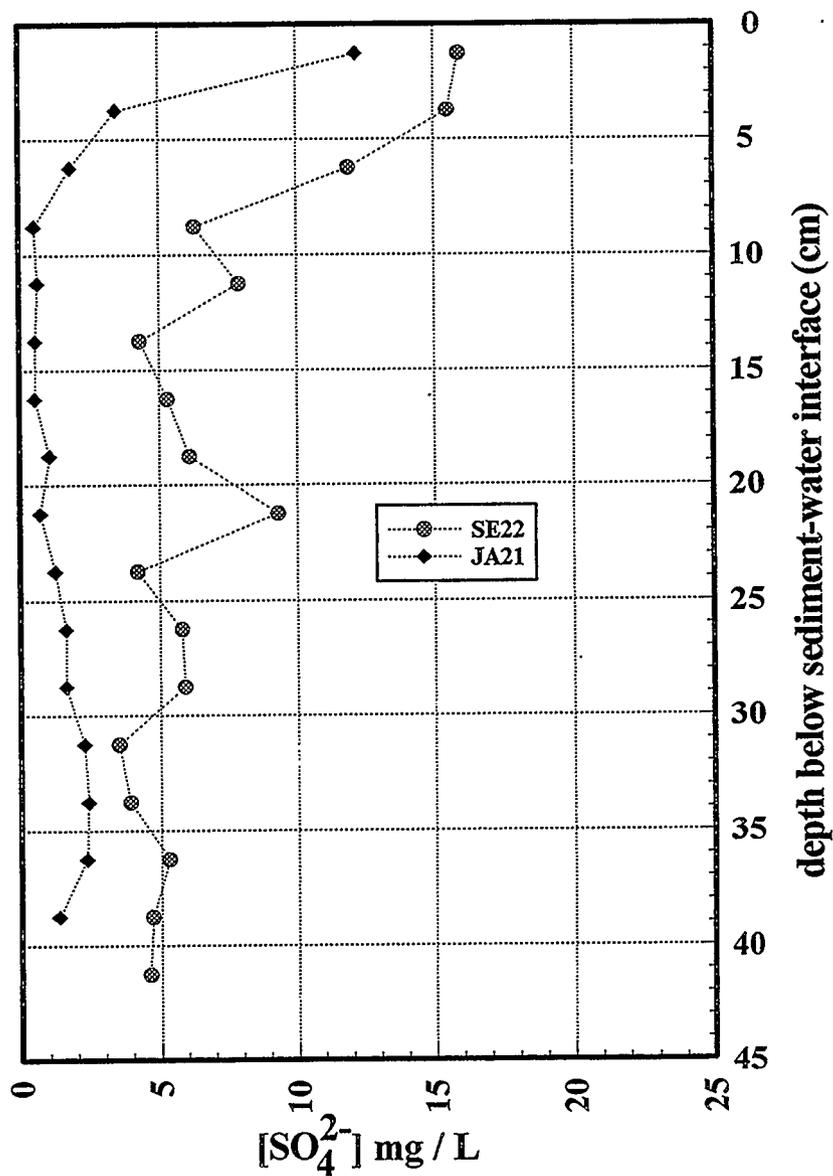


Figure 6.7 Aqueous sulphate concentration profiles for porewaters expressed from cores SE22 and JA21 (Waterton Reservoir).

Table 6.2 Porewater chemical and stable isotopic data.

	pH	Alk as HCO <sub>3</sub> (mg/L)	F (mg/L)	Cl (mg/L)	Br (mg/L)	NO <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)	SO <sub>4</sub> (mg/L)	Li (mg/L)	Na (mg/L)	NH <sub>4</sub> (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	δ <sup>18</sup> O (‰ SMOW)	δD (‰ SMOW)	δ <sup>34</sup> S (‰ VCDT)*
SE22-1	7.72	156.9	N.D.	3.7	N.D.	4.6	N.D.	15.9	<0.1	11.2	0.4	1.4	8.2	22.4	-17.29	-134	<b>6.18</b>
SE22-2	7.57	148.9	N.D.	5.5	N.D.	4.3	N.D.	15.5	<0.1	11.2	0.5	1.0	14.6	39.4	-17.30	-136	<b>26.52</b>
SE22-3	7.83	154.7	N.D.	5.4	N.D.	4.0	N.D.	11.9	N.D.	18.0	0.6	1.1	7.5	18.0	-17.10		<b>36.26</b>
SE22-4	7.79	146.0	N.D.	3.6	N.D.	3.8	3.3	6.3	N.D.	11.1	0.8	0.9	6.0	17.2	-17.28	-133	<i>30.73</i>
SE22-5	7.87	153.9	N.D.	4.9	N.D.	4.5	N.D.	7.9	N.D.	10.2	1.0	1.0	6.6	19.1	-17.05		-2.26
SE22-6	7.87	164.8	N.D.	3.9	N.D.	4.3	N.D.	4.3	N.D.	7.9	0.6	0.4	7.5	15.5	-17.24	-130	
SE22-7	7.89	164.6	N.D.	4.5	N.D.	4.3	N.D.	5.3	<0.1	10.0	1.0	0.8	7.7	20.5	-17.29	-129	
SE22-8	7.61	145.5	N.D.	5.4	N.D.	5.0	N.D.	6.1	N.D.	13.2	1.1	1.2	6.8	19.4	-17.14	-145	<i>21.81</i>
SE22-9	8.25	N.D.	N.D.	5.0	N.D.	4.5	4.4	9.3	N.D.	12.6	1.0	1.0	5.6	15.2	-17.13	-138	<i>7.93</i>
SE22-10	7.77	170.5	N.D.	3.4	N.D.	3.6	N.D.	4.2	N.D.	9.5	1.2	0.8	7.2	19.9	-16.98	-125	<i>7.21</i>
SE22-11	7.88	171.5	N.D.	5.0	N.D.	4.1	N.D.	5.8	<0.1	9.7	1.0	1.0	7.4	2.9	-17.04	-130	<i>6.95</i>
SE22-12	7.83	153.7	N.D.	3.8	N.D.	3.2	N.D.	5.9	N.D.	10.3	0.8	0.6	6.3	18.4	-17.04	-137	<i>7.68</i>
SE22-13	8.02	139.8	N.D.	4.8	N.D.	4.0	3.4	3.5	<0.1	8.6	0.9	0.5	15.1	42.4	-17.18	-125	<b>7.68</b>
SE22-14	7.82	160.6	N.D.	3.6	N.D.	3.4	N.D.	3.9	N.D.	10.8	0.6	0.6	6.7	18.7	-17.29	-128	<i>15.64</i>
SE22-15	7.83	160.8	N.D.	5.1	N.D.	4.6	N.D.	5.3	N.D.	9.3	1.0	0.7	6.5	19.1	-16.99	-128	<i>13.49</i>
SE22-16	7.80	152.5	N.D.	4.7	N.D.	3.4	N.D.	4.7	<0.1	11.3	0.7	0.4	6.8	19.6	-16.97		<i>38.14</i>
SE22-17	7.78	140.6	N.D.	4.8	N.D.	4.3	N.D.	4.6	N.D.	12.3	0.9	0.8	5.6	15.8	-17.24	-136	<i>5.62</i>
JA21-1	N.D.	N.D.	0.1	1.8	N.D.	0.9	N.D.	12.2									<b>10.86</b>
JA21-2	N.D.	N.D.	0.0	1.2	0.0	0.7	N.D.	3.5									<b>22.8</b>
JA21-3	N.D.	N.D.	0.1	2.7	0.0	1.8	N.D.	1.8									10.94
JA21-4	N.D.	N.D.	0.1	1.2	0.0	0.6	N.D.	0.5									
JA21-5	N.D.	N.D.	0.1	0.9	0.0	0.8	N.D.	0.6									<i>23.4</i>
JA21-6	N.D.	N.D.	0.1	1.0	0.0	0.7	N.D.	0.6									
JA21-7	N.D.	N.D.	0.1	1.2	0.0	0.8	N.D.	0.5									
JA21-8	N.D.	N.D.	0.1	2.5	0.0	0.9	N.D.	1.0									<i>5.39</i>
JA21-9	N.D.	N.D.	0.1	1.2	0.0	0.6	N.D.	0.7									<i>26.75</i>
JA21-10	N.D.	N.D.	0.1	1.1	0.0	0.6	N.D.	1.2									<i>8.85</i>
JA21-11	N.D.	N.D.	0.1	1.0	0.0	0.6	N.D.	1.6									
JA21-12	N.D.	N.D.	0.1	1.1	0.0	0.6	N.D.	1.6									
JA21-13	N.D.	N.D.	0.1	1.3	0.0	0.7	N.D.	2.2									
JA21-14	N.D.	N.D.	0.1	2.5	0.0	0.5	N.D.	2.4									
JA21-15	N.D.	N.D.	0.1	1.2	0.0	0.8	N.D.	2.3									
JA21-16	N.D.	N.D.	0.1	1.2	0.0	0.6	N.D.	1.3									

\* Stable sulphur isotopic composition of porewater sulphate determined on microgram - size samples using gas flow combustion mass spectrometry. Italicized values have greater uncertainty owing to small sample size, and bolded values represent mean of several determinations (refer to Table 6.3.)

concentration in deeper porewaters from core JA21 parallel the total sediment sulphur concentration trends (cf. Figure 6.1).

### $\delta^{34}\text{S}$ OF POREWATER SULPHATE

Results of stable sulphur isotope ratio determinations for porewater aqueous sulphate precipitated as  $\text{BaSO}_4$  are illustrated as Figures 6.8 and 6.9 for cores SE22 and JA21, respectively. Symbol sizes on these illustrations are proportional to the uncertainty in determination of isotope ratios for these very small samples, which range in mass from <10 to 250  $\mu\text{g}$   $\text{BaSO}_4$  (refer to Table 6.3). Such small samples preclude conventional analytical methods; the on-line method described earlier was utilized to obtain these data. Also illustrated on these diagrams are corresponding  $\delta^{34}\text{S}$  determinations for total sediment sulphur presented earlier.

$\delta^{34}\text{S}$  values of porewater sulphate in all cases are enriched by between 5‰ and 50‰ (considering only data of high reliability) in comparison with those of total sediment sulphur. A noteworthy feature of the data illustrated for core SE22 (Figure 6.8) is that the  $\delta^{34}\text{S}$  of porewater sulphate is uniform (mean +7.49‰, S.D. = 0.40) over the corresponding interval of uniform total sediment  $\delta^{34}\text{S}$  (mean -6.57‰, S.D. = 0.56). Owing to low porewater sulphate concentrations, insufficient sample was available for analysis to determine the existence of this relationship in core JA21. The low  $\text{BaSO}_4$  yields may confirm the observation that porewaters from core JA21 are more dilute than those of core SE22.

### $\delta^{18}\text{O}$ AND $\delta\text{D}$ OF POREWATERS

Oxygen and hydrogen stable isotope ratios of porewaters expressed from sediments of core SE22 were determined, and analytical results are summarized as Figure 6.10. Data

## WATERTON RESERVOIR

### Core SE22 Sulphur isotope data

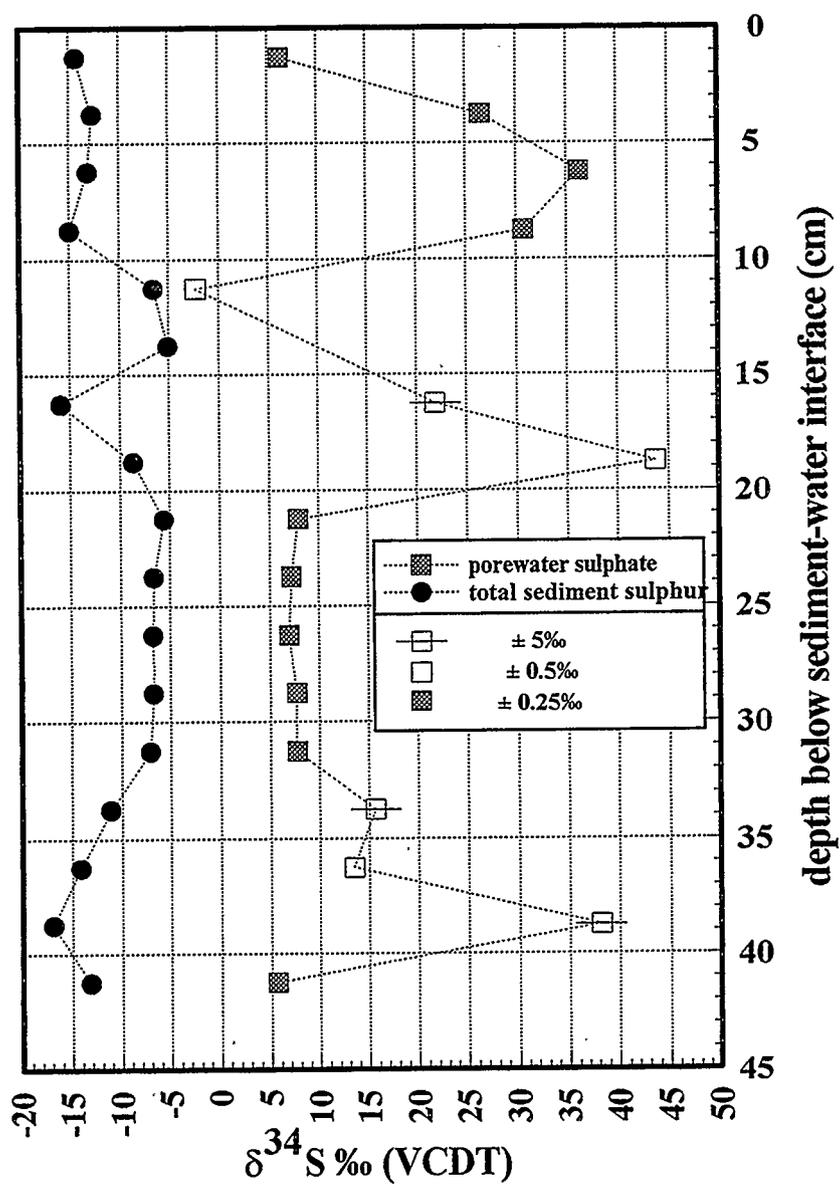


Figure 6.8 Profiles of  $\delta^{34}\text{S}$  of aqueous sulphate and  $\delta^{34}\text{S}$  of total sediment sulphur for core SE22 (Waterton Reservoir). For porewater data, filled squares  $\pm 0.25\text{‰}$ , open squares  $\pm 0.5\text{‰}$  and square with line  $\pm 5\text{‰}$ .

## WATERTON RESERVOIR

### Core JA21 Sulphur isotope data

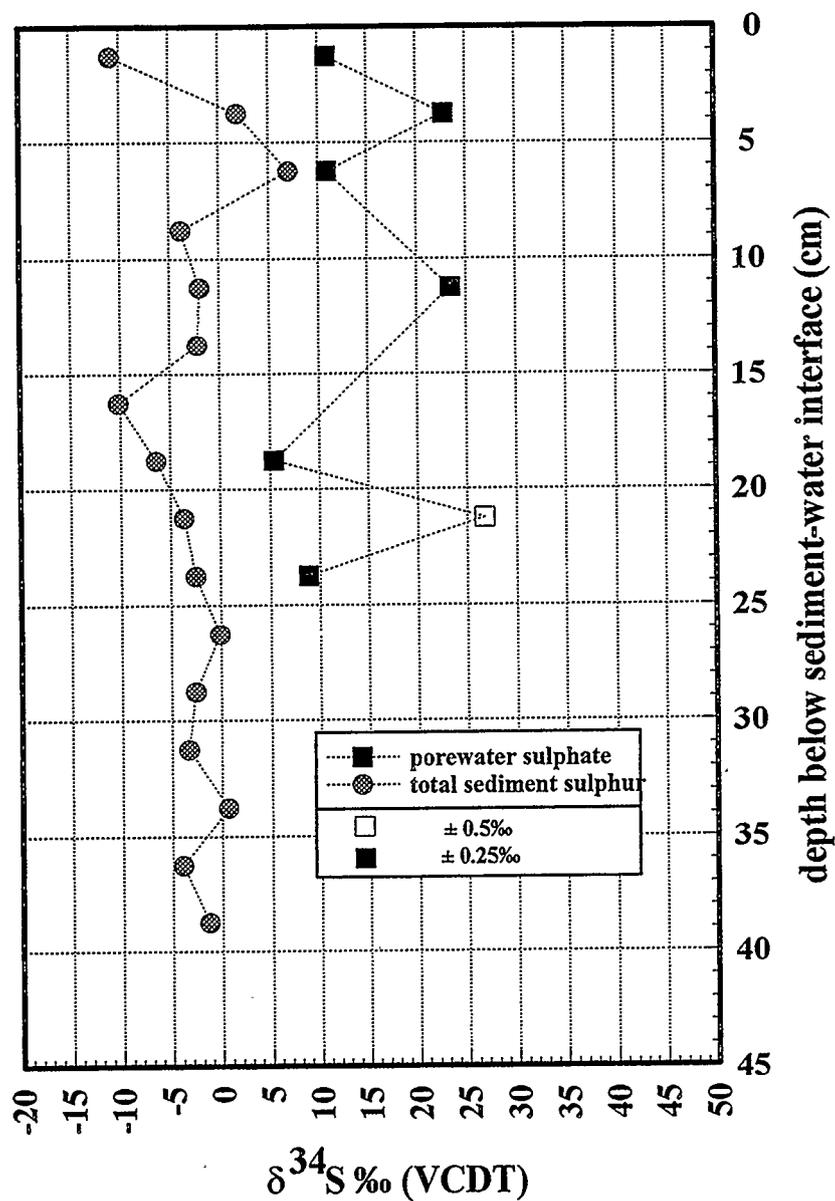


Figure 6.9 Profiles of  $\delta^{34}\text{S}$  of aqueous sulphate and  $\delta^{34}\text{S}$  of total sediment sulphur for core JA21 (Waterton Reservoir). For porewater data, filled squares  $\pm 0.25\text{‰}$  and open square  $\pm 0.5\text{‰}$ .

Table 6.3 Results of porewater sulphate  $\delta^{34}\text{S}$  determinations by GF-C-MS.

sample	$\mu\text{g S}$	$\delta^{34}\text{S}$	qualifying remarks
JA21-1	24.2	+11.55	
" "	26.0	+10.56	late to burn
" "	21.2	+11.03	
" "	25.7	+10.80	
" "	8.2	+10.34	not burned properly
JA21-2	22.0	+23.46	
" "	17.4	+22.13	not burned properly
JA21-3	4.65	+10.94	
JA21-4	2.1	+26.63	no signal
JA21-5	2.2	+23.40	
JA21-6	2.0	+23.16	no signal
JA21-7	2.0	+49.4	no signal
JA21-8	2.7	+5.39	
JA21-9	2.1	+26.75	
JA21-10	4.6	+8.85	
SE22-1	30.7	+6.66	not burned properly
" "	31.4	+6.09	
" "	19.1	+5.79	
SE22-2	18.1	+26.11	
" "	7.5	+26.37	late to burn
" "	13.3	+27.09	not burned properly
" "	2.5	N.D	
SE22-3	10.5	+36.14	
" "	14.8	+36.38	not burned properly
SE22-4	3.4	+30.73	
SE22-5	1.0	-2.26	tiny signal
SE22-6	0.9	+34.09	no signal
SE22-7	1.0	+21.81	tiny signal
SE22-8	0.9	+43.71	tiny signal
SE22-9	9.8	+7.93	
SE22-10	6.4	+7.21	
SE22-11	6.9	+6.95	not burned properly
SE22-12	3.7	+7.68	not burned properly
SE22-13	12.7	+7.85	
" "	4.4	+7.51	not burned properly
SE22-14	1.3	+15.64	
SE22-15	1.3	+13.49	
SE22-16	0.9	+38.14	
SE22-17	3.8	+5.62	
Beauvais Lake water			
MY27 deep	1.8	+5.93	
MY27 shallow	0.9	+10.38	

Samples analysed using gas flow combustion, ion integration mass spectrometry by Dr. A.-L. Norman of the Stable Isotope Laboratory, Department of Physics and Astronomy, The University of Calgary. Refer to Geisemann et al (1994) for description of method. Analytical uncertainties are  $\pm 5\%$  for samples of less than  $2.5 \mu\text{g S}$ ,  $\pm 0.5\%$  for samples between 7 and  $15 \mu\text{g S}$  and  $\pm 0.25\%$  for samples larger than  $15 \mu\text{g S}$ . Italicized values of  $\delta^{34}\text{S}$  have been disregarded for reason summarized in qualifying remarks column.

## Core SE22 - $\delta D$ and $\delta^{18}O$ porewaters

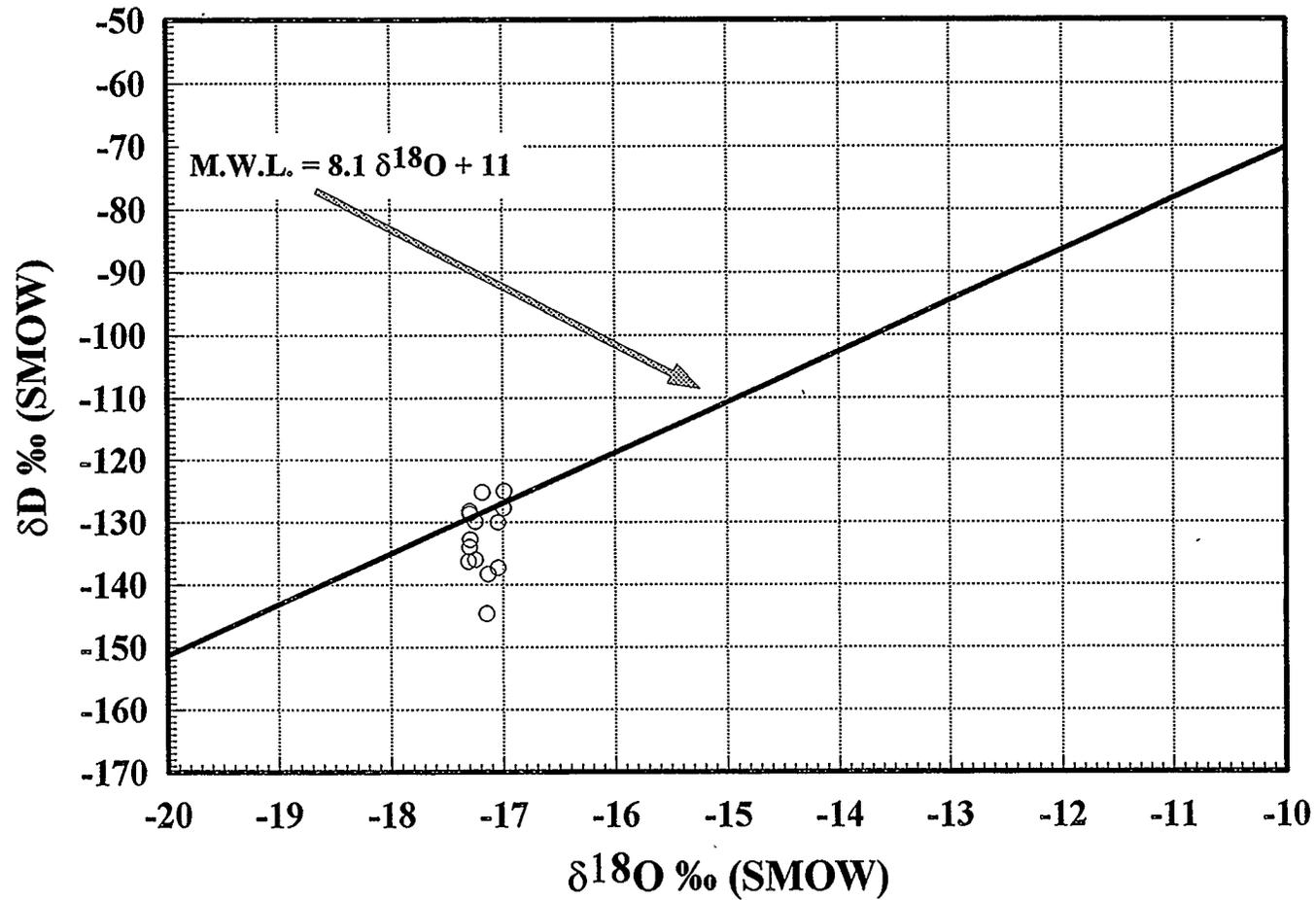


Figure 6.10  $\delta D$  vs  $\delta^{18}O$  for porewaters expressed from core SE22, Waterton Reservoir.

plot in proximity to the global meteoric water line and display a 20‰ range in  $\delta D$  with a corresponding 0.3‰ range in  $\delta^{18}O$ .

## WATER SAMPLE SUITES

The geographic distribution of sulphate concentration data and sulphur isotope ratio determinations of aqueous sulphate for water sample suites are summarized on Figures 6.11 through 6.15. Table 6.4 summarizes location data and facilitates cross-referencing of samples, and Tables 6.5 and 6.6 summarize measurements for aqueous species. In the discussion which follows, data from all suites and miscellaneous water samples are considered collectively; data comprising the most comprehensive sample suite (95AP27) are emphasized.

Table 6.4 Locations of samples comprising water suites.

Location description	Legal description	94MR13	95MR13	95AP27	95AU03	Misc
Waterton River upstream	6-19-3-28W4M			SW10		
Waterton River near Hutterite Colony	15-34-3-28W4M	W2	S4	SW13		
Waterton Reservoir near dock	9-27-4-28W4M	W1	S3	SW14	SW4A SW4B	JA26-W1 JA26-W2
Waterton Reservoir outflow (below dam)	14-26-4-28W4M		S2	SW15		
Cochrane Valley Aquifer @ relief wells	16-30-4-27W4M		S1	SW1		JA26-W3
Cochrane Valley Aquifer @ Lenz Spring	14-28-4-27W4M					G701-5 CVA-1
N. Drywood Ck @ falls	6-5-4-1W5M		S9	SW2	SW1	
N. Drywood Ck @ culvert	3-15-4-1W5M				SW2	
N. Drywood Ck above effluent	12-16-4-30W4M			SW4		
Shell Waterton Complex effluent	12-16-4-30W4M		EFF	SW3		
spring - valley of N. Drywood Ck below Shell	12-16-4-30W4M		SPR	SW5		
N. Drywood Ck above confluence	8-16-4-30W4M			SW6		
S. Drywood Ck above confluence	8-16-4-30W4M			SW7		
Drywood Ck @ confluence	8-16-4-30W4M	W6	S8			
Drywood Ck @ highway #6	11-17-4-29W4M	W5	S7	SW8		
Yarrow Ck @ highway #6	8-8-4-29W4M			SW9		
Drywood west of Gulf Plant	5-14-4-29W4M	W4	S6	SW11		
Drywood east of Gulf Plant	16-12-4-29W4M	W3	S5	SW12		
un-named creek @ NW of Waterton Reservoir	15-28-4-28W4M			SW16		
Beauvais Lake	3-29-5-1W5M					MY27S MY27D

Descriptions of locations comprising water suites. The Shell Waterton Complex effluent pipe emerges near the top of the valley wall, runs parallel to the valley slope and discharges at creek level. The spring in the valley of North Drywood Creek is situated immediately downstream of the effluent discharge location. Abundant calcareous tufa coating the valley wall may suggest that the spring is long-lived. Tufa extends approximately 15 m up the valley wall and for about 25 m downstream.

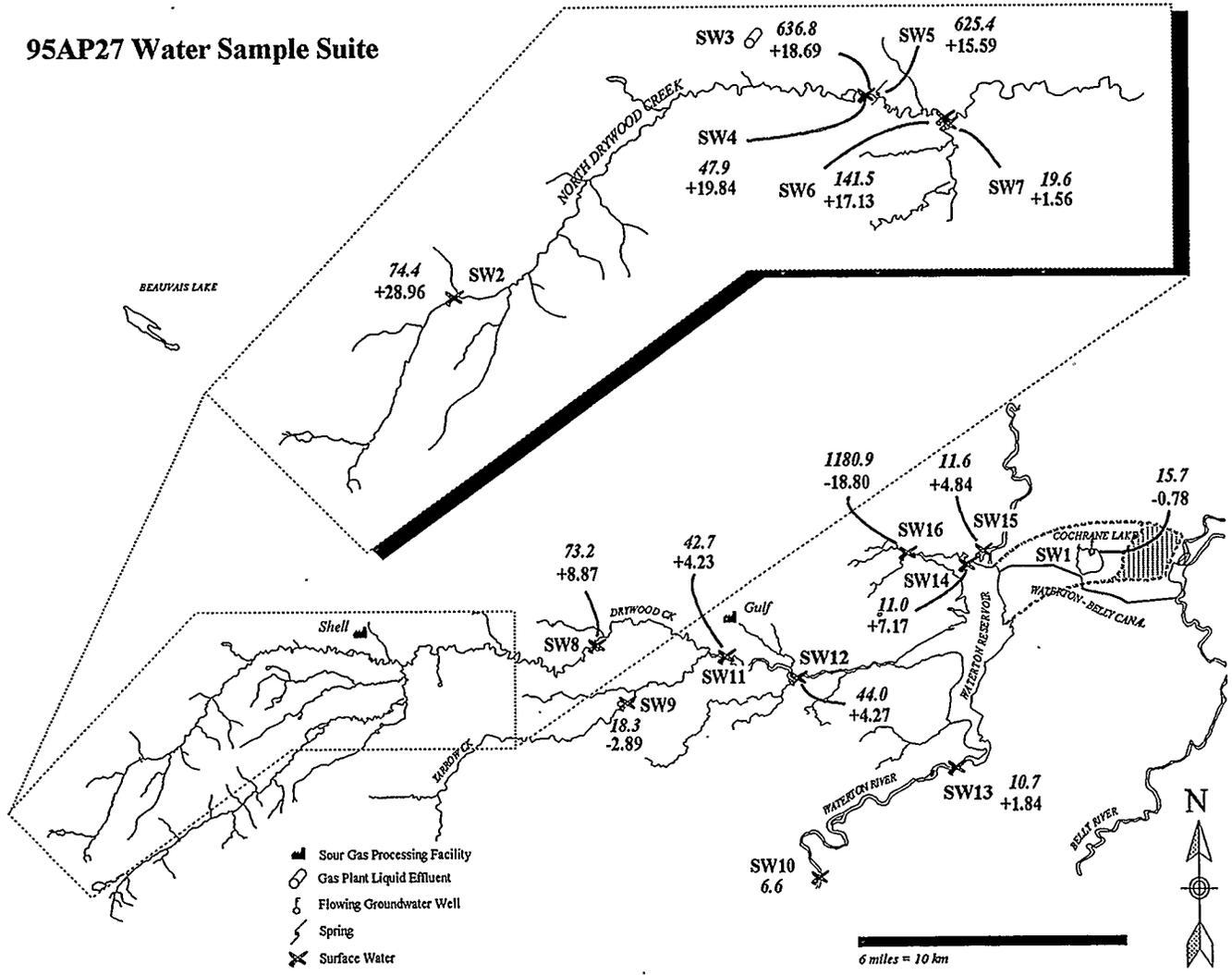


Figure 6.11 Aqueous sulphate concentration (italicized) and  $\delta^{34}\text{S}$  of aqueous sulphate for 95AP27 water suite.

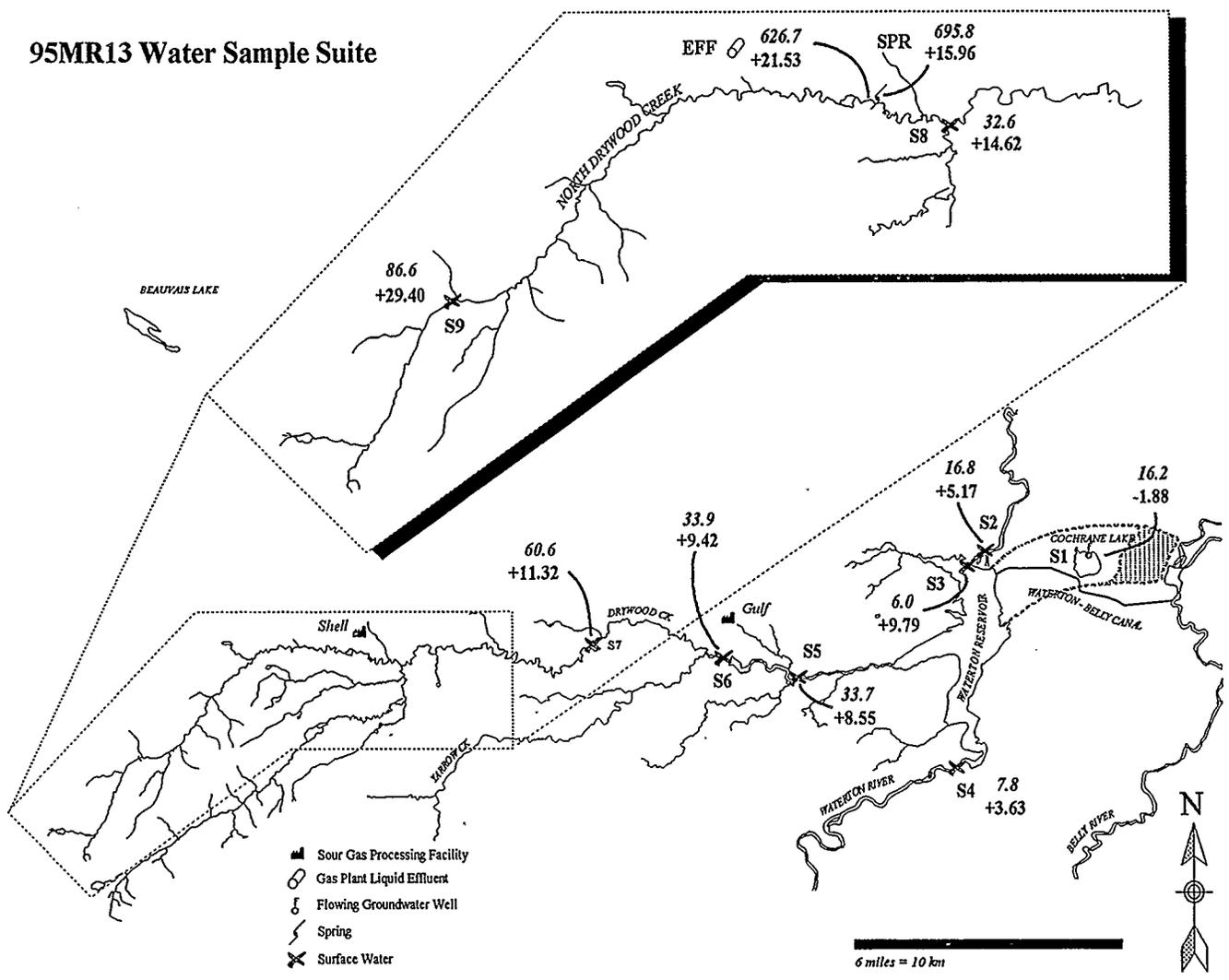


Figure 6.12 Aqueous sulphate concentration (italicized) and  $\delta^{34}\text{S}$  of aqueous sulphate for 95MR13 water suite.

94MR13 Water Sample Suite

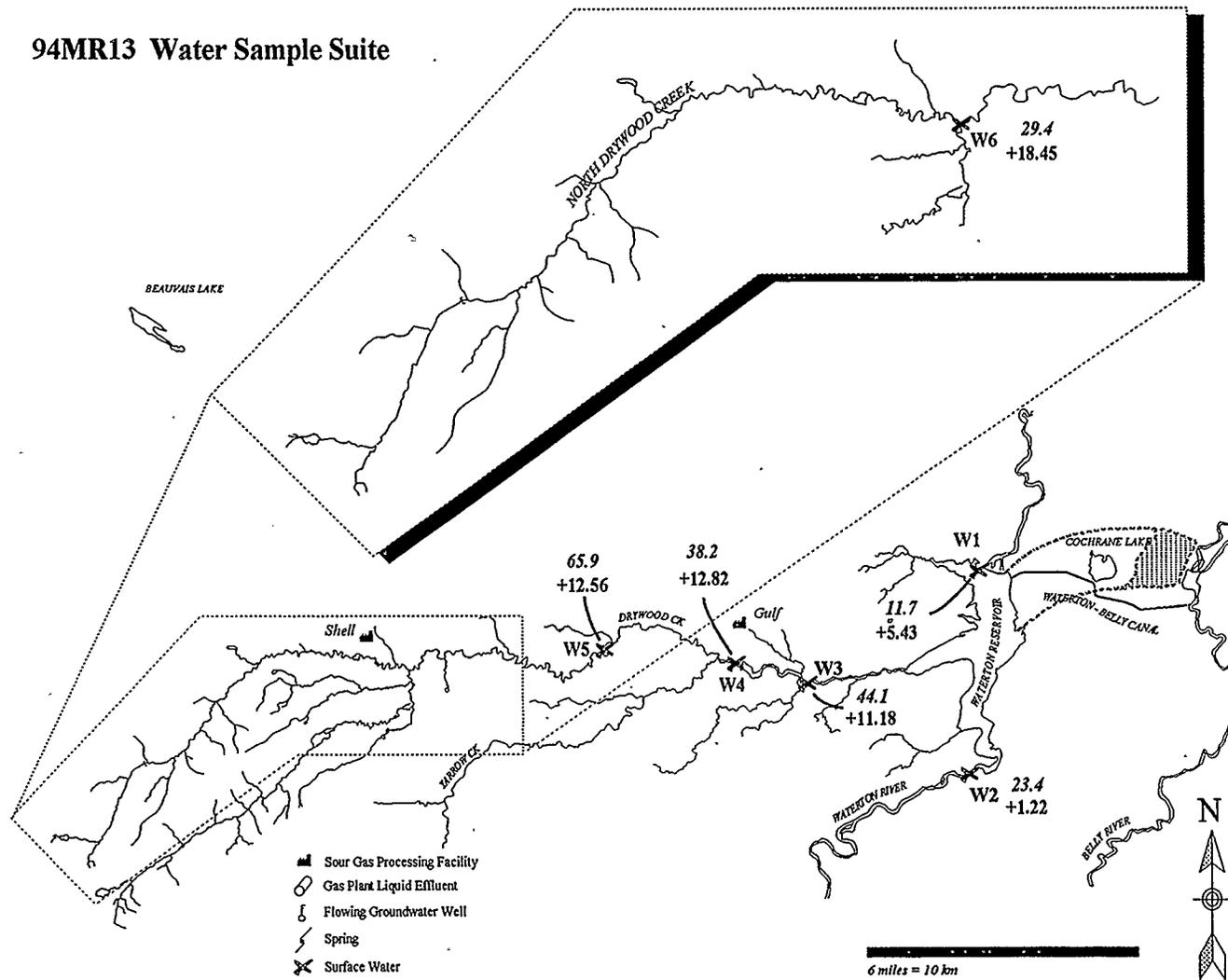


Figure 6.13 Aqueous sulphate concentration (italicized) and  $\delta^{34}\text{S}$  of aqueous sulphate for 94MR13 water suite.

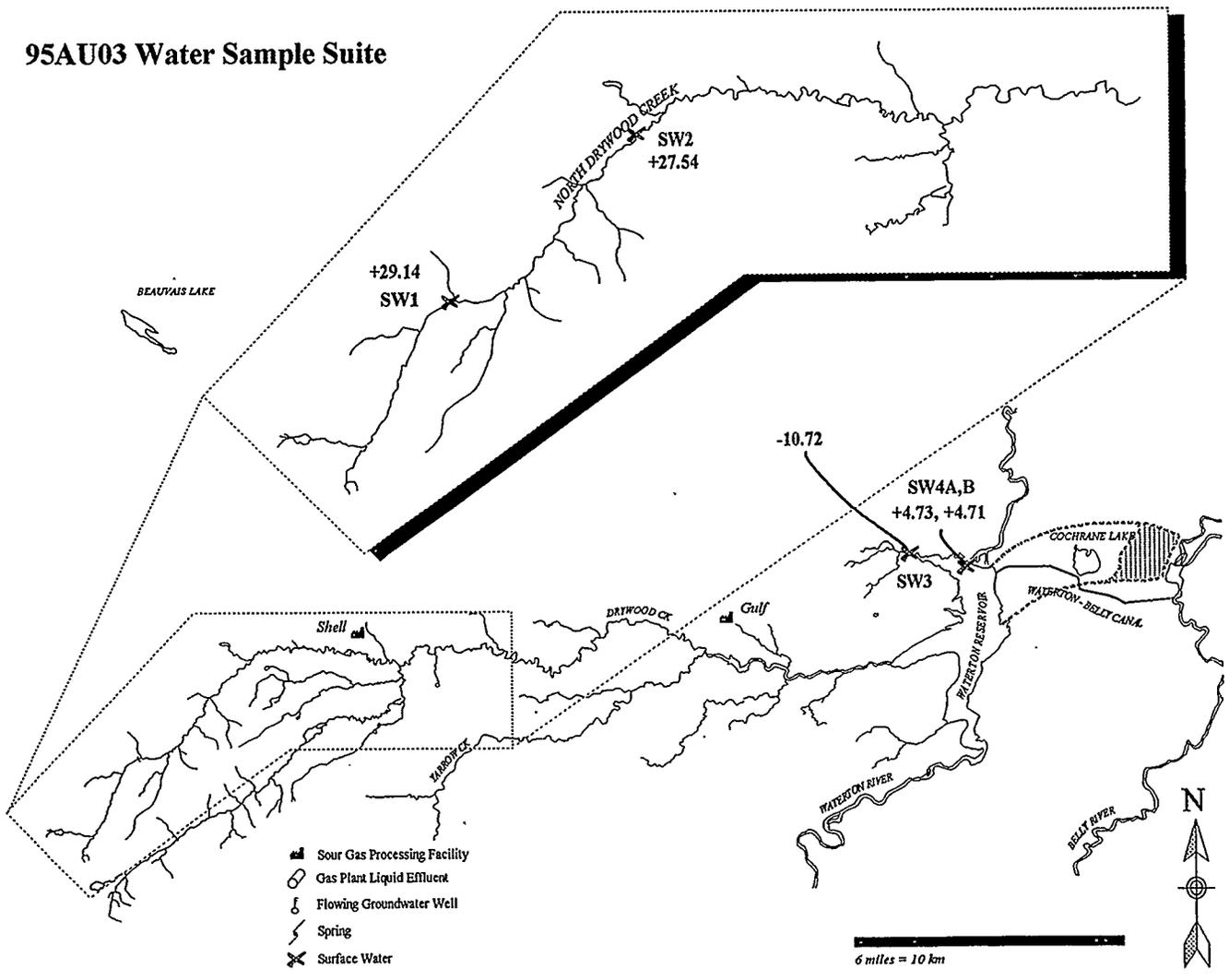


Figure 6.14  $\delta^{34}\text{S}$  of aqueous sulphate for 95AU03 water suite.

## Miscellaneous Water Samples

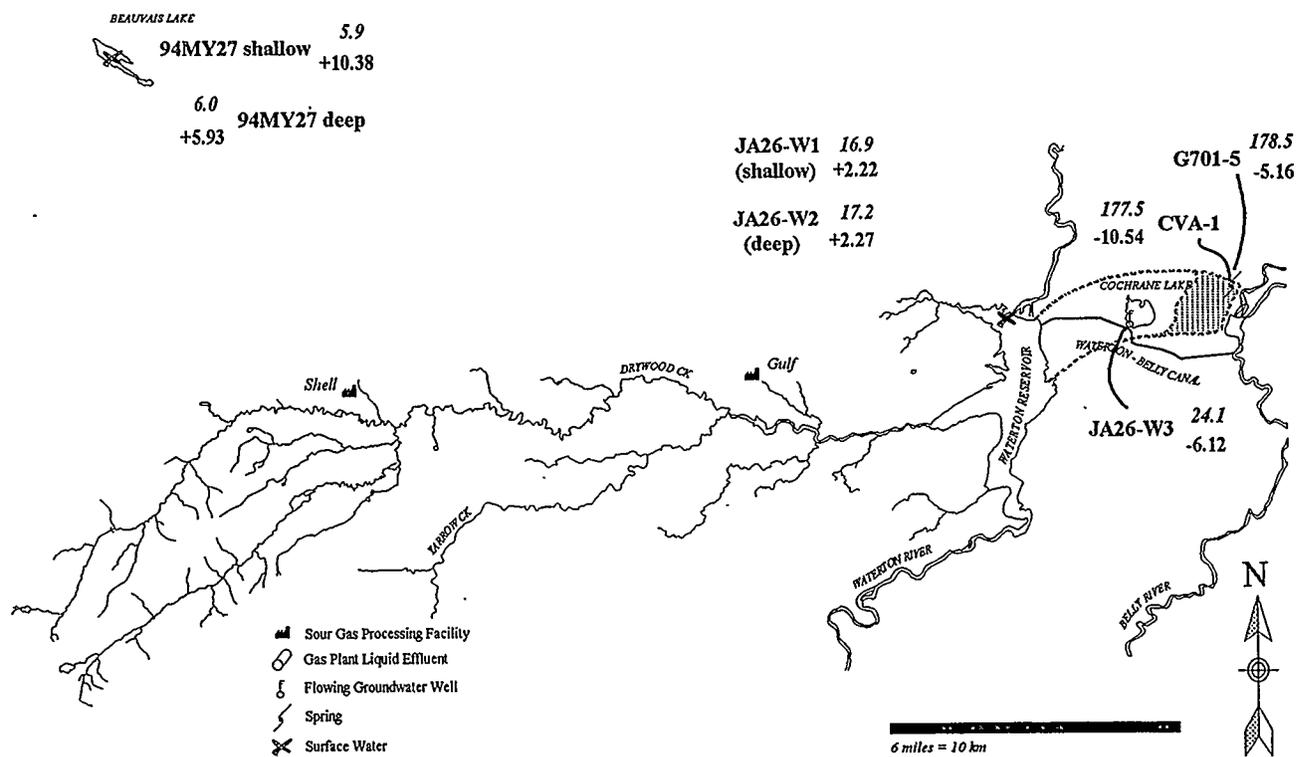


Figure 6.15 Aqueous sulphate concentration (italicized) and  $\delta^{34}\text{S}$  of aqueous sulphate for miscellaneous water samples.

Table 6.5 Summary of concentration measurements for surface water suites.

sample	lab pH	alk as HCO <sub>3</sub> (mg/L)	F (mg/L)	Cl (mg/L)	Br (mg/L)	NO <sub>3</sub> (mg/L)	PO <sub>4</sub> (mg/L)	SO <sub>4</sub> (mg/L)	Li (mg/L)	Na (mg/L)	K (mg/L)	Mg (mg/L)	Ca (mg/L)	Mn (mg/L)	Fe (mg/L)	Sr (mg/L)
JA26-W1	8.27	178.9	0.039	0.691	N.D.	0.52	N.D.	16.912	0.005	3.98	0.920	15.000	39.600	0.006	0.010	0.098
JA26-W2	8.40	181.6	0.038	0.657	N.D.	0.406	N.D.	17.149	0.005	4.00	0.925	15.200	39.900	0.004	0.007	0.100
JA26-W3	8.22	189.6	0.236	0.528	0.011	0.119	N.D.	24.072	0.019	9.27	1.160	19.900	38.800	0.165	0.048	0.520
94MR13-W1	8.26	117.6	0.029	0.651	N.D.	0.681	N.D.	11.687	0.003	2.79	0.980	10.200	26.400	0.006	0.011	0.065
94MR13-W2	8.30	185.7	0.042	1.138	N.D.	0.777	N.D.	23.433	0.005	6.14	2.570	16.800	39.100	0.047	0.044	0.120
94MR13-W3	8.31	148.3	0.069	2.51	N.D.	0.960	N.D.	44.117	0.007	9.64	2.120	20.400	56.500	0.025	0.024	0.168
94MR13-W4	8.31	215.0	0.051	1.954	N.D.	0.837	N.D.	38.212	0.005	8.40	1.510	18.000	52.100	0.016	0.019	0.148
94MR13-W5	8.34	213.3	0.059	2.594	N.D.	1.051	N.D.	65.894	0.006	12.10	1.730	19.000	57.800	0.029	0.021	0.165
94MR13-W6	8.34	117.3	0.041	1.544	N.D.	0.705	N.D.	29.434	0.002	5.67	1.380	15.600	49.300	0.076	0.047	0.120
94MY27S	8.27	212.8	0.108	0.899	N.D.	0.047	N.D.	5.885								
94MY27D	8.23	210.4	0.106	.499	N.D.	0.048	N.D.	6.042								
95MR13-S1	7.99	187.3	0.107	0.518	N.D.	0.033	N.D.	16.177	0.007	6.62	0.775	17.300	33.900	0.117	0.023	0.007
95MR13-S2	7.86	167.9	0.033	0.546	N.D.	0.638	N.D.	16.769	0.003	4.05	0.700	13.40	37.000	0.004	0.010	0.003
95MR13-S3	7.85	129.2	0.025	0.297	N.D.	0.500	N.D.	6.014	0.001	1.52	0.420	9.690	27.000	0.004	0.019	0.001
95MR13-S4	8.36	157.1	0.033	0.741	N.D.	0.451	N.D.	7.777	0.001	2.25	1.930	11.400	31.300	0.059	0.051	0.001
95MR13-S5	8.12	189.5	0.050	1.598	N.D.	0.867	N.D.	33.673	0.002	7.46	1.680	15.700	45.400	0.012	0.022	0.002
95MR13-S6	8.04	204.4	0.049	1.498	N.D.	0.831	N.D.	33.985	0.002	8.11	1.150	16.600	47.300	0.009	0.016	0.002
95MR13-S7	7.98	202.3	0.047	2.283	N.D.	0.997	N.D.	60.608	0.002	12.40	1.390	17.900	52.600	0.008	0.020	0.002
95MR13-S8	8.02	197.4	0.041	1.344	N.D.	0.923	N.D.	32.568	0.005	6.50	1.100	16.000	47.800	0.019	0.020	0.005
95MR13-S9	8.47	110.2	0.020	0.577	N.D.	0.532	N.D.	86.626	0.009	2.75	0.740	15.200	44.100	0.001	0.008	0.009
95MR13-EFF	7.84	381.0	0.108	22.74	0.111	31.775	0.248	626.651	0.020	266.00	11.400	40.300	107.000	0.009	0.028	0.020
95MR13-SPR	7.73	355.7	N.D.	38.284	0.069			695.794	0.032	24.00	2.270	121.000	311.000	0.024	0.024	0.032
95AP27-SW1	7.95	182.2	0.086	0.531	N.D.	0.298	N.D.	15.649	0.006	6.79	0.810	17.400	30.600	0.117	0.020	0.260
95AP27-SW2	7.96	103.9	0.027	0.548	N.D.	0.586	N.D.	74.359	0.006	2.25	0.740	13.800	40.800	0.003	0.008	0.270
95AP27-SW3	7.90	178.9	0.091	18.924	0.048	34.918	N.D.	636.782	0.021	201.00	9.510	40.900	112.000	0.026	0.020	0.350
95AP27-SW4	8.01	167.8	0.036	1.061	N.D.	0.658	N.D.	47.924	0.006	3.24	0.615	16.400	46.400	0.014	0.013	0.140
95AP27-SW5	7.68	426.2	0.048	35.326	0.058	0.377	N.D.	625.379	0.031	23.60	2.300	112.000	295.000	0.022	0.019	0.340
95AP27-SW6	7.79	185.2	0.061	4.154	0.005	2.511	N.D.	141.482	0.008	22.70	1.560	23.100	66.400	0.031	0.017	0.170
95AP27-SW7	7.95	217.3	0.047	0.918	N.D.	0.779	N.D.	19.610	0.004	3.06	0.810	16.800	50.200	0.022	0.010	0.110
95AP27-SW8	8.05	221.5	0.069	2.289	N.D.	1.212	N.D.	73.218	0.007	11.40	1.270	20.700	60.500	0.009	0.017	0.170
95AP27-SW9	8.01	208.4	0.048	0.666	N.D.	1.158	N.D.	18.312	0.005	4.27	0.770	16.800	47.700	0.005	0.009	0.100
95AP27-SW10	8.11	139.6	0.029	0.462	N.D.	0.626	N.D.	6.548	0.002	1.80	0.390	11.000	29.300	0.007	0.009	0.060
95AP27-SW11	8.10	221.4	0.070	1.607	N.D.	0.994	N.D.	42.656	0.006	8.04	1.180	19.100	54.000	0.005	0.010	0.140
95AP27-SW12	8.00	219.4	0.057	1.637	N.D.	1.017	N.D.	43.951	0.006	9.01	1.230	19.100	53.200	0.010	0.010	0.150
95AP27-SW13	7.94	160.6	0.045	0.781	N.D.	0.630	N.D.	10.732	0.002	3.01	1.410	12.600	33.500	0.022	0.026	0.070
95AP27-SW14	8.03	146.6	0.033	0.597	N.D.	0.831	N.D.	10.992	0.004	2.75	0.605	11.300	31.300	0.003	0.009	0.070
95AP27-SW15	8.03	146.8	0.037	0.552	N.D.	0.883	N.D.	11.603	0.004	2.89	0.605	11.600	32.000	0.004	0.009	0.070
95AP27-SW16	7.99	505.9	0.128	7.502	0.045	0.465	N.D.	1180.873	0.069	146.00	12.000	205.000	226.000	0.261	0.256	1.630
95AU03-SW1																
95AU03-SW2																
95AU03-SW3																
94AU03-SW4A																
95AU03-SW4B																
G701-5	7.41	275.3	N.D.	9.1	N.D.	N.D.	N.D.	178.5	0.022	88.30	1.84	28.30	52.30	0.184	0.041	0.675
CVA-1	7.60	297.4	N.D.	9.65	N.D.	N.D.	N.D.	177.5	0.023	90.70	1.93	27.60	46.80	0.168	0.040	0.725

Table 6.6  
Summary of stable isotope measurements for samples from surface water suites

sample	$\delta^{18}\text{O}$ water ‰ (VSMOW)	$\delta\text{D}$ water ‰ (VSMOW)	$\delta^{34}\text{S}$ sulphate ‰ (VCDT)	$\delta^{18}\text{O}$ sulphate ‰ (VCDT)
JA26-W1			+2.22	
JA26-W2			+2.27	
JA26-W3			-6.12	
94MR13-W1			+5.43	
94MR13-W2			+1.22	
94MR13-W3			+11.18	
94MR13-W4			+12.82	
94MR13-W5			+12.56	
94MR13-W6			+18.45	
94MY27S			+10.38	
94MY27D			+5.93	
95MR13-S1			-1.88	
95MR13-S2			+5.17	
95MR13-S3			+9.79	
95MR13-S4			+3.63	
95MR13-S5			+8.55	
95MR13-S6			+9.42	
95MR13-S7			+11.32	
95MR13-S8			+14.62	
95MR13-S9			+29.40	
95MR13-EFF			+21.53	
95MR13-SPR			+15.96	
95AP27-SW1	-16.70	-130.1	-0.78	
95AP27-SW2	-18.52	-141.3	+28.96	+10.36
95AP27-SW3	+0.38	-264.6	+18.69	+9.82
95AP27-SW4	-18.00	-148.9	+19.84	
95AP27-SW5	-17.40	-139.2	+15.59	-2.50
95AP27-SW6	-16.62	-150.1	+17.13	
95AP27-SW7	-18.20	-144.1	+1.56	
95AP27-SW8	-17.47	-143.0	+8.87	
95AP27-SW9	-18.30	-144.6	-2.89	
95AP27-SW10	-17.20	-141.6	N.E.S.	
95AP27-SW11	-18.00	-147.9	+4.23	
95AP27-SW12	-18.70	-147.0	+4.27	
95AP27-SW13	-17.16	-140.2	+1.84	
95AP27-SW14	-17.03	-136.9	+7.17	
95AP27-SW15	-17.10	-136.4	+4.84	
95AP27-SW16	-16.84	-138.1	-18.80	+5.00
95AU03-SW1			+29.14	
95AU03-SW2			+27.54	
95AU03-SW3			-10.11	
94AU03-SW4A			+4.73	
95AU03-SW4B			+4.71	
G701-5	-17.99	-137.7	-5.16	
CVA-1	-18.17	-136.7	-10.54	

Sulphate concentrations reach a maximum of 1181 mg/L and most are less than 20 mg/L. South Drywood Creek, Yarrow Creek and Waterton River and Reservoir waters have low sulphate concentrations. Effluent discharge from Shell Waterton Complex and water flowing from the spring in North Drywood Creek valley topographically below the Shell gas plant have sulphate concentrations in the order of 630 mg/L. Groundwaters discharging from the distal end of the Cochrane Valley Aquifer at Lenz Spring (G701-5 and CVA-1) were characterized by sulphate concentrations of about 180 mg/L in the late summer of 1992.

Figure 6.16 illustrates the relationship between sulphate concentration and sulphur isotope ratio determinations of aqueous sulphate for water suites and miscellaneous waters.  $\delta^{34}\text{S}$  of aqueous sulphate (abbreviated  $\delta^{34}\text{S}_{\text{ate}}$ ) precipitated as  $\text{BaSO}_4$  ranges from about -20‰ to +30‰. Waters characterized by relatively high sulphate concentration have  $\delta^{34}\text{S}_{\text{ate}}$  values of -5‰ or lower, or +15‰ or higher. Significantly, waters collected from North Drywood Creek upstream of Shell Waterton Complex have  $\delta^{34}\text{S}_{\text{ate}}$  values more enriched than the local technogenic sulphur value of approximately +17‰ (Wallick et al, 1984; Twin Butte, 1984) and the most concentrated sulphate solution (95AP27-SW16<sup>1</sup>) has the most depleted sulphur isotopic composition (-18.8‰). The groundwaters discharging into the North Drywood Creek valley in the vicinity of the Shell facility are similar to gas plant effluent in isotopic composition and sulphate concentration. Groundwaters sampled from the Cochrane Valley aquifer have  $\delta^{34}\text{S}_{\text{ate}}$  values of 0‰ or lower.

#### $\delta^{18}\text{O}$ AND $\delta\text{D}$ OF 95AP27 WATER SUITE

Oxygen and hydrogen stable isotope ratios for waters collected April 25th, 1995 are summarized as Figure 6.17. Data generally support a linear trend subparallel to, but not

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<sup>1</sup> although not determined analytically, the high abundance of  $\text{BaSO}_4$  precipitate in sample 95AU03-SW3 from the same location qualitatively suggests a high sulphate concentration.

## All Water Suites

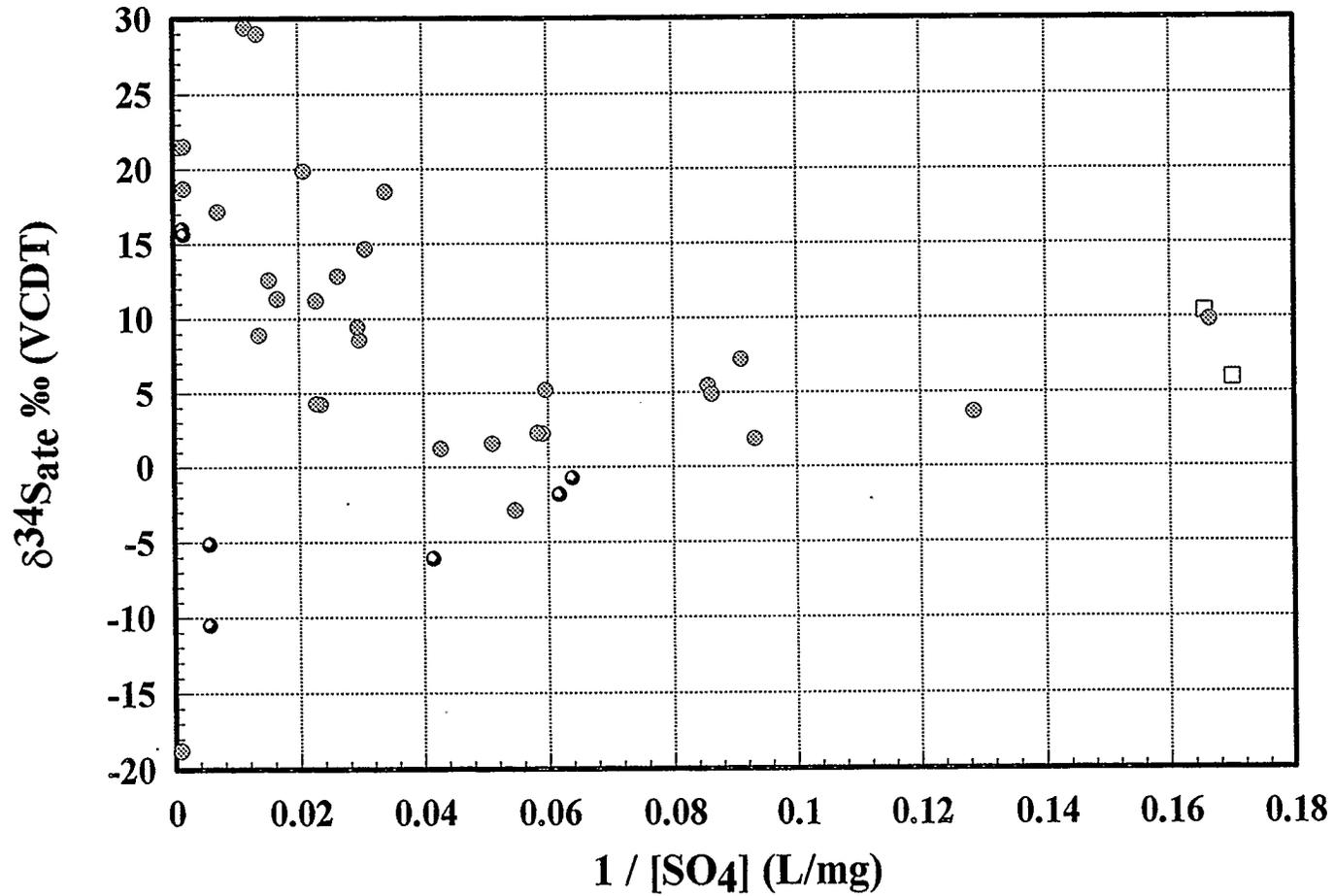


Figure 6.16  $\delta^{34}\text{S}$  of aqueous sulphate vs  $1/\text{sulphate}$  concentration for samples comprising water suites. Spheres represent groundwaters and closed circles surface waters. Beauvais Lake waters represented by open squares.

## $\delta D$ vs $\delta^{18}O$ for 95AP27 waters

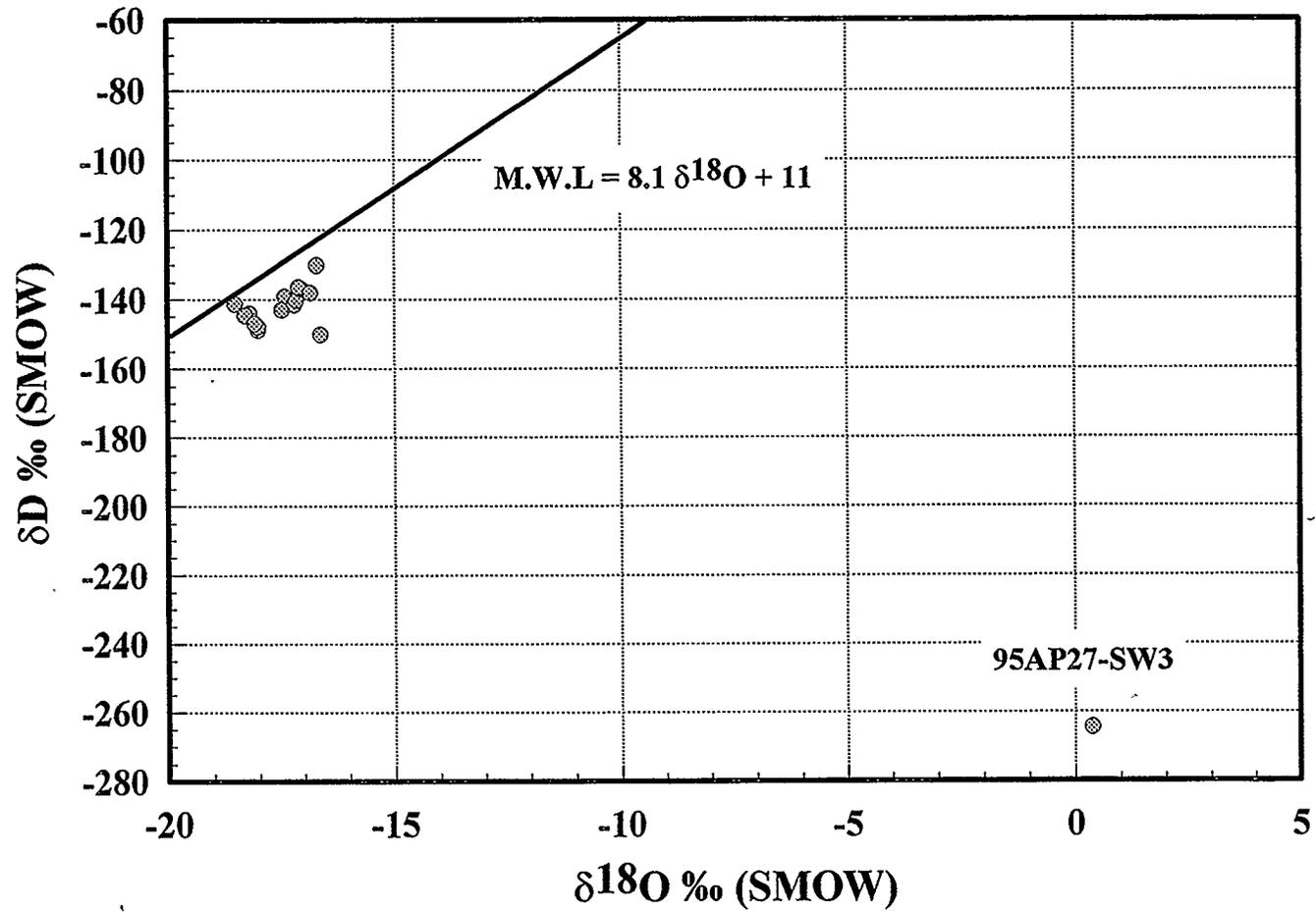


Figure 6.17 Hydrogen and oxygen isotopic data for water samples comprising 95AP27 water suite.

directly on, the global meteoric water line. Sample 95AP27-SW3 (Shell Waterton Complex effluent) is highly enriched in  $^{18}\text{O}$  and depleted in deuterium in comparison with the other waters comprising the suite, and plots away from the global meteoric water line.

## OXYGEN ISOTOPIC COMPOSITION OF SULPHATE

The stable oxygen isotopic composition (abbreviated  $\delta^{18}\text{O}_{\text{ate}}$ ) of selected samples from the 95AP27 water suite is summarized in Table 6.7. Data reported for 95AP27-SW5 is the mean of 2 analyses; all others are from a single determination per sample.

Table 6.7  $\delta^{18}\text{O}$  and  $\delta^{34}\text{S}$  of aqueous sulphate of analysed samples from 95AP27 suite.

		$\delta^{18}\text{O}_{\text{ate}}$ ‰ (SMOW)	$\delta^{34}\text{S}_{\text{ate}}$ ‰ (VCDT)
95AP27-SW2	N. Drywood Ck. @ falls	+10.36	+28.96
95AP27-SW3	Shell Waterton Effluent	+9.82	+18.69
95AP27-SW5	Spring in valley of N. Drywood Ck below Shell	-2.50	+19.75
95AP27-SW16	un-named creek N.W. of Waterton Reservoir	+5.00	-18.80

## GEOLOGIC MATERIALS

Data for total sulphur concentration and stable sulphur isotope ratio determinations for the soil profile sampled are summarized as Table 6.8. Soils in the vicinity of Waterton Reservoir are black chernozems developed on loam (Shields and Lindsay, 1986). Soil sulphur concentrations at the profile examined are lower than those of the reservoir sediments, and sulphur isotope ratios become progressively more enriched with increasing depth in the profile. High water conditions during the summer of 1995 resulted in flooding of the site where the soil profile was examined; it is unclear whether similar circumstances occurred before as reservoir level data for 1995 are presently unavailable.

Table 6.8 Sulphur concentration and  $\delta^{34}\text{S}_{\text{total}}$  for soil profile adjacent to Waterton

Reservoir			
sample	soil horizon	[S <sub>total</sub> ] $\mu\text{mole/g}$	$\delta^{34}\text{S}_{\text{total}}$ ‰ (VCDT)
JA26-S4	Ah	3.3	-3.74
JA26-S3	Ae	4.5	+1.28
JA26-S2	Bh	3.2	+4.10
JA26-S1	C	3.7	+5.21

Rocks of the upper Cretaceous Belly River formation crop out along the cutbank of the Waterton River immediately down stream of Waterton dam. This stratigraphic unit also floors the reservoir, and is exposed along creeks and rivers over much of the reservoir catchment area (Douglas, 1951). Two samples of mudstone intercalations were collected and analysed for [S<sub>total</sub>],  $\delta^{34}\text{S}_{\text{total}}$  and total organic carbon. Table 6.9 summarizes the analytical results.

Table 6.9 Sulphur and carbon concentration and  $\delta^{34}\text{S}_{\text{total}}$  of bedrock in vicinity of Waterton

Reservoir			
	[S <sub>total</sub> ] $\mu\text{mole/g}$	$\delta^{34}\text{S}_{\text{total}}$ ‰ (VCDT)	total organic C (wt%)
WOC-1	0.9	not enough sample	0.01
WOC-2	2.2	+8.38	0.04

## CHAPTER 7 - DISCUSSION AND INTERPRETATION

The total sulphur pool in lake sediments comprises detrital components and sulphur introduced through diagenesis. The former may include sulphur-bearing geologic materials, and organic sulphur from allochthonous (external) or autochthonous (within lake) sources.

Assimilation of sulphur by plants or animals tends not to be isotopically selective (Thode, 1991), hence the sulphur isotopic composition of organisms reflects that of sulphate in the environment in which they grow. Shifts in sulphur isotope ratios reflecting technogenic sulphur impact may be detectable if the isotopic composition of the technogenic sulphur differs from that of the environmental background (Krouse, 1980). In the case of terrestrial plants, aqueous sulphate in the soil solution is the principal form of sulphur available to plants (eg. Schoenau and Germida, 1992), although foliar uptake of atmospheric gaseous sulphur has been documented for some species (Krouse, 1980). In most lakes, sufficient sulphate is available in aerobic habitats to supply the requirements of planktonic algae and bacteria (Cook and Kelly, 1992).

Dissimilatory sulphate reduction, resulting in the formation of Fe-monosulphides or pyrite, is a commonly cited pathway by which diagenetic sulphur is added to lake sediments. Sulphate reducing bacteria require a source of aqueous sulphate; porewater sulphate concentrations in lake sediments commonly decrease abruptly a few centimeters below the sediment-water interface and indicate transport from the sediment surface followed by reduction at depth in the sediment. Studies such as those of Nriagu and Soon (1985), and Rudd et al (1986) have suggested that organosulphur compounds and not metal sulphides are the products of dissimilatory sulphate reduction, however, the time frame of the observations (instantaneous vs. long-term) or the possibility of subsequent sulphur assimilation must be considered. Such controversy underscores the need for additional study.

In this chapter, the contributions and isotopic characterization of the sources of sulphur to the sediments of Waterton Reservoir are discussed. The sources considered include technogenic emissions and liquid effluent, and ambient sulphur sources to surface and groundwaters in the catchment area. The possible contribution of volcanogenic sulphur from the May, 1980 cataclysmic eruption of Mount St. Helens is also considered.

Spatial and temporal variations of sulphur accumulation in the sediments of Waterton Reservoir emphasize the importance of isotopically distinct, local technogenic sulphur sources. The relatively minor role of diagenetic sulphur addition to the sediments of Waterton Reservoir by dissimilatory sulphate reduction is suggested by evidence from porewaters and sediments. Consequently, a record of the local sour gas industry is preserved in the rapidly accumulating reservoir sediments. In contrast, dissimilatory sulphate reduction contributes significantly to sulphur storage in sediments of Beauvais Lake.

## SULPHUR SOURCE CHARACTERIZATION

### Isotopic characterization of local technogenic sulphur

The sulphur isotopic composition of elemental sulphur produced by both the Shell Waterton Complex and the former Gulf Pincher Creek Plant was investigated by the Twin Butte Soils and Water Evaluation Task Force, and data are summarized in Table 3.1. The measurements demonstrate that the sulphur isotopic composition of the H<sub>2</sub>S in the raw gas and the by-product elemental sulphur are similar ( $\delta^{34}\text{S} \sim +17\text{‰}$ ), and both are enriched with respect to sulphur Alberta soils (range of  $\delta^{34}\text{S} +5\text{‰}$  to  $-30\text{‰}$ ; Krouse 1991).

It is reasonable to conclude that technogenic sulphur introduced to the local environment as elemental sulphur dust will have a similarly high  $\delta^{34}\text{S}$  value. Microbial oxidation of elemental sulphur to sulphate is not isotopically selective from the viewpoint of sulphur (eg. Krouse and Tabatabai, 1986), therefore the isotopic composition of sulphate in soil

solutions from aerobic soils or oxygenated groundwater should reflect technogenic additions.

Products of the oxidation of sulphur gases such as the  $H_2S$  or  $H_2S_x$  emitted during liquid sulphur handling or elemental sulphur storage block degassing should also be similar to that of technogenic sulphur because isotope selectivity during oxidation of lower valence state sulphur compounds is small (Krouse, 1994).

Atmospheric sampling experiments conducted during the 1983 Twin Butte study included sulphur isotopic characterization of ambient atmospheric  $SO_2$  and particulate sulphur, and are summarized below. The atmospheric sampling at a downwind location confirms that the technogenic sulphur emitted to the atmosphere from the Shell Waterton incinerator stack is also enriched in  $^{34}S$ .

Table 7.1. Isotopic characterization of ambient atmospheric  $SO_2$  and particulate S

	$\delta^{34}S$ ‰ (CDT)	$\delta^{34}S$ ‰ (CDT)	$\delta^{34}S$ ‰ (CDT)
particles	+19.7	+21.6	+15.8
$SO_2$ trap 1	+21.3	+16.5	+16.4
$SO_2$ trap 2	+25.0	+22.9	+20.7

Atmospheric samples collected over approximately 24 hour periods during October, 1983 from a site located approximately 2km east of Shell Waterton Complex. "trap 2" data are from the second in a sequence of treated filters, and represent  $SO_2$  which passed through "trap 1". Data are from Twin Butte Soils and Water Evaluation Task Force (Twin Butte, 1984).

#### Characterization of ambient aqueous sulphate

Consideration of data from the surface and groundwater sample suites collected for this study, presented previously as Figures 6.11 through 6.15 permits the following generalizations:

- $\delta^{34}S$  of aqueous sulphate of waters from North Drywood Creek upstream of the Shell Waterton Complex ( $\delta^{34}S \sim +29\%$ ; sulphate concentration  $\sim 75$  mg/L) is more enriched than the sulphur recovered at the sour gas plants.

- tributaries of Drywood Creek (South Drywood Creek and Yarrow Creek) dilute the waters of the north branch of Drywood Creek, and add sulphate having a lower  $\delta^{34}\text{S}$  value. This results in  $\delta^{34}\text{S}_{\text{ate}}$  ranging from +4.27 to +11.88‰, and a sulphate concentration ranging from 33.7 to 44.1 mg/L near the mouth of Drywood Creek.
- $\delta^{34}\text{S}$  of Waterton River aqueous sulphate from locations near Waterton Reservoir ranges from +1.2‰ to +3.6‰, and sulphate concentration ranges from 7.8 to 23.4 mg/L.
- the water sample having the highest sulphate concentration (un-named creek at N.W. corner of Waterton Reservoir) is also characterized by the most depleted value of  $\delta^{34}\text{S}$  of aqueous sulphate.
- gas plant effluent water, and the water from the spring in the valley of North Drywood Creek adjacent to the effluent discharge pipe have similar aqueous sulphate concentration and sulphur isotopic composition.

These observations will be elaborated upon in the discussion which follows.

The aqueous sulphate concentration of the upstream reach of North Drywood Creek (74.4 to 86.6 mg/L) is similar to that of pristine groundwater from a southwestern Alberta Foothills setting (64 to 88 mg/L; van Donkelaar et al, 1995). A possible interpretation based solely on sulphate concentration is that discharge of water along North Drywood Creek was sustained by baseflow components on the occasions on which the creek was sampled. However, the sulphur isotopic composition of aqueous sulphate from the North Drywood Creek (+28.96 to +29.40‰) is dramatically different from that of the pristine groundwater (-11.4 to -13.9‰; *ibid*), suggesting the the similarity in concentration is fortuitous, and implicating different sulphur sources for the two.

Hendry et al (1986) used stable sulphur isotopes to suggest that approximately 80% of the aqueous sulphate in groundwaters in oxidized tills of the Lethbridge, Alberta region was derived from oxidation of reduced organosulphur compounds present in the tills. The

sulphur isotopic composition of aqueous sulphate in the weathered till was approximately -9 to -14.5‰, similar to the values reported by van Donkelaar et al (1995).

Results of analyses of groundwater samples obtained from the Cochrane Valley Aquifer further constrain aqueous sulphate source identification in the Twin Butte area, particularly when they are supplemented with data from prior studies. Figure 7.1 displays  $\delta^{34}\text{S}_{\text{ate}}$  vs the inverse of sulphate concentration for selected samples from the present study, supplemented by pristine groundwaters from van Donkelaar et al (1995). Also included are the three groundwaters for which  $\delta^{34}\text{S}_{\text{ate}}$  was determined by the investigators of the Twin Butte Task Force. Krouse (1980) illustrates the utility of such diagrammatic representations for identification of sulphur sources.

A previous hydrologic study has demonstrated that the waters of the gravel facies of the Cochrane Valley Aquifer comprise a mixture of water sourced by leakage from the Waterton Reservoir, and other groundwaters (Vanden Berg and Geiger, 1973). The Cochrane Valley Aquifer gravel facies samples, the pristine spring samples of van Donkelaar et al (1995), and the Twin Butte 1983 groundwaters define a linear trend which forms the lower boundary of the data field represented on Figure 7.1a. Linear regression of the emphasized points on Figure 7.1b defines a line having a y-intercept of -16.42‰. As the y-intercept represents infinite concentration, a sulphur source characterized by a  $\delta^{34}\text{S}$  of close to -16.5‰ is implicated. This compares favorably with a sulphur source isotopic composition of -17‰ suggested by the extrapolation of sulphur isotope determinations on soil B horizon samples from the Twin Butte area (Krouse and Tabatabai, 1986).

### Twin Butte area water data

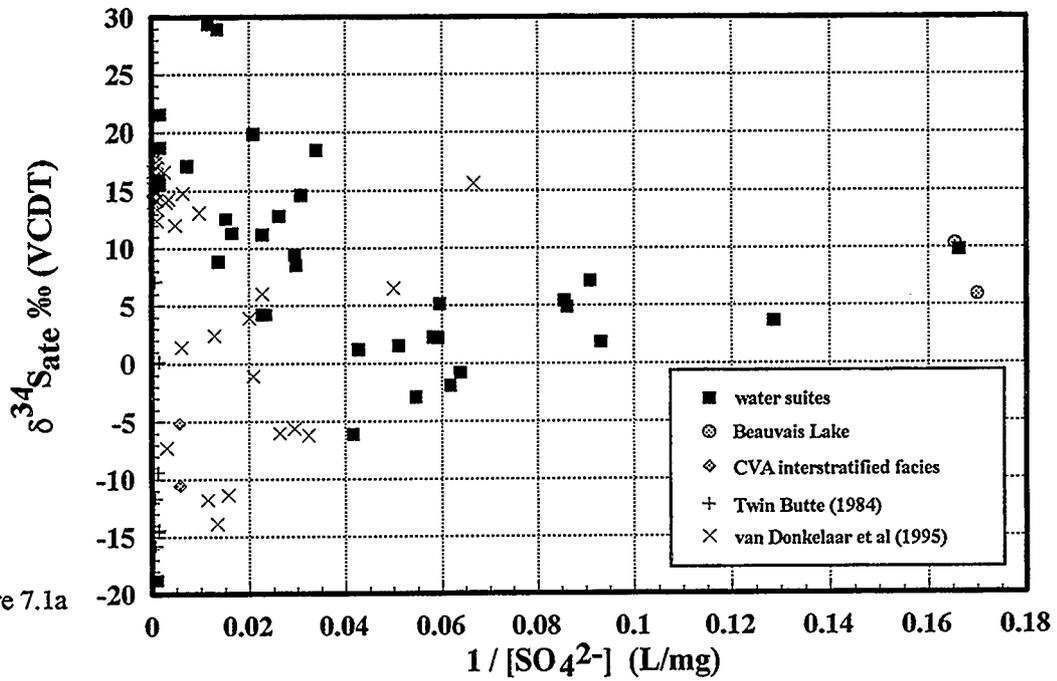


Figure 7.1a

### Twin Butte area "pristine" groundwaters

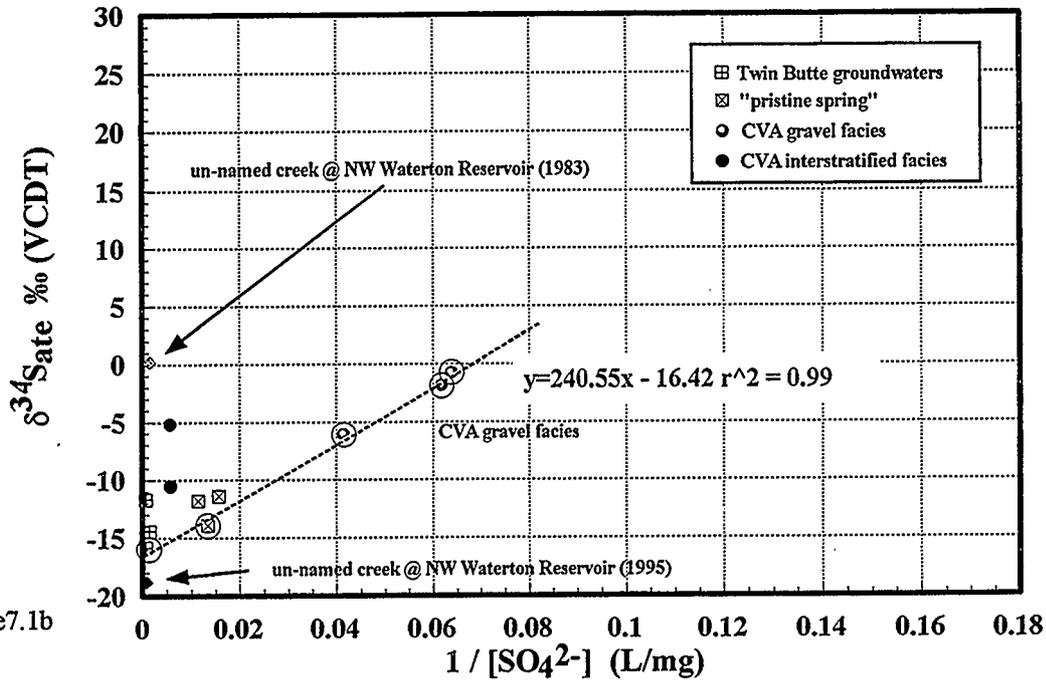


Figure 7.1b

Figure 7.1 Groundwater sulphate source characterization. Figure 7.1a compares water suites with data from van Donkelaar et al, (1995) and the 1983 Twin Butte collection (Twin Butte, 1984). Extrapolation of circled points on Figure 7.1b indicates a sulphur source to groundwater having a  $\delta^{34}\text{S}$  of  $\sim -16.5\text{‰}$ .

The depleted sulphur isotopic composition is consistent with oxidation of reduced sulphur in the glacial tills which mantle the area. The difference in isotopic composition of the presumed till source and that of Hendry et al (1986) may reflect subtleties of Cretaceous bedrock isotopic composition, or a Cordilleran source for some of the tills in the Twin Butte area, or both. Stalker and Harrison (1977) described the presence of Cordilleran drift underlying Laurentide drift from exposures on the banks of Drywood Creek, in the vicinity of the Highway #6 crossing. Points representing samples obtained from Lenz Spring (at the distal end of the Cochrane Valley Aquifer and where the aquifer is interstratified with impermeable materials) lie off the trend, suggesting addition of sulphate having a relatively enriched sulphur isotopic composition.

Surface waters from the un-named creek flowing into the northwest corner of Waterton Reservoir have the highest aqueous sulphate concentration reported in this study (1180 mg/L, 95AP27-SW16). The  $\delta^{34}\text{S}$  of the sulphate from the sample (-18.8‰) is close to that of the inferred groundwater sulphate source, suggesting that groundwater sustains the discharge of the creek. Interestingly, a sample collected later in the year (95AU03-SW3) has a higher  $\delta^{34}\text{S}_{\text{ate}}$  (-10.11‰), and a sample from the same watershed collected in October 1983 had a sulphate concentration of 686 mg/L and a  $\delta^{34}\text{S}_{\text{ate}}$  of +0.2‰ (Twin Butte, 1984). This observation will be discussed later.

Figure 7.2 illustrates  $\delta\text{D}$  vs  $\delta^{18}\text{O}$  for water samples of the 95AP27 suite, supplemented with data from van Donkelaar (1993) (also summarized in van Donkelaar et al, 1995) and the Twin Butte Task Force study. Also illustrated are samples comprising a suite of waters collected from Waterton Reservoir and the Cochrane Valley Aquifer during a preliminary study by the author during the late summer of 1992. Significantly, several of the data points representing surface water samples of the 1983 Twin Butte study are enriched in  $^{18}\text{O}$  and deuterium in comparison to other data points, demonstrating that evaporation has affected those waters. This is consistent with climatic history of the Twin Butte area; dry

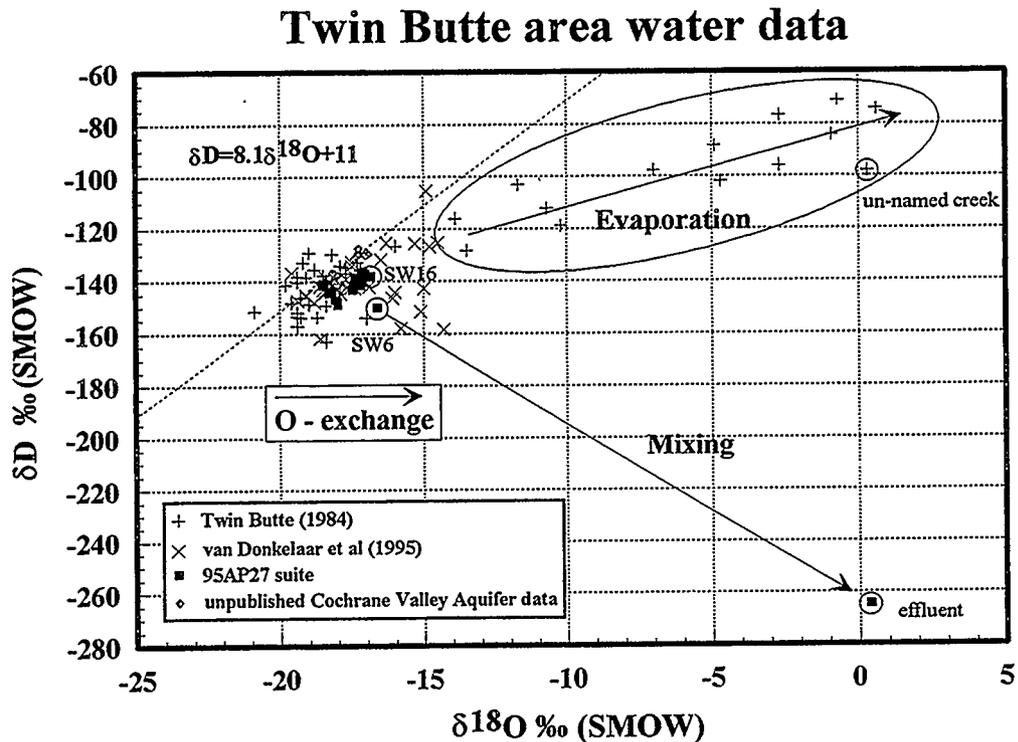


Figure 7.2  $\delta D$  vs  $\delta^{18}O$  for Twin Butte area surface and groundwaters. Refer to text for discussion of emphasized points

conditions in 1983 would contribute to the moisture deficit leading to the drought of 1984.

The data point representing the un-named creek sample from 1983 lies along the evaporation trend, however in 1995, the sulphate concentration was higher, and oxygen and deuterium isotope ratios for the 95AP27-SW16 sample do not support evaporative concentration of the water, as the point lies close to the global meteoric water line. The variability of sulphate concentration and  $\delta^{34}S_{ate}$  in this small watershed warrants additional investigation.

The preceding discussion suggests by analogy to the study of Hendry et al (1986), that aqueous sulphate having negative  $\delta^{34}S$  values may be derived from a glacial till source.

The observation that the  $^{34}\text{S}$ -enriched aqueous sulphate from Drywood Creek generally becomes progressively depleted in a downstream direction is consistent with addition of dilute and  $^{34}\text{S}$ -depleted groundwater to the creek, via direct recharge or, indirectly by groundwater contributions to tributaries. It also requires a source or sources of the  $^{34}\text{S}$ -enriched sulphate.

In the narrow, elongate mountain valleys, the volume of till with which groundwater could interact is expected to be less than in the more gentle topography of the adjacent foreslopes and plains. This suggests that the sulphur isotopic composition of sulphate in water samples from a headwaters setting may reflect the isotopic composition of the bedrock in the headwaters area. Variations of  $\delta^{34}\text{S}$  of marine sulphate through the Phanerozoic are well documented (eg. Claypool et al, 1980); corresponding data for the Precambrian are fewer. Ueda et al (1990) extracted trace sulphur from samples obtained from near the base of the ~1.9 Ga Belcher Group, and suggest that early Proterozoic seawater sulphate is characterized by a  $\delta^{34}\text{S}$  of +27.8‰. The relatively small volume of Mississippian and Upper Devonian marine carbonate bedrock cropping out on the peaks of mountains west of Twin Butte would be expected to contribute sulphate having a  $\delta^{34}\text{S}$  in the range of +21 to +29‰ (Claypool et al, 1980). Determination of  $\delta^{34}\text{S}$  of sulphate presumably associated with the tidal flat and algal carbonates which comprise part of the of Purcell Supergroup (Tippett et al, 1991) may implicate these as the source of enriched sulphate to North Drywood Creek.

Significantly,  $\delta^{34}\text{S}_{\text{ate}}$  of water samples obtained from similar distances along the watershed of North Drywood Creek (95AP27-SW4,  $\delta^{34}\text{S}_{\text{ate}}$  +19.84‰) and South Drywood Creek (94AP27-SW7,  $\delta^{34}\text{S}_{\text{ate}}$  +1.56‰) are different even though the bedrock geology of the headwaters areas are similar. This suggests that local phenomena control the sulphur isotopic composition of aqueous sulphate in North Drywood Creek. Among the possibilities is introduction of deep formation waters via discharge along a fault surface.

Clearly, the identification of the enriched sulphate source should be pursued by additional investigations.

A second source of  $^{34}\text{S}$ -enriched sulphate to the Drywood Creek watershed is effluent water discharged by the Shell Waterton Complex. The effluent comprises a mixture of surface run-off from the plant site and sulphur storage area, sanitary wastewater, and water used and produced during sour gas processing operations. Wastewater is treated prior to being released to the Drywood Creek watershed to comply with regulated limits for chemical oxygen demand, total suspended solids, ammonia nitrogen, oil and grease, pH and chloride concentration (Alberta Environment, 1991). The aqueous sulphate concentration of effluent water is not limited by regulatory agencies. Data obtained from daily water analyses of effluent water submitted to Alberta Environment indicates that the mean daily effluent discharge rate between 1989 and 1994 was 1236 m<sup>3</sup>/d (S.D. 303, n=1825), having a mean sulphate concentration between 1991 and 1994 of 977 mg/L (S.D. 184, n=1376).

Comparison of the sulphate concentration data for the effluent and the nearby spring may lead to the conclusion that the spring is fed by a leak in the effluent pipe. However, consideration of stable sulphur isotopes of the aqueous sulphate, and of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of the waters, indicates otherwise.

The  $\delta^{34}\text{S}_{\text{ate}}$  of effluent water is enriched (+18.7‰ and +21.5‰), reflecting the isotopic composition of sulphur recovered at the gas plant, perhaps mixed with sulphate derived from purchased sulphuric acid utilized in treating the demineralizers at the SCOT plant (Norris Graham, pers. com. 1995) or, with waters withdrawn from North Drywood Creek. The  $\delta^{34}\text{S}_{\text{ate}}$  of spring waters is also enriched (+15.6‰ and +16.0‰) suggesting a large contribution of technogenic sulphur to the groundwater. This interpretation is supported by data from the earlier Twin Butte study; the  $\delta^{34}\text{S}_{\text{ate}}$  of the spring water was

+7.1‰ in 1983<sup>1</sup>. This suggests that over the intervening decade, the proportion of technogenic sulphur affecting the <sup>34</sup>S-depleted groundwater has increased.

Oxygen and hydrogen isotopes of water clearly demonstrate that the spring is not sourced by a leak in the effluent pipe.  $\delta D$  and  $\delta^{18}O$  of the spring (-139.2‰ SMOW and -17.4‰ SMOW, respectively) lies close to the global meteoric water line (Figure 7.2), whereas the effluent water is strongly depleted in deuterium (-264.6‰ SMOW) but enriched in <sup>18</sup>O (+0.4‰ SMOW). The hydrogen isotopic data for the effluent water is consistent with water originating by condensation of steam (the light isotopes would preferentially enter the vapour phase; vapour removal and subsequent condensation would produce liquid water depleted in both <sup>18</sup>O and deuterium), however the oxygen isotopic composition of effluent water requires additional explanation.

Included in the wastewater processing scheme is pH adjustment to raise pH to between 6.0 and 9.5 prior to discharge. Addition of lime to the water to achieve this, and oxygen isotope exchange between the water and lime having an enriched oxygen isotopic composition could explain the observed relative enrichment in <sup>18</sup>O which characterizes the effluent water.

The oxygen isotopic composition of effluent water may permit recognition of mixtures of effluent and environmental waters. Sample 95AP27-SW6 represents water from North Drywood Creek below the effluent discharge site but above the confluence with South Drywood Creek. This known mixture is displaced from the meteoric water line in the direction of the isotopic composition of the effluent (Figure 7.2). Other ground and surface waters similarly displaced from the main data field may suggest addition of effluent water, however oxygen exchange with carbonate minerals in the till, or with lime applied

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<sup>1</sup> curiously, the sulphate concentration of the spring in 1983 was 1456mg/L but  $\delta^{18}O$  and  $\delta D$  data do not support evaporative concentration of the water.

to ameliorate soils in the vicinity of the plant, cannot be excluded as causes of the observed shift.

To summarize, at least 3 sources of sulphate to surface and ground waters are implicated to explain the distribution of points on Figure 7.1a. Sulphate depleted in  $^{34}\text{S}$  ( $\sim -16.5\%$ ) may be derived from the tills which mantle the Twin Butte area, and  $^{34}\text{S}$ -enriched sulphate is contributed by both technogenic ( $\sim +17\%$ ) and an unknown source in the headwater region of North Drywood Creek ( $\sim +29\%$ ). Sulphate having intermediate sulphur isotopic composition may be inferred to be a mixture of these sources. The presence of a source more enriched than the local industry precludes the use of  $\delta^{34}\text{S}_{\text{ate}}$  to identify technogenic S unless water originating from the north branch of Drywood Creek can be excluded.

#### Estimate of technogenic sulphur deposition to Waterton Reservoir

Incinerator stack emissions data presented earlier demonstrate that significant quantities of technogenic sulphur have been introduced to the environment in the general Twin Butte area. Determination of actual annual flux to Waterton Reservoir is desirable, however such estimates could not be made from the available information.

Thimm and Weleschuk (1990) presented a map of average ground-level total sulphation in the Twin Butte area for 1976, the first year of diminished emissions levels following the start-up of the SCOT plant at Shell Waterton Complex (Figure 7.3). The Gulf Pincher Creek Plant was also in operation at this time. The map portrays quantities of gaseous sulphur species present in the atmosphere and retained by both lead peroxide, and zinc acetate -coated surfaces contained in louvered "birdhouses" installed on posts approximately 1.5 m above the ground surface. Traps are collected and analysed on a monthly basis to permit estimation of average sulphation levels, expressed as  $\text{mg SO}_3/100 \text{ cm}^2/\text{d}$ . Data from approximately 60 of such stations constrain the contours on the map. Contours illustrate a dispersal plume extending over 20 km east-northeast from

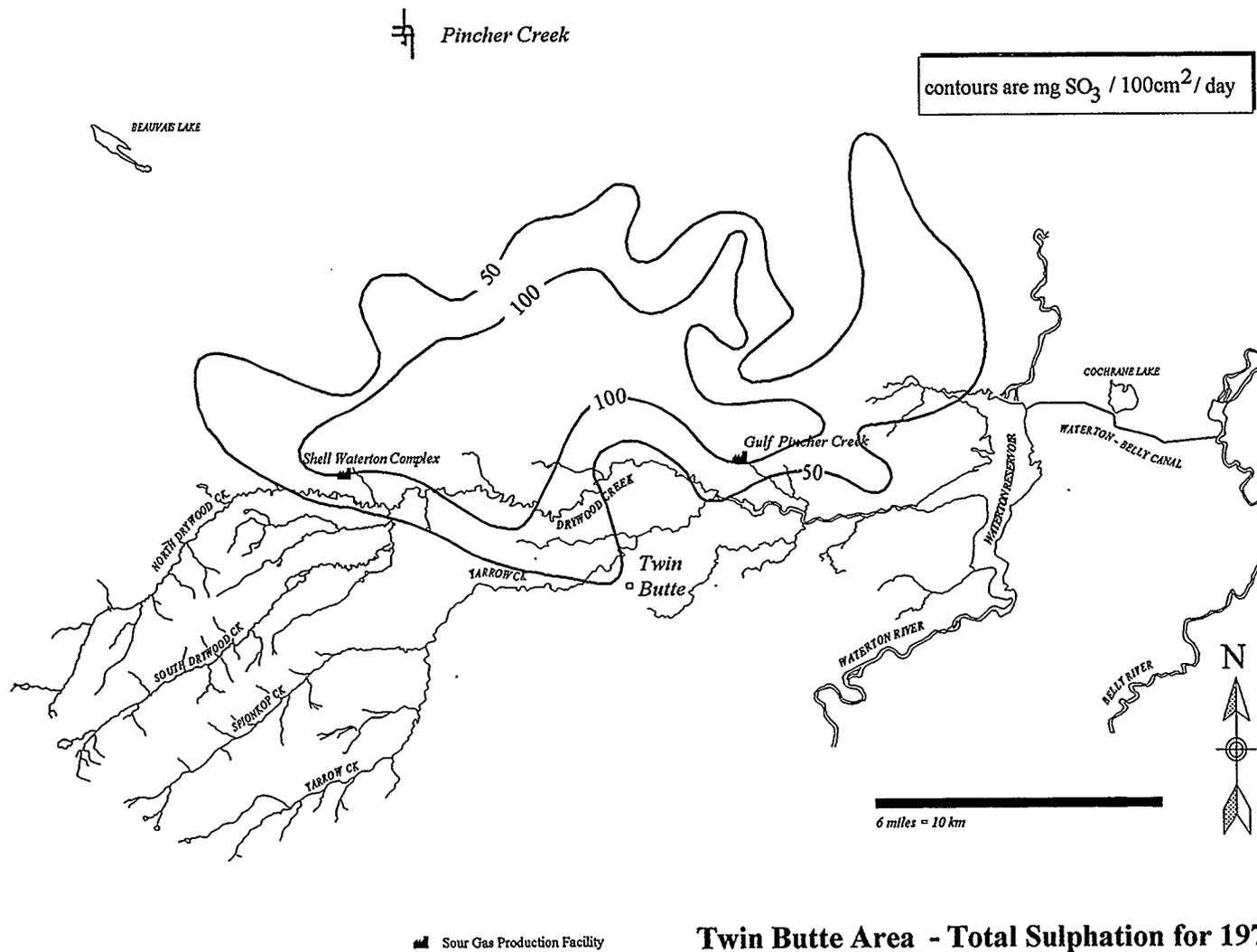


Figure 7.3 Twin Butte area total sulphation for 1976. Contours constrained by a network of approximately 60 static detectors which provide monthly average  $\text{SO}_2$  and  $\text{H}_2\text{S}$  exposure information. After Thimm and Weleschuk (1990).

the Shell plant, and including portions of the Drywood Creek watershed. Significantly, the small watershed of the un-named creek flowing into the northwest corner of Waterton Reservoir appears to have experienced deposition of atmospherically-transported sulphur.

Soils were collected in proximity to 14 lakes (usually 4 sites from each lake) in the general Twin Butte area during the 1983 investigations of the Twin Butte Soils and Water Evaluation Task Force. By the time of the soil survey, approximately 511315 tonnes of S had been emitted by the local sour gas industry. The  $\delta^{34}\text{S}_{\text{total}}$  of litter horizon samples in particular, demonstrated areas which had been exposed to technogenic sulphur as evidenced by enriched sulphur isotope ratios, reaching +12.1‰ adjacent to a lake in close proximity the Shell Waterton Complex (Figure 7.4). More distant areas were characterized by  $\delta^{34}\text{S}_{\text{total}}$  values of less than 0‰. Litter horizon total sulphur concentration data were of less utility in identifying the area of technogenic sulphur deposition. In contrast to the litter horizon data, samples from deeper soil horizons were characterized by relatively depleted  $\delta^{34}\text{S}_{\text{total}}$  (Table 7.2).

Table 7.2  $\delta^{34}\text{S}_{\text{total}}$  and  $[\text{S}_{\text{total}}]$  for Twin Butte Area soils

HORIZON	$\delta^{34}\text{S}_{\text{total}}$ ‰ (CDT)			[ $\text{S}_{\text{total}}$ ] μmole/g S		
	mean	S.D.	n =	mean	S.D.	n =
Litter	+1.8	8.8	47	39.5	11.3	47
A	-7.0	5.7	55	15.0	6.3	55
B	-8.0	4.5	24	6.9	4.0	25
C	-9.0	0.5	5	8.5	5.1	5

The litter horizon is characterized by the highest sulphur concentration and is enriched in  $^{34}\text{S}$  in comparison with deeper soil horizons. Soils were collected in 1983 (Twin Butte Task Force, 1984), and include areas from which deposition of technogenic sulphur is implicated by the network of sulphation stations in the area.

The spatial distribution of enriched litter horizon  $\delta^{34}\text{S}_{\text{total}}$  values confirms the general trend of the sulphur dispersal plume, however a broader areal extent is suggested by the isotope data. This probably reflects the higher technogenic emissions levels in the years preceding the 1976 compilation. Data for un-named lake #2, located west of Waterton

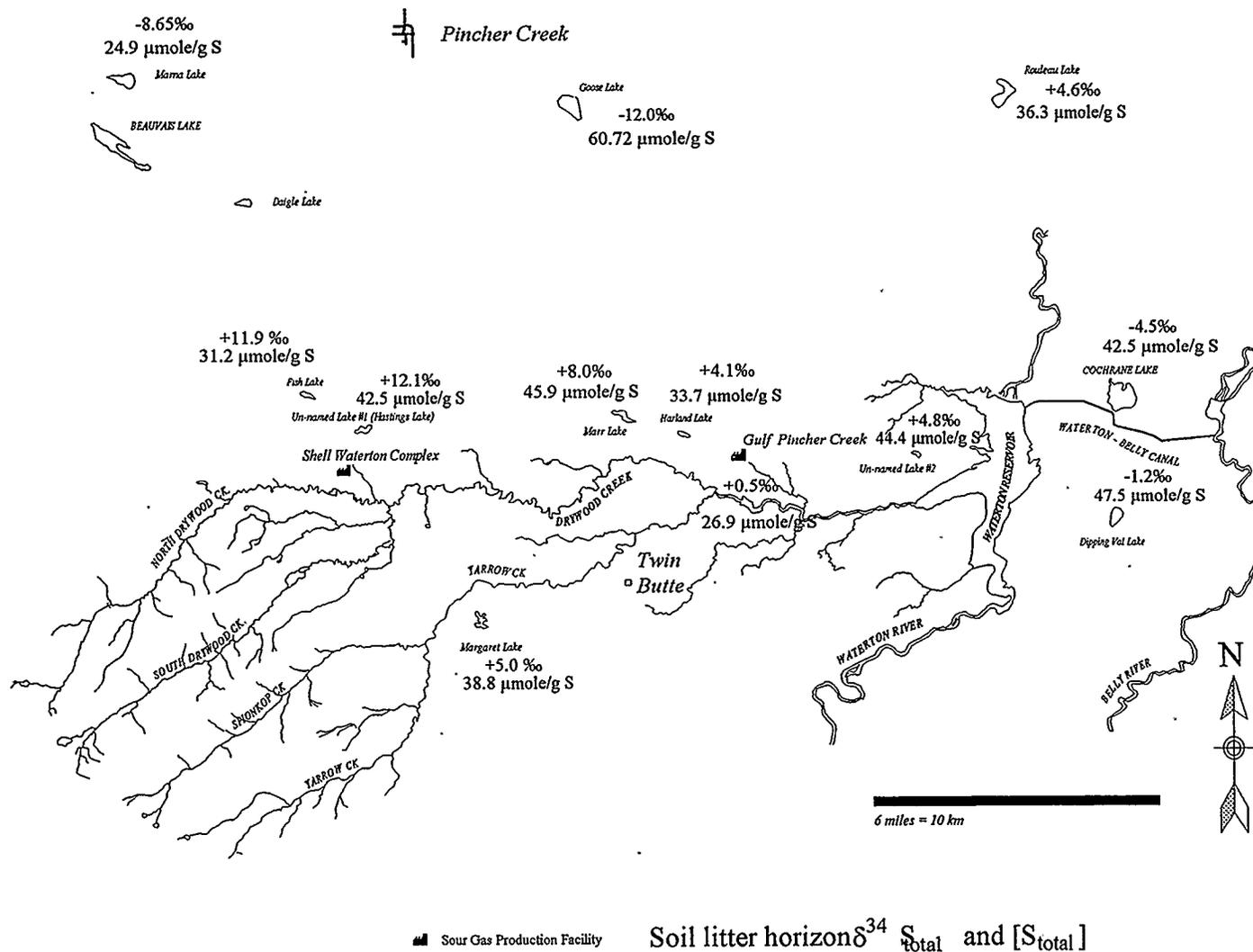


Figure 7.4 1983 litter horizon  $\delta^{34}\text{S}_{\text{total}}$  and  $[\text{S}_{\text{total}}]$  measurements. Data from Twin Butte Soils and Water Evaluation Task Force (Twin Butte, 1984).

Reservoir, suggest a technogenic sulphur contribution to the litter horizon when compared with reported values for Cochrane and Dipping Vat lakes, located to the east of Waterton Reservoir.

Collectively, the sulphation contours and litter horizon stable sulphur isotope data indicate that it is reasonable to assume that at least the northern portion of Waterton Reservoir has, in the past, experienced deposition of technogenic sulphur.

The estimate which follows is an attempt to estimate the maximum possible industrial sulphur contribution to Waterton Reservoir, based on sulphation levels reported by Thimm and Weleschuk (1990). Assuming a 1976 sulphation level of 50 mg SO<sub>3</sub>/100 cm<sup>2</sup>/d (7.3 kg S/ha/yr) over the entire area of Waterton Reservoir (ie 10.9x10<sup>6</sup>m<sup>2</sup>), the total contribution to Waterton Reservoir of sulphur species detected by the sulphation network was approximately 8 tonnes S/yr.

The maximum annual emission level occurred in 1972, when the local industry emitted approximately three times as much S as in 1976. This suggests that the maximum technogenic contribution may have been approximately 24 tonnes S/yr in 1972.

To place this crude estimate in context, it is worthwhile to consider the sulphate load carried by the principal sources of water to Waterton Reservoir. The Environment Canada hydrometric gauging station on Drywood Creek is located near the mouth of the creek. Three water samples collected from near this location suggest a mean sulphate concentration of 40.6 mg/L for Drywood Creek. Using a mean discharge rate of 2.99 m<sup>3</sup>/s for Drywood Creek, an annual sulphate load of approximately 3830 tonnes (or 1264 tonnes S/yr) is calculated.

This estimate includes technogenic sulphur introduced as liquid effluent discharged into North Drywood Creek. The annual technogenic effluent sulphate contribution is

approximately 435 tonnes (or 144 tonnes S/year), or about 11% of the total Drywood Creek sulphate load.

The discharge rate of the Waterton River at the reservoir can be estimated at 20.1 m<sup>3</sup>/s by subtracting the discharge of Drywood Creek from the total discharge from Waterton Reservoir. The latter comprises the Waterton River near Glenwood (mean discharge of 15.57 m<sup>3</sup>/s<sup>2</sup>) and the Waterton-Belly Diversion canal (mean discharge 7.52 m<sup>3</sup>/s). The sulphate concentration of the Waterton River near the mouth is approximately 9.3 mg/L (based on samples 95MR13-S4 and 95AP27-SW13); the calculated annual sulphate load is 3170 tonnes (or 1046 tonnes S/year).

These calculations demonstrate that the estimated maximum direct technogenic sulphur contribution to the waters of Waterton Reservoir is small, accounting for only about 7 to 8% of the total sulphur load, and that the Waterton River and Drywood Creek contribute approximately equally to the ~7000 tonne per year aqueous sulphate supply to Waterton Reservoir.

Given the small direct technogenic sulphur contribution and the <sup>34</sup>S enrichment characteristic of aqueous sulphate carried by North Drywood Creek, it would seem tenuous to suggest that a technogenic signal could be recognized in the sediments of Waterton Reservoir. Interpretations presented later will however suggest that a record of the activities of the local sour gas industry is in fact preserved.

## SULPHUR ACCUMULATION IN SEDIMENTS OF WATERTON RESERVOIR

### Evidence from porewaters for dissimilatory sulphate reduction

Although situated generally downwind from the local sour gas industry, the sediments of Waterton Reservoir have remarkably little sulphur in comparison with sediments from

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<sup>2</sup> the discharge of the Waterton River at Glenwood includes the contribution from Foothills Creek

## [Stotal] of Pristine Oligotrophic Lakes compared to Waterton Reservoir

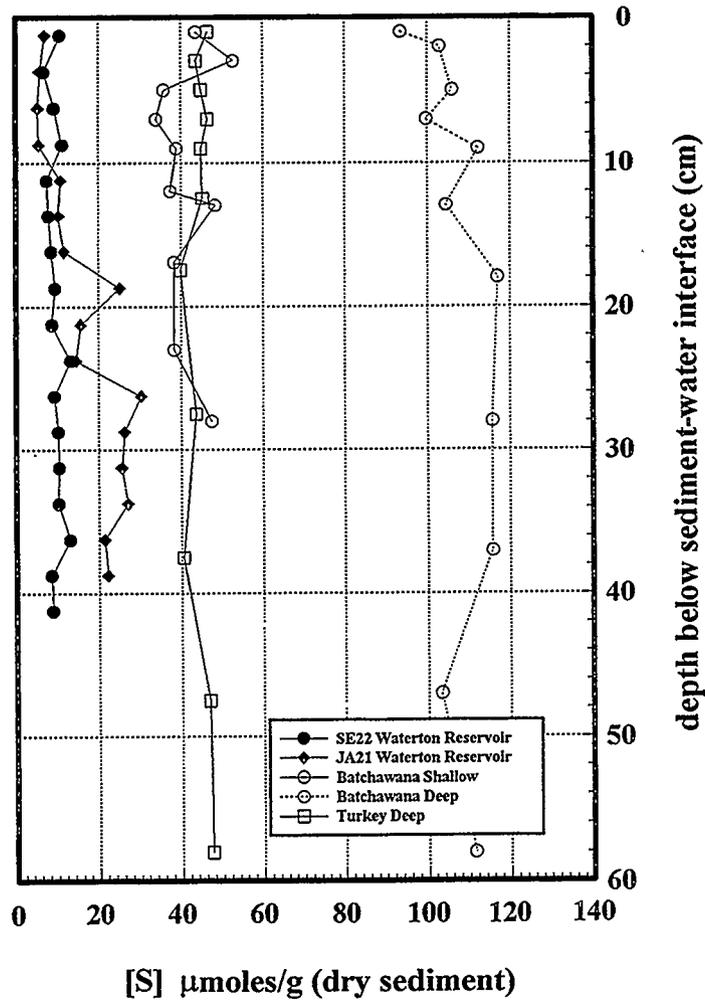


Figure 7.5 The total sulphur concentration of sediments from Waterton Reservoir are compared with published data for pristine oligotrophic lakes. Data for Batchawana and Turkey Lakes, situated in a pristine Ontario watershed, is from Nriagu and Soon (1985).

Beauvais Lake (compare Figures 6.1 and 6.2). The low sulphur concentration is further emphasized when sediments of Waterton Reservoir are compared with those of two oligotrophic lakes in a pristine, forested watershed in northern Ontario (Figure 7.5). In contrast, sediments of oligotrophic Big Moose Lake, an acidified lake in Adirondack Park,

N.Y., where sulphate concentrations have increased almost 5-fold in the last century (Fry, 1986), contain as much as 560  $\mu\text{mole/g S}$  in post-industrial sediments (White et al, 1989).

Interstitial water chemistry is a particularly sensitive tool for the study of diagenetic reactions. Readily measurable changes in porewater chemical concentrations can reflect almost undetectable changes in sediment composition. To address the low total sulphur concentrations characteristic of the sediments of Waterton Reservoir, evidence from porewater concentration profiles and the stable sulphur isotopic composition of porewater sulphate will be discussed to ascertain if the process of dissimilatory sulphate reduction is occurring in the sediments of Waterton Reservoir.

#### Aqueous sulphate concentration and stable sulphur isotope profiles

The aqueous sulphate concentration of porewaters expressed from sediments of Waterton Reservoir decreases abruptly below approximately 7.5 cm depth below the sediment-water interface (Figure 6.7). Such concentration profiles are common in freshwater sediments, and are interpreted to indicate sulphate transport from the sediment surface followed by dissimilatory sulphate reduction at depth in the sediment. This can be substantiated by an increase in porewater sulphide concentration which may be depth-coincident (eg. Carignan, 1988). The depth of the anoxic interface, below which sulphate reduction occurs, varies with position in a lake and with season, in response to textural changes in sediments resulting from the activities of benthic organisms (ibid.). Deepening of the oxic-anoxic boundary during the winter may reflect changes in organic carbon supply, and effects related to decreasing temperature (Cook and Kelly, 1992).

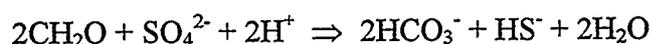
Efforts to measure porewater sulphide concentration of Waterton Reservoir porewaters failed, and recovery of aqueous sulphide as CdS for either gravimetric determination or stable sulphur isotope characterization was compromised by co-precipitation of  $\text{CdCO}_3$  (otavite). Subtle changes in sediment colour during storage lend support to existence of reducing conditions within the sediments of Waterton Reservoir. The stable sulphur

isotopic composition of porewater sulphate however, provides the most conclusive evidence for sulphate reduction in the sediments of Waterton Reservoir.  $\delta^{34}\text{S}_{\text{total}}$  of reservoir sediments is, without exception, depleted in comparison with the isotopic composition of porewater sulphate expressed from the same sample. The amount of depletion (considering only the most reliable  $\delta^{34}\text{S}_{\text{ate}}$  analyses, the solid symbols on figures 6.8 and 6.9) ranges from 3.9 to 49.4‰, and averages 21.2‰. Similarly,  $\delta^{34}\text{S}_{\text{ate}}$  of porewater sulphate is more enriched than the  $\delta^{34}\text{S}_{\text{ate}}$  of reservoir water sulphate (mean +5.26‰, n=7) on average by 10.2‰.

The depleted  $\delta^{34}\text{S}_{\text{total}}$  of the sediments, and enriched  $\delta^{34}\text{S}_{\text{ate}}$  of corresponding porewaters in comparison with  $\delta^{34}\text{S}_{\text{ate}}$  of reservoir water is consistent with the fractionation of sulphur isotopes resulting from dissimilatory sulphate reduction, the only known process by which sulphur isotope fractionation of this magnitude can be realized. Isotope effects accompanying dissimilatory reduction predict enrichment of  $^{34}\text{S}$  in the remaining unreacted sulphate and depletion of  $^{34}\text{S}$  in the product sulphide.

#### Porewater alkalinity

Dissimilatory sulphate reduction can be approximated by:



The stoichiometry of dissimilatory sulphate reduction suggests that 2 moles of  $\text{HCO}_3^-$  should result from the reduction of each mole of  $\text{SO}_4^{2-}$ . If sulphate reduction is occurring, it is reasonable that the porewater bicarbonate concentration should reflect this. In the case of core SE22 for which both porewater sulphate and  $\text{HCO}_3^-$  concentrations were measured, sulphate decreases from a maximum of 15.9 mg/L in the top 7.5 cm to about 5.5 mg/L below, a difference of 10.4 mg/L. This should correspond to an increase in porewater alkalinity of approximately 13.3 mg/L, however this is not observed. Figure 7.6 summarizes alkalinity data for porewaters from core SE22. The porewater alkalinity measurements lie within the observed range of reservoir water alkalinity determinations.

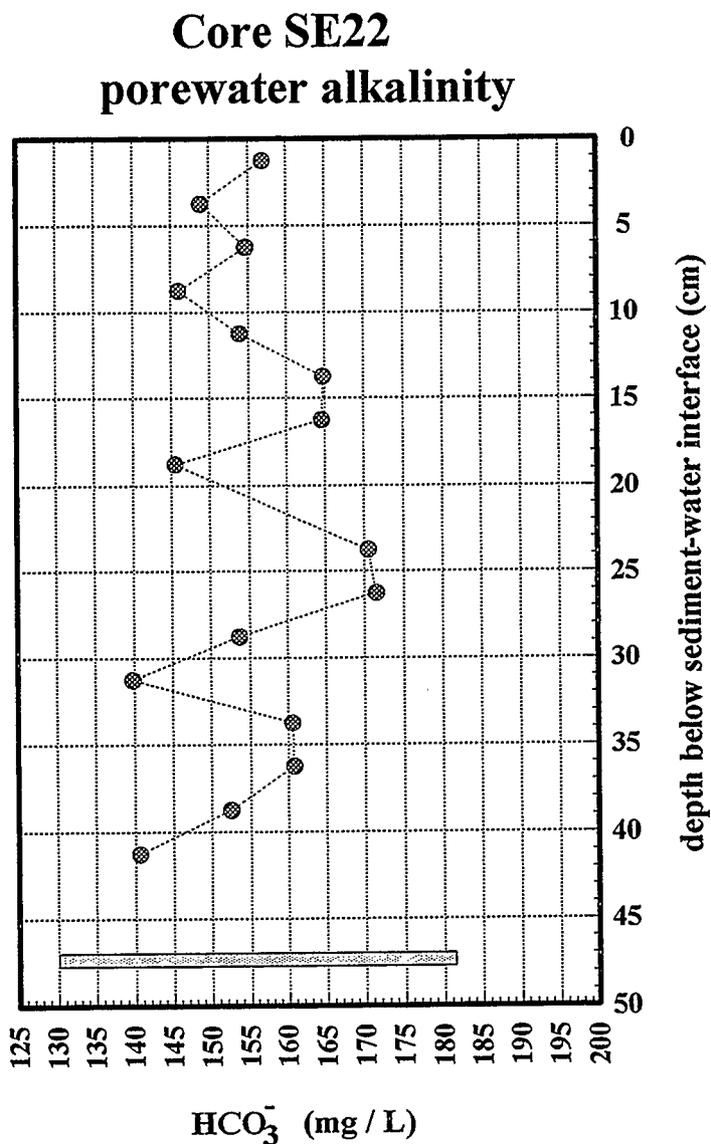


Figure 7.6 Alkalinity data for porewaters expressed from core SE22, Waterton Reservoir. Horizontal bar represents range of measured alkalinity for samples from water column of Waterton Reservoir.

Saturation indices (S.I. values) provide an indication of how close a mineral is to equilibrium with the solution under consideration, and are determined by comparing the ion activity product (IAP) of a solution with the equilibrium constant of the mineral ( $K_{eqT}$ ) at a given temperature.

Porewaters from core SE22 were speciated at 10°C using SOLMINEQ.88 (Kharaka et al, 1988) to determine if the precipitation of calcite or aragonite could account for the observed deficiency in alkalinity. In all samples except SE22-13, porewaters are slightly undersaturated with respect to these carbonate minerals, characterized by  $\log (IAP/KT)_{\text{calcite}}$  values ranging from -0.074 to -0.357 and  $\log (IAP/KT)_{\text{aragonite}}$  values varying between -0.212 and -0.589. In the case of SE22-13, calculated saturation indices for calcite (+0.228) and aragonite (+0.135) suggest carbonate precipitation. Porewaters from this sample were also characterized by the highest  $\text{Ca}^{2+}$  concentrations observed.

It should be emphasized that the large charge balance error in the analyses of these porewaters compromises the use of this approach, and that the suggestion that the alkalinity deficiency cannot be explained by precipitation of carbonate minerals is tentative at best.

#### Limits to dissimilatory sulphate reduction

If the diminishing porewater sulphate concentrations with depth signify sulphate reduction, why are sediments of Waterton Reservoir characterized by such low total sulphur concentrations? Sulphate reduction rates for temperate dimictic lakes commonly are in the range of 0.02 to 0.2 mmole/m<sup>2</sup>/day (Cook and Kelly, 1992). The sediment surface area of Waterton Reservoir can be approximated by multiplying the reservoir surface area (approximately  $10.9 \times 10^6 \text{ m}^2$ ) by a factor of 1.5 to account for reservoir bottom topography (this estimate probably overstates the surface area). Utilizing the typical sulphate reduction rates, in principle between 0.74 and 7.4 tonnes/yr sulphate could be reduced in the sediments of Waterton Reservoir.

The sulphate load to the Waterton Reservoir from Drywood Creek and the Waterton River has previously been estimated to be of the order of 7000 tonnes  $\text{SO}_4^{2-}$ /yr. The short residence time of water in the reservoir assures a continuous supply of sulphate. Clearly,

sulphate supply is not a limiting factor in dissimilatory sulphate reduction in the sediments of Waterton Reservoir.

The cores from Waterton Reservoir were obtained from settings situated below wave base to eliminate artifacts resulting from sediment remobilization. The absence of evidence of a benthic fauna suggests that in such deep water settings, an increase in sediment permeability through bioirrigation is not expected. Diffusion is possibly the only mechanism by which aqueous sulphate from the reservoir can enter the rapidly accumulating sediments. The mean water temperature of the Waterton River at Waterton Lakes National Park is  $6.2 \pm 5.5^\circ\text{C}$ ; at such low temperatures the diffusion coefficients of electrolytes in aqueous solution are considerably smaller than at  $25^\circ\text{C}$  (Freeze and Cherry, 1979).

The chlorophyll  $a^3$  concentration of lake waters is used as a measure of the trophic status of a lake (Prepas, 1990). Although the parameter was not measured in samples, obtained for this study, the exclusion of aquatic plants in the shore zone by the large annual variation in reservoir water level, and the absence of evidence of a benthic fauna suggests that Waterton Reservoir is nutrient-poor. The mean concentration of chlorophyll  $a$  in the Waterton River near Waterton Lakes National Park between 1982 and 1993 as determined by Environment Canada was  $1.7 \pm 1.3 \mu\text{g/L}$  ( $n=155$ ). Although nutrients may be introduced by effluent discharge to Drywood Creek, the evidence suggests Waterton Reservoir is oligotrophic.

The low primary productivity suggests that the supply of organic matter is predominately detrital organic matter introduced by riverine transport, or reservoir bank erosion by wind-driven waves. The high reservoir sedimentation rate may result in a dilution of the detrital organic matter, limiting availability to the decomposing organisms of the food web which supply suitable organic substrates to the sulphate reducing bacteria. Low rates of organic

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<sup>3</sup> Chlorophyll  $a$  is a photosynthetic pigment

carbon supply have been implicated to explain low rates of sulphur accumulation in an ultraoligotrophic, acidic lake (Cook et al, 1990), although at approximately 100  $\mu\text{mole/g}$ , total sulphur concentrations are far higher than those of Waterton Reservoir.

The higher  $\delta^{34}\text{S}$  values of porewater sulphate in comparison with that of lake water sulphate and total sediment sulphur indicates that dissimilatory sulphate reduction has occurred in the sediments of Waterton Reservoir. However, it is suggested that the low availability of organic carbon may limit the relative contribution of sulphate reduction to sulphur storage in the sediments. The possibility of sediment properties and cold temperatures diminishing sulphate availability to the sediments, leading to circumstances where rapid sediment accumulation traps porewaters at a rate which outpaces sulphate diffusion, warrants further investigation.

#### Geochronology of Waterton Reservoir sediments

Dating of sediments of Waterton Reservoir by Flett Research Ltd. (Winnipeg, Manitoba) was attempted using the  $^{210}\text{Pb}$  radiometric dating method (Oldfield and Appleby, 1984). In this method, the decay of “unsupported”  $^{210}\text{Pb}$  introduced via atmospheric deposition<sup>4</sup> is compared with that of “supported”  $^{210}\text{Pb}$  derived from decay of  $^{226}\text{Ra}$  in detrital particles. Decay of the “unsupported” lead results in a decrease in  $^{210}\text{Pb}$  activity with progressive burial.  $^{210}\text{Po}$  activity is measured as a surrogate to measuring of  $^{210}\text{Pb}$  owing to weak  $\beta$  and  $\gamma$  emissions during  $^{210}\text{Pb}$  decay. As no decrease in radiogenic daughter  $^{210}\text{Po}$  activity with depth in the core could be detected, no sedimentation rate could be calculated, and dating of the sediments was not possible.

In the absence of geochronological control for sediments of Waterton Reservoir, interpretations of core profiles are necessarily speculative. However, similarity in shape of  $\delta^{34}\text{S}_{\text{total}}$  profiles of the Waterton Reservoir sediment cores (Figure 6.3), and the occurrence

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<sup>4</sup>  $^{210}\text{Pb}$  is a radiogenic daughter of  $^{226}\text{Rn}$  decay.  $^{226}\text{Rn}$  is a gas, and is dispersed by atmospheric processes.

of a depth-coincident inflection in this profile in both suggests that correlation between the two deep-water cores is possible.

Assuming that the longer of the two cores (SE22, 42.5cm) penetrated the entire sediment accumulation and knowing that deposition of sediments in the reservoir began in 1965, a sedimentation rate of approximately 1.5 cm/yr is indicated<sup>5</sup>. The inflection in the core profile occurs at a depth of 16.25 cm below the sediment-water interface; the top of the interval represented by the 2.5 cm thick sample is at 15 cm depth, or 27.5 cm above the base of the core. If the sedimentation rate has been constant, and assuming no compaction, this corresponds to approximately 18.3 years of sedimentation, implying deposition by about mid-1983. Similarly, the age of the top interval of uniform  $\delta^{34}\text{S}_{\text{total}}$  and  $\delta^{34}\text{S}_{\text{ate}}$  in core SE22 can be estimated to be approximately 1980.

Accepting this temporal framework and extending it to core JA21, a change in sediment sulphur storage in about 1983 is apparent, as sulphur concentration is higher in sediments older than this (Figure 6.1).

Studies of oligotrophic lakes in eastern North America have demonstrated that sulphur concentration of deep water sediments tends to be greater than that of shallow waters sediments (eg Batchawana lake data of Nriagu and Soon (1985) and data from Lac Tantaré from Carignan (1988)). As both of the cores from Waterton Reservoir are from deep water settings, it is suggested that phenomena related to sediment source at a local scale may explain the differences in total sediment sulphur concentration and isotopic composition exhibited by the sediment profiles.

#### Importance of the detrital sulphur contribution

Accepting that erosion of surficial geologic materials supplies a portion of the sediment to each of the lakes examined, it is appropriate to consider the total sulphur concentration of

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<sup>5</sup> Core SE22 was collected in September 1993 therefore 28 years of sedimentation are represented.

these materials to ascertain the magnitude of sulphur enrichment of the sediments over that of the detrital source materials.

Data generated in 1983 by the Twin Butte Soils and Water Evaluation Task Force include soil sulphur concentration and  $\delta^{34}\text{S}_{\text{total}}$  for soil suites collected from 14 sites in the area. Typically 4 samples from each site were collected and analysed; the data are summarized in Table 7.2. Tills in the area are uncharacterized with respect to sulphur concentration and isotopic composition, however  $\delta^{34}\text{S}_{\text{ate}}$  of local groundwaters suggests that sulphate is derived from a  $^{34}\text{S}$ -depleted source, characterized by a  $\delta^{34}\text{S}$  of approximately -16.5‰ as discussed earlier. This is consistent with oxidation of reduced sulphur in the tills (eg Hendry et al, 1989), although other sources cannot be excluded with the available data.

Surficial geologic materials cropping out along the perimeter of Waterton Reservoir are typically undercut, a process facilitated by strong winds which characterize the area. Cutbanks on creeks and the exposed shoreline of Waterton Reservoir demonstrate that the soil A horizon in un-tilled settings tends to resist erosion owing to retention of particulate material by intertwined roots. This suggests that the bulk of the potential allochthonous sediment introduced to area lakes or to Waterton Reservoir is derived from deeper soil horizons or till. Strong winds characteristic of the region provide a mechanism by which litter (or the tilled layer in cultivated land) in could also be introduced. Occasional drought conditions may contribute to soil deflation.

The mean total sulphur concentration of core SE22 (9.5  $\mu\text{mole/g S}$ ) and of core JA21 (16.5  $\mu\text{mole/g S}$ ) is only slightly higher than that of soil B and C horizon in the Twin Butte area (approximately 7.7  $\mu\text{mole/g S}$ , Table 7.2). Core MY27 from Beauvais Lake (mean  $[\text{S}_{\text{total}}]$  254.5  $\mu\text{mole/g S}$ ) has significantly more sulphur than local soils. This suggests that the bulk of the sulphur in sediments of Waterton Reservoir may be detrital in origin, and that considerable sulphur has been added to the pre-industrial sediments of Beauvais Lake.

The mean  $\delta^{34}\text{S}_{\text{total}}$  of Waterton Reservoir sediments from core SE22 (-10.56‰) is slightly  $^{34}\text{S}$ -depleted compared to that of local soil B and C horizon material, however that of core JA21 (-2.74‰) is enriched with respect to materials potentially derived from these soil horizons. The  $\delta^{34}\text{S}_{\text{total}}$  of Beauvais Lake sediments (mean -3.34‰) is similarly enriched.

The total sediment sulphur concentration of sediments of core SE22 generally decreases from the base of the core towards the top; the trend in sediments of core JA21 is more pronounced. The sediments of the sulphur-rich interval of core JA21 are characterized by sulphur concentrations of 25.4  $\mu\text{mole/g}$ . This is about 2.5 times more sulphur than of core SE22, and about 3.2 times as much as local soil B and C horizon material. Assuming that soil detrital material accounts for approximately 7.7  $\mu\text{mole/g}$  S of the total sediment sulphur in core JA21 (because the mean sulphur content of surrounding soils is 7.7  $\mu\text{mole/g}$ ), approximately 17.7  $\mu\text{moles/g}$  S has been added to the sediments in the lower part of core JA21. Addition of sulphur to the sediments of core SE22 (mean sulphur concentration 9.5  $\mu\text{mole/g}$ ) has been smaller, approximately 1.8  $\mu\text{mole/g}$  S.

Porewater aqueous sulphate concentration profiles, and the  $^{34}\text{S}$ -enrichment of porewater sulphate relative to both reservoir water sulphate and total sediment sulphur, demonstrate that dissimilatory sulphate reduction occurs in sediments of Waterton Reservoir. Addition of  $^{34}\text{S}$ -depleted sulphide produced by dissimilatory sulphate reduction could explain both the small increment of sulphur added to sediments of core SE22 and the observed relative  $^{34}\text{S}$ -depletion of sediments of core SE22 compared to surrounding soil materials. The low total organic carbon content of the sediments may limit the extent of sulphur added by dissimilatory reduction.

Such a scenario does not satisfactorily explain the  $^{34}\text{S}$ -enrichment that is characteristic of the higher sulphur content sediments of core JA21.  $\delta^{34}\text{S}_{\text{total}}$  of core JA21 is generally enriched by at least 3‰ compared to that of core SE22. Isotope balance considerations suggest that addition of a small quantity of  $^{34}\text{S}$ -enriched material derived from the litter

horizon to the sediments of core JA21, coupled with addition of  $^{34}\text{S}$ -depleted sulphide sulphur (reflecting the increased organic carbon content of the litter) is a possible explanation of the observed stable sulphur isotope and sulphur concentration data. Total sulphation data for 1976 (Figure 7.3), and stable sulphur isotope data for litter horizon samples collected during 1983 (Figure 7.4) confirm the prior existence of a zone of technogenic sulphur deposition in the vicinity of the northern portion of Waterton Reservoir. Litter from the vicinity of un-named lake #2, west of the reservoir, was characterized by a  $\delta^{34}\text{S}_{\text{total}}$  of +4.4‰ in 1983 (Twin Butte Task Force, 1984). Core JA21 was obtained from a location near Waterton Dam (Figure 4.1), at the north end of the reservoir, and directly downwind of the Gulf Pincher Creek sour gas plant.

It is suggested that technogenic sulphur, delivered by dispersal in the atmosphere and deposited by wetfall and dryfall processes, and assimilated by vegetation and soil ecosystems, has subsequently (and locally) been introduced as detrital sediment to Waterton Reservoir. Assimilatory reduction of sulphate is not isotopically selective from the viewpoint of sulphur therefore the  $\delta^{34}\text{S}$  of technogenic sulphur-impacted organic matter will tend to approach that of the emissions (Krouse, 1980).

A complementary hypothesis is that  $^{34}\text{S}$ -enriched elemental sulphur from by-product sulphur storage and handling facilities may contribute to the total sulphur pool in core JA21. In the autumn of 1983, the elemental sulphur block at the then recently shut-down Gulf Pincher Creek Plant (comprising some 115000 tonnes), was removed from the site using a combination of remelting methods and mechanical disaggregation. Between August and mid-October 1983, 75365.2 tonnes were broken mechanically and bulk hauled to the Shell Waterton Complex (Gulf, 1983). Block break-up operations were restricted to periods of windspeeds less than 30 kph, and a water fog was used in an effort to reduce transport of elemental sulphur dust. Nevertheless, monitoring of downwind soils indicated an increase in elemental sulphur in the soils (*ibid.*).

The sulphur storage area of the Gulf Pincher Creek Plant was situated approximately 8 km from the northwestern corner of Waterton Reservoir, and about 4.8 km from the watershed of the un-named creek which flows into the northwestern arm of Waterton Reservoir. Wind data submitted in support of a reduction in maximum incinerator stack emissions (Gulf, 1972) indicate that the prevailing winds in the vicinity of the Gulf Plant are generally from the southwest. Interestingly, the aqueous sulphate from the water sample collected from the un-named creek in October 1983 by investigators of the Twin Butte Task Force had a  $\delta^{34}\text{S}_{\text{ate}}$  of +0.2‰. Samples collected from the same creek during 1995 are characterized by  $\delta^{34}\text{S}_{\text{ate}}$  values in the range of -18.8‰ to -10.11‰, perhaps implicating a higher proportion of technogenic sulphur in the past.

The total sulphur concentration spike in core JA21 at 18.75 cm depth, and the broader zone of higher total sulphur concentrations in the older sediments of the core may suggest that sulphur dust contributions occurred in the past and were not restricted to the final elemental sulphur storage block disaggregation.

The contributions to the reservoir sediments may be indirect, as elemental sulphur could be converted by to sulphate by ubiquitous sulphur oxidizing bacteria in the soils and subsequently be assimilated through the roots of vegetation, and introduced as detrital organic matter. On the otherhand, elemental sulphur (which is insoluble in water) could be transported to the sediments of Waterton Reservoir via the un-named creek or more directly by the prevailing wind. Elemental sulphur can be reduced to sulphide by some genera of sulphate reducing bacteria (Cook and Kelly, 1992), however the low organic carbon content of the sediments may restrict the extent of dissimilatory reduction, as discussed earlier.

## SULPHUR ACCUMULATION IN SEDIMENTS OF BEAUVAIS LAKE

Accumulation of sediments in Waterton Reservoir began about nine years after sour gas processing began in the Twin Butte area. Consequently, sediments of Beauvais Lake were collected to characterize the quantity and isotopic composition of sulphur in pre-industrial sediments. Prior work has demonstrated the presence of Mazama tephra (~6800 years B.P.) in sediments of Beauvais Lake at a depth of approximately 340 cm below the sediment-water interface, suggesting a sedimentation rate of 0.5 mm/yr (Powers, 1994). In other words, sediments below approximately 6 cm in the core<sup>6</sup> should be of pre-colonial age (establishment of homesteads in the Beauvais Lake area occurred in 1882).

Three components to the sulphur isotope stratigraphy of lake sediment cores were identified by Fry (1990), applicable to settings where the isotopic composition of technogenic sulphur differs from that of the ambient environment, and where sulphate reduction is limited by sulphate availability:

- a uniform baseline reflecting sources of sulphur in precipitation, soils and watersheds, preserved in the pre-industrial sediments;
- sedimentation of materials incorporating technogenic sulphur, resulting in a shift of the sulphur isotopic composition of the post-industrial sediments towards that of the industrial source (Krouse, 1980);
- and dissimilatory sulphate reduction, adding sulphur strongly depleted in <sup>34</sup>S owing to the isotope selectivity characteristic of the process.

In contrast to those of Waterton Reservoir, the sediments of Beauvais Lake are rich in sulphur despite Beauvais Lake having a lower aqueous sulphate concentration (6 mg/L, n=2 this study; <6 mg/L, n=4 during 1984 ref: Crosby, 1990b) than waters of Waterton

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<sup>6</sup> disruption of the core during acquisition precludes accurate geochronology; the depth and age cited is intended for illustrative purposes only.

Reservoir. The dramatic decline in sulphur concentration in the top 10 cm of core MY27 corresponds to a facies change to bioturbated sediments.

Sediments collected from Beauvais Lake confirm the tendency to uniform isotopic composition and suggest that a  $\delta^{34}\text{S}_{\text{total}}$  of about -5‰ characterizes pre-industrial lake sediment sulphur in the Twin Butte area (Figure 6.4). However, the stable sulphur isotopic composition of the surficial sediments appears to be enriched in  $^{34}\text{S}$  by about 4‰ over that of older sediments. Whether this reflects a shift in isotopic composition toward local technogenic emissions or other  $^{34}\text{S}$ -enriched sources, or sulphur isotope selectivity associated with bioturbation processes is unknown. The characteristic signature of sulphate fertilization (increased total sulphur concentration and strongly depleted  $\delta^{34}\text{S}_{\text{total}}$ ) is not present in the surficial sediments of core MY27.

It is interesting to speculate if the higher sulphur concentration observed in sediments of Beauvais Lake are a consequence of long-term dissimilatory sulphate reduction. Beauvais Lake is presently a mesotrophic lake (Crosby, 1990b); the extent to which cultural changes (establishment of a small cottage community of approximately 45 cottages and a provincial park) in the small catchment area have affected lake water chemistry are uncertain. Sediments of Beauvais Lake are characterized by approximately 7% total organic carbon throughout the length of core MY27, perhaps suggesting that present levels of bioproductivity can be extrapolated to the past.

The  $\delta^{34}\text{S}$  of aqueous sulphate was determined on microgram-sized samples obtained from shallow and deep waters obtained from Beauvais Lake. Significantly, isotopic composition of sulphate from the deep water sample ( $\delta^{34}\text{S}_{\text{ate}} = +5.9\text{‰}$ ) and the shallow water sample ( $\delta^{34}\text{S}_{\text{ate}} = +10.4\text{‰}$ ) are different, although the sulphate concentration of the two are similar (~6 mg/L). This may reflect incomplete mixing, with the shallow water sample reflecting the contemporary isotopic composition of precipitation and runoff from the small catchment area of the Beauvais Lake basin (7.1 km<sup>2</sup>; Crosby, 1990b). Most of the inflow

to the lake is provided by diffuse surficial runoff and precipitation; there are only two intermittent streams in the basin (*ibid.*).

Evidence from prior temperature and dissolved oxygen studies of Beauvais Lake demonstrate that the lake becomes thermally stratified, and bottom waters have in the past become anoxic in the winter and also during the summer (Crosby, 1990b). Although anoxic lake bottom waters are not a prerequisite for dissimilatory sulphate reduction, development of anoxic condition would exclude aerobic organisms and potentially favour the sulphate reducers. Kelly and Rudd (1984) found that sandy epilimnetic sites were conducive to sulphate reduction because decomposition processes caused oxygen concentrations to decrease rapidly within millimeters below the sediment-water interface in control and experimentally-acidified lakes.

The sulphur concentration of the Beauvais Lake sediments cannot be attributed solely to sedimentation of autochthonous organic material. Freshwater algae contain sulphur in a ratio of approximately 1 S atom to 100 C atoms (Cook and Kelly, 1992). Assuming that decomposition processes do not alter this abundance ratio, the 7.3% total organic carbon present in sediments of Beauvais Lake would contribute approximately 0.073% S, or ~23  $\mu\text{mole S/g}$ . This accounts for only about 9% of the total sulphur observed in the sediments of Beauvais Lake.

Beauvais Lake and Waterton Reservoir differ in several important respects. The sedimentation rate of Beauvais Lake (~0.5 mm/yr; Powers, 1994) is typical of lakes; that of Waterton Reservoir (15 mm/yr) is extraordinary. Water residence times also differ dramatically (4 years for Beauvais Lake (Crosby, 1990b) vs. 0.16 years for Waterton Reservoir). Organic productivity of the two lakes also differs (Beauvais Lake is mesotrophic, Waterton Reservoir is oligotrophic). These contrasts lead to differences in the relative contributions of detrital sulphur and diagenetic sulphur to the sediments of these lakes, and may preclude any comparison of the pre-industrial sulphur isotopic

background value from Beauvais Lake with the sulphur isotopic composition of sediments from Waterton Reservoir.

#### POSSIBLE CONTRIBUTION OF VOLCANOGENIC SULPHUR

The decrease in total sulphur concentration of the sediments in core JA21, inferred to be related to the cessation of activities at the Gulf Pincher Creek plant, supports the sediment chronology suggested earlier. The uniformity of the sulphur isotopic composition of total sediment sulphur and of porewater sulphate in core SE22 at depths greater than 20 cm below the sediment-water interface and postulated to occur in sediments deposited before 1980 is striking. As these sediments have not been appreciably enriched in sulphur compared to the surrounding soils, the observed sulphur isotope uniformity may reflect a more subtle process.

It is postulated that the sediments and porewaters of core SE22 may provide a geochemical record of the May, 1980 eruption of Mount St. Helens, a volcano located approximately 680 km to the southwest of the Waterton Park area.

Review of Environment Canada historical water quality data for the Waterton River near Waterton Lakes National Park revealed anomalously high sulphate concentrations in samples collected on June 12, and July 16, of 1980. Measured sulphate concentrations were 6.2 and 5 times higher than the mean concentration for June and July<sup>7</sup> (respectively, 4.2 mg/L  $\pm$  1.3, n=27 and 4.4 mg/L  $\pm$  1.0, n=25). The timing of the sulphate concentration peaks reported during 1980 is especially interesting. At this time of year, sulphate concentration of the Waterton River typically is at or near the annual minimum, and discharge is at the annual peak, or, in the case of July, declining from peak levels as spring melt and orographic precipitation abate. The sample of Waterton River water collected by

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<sup>7</sup> mean sulphate concentration calculated from Environment Canada records culled to  $\pm$ 5% charge balance and omitting June and July, 1980 and disregarding apparently spurious data from Nov 30, 1968.

Environment Canada on May 15, 1980 had a sulphate concentration of 5.0 mg/L, slightly lower than the mean May concentration of  $5.4 \pm 1.6$  mg/L.

Mean discharge for June of 1980 measured on the Waterton River near Waterton Lakes National Park was  $56 \text{ m}^3/\text{s}$ , less than the June average of  $70.5 \text{ m}^3/\text{s}$ . Multiplying discharge rate and sulphate concentration yields the sulphate load for the time period under consideration. If the observed sulphate concentration on June 12, 1980 is extrapolated over the entire month,  $3.8 \times 10^3$  tonnes of sulphate was carried by the Waterton River in 30 days. This exceeds, by a factor of approximately 1.3, the average annual sulphate load for the same station, calculated assuming a mean sulphate concentration of 5.0 mg and a mean annual discharge of  $18.8 \text{ m}^3/\text{s}$ .

Sulphur dioxide emissions from volcanoes can be safely monitored from remote sites by correlation spectrometers (COSPEC), and are used in an effort to forecast eruptions. Data collected in May of 1980, during the pre-cataclysmic, phreatic eruption phase of Mount St. Helens, indicate  $\text{SO}_2$  emissions levels of up to 40 tonnes / day (Casadevall et al 1981). During the period from May 25 to June 3 rates of 130 to 260 tonnes/d were observed, increasing abruptly June 6 to 1000 tonnes/d and remaining at a high level (500 to 3400 tonnes/d) through December (ibid).

Unstable magmatic gases such as  $\text{SO}_2$  very rapidly form an aerosol of liquid  $\text{H}_2\text{SO}_4$  droplets which become adsorbed on the ash particles. Sulphuric acid is an effective desiccant and absorbs water and other acid components from the plume. Reactions between the acid and the substrate lead to formation of salt crusts, as ions are leached from the ash (Taylor and Stoiber, 1973).

Anecdotes from residents of Alberta indicate that ash from Mount St. Helens was deposited throughout much of southern Alberta in the days following the May 18th plinian eruption. Continuous ambient air quality data were collected by Alberta Environment for

the period March 1 to May 31, 1980 from a mobile laboratory situated in the vicinity of the village of Twin Butte (Alberta Environment, 1980). These data displayed no increase in ambient SO<sub>2</sub> which could be related to the eruption, an observation easily rationalized by the 4 minute half-time of SO<sub>2</sub> in the presence of water vapour (Dana et al 1975).

The high sulphate concentrations observed in the Waterton River may be explained by dissolution of sulphate salts from wind-carried ash deposited on snowfields in alpine and sub-alpine areas of the headwater region of the Waterton River (ie. Glacier National Park, Montana and Waterton Lakes National Park, Alberta). Modelling of air mass trajectories (Miller et al 1981) suggests that dispersal of ash by air masses between 3 and 7 km elevation would have carried ash to the region in approximately 12 to 18 hours following the eruption. Snowmelt associated with warming temperatures, or precipitation, could dissolve adsorbed sulphate salts and flush sulphate into the watershed.

As no rainfall pH or ionic concentration data could be located for weather stations in the region, it is difficult to assess the potential contribution related to rainout of SO<sub>2</sub> originating from Mount St. Helens. Reported precipitation quantities for May, 1980 at Waterton River Cabin (197.2 mm) and Pincher Creek Airport (125mm) were higher than average, with the bulk of the precipitation falling after May 21st (ie post-eruption). Reported precipitation amounts from June and July 1980 at both Waterton River Cabin and Pincher Creek Airport were lower than average.

Consideration of daily discharge data for the Waterton River and Drywood Creek, and daily water level measurements of Waterton Reservoir suggests that residence times during June of 1980 were of the order of 28 days, about 1.5 times longer than mean June residence time (approximately 18 days). Similarly, data for July 1980 indicated that July residence times for Waterton Reservoir were approximately 135 days or 3.3 times the normal (about 40 days). The longer residence times reflect the fact that the reservoir was

filling following diversion of water via the Waterton-Belly Canal during the latter half of April and the first half of May.

Longer than normal residence time of water in the Waterton Reservoir combined with higher sulphate concentrations may have promoted an increase in sulphate diffusion to sediments which accumulated prior to 1980. This may explain the increase in porewater sulphate concentration from about 0.7 to 1.8 mg/L observed below approximately 22.5 cm depth in core JA21 (anion concentration data for this profile are considered more reliable than corresponding data for core SE22). Unfortunately sulphate for isotope characterization of these waters could not be recovered. It is noteworthy that the  $\delta^{34}\text{S}_{\text{ate}}$  of porewater sulphate in core SE22 from samples deeper than about 20 cm below the sediment-water interface is consistently near +7.5‰, close to the  $\delta^{34}\text{S}$  values determined on samples of Mount St. Helens ash (Dr. H.R. Krouse, pers. com. 1995). The only published sulphur isotope data available for Mount St. Helens is a determination of  $\delta^{34}\text{S}$  of aqueous sulphate (+9.5‰) from the pond in Mount St. Helens crater, collected prior to the eruption (Barnes et al, 1981).

Uniformity of the  $\delta^{34}\text{S}_{\text{ate}}$  of the porewaters, especially in core SE22, may indicate that the pre-existing isotopic signature of porewater sulphate was “overwhelmed” by addition of volcanogenic sulphate diffusing down into the sediments which had accumulated to that moment in time. It is postulated that the isotopic composition of the porewater sulphate has been essentially unchanged because insufficient organic carbon was available to permit reduction of sulphate by dissimilatory reduction.

The small catchment area of Beauvais Lake (~7 km<sup>2</sup>, Crosby, 1990b) may limit the potential volcanogenic sulphur contribution to sediments of Beauvais Lake. However, the <sup>34</sup>S-enrichment observed in the uppermost 10 cm of sediments in core MY27 is intriguing, particularly in light of the upwind location of Beauvais Lake with respect to either of the local technogenic sulphur sources.

## SUMMARY

Although situated generally downwind of two sour gas plants which together have emitted in excess of 500 000 tonnes of sulphur to the environment during more than 35 years of activity, deep-water sediments of Waterton Reservoir contain remarkably little sulphur. The total sulphur concentration of the reservoir sediments is less than 30  $\mu\text{mole/g}$  (as S). Analytical results indicate that total sediment sulphur concentration and total sediment sulphur isotope ratios vary with location and time. Specifically, total sediment sulphur concentration of younger sediments is less than that of older sediments, and both total sediment sulphur concentration is elevated and total sediment  $\delta^{34}\text{S}$  is enriched at the northern end of the reservoir in comparison with a location near the center of Waterton Reservoir.

The shoreface of Waterton Reservoir is actively eroded by wind-driven waves during periods of high water level, providing a local sediment source. Comparison of sediment sulphur concentration data with that of soils from the vicinity indicates that diagenetic addition of sulphur has been minor. Consequently, the variations in the isotopic composition of the sediments reflect changes in the isotopic composition of the detrital components.

It is suggested that the observed variations reflect the cessation of sulphur recovery operations at the former Gulf Pincher Creek Plant, which was decommissioned in 1984.  $^{34}\text{S}$ -enriched technogenic sulphur assimilated by vegetation and in turn introduced to the reservoir as detrital organic matter, or alternatively, as windblown elemental sulphur, may explain both the enriched sulphur isotopic composition and the slightly elevated total sulphur concentration characteristic of sediments at the northern end of Waterton Reservoir. The area is  $\sim 8\text{km}$  directly downwind from the site of the former gas plant.

Suites of water samples, collected over the course of a single day from the catchment area of Waterton Reservoir, provide an instantaneous characterization of the watershed and permit identification of sources of sulphur. Ambient environmental sulphur includes sulphate from at least two distinct sources. A sulphate source characterized by a  $\delta^{34}\text{S}$  of approximately  $-16.5\text{‰}$  is considered to reflect oxidation of reduced sulphur in the glacial tills which mantle the area. Aqueous sulphate from the subalpine headwater area of North Drywood Creek has a  $\delta^{34}\text{S}$  of  $\sim +29\text{‰}$ , presumably reflecting the sulphur isotopic composition of exposed Precambrian and Paleozoic bedrock. Tributaries dilute the waters of North Drywood Creek and add sulphate having a depleted isotopic composition, presumably reflecting the addition of groundwater.

Integration of discharge data from hydrometric stations with analytical results permits estimation of the sulphate load carried by the two principal water sources to Waterton Reservoir. The load calculations demonstrate that the maximum possible contribution of technogenic sulphur (comprising atmospheric emissions and liquid effluent) to Waterton Reservoir is small in comparison with sulphur contributed by the ambient environment. Maximum technogenic contributions from these sources are only 8% of the total sulphur load. Drywood Creek and the Waterton River combined provide approximately 7000 tonnes  $\text{SO}_4^{2-}/\text{yr}$  ( $\sim 2310$  tonnes S/yr) to Waterton Reservoir.

The short residence time of water in Waterton Reservoir (approximately 60 days) ensures an unlimited supply of sulphate, yet diagenetic sulphur addition is small. It is postulated that the high sedimentation rate and low bioproductivity of Waterton Reservoir limits the availability of suitable organic carbon substrates for the sulphate-reducing bacteria. Consequently, the process is of only minor importance to sulphur storage in the reservoir sediments, and overprinting of the depositional component of the sulphur isotope stratigraphy is minimal.

Evidence from historical water chemistry data suggests that ashfall from the May 1980 cataclysmic eruption of Mount St. Helens influenced the chemistry of the Waterton River. Leaching of sulphate salts associated with the volcanic ash deposited within the 1500km<sup>2</sup> catchment area of Waterton Reservoir may explain the larger than typical sulphate load that was carried during peak river discharge in 1980.

## CHAPTER 8 - CONCLUSIONS

Two sour gas plants located in the vicinity of Waterton Reservoir have emitted in excess of 500 000 tonnes of sulphur to the environment during more 35 years of sulphur recovery operations. Chemical and stable isotopic characterization of the principal sources of water to Waterton Reservoir (the Waterton River and Drywood Creek) indicate that approximately 2310 tonnes S/yr is provided to the reservoir by ambient environmental sources. An unusually large sulphate load may have accompanied the eruption of Mount St. Helens during the spring of 1980. The peak technogenic contribution was approximately 24 tonnes S/yr in 1972. Although sulphur is available, analytical results demonstrate that the sediments of Waterton Reservoir contain remarkably little sulphur, less than 30  $\mu\text{mole/g}$ . In contrast, sediments of nearby Beauvais Lake generally are characterized by sulphur concentrations higher than 250  $\mu\text{mole/g}$ .

Ambient environmental sulphur includes sulphate from at least two distinct sources which can be distinguished by stable sulphur isotope ratio measurements. Sulphate having a  $\delta^{34}\text{S}$  of approximately -16.5‰ is considered to reflect oxidation of reduced sulphur in the glacial tills which mantle the area. Aqueous sulphate from the subalpine headwater area of Drywood Creek has a  $\delta^{34}\text{S}$  of approximately +29‰. The source of the  $^{34}\text{S}$ -enriched sulphate has not been positively identified, but is considered to reflect bedrock sulphur sources. Significantly, the discovery of a sulphate source having a sulphur isotopic composition more enriched than that of local technogenic emissions compromises the use of sulphur isotopes as a tracer of technogenic sulphur unless possible contributions of the unidentified, enriched source can be excluded.

The sulphur isotopic composition of liquid effluent discharged by the Shell Waterton Complex is similar to that of a nearby spring, however determination of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  of the waters demonstrate that the spring is not sourced by a leak in the effluent pipe. Comparison of the sulphur isotopic composition of water from the spring in 1983 with

that of 1995 suggests that the relative contribution of technogenic sulphur to the spring has increased.

The total sulphur pool in lake sediments comprises detrital components and sulphur introduced through diagenetic processes mediated by bacteria. At Waterton Reservoir, water management practices have created circumstances inhospitable for establishment of an aquatic community in the littoral zone. Consequently, the shoreface is actively eroded by impinging waves, driven by the strong winds characteristic of the region, and sediments accumulate quickly. Although the rapid throughput of water ensures a large aqueous sulphate supply, it is postulated that low bioproductivity limits the availability of suitable organic carbon substrates to the sulphate-reducing bacteria. As a result, addition of diagenetic sulphur is small, and the characteristic stable sulphur isotope overprint of dissimilatory sulphate reduction is minimal. The sulphur isotope stratigraphy of sediments of Waterton Reservoir is dominated by the detrital component.

The stable isotopic composition of the technogenic sulphur is distinct from that of soils in the vicinity of the reservoir, permitting recognition of technogenic sulphur if subsequent isotopic fractionation is not significant. Assimilation of sulphur by organisms is not isotopically selective, thus the isotopic composition of affected organisms is shifted towards that of the technogenic source.

Spatial and temporal variations in both total sediment sulphur concentration and  $\delta^{34}\text{S}$  exhibited by sediments of Waterton Reservoir are interpreted to reflect proximity to a local technogenic sulphur source. It is suggested that the observed variations result from the cessation of sulphur recovery operations at the former Gulf Pincher Creek Plant which was decommissioned in 1984. The interpretation is compromised by the absence of precise geochronologic control, and the lack of data constraining apportionment of total sulphur. It is postulated that the observed variations in total sediment sulphur concentration and  $\delta^{34}\text{S}$  reflect local addition of technogenic sulphur as wind-blown elemental sulphur dust, or

as detrital organic matter which has, during growth, assimilated sulphur from local technogenic sources. Clearly, a more comprehensive understanding could be gained by isolation and characterization of the individual components of the total sulphur pool.

Integration of the total sulphation data collected by regulatory agencies with chemical and isotopic characterization of soils could provide important information regarding short-term retention of technogenic sulphur by soils and vegetation. Characterization of suspended particulate matter and of soil profiles along the length of Waterton Reservoir could further constrain local sediment source variations.

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