
Abundances of Oxygen and Organics in the Red Deer River: Comparison with Marmot Basin Streams*

B.L. Baker¹ and S.A. Telang²

Abstract:

Comparison of water quality data for two watersheds in Alberta—the Red Deer River and Marmot Basins, showed minor differences in oxygen levels and major differences in total organic carbon, and refractory and some labile organic compounds. Dissolved oxygen in both basins was very similar—11.0 mg/L for the Marmot streams and 9.3 mg/L for the Red Deer River. Major differences occurred in the winter months when the dissolved oxygen level in the Red Deer River dropped to less than 3.0 mg/L at three downstream sampling stations, whereas in the Marmot Basin, it consistently remained near 11.0 mg/L. Biochemical and chemical oxygen demands in the Red Deer River average 2.0 mg/L and 6.3 mg/L respectively, and in the Marmot Basin they averaged 2.0 mg/L and 4.0 mg/L, respectively. The higher chemical oxygen demand in the Red Deer River suggests higher abundances of oxidizable chemical constituents. Total organic carbon in the Red Deer River averaged 7.2 mg/L, whereas in the Marmot Basin streams it averaged 4.2 mg/L. Refractory organic compounds (humic-fulvic acids and tannins and lignins) in the Red Deer River average 8.2 mg/L and labile compounds 146 µg/L; in the Marmot Basin they averaged 0.9 mg/L and 054 µg/L, respectively. These differences in abundances are attributed to the larger drainage area in the Red Deer basin as compared with the Marmot Basin—24,000 km² and 9.4 km², respectively. Further, the Red Deer basin includes forested, agricultural and some urban areas, whereas the Marmot Basin is exclusively forested area.

Résumé:

La comparaison de la qualité de l'eau des bassins versants des rivières Red Deer et Marmot, en Alberta, montre que les niveaux d'oxygène diffèrent peu d'une rivière à l'autre, tandis que les taux de carbone organique, de composés réfractaires et de certains composés organiques labiles sont très inégaux. L'oxygène dissout dans les deux bassins était très semblable — 11.0 mg/L pour la rivière Marmot et 9.3 mg/L pour la rivière Red Deer. Les plus importantes différences se manifestent pendant l'hiver lorsque le niveau d'oxygène dissout dans la rivière Red Deer tombe à moins de 3.0 mg/L dans trois stations d'échantillonnage, alors que dans le bassin de la Marmot, il se maintient autour de 11.0 mg/L. Les besoins en oxygène biochimique et chimique dans la rivière Red Deer sont d'une moyenne de 2.0 mg/L et de 6.3 mg/L respectivement; dans le bassin de la Marmot, la moyenne est de 2.0 mg/L et 4.0 mg/L respectivement. La demande élevée d'oxygène chimique dans la Red Deer permet de supposer que de fortes doses de composants chimiques oxydables sont présentes. La part totale de carbone organique dans la Red Deer est de 7.2 mg/L, alors que pour la Marmot, elle est de 4.2 mg/L. Les composés organiques réfractaires (acides humique-fulviques, tanins et lignines) dans la Red Deer sont de

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¹ Professor, Kananaskis Centre for Environmental Research, The University of Calgary, Calgary, Alberta.

² Professor, Kananaskis Centre for Environmental Reserach, The University of Calgary, Calgary, Alberta.

8.2 mg/L et les composés labiles représentent 146 µg/L; pour la Marmot, ils sont respectivement de 0.9 mg/L et de 054 µg/L. Ces différences de proportion s'expliquent par le fait que la zone d'écoulement de la Red Deer (24,000 km²) est plus étendue que celle de la Marmot (9.4 km²). De plus, le bassin de la rivière Red Deer comprend des zones forestières, agricoles et urbaines alors que la Marmot ne traverse qu'une zone forestière.

Introduction

Eighty percent of the readily available total fresh water supply in Alberta flows through the sparsely populated northern region. The other twenty percent flows through the more densely populated central and southern regions (Baker et al. 1982). In the 1970s, the growing urban, rural, industrial, and agricultural activities in central and southern Alberta aroused interest amongst the local citizens concerning the impact of these activities on water quality in their region. To assess the impact of some of these activities, two studies were undertaken, one in the Marmot Basin and the other in the Red Deer River basin. The Marmot study dealt with the effects of forest clearcutting on organic compounds in surface waters of the basin. The study included an evaluation of source, transport, processes and fate of organic compounds in stream waters. Results of the Marmot Basin study have been published separately (Telang et al. 1981; Telang and Hodgson, 1983).

The Red Deer River study was undertaken to evaluate the result of damming the Red Deer River on organic compounds in the river. Dam construction, however, did not start during the course of this study and the delay led to the assessment of abundance of naturally occurring organic substances in the river water. The occurrence and distribution of organic compounds in the Red Deer River is presented in the results section of this paper and a comparison with the Marmot Basin is included in the discussion section.

Study Area

The Red Deer River is located in south-central Alberta (Figure 1). Its headwaters are in the Rocky Mountains of Alberta and the river flows eastward across the prairies before joining the South Saskatchewan River in Saskatchewan. The study area extends from Sundre to East Coulee—a distance of 275 km. This stretch includes a forested area and an agricultural area, as well as an extensive transition zone. The upper portion of the study area (between Sundre and 50 km downstream from Red Deer) has several tributaries that contribute to the organic load of the Red

Deer River and is characterized by extensive natural vegetation with only limited agricultural activity. The downstream portion (between 50 km downstream from Red Deer and East Coulee) is in sharp contrast with no significant tributaries entering the river and land use is almost entirely agricultural.

The Red Deer River provides water to about 10 percent of the provincial population. It flows through two small cities, Red Deer and Drumheller, which release treated effluent into the river. No major industries are located near the river. Some muskeg areas in the upper drainage basin contribute substances to the river through two tributaries. For about four months each year the river is ice-covered (from December to April).

The Red Deer drainage area is about 24,000 km² ranging from the Rocky Mountains eastward to points well within the prairies area. The total area lies within the confines of 50° and 53° north latitude, and 112° and 116° west longitude. The local bedrock is Cretaceous sandstone and shale with soil of orthic black loam on an undulating morainal structure. Natural vegetation is dominantly spruce, aspen, and balsam poplar with willow.

The climate is characterized by short, cool summers and long, cold winters. The mean precipitation is about 450 mm, 75 percent of which is snow. The average summer temperatures range from 10°C to 15°C, and the winter temperatures range from -35° to -5°.

The drainage basin is characterized by five major tributaries to the Red Deer River along with at least five very minor stream tributaries. The mean annual flow of the Red Deer River leaving the study area is 50,100 litres per second (Lps), seasonally varying from 6800 to 205,000 Lps. The contribution of the major tributaries accounts for about 50 percent of the Red Deer River flow. The river bed is primarily quarternary alluvial gravel and sand. One of the upstream tributaries shares this character whereas the remainder have muddy stream beds. In the forested areas, vegetation hangs over the water surface of tributaries.

Methodology

Eight sampling sites were chosen in the 275 km stretch of the Red Deer River (Figure 1). During the study period (May 1977 to May 1978), water samples were collected at each site every three months to represent the four seasons of the year. The samples were collected in acid-washed (35 mL saturated sodium dichromate per litre of concentrated H₂SO₄ followed by rinsing with double-distilled water) glass bottles. Each sampling trip required a collection period of ten hours. Wintertime sampling required more time for drilling holes through ice which varied in thickness from 45 to 100 cm. Dissolved oxygen levels were determined at the time of sampling, samples for phenol were preserved against bacterial and chemical oxidation with copper sulphate and phosphoric acid (APHA, 1971). Water samples were stored at 4°C until analyzed (usually less than 24 hours after sampling). Dissolved oxygen and biochemical oxygen demand levels were

determined using the modified Winkler method, and the chemical oxygen demand by the dichromate oxidation method (APHA, 1971). Colorimetric methods were used for the determination of phenols, tannins and lignins (APHA, 1971) and carbohydrates (Antia and Lee, 1963; Strickland and Parsons, 1972). Humic substances were determined using a Dohrmann D-50 organic carbon analyzer. Solvent extraction, acid-base treatment and chromatography techniques were used for the determination of hydrocarbons (Peake et al. 1972), amino acids (Roach and Gehrke, 1969a, 1969b) and fatty acids (Peake et al. 1974).

Results

Seasonal variations were observed in the abundance of oxygen and organic constituents (Table 1). Each reported value represents the average of eight sampling locations spanning 275 km of river course. The spring, summer, autumn, and winter seasons correspond to June, August, November, and January sampling months.

In general, maximum values for most of the parameters measured were observed in the spring and autumn with the spring maximum more pronounced than the autumn maximum. These maxima were attributed to springtime flushing of organic compounds in the drainage basin and to leaching of fallen leaves in the autumn.

Oxygen Levels

Levels of dissolved oxygen in the Red Deer River averaged 9.6 mg/L. Except for winter months, most of the river waters were 80 to 200 percent saturated with dissolved oxygen. Saturation concentrations of dissolved oxygen vary indirectly with temperature and range from 14.6 mg/L at 0°C to 7.6 mg/L at 30°C. During the winter, under ice cover, dissolved oxygen levels dropped consistently between Sundre and Drumheller (from 11.6 to 2.7 mg/L) (Figure 2) representing a drop in saturation levels from 82 to 19 percent. For clarity, only three sampling sites have been shown in Figure 2. The dissolved oxygen levels at other sampling sites followed the general patterns shown in Figure 2. The levels of dissolved oxygen at East Coulee were similar to those at Drumheller.

In the literature, decreases in dissolved oxygen (DO) levels have been reported for ice covered lakes, streams, and rivers (Maquire and Watkin, 1975; Beak, 1977; Penttinen et al., 1978, 1979). Maquire and Watkins (1975)

Figure 1: Red Deer River Basin

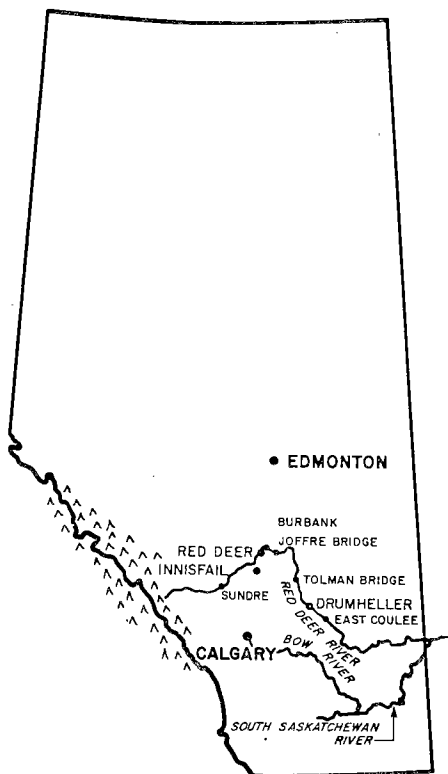
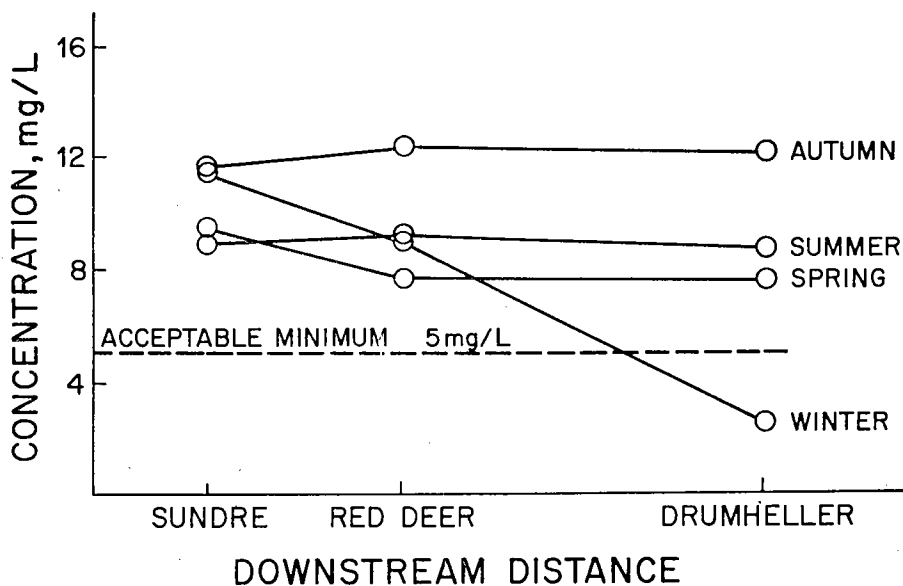


Table 1. Abundances of oxygen and organic constituents in the Red Deer River (mg/L).

Parameter	Spring		Summer		Autumn		Winter		
	Range	Average	Range	Average	Range	Average	Range	Average	
Dissolved Oxygen	7.7- 9.6	8.4	8.7-13.6	10.1	11.7-14.6	12.6	2.7-11.6	7.3	9.6
Chemical Oxygen Demand	3.1-19.8	12.1	3.0- 5.9	4.0	3.2-10.5	7.3	0.0- 3.9	1.8	6.3
Biochemical Oxygen Demand	1.0- 1.5	1.2	0.9- 2.2	1.5	2.9- 6.4	4.1	0.2- 3.4	1.5	2.1
Total Organic Carbon	6.0-13.0	9.1	6.0- 8.0	7.1	6.0- 8.0	7.2	5.0- 6.0	5.5	7.2
Humic and Fulvic Acids	0.9- 5.7	3.0	8.0- 8.2	8.1	--	--	--	--	5.5
Tannins and Lignins	0.48-3.24	1.06	0.04-0.11	0.08	0.56-0.75	0.63	0.78-1.04	0.92	0.67
Carbohydrates (µg/L)	210 - 710	480	10	10	10-50	20	10-20	10	13.0
Amino Acids (µg/L)	14 - 55	32	5-25	16	5-27	10	6-11	7	16
Hydrocarbons (µg/L)	--	--	--	0.12	--	--	--	--	--
Phenols (µg/L)	<1	<1	<1	<1	<1	<1	<1	<1	<1

Figure 2: Seasonal Variations in Dissolved Oxygen Levels Along the Red Deer River.



attributed the DO depression in Silver Lake, Ontario to prevention of atmospheric oxygen mixing with the water due to ice cover. Penttinen et al. (1978, 1979) ascribed the chronic low DO problems in the Red Deer River to the introduction of organic compounds to the river from tributaries. DO depletion was also observed in the Willamette River in Oregon (Rickert et al., 1976). In the Willamette River, DO depletion was not due to ice cover but to the input by pulp mills in addition to natural background oxygen demands from essentially pristine streams. Oxygen uptake by sediments is also possible and is found to be related almost entirely to bacterial activity in the sediments. Very little uptake was seen in sediments that had been sterilized to prohibit bacterial activity (Brewer et al., 1977).

In the present study, decreased DO levels were not directly attributed to increased contribution of organic compounds to the Red Deer River from tributaries. The abundance of total organic carbon in the winter months was nearly the same at all the eight sampling sites in the Red Deer River (5.0 to 6.0 mg/L). Further, total organic levels were less than in other seasons. The depleted oxygen level in

the river water was, therefore, attributed to the combined effects of relatively high oxygen demands and to reduced oxygen exchange between the river waters and the atmosphere due to thick ice cover and the low flow rate of the river. Depletion of oxygen due to oxygen uptake by bacterial activity in the sediments was not measured and could therefore not be assessed under the cold winter conditions.

Chemical oxygen demand (COD) levels averaged 6.3 mg/L throughout the year (Table 1) with a bimodal seasonal variation of high springtime and autumn levels of 12.2 mg/L and 7.3 mg/L, respectively. A different seasonal pattern emerged for biochemical oxygen demand (BOD) with gradually increasing levels from springtime through to the autumn where maximum levels of 4.1 mg/L were recorded. The yearly average was 2.2 mg/L (Table 1). High COD levels in the spring and autumn reflect increased input of chemical constituents associated with springtime flushing and autumn leaf-fall. The steady increase in BOD throughout the warmer periods of the year reflected an increase in microbial activity that reached a maximum in the autumn.

Organic Compounds

Total organic carbon (TOC)

Total organic carbon in the Red Deer River basin averaged 7.2 mg/L. A seasonal variation was noted that compared well with the COD seasonal variation but was less pronounced (Table 1). Analyzed organic compounds in the Red Deer River amounted to 50 percent of the total organic carbon. Among these compounds, the most dominant were the refractory compounds: humic and fulvic acids constituted 39 percent of the total organic carbon; tannins and lignins were next with nine percent, and labile compounds such as carbohydrates, amino acids, fatty acids, hydrocarbons and phenols were two percent.

Humic and fulvic acids

These high molecular weight polymeric compounds averaged 5.5 mg/L in the warmer months of the year in the waters of the Red Deer River. Springtime abundances were low (3.0 mg/L) compared with the summer time levels (8.1 mg/L). The levels of humic and fulvic acids were considerably higher than the levels observed in pristine mountain streams (0.8 mg/L; Telang et al., 1981).

Tannins and lignins

Tannins and lignins are very complex polycyclic aromatic compounds of plant origin. In the waters of the Red Deer River they averaged 0.67 mg/L with maximum levels observed during the winter months (0.92 mg/L). Minimum levels were noted during the summer (0.08 mg/L). Levels of tannins and lignins in the Red Deer River were higher than those for sea water (0.02-0.05 mg/L; Pocklington and MacGregor, 1973), and in water of the Marmot Basin (0.10 mg/L; Telang et al., 1981).

Carbohydrates

Dissolved carbohydrates averaged 130 $\mu\text{g/L}$ in the Red Deer River with a seasonal maximum observed in the spring (480 $\mu\text{g/L}$) followed by minimal levels throughout the remainder of the year (Table 1). Carbohydrates have been widely studied in surface waters and their levels in the Red Deer River are in the same range as other water (100-700 $\mu\text{g/L}$); Handa, 1966; Lewis and Rakestraw, 1955; Telang et al., 1981).

Amino acids

Sixteen amino acids were identified in the waters of the Red Deer River. These amino

acids were present in two forms—free amino acids and combined amino acids. The concentration of free amino acids ranged from 0.9 to 15 $\mu\text{g/L}$ and combined acids from 1.0 to 47.0 $\mu\text{g/L}$. The average for total amino acids was 16 $\mu\text{g/L}$. Maximum abundances were observed in the spring followed by a steady decrease for the balance of the year—from 32 $\mu\text{g/L}$ down to 7 $\mu\text{g/L}$. The most abundant acids were aspartic, glutamic, glycine, proline, and serine. Amino acids were less abundant in the Red Deer River than in other waters (16-125 $\mu\text{g/L}$, Degens et al., 1964; 50 $\mu\text{g/L}$; Sevenov et al., 1968, 15-220 $\mu\text{g/L}$; Peake et al., 1972).

The distribution of individual amino acids varied considerably. In the free acid form, aspartic and glutamic acid were most abundant accounting for 25 percent and 24 percent, respectively. Glycine, proline and serine were next most abundant and individually ranged between 5 and 8 percent. Of the combined amino acids, aspartic acid and glutamic acid were again the most abundant of the detected acids (25 percent and 17 percent, respectively). Glycine, proline and serine again were the next most abundant, each representing about 12 percent of total combined amino acids.

Hydrocarbons

The one sample studied for hydrocarbons (Table 1) showed very low abundance of alkane hydrocarbons—0.12 $\mu\text{g/L}$ with polycyclic aromatic hydrocarbons below detection limits of 0.10 $\mu\text{g/L}$. The abundance of hydrocarbons in the Red Deer River water agreed with the range of other waters (0.05 to 1.0 $\mu\text{g/L}$; Peake and Hodgson, 1966; Peake et al., 1972; Telang et al., 1981).

Phenols

Detection limits for phenols were 1 $\mu\text{g/L}$. In the Red Deer River water, phenol levels never reached the detection limit of 1 $\mu\text{g/L}$, and were less abundant than in other surface waters (2.0 to 6.0 $\mu\text{g/L}$; Environment Canada, 1961-73, Telang et al., 1981).

Discussion

One of the purposes of the present study was to compare the occurrence and distribution of oxygen and organic constituents of two very different but relatively pristine drainage basins of Alberta—the Red Deer River and the Marmot Basin. Comparative data of the two basins are shown in Table 2. Marmot is a small basin (9.4 km²) located in the Kananaskis

Table 2. Comparison of water quality in Marmot and Red Deer (mg/L)

Constituent	Marmot	Red Deer
Dissolved Oxygen	11.0	9.6
Chemical Oxygen Demand	4.0	6.3
Biochemical Oxygen Demand	2.0	2.1
Total Organic Carbon	4.2	7.2
Humic and Fulvic Acids	0.8	5.5
Tannins and Lignins	0.10	0.67
Carbohydrates	0.04	0.13
Amino Acids ($\mu\text{g/L}$)	10.0	16.0
Hydrocarbons ($\mu\text{g/L}$)	0.05	0.12
Phenols ($\mu\text{g/L}$)	1.7	<1.0

range of the Rocky Mountains of Alberta at an altitude between 1600 and 2800 metres (Telang et al., 1981). The basin has been designated as a research area, is unpopulated, and part of the basin has been subjected to various logging practices. One main stream is fed by three tributaries with a mean annual flow of 100 Lps ranging between 10 and 410 Lps. In contrast, the Red Deer River basin has an area of 24,000 km² containing forested foothills, parkland and prairie. Its altitude varies from 840 to 1040 metres. The population is about 200,000 with occupations principally agriculture and forestry. Two cities—Red Deer and Drumheller—on the main Red Deer River each have populations between 35,000 and 45,000. The mean annual flow of the Red Deer River is 50,100 Lps varying between 6,800 and 205,000 Lps. The Red Deer River originates in the Rocky Mountains and is fed by about a dozen tributaries. Limited industrial activity takes place in the basin, but it has virtually no direct impact on the river waters. Compared with many rivers of the world which serve large populations and extensive industry, the Red Deer River is relatively pristine.

Although the Red Deer River is relatively

pristine, it does have water quality problems which are associated with low dissolved oxygen levels. During the wintertime, under ice cover, dissolved oxygen (DO) levels decrease to unacceptably low levels (between Tolman Bridge and East Coulee, Figure 1). This is not observed in the Marmot Basin because of its steep topography and very rough stream bed that permit aeration of the flowing water in spite of extensive ice cover (Telang et al., 1981).

Oxygen levels and demands in the two river systems are similar. The annual mean values for dissolved oxygen are within ten percent of each other at 10.0 mg/L, biochemical oxygen demand is the same at 2.0 mg/L, and the chemical oxygen demand in Red Deer is slightly higher—6.3 mg/L as compared with 4.0 mg/L in Marmot (Table 2). In terms of these parameters these are only minor differences between the two systems even though the physiography, vegetation, soils, land use and population are so different. In terms of gross organic constituents of the waters, differences are apparent. The Marmot Basin is forested throughout the basin; whereas, the Red Deer basin contains not only forested areas, but also muskeg,

agriculture and urban areas. The principal Red Deer River tributaries draining muskeg and forest areas have the potential to acquire a wide variety of organic compounds (Baker et al., 1982). In terms of total organic carbon (TOC), the Red Deer River contains almost twice as much organic carbon as does the Marmot, 7.2 mg/L as compared with 4.2 mg/L. In both systems seasonal variations are observed in TOC. These variations are greater in the Red Deer River where TOC levels vary along the river course from 6.0 to 13.0 mg/L. This variation is most noticeable during spring runoff; whereas, in other seasons, these changes remain within 1.0 mg/L of the mean annual value. In contrast, Marmot TOC varies between 3.3 and 4.8 mg/L throughout the year. Abundance of humic and fulvic acids show similar patterns. Mean values in the Red Deer River are seven times as high as in the Marmot Basin (Table 2). Differences in soil conditions probably are responsible for the increased amount of humic and fulvic materials in the waters of the Red Deer River. Soils in the Marmot Basin are grey-wooded, podzolic, regosolic, and greysolic; whereas, the Red Deer Basin soils are basically orthic black loam with glacial till. In addition, the relatively extensive areas of muskeg in the Red Deer Basin undoubtedly contribute to the abundance of humic materials in the waters (muskeg areas account for slightly more than one percent of the total drainage basin). In terms of tannins and lignins, once again the Red Deer River is characterized by high levels—almost seven times higher than in the Marmot Basin. The source of these organic constituents is primarily lignaceous materials from trees. Decomposing vegetation is leached by local precipitation and the leachate ultimately reaches the surface water-courses. Although the annual precipitation in the Marmot Basin is more than twice that of the Red Deer basin (1080 mm compared with 450 mm), the amount of treed area in the Red Deer basin is about three orders of magnitude greater and therefore contributes much larger quantities of tannins and lignins to the watercourse.

Some minor differences are observed in total abundances of the labile organic compounds in waters of the two basins. Carbohydrates are observed at about 44 $\mu\text{g/L}$ in the Marmot Basin; whereas, in the Red Deer River they were present at 130 $\mu\text{g/L}$ on a mean annual basis.

In the two basins, hydrocarbon abundance is not significantly different, although in

the Red Deer River it is 2.5 times that in the Marmot. Phenolic abundance is much the same in both basins, with the implication that industrial input of both hydrocarbons and phenols is virtually nonexistent. Amino acid abundance in the two river systems is also very similar. The larger abundance in the Red Deer system reflects a larger basin and thus greater opportunity for the natural introduction of organic materials from natural systems in the basin.

The above comparisons show that, although the two basins vary greatly in size and vegetation type, the general water quality as shown by gross oxygen and oxygen demand characteristics is really quite similar. Differences in refractory and labile abundances are evident and probably occur because in the larger basin the input of organic substances to river water is much greater than in the smaller basin.

Conclusions

A wide variety of organic compounds are found in relatively pristine rivers in Alberta. Abundances of organic compounds in the Red Deer River varied from less than 0.12 $\mu\text{g/L}$ for hydrocarbons to 5.5 mg/L for humic substances. Comparison with findings in the Marmot Basin, a pristine mountain drainage basin, revealed that the organic water quality of the two basins was not significantly different despite the difference in area, land use and topography. The larger Red Deer River drainage basin was characterized by significantly greater abundances of gross organic constituents such as humic and fulvic acids and tannins and lignins, and labile constituents such as carbohydrates and amino acids. These increased abundances were evidently sufficient through their chemical oxygen demands to decrease the abundance of dissolved oxygen in the Red Deer River, during winter months, to undesirably low levels.

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