Occurrence and Distribution of Organic and Oxygen Compounds in Mountain Streams of the Marmot Basin

S. A. TELANG, G. W. HODGSON, AND B. L. BAKER

ABSTRACT

The nature and abundance of O₂ and organic compounds were examined in the streams of the Marmot basin. Levels of dissolved O₂ in mountain streams of the Marmot basin averaged 11,000 μg/liter. The streams were 90-105% saturated with dissolved O₂. Biochemical and chemical demand averaged 2,000 and 4,000 μg/liter, respectively. Total organic C in mountain streams averaged 4,000 μg/liter. Analyzed organic compounds in stream waters constituted 25% of the total organic C, refractory compounds accounted for 23%, and labile compounds 2%. Refractory organic compounds, humic and fulvic acids, averaged 790 μg/liter and tannins and lignins 100 μg/liter. Averages of labile compounds were: hydrocarbons, 0.05 μg/liter (sum of individual compounds in the range of C₁₅-C₂₀); phenols, 2 μg/liter; fatty acids, 2 μg/liter; carbohydrates, 45 μg/liter; and total amino acids, 10 μg/liter (sum of 16 protein amino acids). Seasonal variations in abundances of organic compounds were observed.

Additional Index Words: humic and fulvic acids, tannins and lignins, hydrocarbons, phenols, fatty acids, carbohydrates, amino acids.


Until recently, water quality with respect to chemistry was usually considered in terms of dissolved inorganic elements or suspended particulate matter due to ease of detection and quantification. Organic constituents were seldom given equal consideration. However, recent advances in the analysis of organic compounds, particularly techniques of separation and methods of identification, have made it possible to detect and quantify a variety of organic compounds that occur in trace amounts in water. Most of the attention, however, has been directed towards the analysis of organic compounds that are introduced into water systems by man's activities. These compounds include herbicides, insecticides, plasticizers, and crude oil. Very little attention has been given to organic compounds that occur naturally in pristine unpolluted waters.

In 1974, we, therefore, initiated a study of organic compounds in the mountain streams of the Marmot basin. The purpose of the study was to gain a better understanding of the occurrence and distribution of natural organic compounds in a pristine unpolluted stream water. This paper, dealing with the occurrence and distribution of organic compounds in the Marmot basin streams, is the first such study of organic compounds in pristine mountain waters.

STUDY AREA

The Marmot Creek drainage basin is in the Kananaskis range of the eastern Rocky Mountains, in Alberta, Canada (Fig. 1). The basin was set aside as a research area in 1962 by the East Slope (Alberta) Watershed Research Program to study forest hydrology (Jeffrey, 1964). The basin, totaling about 9.4 km² in area (Swanson, 1977), consists of three subbasins—Twin Fork, Middle Fork, and Cabin Creek. The three major streams flowing from these basins combine to form a single larger stream (Main Marmot) which drains the basin. The basin is situated at longitude 115°09'15"W, latitude 50°56'57"N, and an altitude of 1,585-2,805 m. The Marmot basin is an unpopulated region. The nearest town is Canmore some 60 km away with a population of about 3,000. The basin is a protected research area with access limited only to researchers. Occasionally a few hikers, and cross country skiers use the basin for recreational purposes.

The climate is characterized by short, cool summers and long, cold winters. The mean precipitation is 1,080 mm, about 75% of which is snow (Singh and Kalra, 1972). Rain occurs during the June-September period. The average July temperature ranges from 18 to 2°C; average January temperature ranges from −6 to −18°C. Thawing periods occur frequently in all winter months due to chinook winds. Weeklong short periods with a maxima of about 10°C are common during the winter months (Kirby and Ogilvie, 1969).

The vegetation is dominated by spruce-subalpine fir forests. The main types of soil are brunisolic grey-wooded, podzolic, regosolic, local greyolic, and organic soils (Stevenson, 1967; Karkonis, 1972). The basin is underlain by Mesozoic formations consisting mainly of shale and sandstone with lesser amounts of limestone, conglomerate, and coal (Mutch, 1977). The stream bed comprises sands, gravels, and boulders and is inhabited by stream microflora including benthic invertebrates, algae, and bacteria. A variety of wildlife is also seen in the basin. Significant differences are not observed in the vegetation, soil, and bedrock of the several basins except that in the Cabin Creek subbasin limestone appears to be the dominant bedrock.

Streams draining the Marmot basin are of first and second order (Mutch, 1977). They are small, perennial, and turbulent with an average daily discharge of 50 liters/sec each for Twin and Middle Fork subbasins, 20 liters/sec for Cabin Creek, and 130 liters/sec for the Main Marmot. The peak discharge for streams occurs in June (Water Survey of Canada, Calgary District). Streams are shaded throughout the year by vegetation. The pH of stream waters is generally around 8.0. Stream water temperatures vary from 0 to 2°C in March to nearly 10°C in July (Mutch, 1977). The buildup of ice cover over streams starts in November and breakup occurs in May.

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2 Professional Associate, Director and Professor, and Professional Associate, respectively, Kananaskis Centre for Environ. Res., Univ. of Calgary, Alberta T2N 1N4, Canada.
METHODOLOGY

One sampling site was chosen on each of the four Marmot basin streams (Fig. 1). During the study period (1974–78), water samples were collected on the 18th of each month to study abundances and seasonal variations of oxygen and organic compounds. An analysis of organic compounds is time consuming and, therefore, a regular schedule for sampling was adopted. It was difficult to accommodate sampling of specific events in the regular sampling program. Depending on weather and road conditions, water sampling was carried out over a period of 1–2 hours. Water samples were stored at 0°C and analyzed within 24 hours. Dissolved O₂ levels were determined immediately after sampling. Dissolved and biochemical O₂ demand levels were determined by the modified Winkler method, and the chemical O₂ demand by the dichromate oxidation method (APHA, 1971). Colorimetric methods were used for the determination of phenols, tannins and lignins (APHA, 1971), and carbohydrates (Strickland and Parsons, 1972). Humic substances were determined as organic C (Peake, 1974). Total organic C was determined using a Beckman Model 915 C analyzer. Solvent extraction, acid-base treatment, and chromatography techniques were used for the determination of hydrocarbons (Peake et al., 1972), amino acids (Degens and Reuter, 1964; Roach and Gehrke, 1969), and fatty acids (Peake et al., 1974).

RESULTS AND DISCUSSION

Seasonal variations in abundances of O₂ levels and all organic constituents were observed (Table 1 and Fig. 2). To facilitate handling, the monthly data were grouped by season, designated as winter (January–April), spring (May–August), and fall (September–December) (Table 1). In general, maximum values for organic compounds were observed in the months of January or February (winter), May or June (spring), and October or November (fall). The winter maxima was attributed to the low volume of water which allowed the concentration and preservation of organic compounds, the spring maxima to leaching of soil matter by spring runoff, and the fall maxima to leaching of autumn leaf-fall material.

Oxygen Levels

Levels of dissolved O₂ in streams of the Marmot basin averaged 10,970 μg/liter. Throughout the year stream waters were 90–105% saturated with dissolved O₂. During the period of ice cover from November to April, dissolved O₂ levels remained high (11,200–11,700 μg/liter), but percentage saturation values were low. Mutch (1977) suggested that the thick ice cover and the low discharge of water causes reduced O₂ exchange between the stream waters and the atmosphere. During the spring runoff period and the summer months, levels of dissolved O₂ in the Marmot Creek basin waters dropped between 9,800 and 10,800 μg/liter. This seasonal variation was attributed to a rise in temperature, which would affect the solubility of O₂ in water (Hynes, 1966), and to variations in biochemical and chemical demands.

Biochemical O₂ demand levels averaged 1,960 μg/liter (Table 1). The demand increased steadily from September (1,000 μg/liter) to February (3,000 μg/liter), then gradually declined to low levels in August (1,000 μg/liter). In the September–February period, chemical oxygen demand also showed an overall increase (from 1,000–7,000 μg/liter). The steady increases in biochemical and chemical O₂ demands during this period suggested an increase in microbial activity (e.g., bacterial

Table 1—Abundances of O₂ and organic compounds in stream waters of the Marmot basin (conc. μg/liter).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Winter</th>
<th>Spring</th>
<th>Fall</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved O₂</td>
<td>11,370</td>
<td>10,550</td>
<td>11,000</td>
<td>10,970†</td>
</tr>
<tr>
<td>Biochemical O₂ demand</td>
<td>2,300</td>
<td>1,600</td>
<td>1,980</td>
<td>1,980†</td>
</tr>
<tr>
<td>Chemical O₂ demand</td>
<td>4,040</td>
<td>5,730</td>
<td>2,180</td>
<td>3,980†</td>
</tr>
<tr>
<td>Total organic C</td>
<td>4,800</td>
<td>4,400</td>
<td>3,250</td>
<td>4,150‡</td>
</tr>
<tr>
<td>Humic and fulvic acids</td>
<td>620</td>
<td>1,020</td>
<td>700</td>
<td>790‡</td>
</tr>
<tr>
<td>Tannins and lignins</td>
<td>105</td>
<td>115</td>
<td>88</td>
<td>1021†</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0.05</td>
<td>-</td>
<td>1.2</td>
<td>0.05‡</td>
</tr>
<tr>
<td>Phenols</td>
<td>2.1</td>
<td>6.4</td>
<td>6.4</td>
<td>2.23‡</td>
</tr>
<tr>
<td>Total fatty acids</td>
<td>3.11</td>
<td>1.7</td>
<td>1.45</td>
<td>2.04†</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>41</td>
<td>63.2</td>
<td>28.8</td>
<td>44.2†</td>
</tr>
<tr>
<td>Total amino acids</td>
<td>8.8</td>
<td>10.42</td>
<td>10.1</td>
<td>9.77†</td>
</tr>
</tbody>
</table>

† 1974–78.
‡ 1975–77.
§ 1976–78.
# Spring months of 1975 and 1976.
†† For two undisturbed streams.
activity). Studies on microbial populations in the stream waters of the Marmot Creek drainage basin substantiated this hypothesis (Geesey et al., 1978). It is possible that an increased organic load resulted in increases of certain organic compounds, such as carbohydrates and amino acids, which may have been utilized as a food source by microorganisms (Dugan, 1975) in the presence of O2.

**Organic Compounds**

**TOTAL ORGANIC C**

Total organic C in the streams of the Marmot basin averaged 4,150 µg/liter. Seasonal peaks were observed in January (5,000 µg/liter); April (6,000 µg/liter); and September (4,000 µg/liter). Analyzed organic compounds in the waters of Marmot basin amounted to 25% of the total organic C. Among these compounds, the most dominant were the refractory compounds, humic and fulvic acids, constituting 19% of total organic C; tannins and lignins were next with 4%; and labile compounds, such as hydrocarbons, phenols, carbohydrates, fatty acids, and amino acids, were 2%.

**HUMIC AND FULVIC ACIDS**

Humic and fulvic acids mentioned in this paper refer to organic compounds that are not extractable with benzene. They are high molecular weight polymeric compounds derived from the lignins of vascular plants. The distinction between humic and fulvic acids is made largely on the basis of their molecular weight and solubility. Humic acids are soluble at all pH values above 2; fulvic acids are completely soluble in water at all pH values. Humic and fulvic acids in the waters of the Marmot basin averaged 790 µg/liter, and their levels in mountain streams were slightly less than those in pristine river waters (Table 2). Seasonal abundance peaks were observed in February (750 µg/liter), May (1,350 µg/liter) and October (1,250 µg/liter). Fulvic acids were dominant, accounting for 70-90% of the total humic material.

**TANNINS AND LIGNINS**

Tannins and lignins are very common complex polycyclic aromatic compounds of plant origin. In undisturbed streams of the Marmot basin their abundances averaged 102 µg/liter. Seasonal abundance peaks were observed in January (100 µg/liter), May (175 µg/liter), and September (70 µg/liter). Levels of tannins and lignins in the Marmot basin waters were higher than those in sea waters, but were near the lower range for rivers (Table 2).

**HYDROCARBONS**

Hydrocarbon levels in the stream waters of the Marmot basin were extremely low (0.05 µg/liter) as compared to other stream and river waters (Table 2). The carbon preference index determination indicated that the hydrocarbons were of both aquatic and terrestrial origin (Telang et al., 1981).

**PHENOLIC COMPOUNDS**

In the streams of the Marmot basin phenolic compounds averaged 2.23 µg/liter. Their levels in the Marmot basin waters were comparable to those in stream and river waters (Table 2). Phenolic compounds were abundant only during the summer and early fall months. During the months of June to September, the levels of phenolic compounds increased steadily from <1 µg/liter to 4 µg/liter and remained high (3 µg/liter) until the leaf-fall was over in October. Efficient leaching of phenolic compounds from soil and plant material during the rainy season may account for these high values. During the late fall, winter months, the early runoff period (November–May), however, their levels dropped below the detection limit of 1 µg/liter.

**FATTY ACIDS**

Total fatty acids content in streams of the Marmot basin averaged 2.08 µg/liter. Seasonal maxima were observed in March (4 µg/liter), June–July (2.5 µg/liter), and December (4 µg/liter). Fatty acids have been widely studies in surface waters and were far less abundant in Marmot basin waters than in other surface waters (Table 2).

<table>
<thead>
<tr>
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<th>Other stream waters</th>
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<tbody>
<tr>
<td>Total organic C</td>
<td>4,150</td>
<td>1,000–20,000</td>
</tr>
<tr>
<td>Humic and fulvic acids</td>
<td>790</td>
<td>900†</td>
</tr>
<tr>
<td>Tannins and lignins</td>
<td>102</td>
<td>20–50‡</td>
</tr>
<tr>
<td>Hydrocarbons</td>
<td>0.05</td>
<td>0.3–1.0†</td>
</tr>
<tr>
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<td>2.23</td>
<td>2.0–6.0†</td>
</tr>
<tr>
<td>Total fatty acids</td>
<td>2.08</td>
<td>80–90†</td>
</tr>
<tr>
<td>Carbohydrates</td>
<td>44.3</td>
<td>100–700‡</td>
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<tr>
<td>Total amino acids</td>
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<td>250–750†</td>
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† River water.  
‡ Sea water.  
§ Stream water.  
¶ Lakes and reservoirs.

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Even-C-numbered fatty acids predominated in stream waters. The saturated acids, palmitic and stearic (C16 and C18), accounted for 10–25% of the acids detected in the C12–C16 range. Of the odd-C-numbered acids, C17, C19, and C17, accounted for 3–5% of the total acids. Even-C-numbered acids contained one double bond were also detected in the C14 to C12 range. Of these, the most common were C16 and C18, unsaturated fatty acids. The C14, unsaturated acid was slightly more abundant (7–14%) than the C16, unsaturated acid (3–9%).

Table 2—Comparison of organic compounds in stream waters of the Marmot basin with those of other surface waters (conc. µg/liter).

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Carbohydrates

Dissolved carbohydrates averaged 44.3 µg/liter in the Marmot Creek basin waters. Seasonal peaks were observed in February (65 µg/liter), June (100 µg/liter), and October (45 µg/liter). Like fatty acids, carbohydrates have been widely studied in surface waters and their levels in the Marmot basin water were less than those in other waters (Table 2).

Seven monosaccharides were also identified in the Marmot Creek basin waters by gas chromatography. Three of the monosaccharides were pentoses—arabinose, ribose, and xylose—and four were hexoses—mannose, galactose, rhamnose, and glucose. They were identified as trimethylsilyl derivatives.

Of the seven monosaccharides, glucose was by far the most abundant, averaging about 40% of the total identified monosaccharides. The next most abundant monosaccharides were xylose, averaging about 20%; galactose, averaging about 15%; and mannose, about 10%. The remaining three monosaccharides—rhamnose, ribose, and arabinose—each averaged about 6-8% of the total detected monosaccharides.

Amino Acids

Sixteen amino acids were identified in stream waters of the Marmot Creek drainage basin. The concentration of free amino acids ranged from 0.9 to 6.5 µg/liter and combined amino acids ranged from 2 to 10 µg/liter. The average for total acids was 9.77 µg/liter (Table 1). Seasonal abundance maxima were observed in March (11 µg/liter), June (11 µg/liter), and September (15.8 µg/liter). The most abundant acids were aspartic acid, glutamic acid, glycine, alanine, ornithine, proline, and serine. Amino acids also have been extensively studied in natural waters, and like hydrocarbons, fatty acids, and carbohydrates, they were less abundant in the Marmot basin waters than in other waters (Table 2).

The distribution of individual amino acids showed considerable variation in the waters of the Marmot basin. Of the free amino acids, glycine was by far the most abundant, accounting for nearly 17% of the total measured free acids. Aspartic acid, glutamic acid, and ornithine were the next most abundant and individually ranged from 10 to 12%. Alanine, proline, and serine rated next in abundance. Individually they were in the range of 6-8%. Of the combined amino acids, glycine, aspartic, and glutamic acid were again by far the most abundant of the detected acids (17, 17, and 23%, respectively). Ornithine and alanine were next in abundance, each representing 8%. Proline and serine were present to the extent of 6 and 5%, respectively.

An analysis of amino acid data revealed one major heterogeneous source of amino acid in the waters of the Marmot basin. Amino acids occur in the environment either as free amino acids or as polypeptide polymers (proteins) with repeating sequences of amino acids in extensive chains. In the peptide form, individual amino acids survive environmental stress much better than in the free amino acid state. If a polypeptide survives as such from its biotic source to the stream water, it should still display the same relative abundance of individual amino acids when they are finally released in the laboratory acid hydrolysis method as in the original source material. Accordingly, a single source of combined amino acids (proteins or peptides) would result in the same relative abundance of component acids in the surface waters of local streams. Variations between abundance ratios of two amino acids in the stream waters and the ratios observed in suspected source materials would indicate more than one source of amino acids in the stream waters. A variation in the relative abundance of one amino acid to another in the combined form, from stream to stream, would also indicate more than one source of amino acids in the stream waters. The ratios of three pairs of amino acids found in the Marmot basin waters were examined to test the last hypothesis. In the combined form, the ratios of serine to glycine, threonine to glycine, and aspartic acid to glutamic acid for the four streams ranged from 0.06 to 0.11, 0.1 to 0.25, and 0.7 to 0.8, respectively. The narrow range of ratios for individual pairs of amino acids suggested a common heterogeneous source, since there was no indication of different suites of acids as might have been revealed by variable abundance ratios for pairs of acids.

CONCLUSIONS

A wide variety of organic compounds are found in clear, highly oxygenated pristine mountain streams of the Marmot basin. Abundances of organic substances vary from as low as 0.05 µg/liter for hydrocarbons to as high as 790 µg/liter for humic substances. Seasonal variations are observed in O2 levels and abundances of organic compounds, aquatic organisms, terrestrial vegetation, and wildlife are sources of organic compounds in the basin’s stream waters.

ACKNOWLEDGMENT

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