

DISTRIBUTION OF ORGANIC CONSTITUENTS IN LAKE WATERS AND SEDIMENTS OF THE McMURDO SOUND REGION IN THE ANTARCTIC

Genki MATSUMOTO,

*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
1-1, Fukazawa 2-chome, Setagaya-ku, Tokyo 158*

Tetsuya TORII

Chiba Institute of Technology, Tsudanuma, Narashino 275

and

Takahisa HANYA

*Department of Chemistry, Faculty of Science, Tokyo Metropolitan University,
1-1, Fukazawa 2-chome, Setagaya-ku, Tokyo 158*

Abstract: During the 1976–77 austral summer, geochemical studies were carried out to elucidate the distribution of organic constituents in lake waters, sediments, soils and epibenthic algae collected from Ross Island and the Dry Valleys of the McMurdo Sound region.

The contents of the total organic carbon (TOC) and organic carbon extractable with ethyl acetate (EOC) of lake waters showed a wide range of variation depending on the sampling depths and locations. TOC, total-N and EOC of sediments and soils showed low values, which may reflect the low productivity of the lakes and their environments. The contents of hydrocarbons of lake waters, sediments and soils were fairly low, but characteristic, branched and unsaturated, hydrocarbons were found as the major constituents. Generally the contents of fatty acids of lake waters, sediments and soils were also low and their constituents showed a pattern similar to that of algal fatty acids. *m*- and *p*-Hydroxybenzoic and *o*- and *p*-hydroxyphenylacetic acids were identified and the presence of *o*-hydroxybenzoic and vanillic acids was suggested for lake waters and sediments. *p*-Hydroxybenzoic acid is dominant among the phenolcarboxylic acids identified. The lack of syringic, *p*-coumaric and ferulic acids in lake waters, sediments and soils must reflect the absence of vascular plants. The analytical results for epibenthic algae suggest that they are one of the important source organisms of organic compounds found in lake waters and sediments.

1. Introduction

The Antarctic is the unique continent where vascular plants are absent, except

in the Antarctic Peninsula, on the earth (GREEN *et al.*, 1967). So, the organic constituents in lake waters and sediments on the continent are expected to be considerably different from those in the Temperate and Torrid Zones. Although numerous studies of inorganic constituents in this area have been carried out, the kinds and amounts of organic constituents have yet been scarcely known. PARKER *et al.* (1974) reported the high concentrations and rapid seasonal fluctuations of total organic carbon (TOC) in Lake Bonney. The high concentrations of TOC and extractable organic carbon (EOC) and low concentrations of fatty acids in the bottom waters of Lakes Vanda, Bonney and Fryxell have also been reported from the geochemical point of view (TORII and WAGURI, 1975; MATSUMOTO and HANYA, 1977).

To elucidate the feature of organic constituents in cold desert lakes, the authors report here the analytical results of TOC, EOC, hydrocarbons, fatty acids and phenolcarboxylic acids in lake waters, sediments, soils and epibenthic algae collected from Ross Island and the Dry Valleys of the McMurdo Sound region in the Antarctic, and discuss the source organisms of the organic compounds found there.

2. Experimental

2.1. Description of samples

During the 1976–77 season, lake waters, sediments, soils and epibenthic algae were collected from Ross Island and the Dry Valleys of the McMurdo Sound region (Fig. 1). The lake water samples were collected with a Kitahara-type water sampler made of stainless steel with a stainless steel wire, except for surface waters which

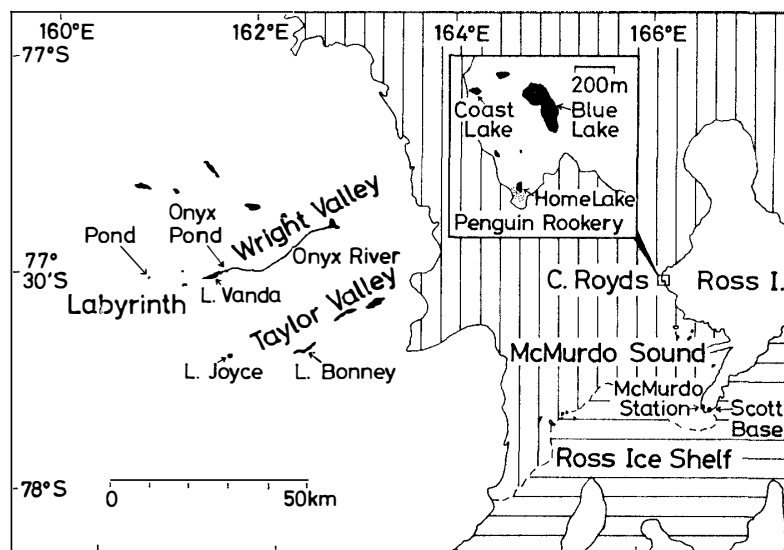


Fig. 1. Sampling locations in Ross Island and the Dry Valleys of the McMurdo Sound region.

were directly collected into 2 l brown glass bottles with teflon caps, and then were transferred into glass bottles and acidified ($\text{pH} < 2$) with concentrated hydrochloric acid (5 ml/2 l) to prevent the change due to biological activity. The water samples were stored at the temperature below 5°C until the analysis.

Surface lake sediments, soils and epibenthic algae were collected with a small scoop made of stainless steel except for the sediments of Lakes Bonney and Joyce, and were transferred into 500 ml glass bottles or wrapped with teflon sheets. At Lakes Bonney and Joyce, the sediments were collected with a Kitahara-type water sampler together with bottom waters. The samples were stored at the temperature below 0°C .

2.2. Analyses of water samples

TOC was determined by MENZEL and VACCARO method (1964). The water samples (1.0–1.5 l) were treated 3 times with ethyl acetate (300 ml, $150\text{ ml} \times 2$) under acidic conditions ($\text{pH} < 2$) in a 2 l separating funnel, then the organic extracts were combined and concentrated to 5.0 ml under reduced pressure at the temperature below 30°C . To determine EOC, the duplicate 50 μl concentrates were taken with a syringe and transferred to 10 ml glass ampoules. The ethyl acetate was removed completely under the same conditions described above. Five ml redistilled water were added to the ampoules and their organic carbon was determined by MENZEL and VACCARO method (1964).

To determine organic compounds, the concentrates were hydrolyzed with 0.5 M potassium hydroxide methanol (5 ml, 80°C , 2 hours) and extracted with 60 ml ethyl acetate after acidification ($\text{pH} < 2$) with concentrated hydrochloric acid and addition of 5 ml redistilled water. The extracts were evaporated to dryness, redissolved in 50 μl benzene: ethyl acetate (1:1), and chromatographed through a silica gel column ($180 \times 4\text{ mm}$ i.d., 100 mesh, 5% water). Hydrocarbons, fatty acids and phenolcarboxylic acids were eluted with 2 column volumes of hexane, 3 column volumes of benzene: ethyl acetate (95:5), and 4 column volumes of benzene: ethyl acetate (1:1), successively. The benzene: ethyl acetate (95:5) eluates were concentrated and methylated with 15% boron trifluoride methanol solution (80°C , 2 hours). The benzene: ethyl acetate (1:1) eluates were also concentrated and trimethylsilylated (TMS) with 25% N,O-bis (trimethylsilyl) acetamide acetonitrile solution (1 hour, room temperature). Hydrocarbons, methyl esters of fatty acids and TMS derivatives of phenolcarboxylic acids were determined by using a Shimadzu LKB 9000 Gas Chromatograph-Mass Spectrometer (GC-MS). The GC-MS conditions are described on each chromatogram. In this study, great care was taken to avoid contamination of the samples throughout the experiments. According to 4 replicate addition experiments by using authentic compounds, the analytical uncertainty was within $\pm 12\%$.

2.3. Analyses of sediments, soils and epibenthic algae

TOC and total-N were determined by dry combustion using a CHN Analyzer (Yanako MT2 CHN Corder) after treatment with 6 M hydrochloric acid to remove inorganic carbon.

To determine EOC and organic compounds, wet samples (5–30 g) of sediments, soils and epibenthic algae were homogenized by stirring for 10 minutes (1.0×10^4 rpm) with an Ace Homogenizer AM 7 (Nihon Seiki Ltd.). Homogenized samples were refluxed for 2 hours with 0.5 M potassium hydroxide methanol solution, then centrifuged (3.0×10^3 rpm). Alkaline methanol extracts and residues were acidified ($\text{pH} < 2$) separately with concentrated hydrochloric acid, and the residues were treated 3 times with 100 ml ethyl acetate by repeatedly stirring and centrifugation. The ethyl acetate extracts and the methanol extracts were combined and washed 5 times with 30 ml distilled water and concentrated. EOC and organic compounds were determined by the same methods as in the case of the water samples.

3. Results and Discussion

3.1. TOC, EOC and total-N

Table 1 and Fig. 2 show the TOC and EOC values of the water samples collected from Ross Island and the Dry Valleys of the McMurdo Sound region. The TOC and EOC values of the lake waters ranging from 0.31 to 110 mgC/l and from 0.05 to

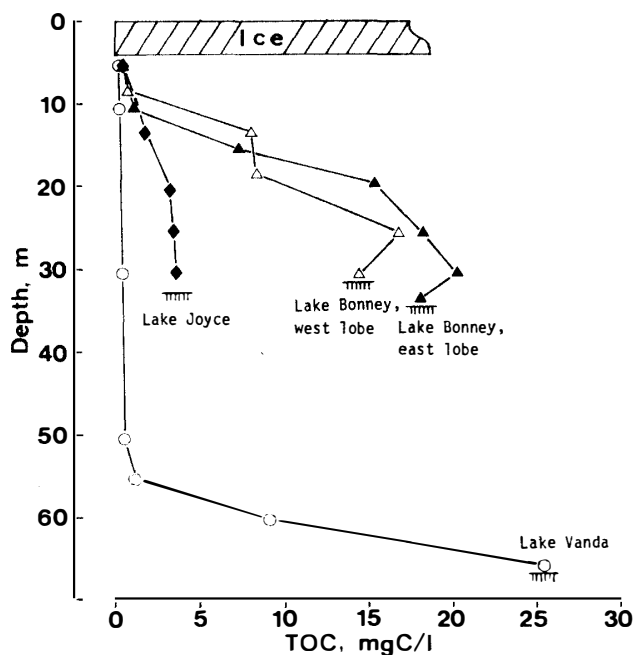


Fig. 2. Vertical distribution of the TOC values in waters of Lakes Vanda, Bonney and Joyce.

Table 1. TOC and EOC of water samples collected from Ross Island and the Dry Valleys of the McMurdo Sound region.

Sample (depth, m)	Sampling date	TOC (mgC/l)	EOC (mgC/l)	EOC/TOC × 100(%)
Ross Island				
Blue Lake (surface)	Dec. 8, 1976	0.43	0.08	19
Home Lake (surface)	Dec. 8, 1976	110	8.5	7.7
McMurdo Station, dumping site (surface)	Jan. 18, 1977	61	7.6	12
Wright Valley				
Onyx River (surface)	Dec. 13, 1976	0.72	0.10	14
Lake Vanda (5.4)	Dec. 13, 1976	0.31	0.05	16
(10.4)		0.32	nm	—
(30.4)		0.32	0.06	19
(50.4)		0.46	0.14	30
(55.4)		1.2	0.26	22
(60.4)		9.2	0.71	7.7
(65.9)		25	1.5	6.0
Unnamed pond, Labyrinth (surface)	Jan. 3, 1977	3.0	0.48	16
Taylor Valley				
Lake Bonney, east lobe (5.4)	Dec. 24, 1976	0.52	0.10	19
(10.4)		1.1	nm	—
(15.4)		7.4	nm	—
(19.4)		15	2.5	17
(25.4)		18	nm	—
(30.4)		20	nm	—
(33.4)		18	3.4	19
Lake Bonney, west lobe (5.4)	Dec. 21, 1976	0.44	0.11	25
(8.4)		0.75	nm	—
(13.4)		8.1	nm	—
(18.4)		8.4	0.29	3.5
(25.4)		17	nm	—
(30.4)		15	0.51	3.4
Pearce Valley				
Lake Joyce (5.4)	Dec. 18, 1976	0.31	nm	—
(13.4)		1.7	nm	—
(20.4)		3.2	nm	—
(25.4)		3.4	nm	—
(30.4)		3.4	0.51	15

nm: Not measured.

8.5 mgC/l, respectively, are remarkably different according to the sampling depths and locations. The highest values of TOC and EOC are found at Home Lake in Ross Island, where the water is strongly influenced by the excretions of Adélie Penguin and skua around the lake. The high values are also found in the water of the dumping site at McMurdo Station. In the waters of Lake Vanda, the TOC and EOC values (Fig. 2) remarkably increase from a depth of 50.4 m toward the bottom and reach the maximum values of 25 mgC/l and 1.5 mgC/l, respectively, at the bottom (65.9 m). These distribution pattern are similar to the density profile (WILSON and WELLMAN, 1962; TORII *et al.*, 1975). In the waters of Lake Joyce, the TOC values also increase with depth toward the bottom, although the values are generally low. At the east and west lobes of Lake Bonney, the TOC values of the waters show the same tendency but decrease near the bottom (Fig. 2). The difference of the vertical distribution of the TOC values among the three lakes is considered to be related to the vertical microbial community and their activity, temperature and salinity profiles, etc.

The percentages of EOC to TOC for the waters are ranging from 3.5 to 30% with the maximum value at the depth of 50.4 m in Lake Vanda. These values are similar to those of river waters of the Ogasawara Islands (MATSUMOTO and HANYA, 1978).

Table 2. TOC, total-N, and EOC of sediments, soils, and epibenthic algae collected from Ross Island and the Dry Valleys of the McMurdo Sound region.

Sample	Sampling date	TOC (mgC/g)	Total-N (mgN/g)	EOC (mgC/g)	TOC/ Total-N	EOC/TOC × 100 (%)
Sediments						
Home Lake	Dec. 8, 1976	41	11	4.2	3.7	10
Lake Vanda, south-east side (shallow bottom)	Jan. 1, 1977	0.42	0.069	0.046	6.1	11
Unnamed pond, Labyrinth	Jan. 3, 1977	0.59	0.11	0.074	5.4	13
Lake Bonney, west lobe	Dec. 21, 1976	1.8	0.31	0.51	5.8	28
Lake Joyce	Dec. 18, 1976	4.1	0.63	0.46	6.5	11
Soils						
Lake Vanda, east side	Jan. 1, 1977	0.71	0.23	0.092	3.1	13
Lake Bonney, west lobe, west side	Dec. 22, 1976	0.14	0.038	0.036	3.7	26
Epibenthic algae						
Coast Lake	Dec. 8, 1976	240	32	12	7.5	5.0
Onyx Pond	Dec. 16, 1976	6.1	0.98	nm	6.2	—
Lake Vanda, south-east side	Jan. 1, 1977	5.4	0.68	0.39	7.9	7.2

nm: Not measured.

The TOC, total-N and EOC values of sediments, soils and epibenthic algae are summarized in Table 2. The epibenthic algae were identified to be blue-green algae, *Oscillatoria* spp., *Phormidium* spp. and *Calothoria* spp. being the main species, by FUKUSHIMA (personal communication). The contents of TOC, total-N and EOC of sediments and soils are low, except for Home Lake, which may reflect the low productivity of the lakes and their environments. The primary productivity measurement in Lakes Vanda and Bonney reported by GOLDMAN *et al.* (1967) yielded the low values of 29 mgC/m² day to a depth of 60 m and 31 mgC/m² day to a depth of 10 m, respectively. The highest values of TOC, total-N and EOC of sediments are found at Home Lake as in the case of the lake water. However, the low values of epibenthic algae collected from Onyx Pond and Lake Vanda may be attributed to the sandy materials adhered to the algae as impurity.

The average ratios of the TOC to total-N values for sediments, soils and epibenthic algae are 5.6, 3.4 and 7.1, respectively. The intermediate value for sediments may be a result of the mixing of the soils of low values with the algae of high values throughout the sedimentation. The difference of these values might, however, be due to the extent of the contribution of inorganic nitrogen compounds, the difference of the kinds of source organisms, and the degree of the decomposition of organic matter. The percentages of the EOC to TOC values for sediments varied from 10 to 28%, which are similar to those of Syowa Oasis (MATSUMOTO *et al.*, unpublished).

3.2. Hydrocarbons

Fig. 3 shows the gas chromatogram of the hydrocarbon fractions obtained from water (65.9 m depth), sediments (shallow bottom), soil (east side) and epibenthic algae collected at Lake Vanda. The constituents of the hydrocarbons are remarkably different among the kinds of the samples. The major constituents of the hydrocarbons for the water, sediment, soil and epibenthic algae are branched- $C_{18:0}$ (carbon chain length: numbers of unsaturation) and $C_{17:0}$; $C_{17:1}$, $C_{18:1}$ and $C_{19:1}$; $C_{23:0}$, $C_{25:0}$ and $C_{27:0}$; and $C_{17:1}$, $C_{18:1}$ and $C_{19:1}$, respectively.

Table 3 lists the range of carbon chain length, their total concentrations and major constituents (including tentatively identified hydrocarbons) with approximate percentages (more than 10%) in the samples. Hydrocarbons are found in the range of $C_{12:0}$ to $C_{36:0}$ including branched and unsaturated at the low concentrations except for the water of the dumping site at McMurdo Station and the sediment at Home Lake. The source of the hydrocarbons of the dumping site may, in part, DFA (Diesel Fuel for Antarctica) widely used at the station, because the major constituents are lower molecular weight alkanes ($<C_{20}$).

The major constituents of hydrocarbons of the samples are principally lower or higher ($\geq C_{20}$) molecular weight saturated and/or unsaturated hydrocarbons, although the constituents are different according to the kinds of samples and the

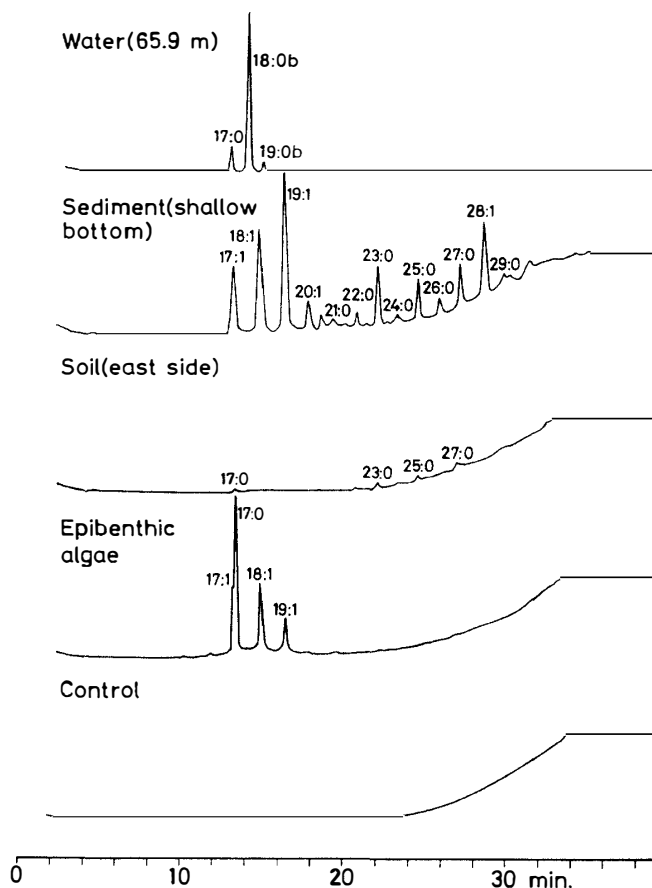


Fig. 3. Gas chromatograms of the hydrocarbon fractions obtained from water, sediment, soil and epibenthic algae collected at Lake Vanda. Conditions: Column, glass column (200 cm \times 3 mm i.d.), packed Nishio 1% OV-1 (water) or Shimadzu 1.5% OV-1 (sediment, soil, epibenthic algae and control) on 80–100 mesh Chromosorb W; temperature, injection, 290°C, column, programmed from 100–285°C at 6°C/min, molecular separator, 300°C, ion source, 330°C; carrier gas, helium at 30 ml/min; detector, total ion collector at 20 eV; recorder range, 10 mV. 18:0b and 19:0b: Branched- $C_{18:0}$ and - $C_{19:0}$ alkanes, respectively.

locations (Table 3). The presence of unsaturated hydrocarbons as the major constituents is quite different from the cases of the Tokyo area (MATSUMOTO, unpublished) and the Ogasawara Islands (MATSUMOTO and HANYA, 1978), where saturated hydrocarbons are only dominant in straight chain hydrocarbons.

Generally, lower molecular weight aliphatic hydrocarbons are present dominantly in algae, *i.e.*, blue-green algae (HAN *et al.*, 1968; HAN and CALVIN, 1969; GELPI *et al.*, 1970; ORÓ *et al.*, 1970; WEETE, 1976). Therefore, the major sources of the lower molecular weight saturated and unsaturated hydrocarbons found in the lake waters and sediments may be algae such as blue-green algae as shown in

Table 3. Hydrocarbons found in waters, sediments, soils and epibenthic algae collected from Ross Island and the Dry Valleys of the McMurdo Sound region.

Sample	Range	Concentration	Major constituents (carbon chain length: numbers of unsaturation, approximate%)
Waters*		($\mu\text{g/l}$)	
Home Lake (surface)	C ₁₅ -C ₃₁	4.8	C _{17:2} (75)
Lake Vanda (60.4 m)	C ₁₆ -C ₃₄	0.24	C _{19:0} (13), C _{21:0} (11)
(65.9 m)	C ₁₆ -C ₃₂	6.5	branched-C _{18:0} (75), C _{17:0} (14)
Unnamed pond, Labyrinth (surface)	C ₁₆ -C ₃₃	0.22	C _{27:0} (13), C _{26:0} (13), C _{25:0} (12), C _{24:0} (10)
McMurdo Station dumping site (surface)	C ₁₃ -C ₃₆	170	C _{15:0} (15), C _{14:0} (13)
Sediments		($\mu\text{g/g}$)	
Home Lake	C ₁₄ -C ₂₉	40	C _{17:0} +C _{17:1} +pristane(48), C _{15:0} (29)
Lake Vanda, south-east side (shallow bottom)	C ₁₅ -C ₃₅	0.13	C _{19:1} (22), C _{18:1} (13)
Unnamed pond, Labyrinth	C ₁₅ -C ₃₄	1.1	C _{17:0} +C _{17:1} (97)
Lake Bonney, west lobe	C ₁₄ -C ₃₄	5.2	C _{29:2} (92)?
Lake Joyce	C ₁₄ -C ₃₅	0.51	C _{27:1} (28), C _{25:1} (21), C _{29:1} (16)
Soils		($\mu\text{g/g}$)	
Lake Vanda, east side	C ₁₅ -C ₃₂	0.046	C _{23:0} (23), C _{27:0} (10), C _{25:0} (10)
Lake Bonney, west lobe, west side	C ₁₇ -C ₃₅	0.014	C _{27:0} (18), C _{25:0} (11), C _{26:0} (10), C _{29:0} (10)
Epibenthic algae		($\mu\text{g/g}$)	
Coast Lake	C ₁₂ -C ₃₆	140	C _{18:1} (20), C _{17:1} (12), C _{19:1} (10)
Onyx Pond	C ₁₄ -C ₃₁	15	C _{17:0} +C _{17:1} (67), branched-C _{18:1} (11)?
Lake Vanda, south-east side	C ₁₂ -C ₃₅	11	C _{17:0} +C _{17:1} (61), C _{18:1} (24), C _{19:1} (11)

*Table indicates only the water samples, in which hydrocarbons were detected.

Table 3. On the other hand, higher molecular weight aliphatic hydrocarbons are distributed in fungi (ORÓ *et al.*, 1966; WEETE, 1976) and bacteria (HAN and CALVIN, 1969; ALBRO, 1971), but GELPI *et al.* (1968, 1970) also reported the presence of higher molecular weight unsaturated hydrocarbons in a blue-green algae, *Anacystis montana*, and a golden-brown algae, *Botryococcus braunii*. Therefore, the higher molecular weight saturated and unsaturated hydrocarbons must have originated mainly from those organisms in the lakes and their environments (MEYER *et al.*, 1962; HOLM-HANSEN, 1963; DI MENNA, 1966; SUGIYAMA *et al.*, 1967; GOLDMAN, 1970; BENOIT and HALL, 1970; CAMERON *et al.*, 1970; HOROWITZ *et al.*, 1972; KOOB and LEISTER, 1972; KRISS *et al.*, 1977). The presence of branched-C_{18:0} is of interest, but its source organisms could not be elucidated.

3.3. Fatty acids

Fig. 4 indicates the mass fragmentograms of the fatty acid fractions obtained

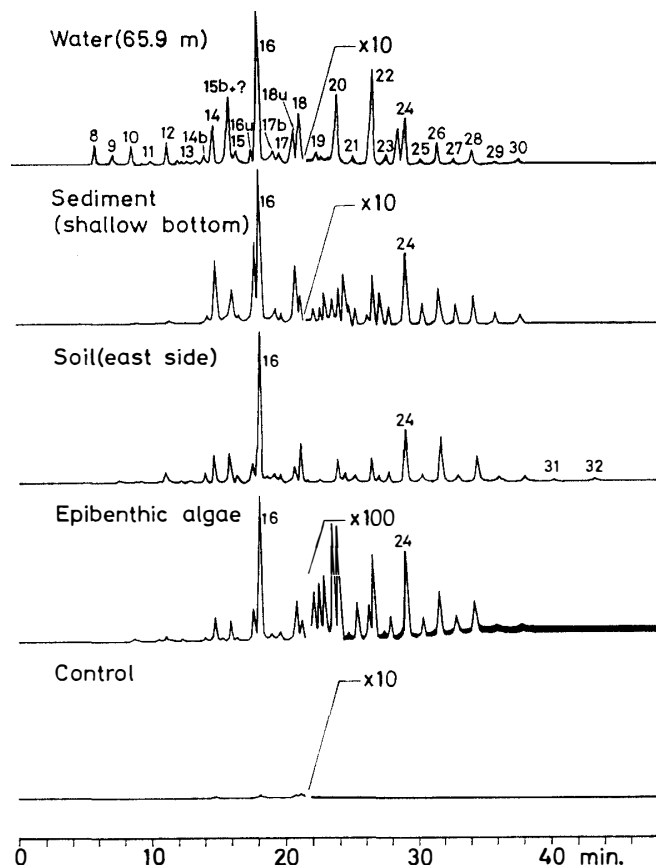


Fig. 4. Mass fragmentograms of the fatty acid fractions obtained from water, sediment, soil and epibenthic algae collected at Lake Vanda. Conditions: Column, glass column (200 cm \times 3 mm i.d.), packed Shimadzu 1.5% OV-1 on 80–100 mesh Chromosorb W; multiplier gain, 2 at 20 eV; other conditions are same as in Fig. 3. 14b, 15b, and 17b: Branched (iso+anteiso)-C₁₄, -C₁₅, and -C₁₇ fatty acids, respectively. 16u and 18u: Unsaturated-C₁₆ and -C₁₈ fatty acids, respectively.

from water, sediment, soil and epibenthic algae collected at Lake Vanda. The mass number m/e 74 is the base peak of the methyl esters of straight chain fatty acids. On the chromatogram, fatty acids are found with the dominance of even carbon numbered acids ranging from C_{8:0} to C_{32:0} including unsaturated and branched acids. Table 4 lists the range of carbon chain length of the acids, their total concentrations and the major constituents with their percentages (more than 10%) of the samples. Fatty acids in the waters, sediments, soils and epibenthic algae are found in the range of C_{8:0} to C_{32:0}, C_{8:0} to C_{32:0}, C_{10:0} to C_{37:0} and C_{8:0} to C_{32:0}, respectively. Generally, the range of carbon chain length is narrow, except for soil collected at the west side of the west lobe of Lake Bonney, compared with those of the Tokyo area (MATSUMOTO, unpublished) and the Ogasawara Islands (MATSUMOTO and

Table 4. Fatty acids found in waters, sediments, soils, and epibenthic algae collected from Ross Island and the Dry Valleys of the McMurdo Sound region.

Sample	Range	Concentration	Major constituents (%)
		($\mu\text{g/l}$)	
Waters			
Blue Lake (surface)	C ₁₂ -C ₃₂	5.9	C ₁₆ (39), C ₁₈ (16), C _{18u} (11), C _{16u} (10)
Home Lake (surface)	C ₈ -C ₂₈	1600	C _{18u} (32), C ₁₆ (29), C _{16u} (28)
McMurdo Station, dumping site (surface)	C ₈ -C ₃₀	2900	C _{18u} (33), C ₁₆ (31), C ₁₈ (24)
Onyx River (surface)	C ₁₄ -C ₃₀	4.6	C ₁₆ (25), C _{16u} (12), C _{18u} (11)
Lake Vanda (5.4 m)	C ₁₄ -C ₃₂	4.8	C ₁₆ (26), C ₁₈ (11), C _{18u} (10)
(30.4 m)	C ₁₄ -C ₃₀	4.0	C _{18u} (32), C ₁₆ (31), C _{16u} (14)
(50.4 m)	C ₁₂ -C ₂₈	7.8	C _{18u} (63), C ₁₆ (12)
(55.4 m)	C ₁₂ -C ₃₀	61	C _{16u} (63), C _{18u} (20)
(60.4 m)	C ₁₂ -C ₃₀	16	C _{16u} (35), C _{18u} (31), C ₁₈ (20)
(65.9 m)	C ₈ -C ₃₀	7.6	C _{18u} (31), C ₁₆ (23)
Unnamed pond, Labyrinth (surface)	C ₁₂ -C ₃₀	7.1	C ₁₆ (59), C ₁₈ (10)
Lake Bonney, east lobe (5.4 m)	C ₁₂ -C ₃₂	9.3	C _{18u} (35), C ₁₆ (34)
(19.4 m)	C ₈ -C ₃₀	8.6	C _{18u} (26), C ₁₆ (25), C ₁₄ (17)
(33.4 m)		nm	
Lake Bonney, west lobe (5.4 m)	C ₁₂ -C ₁₈	2.7	C ₁₆ (30), C _{16u} (29), C _{18u} (17), C ₁₈ (16)
(18.4 m)	C ₁₂ -C ₁₈	2.5	C ₁₆ (38), C ₁₄ (20), C _{18u} (16), C _{16u} (14)
(30.4 m)	C ₈ -C ₃₂	6.2	C ₁₆ (17), C ₁₂ (15), C ₁₄ (15), C _{16u} (15)
Lake Joyce (30.4 m)	C ₁₀ -C ₂₈	5.9	C _{18u} (40), C ₁₆ (20), C ₁₈ (16)
Sediments		($\mu\text{g/g}$)	
Home Lake	C ₈ -C ₃₂	2000	C ₁₆ (33), C _{18u} (18), C _{16u} (14)
Lake Vanda, south-east side (shallow bottom)	C ₁₀ -C ₃₂	8.4	C _{18u} (40), C _{16u} (33), C ₁₆ (13)
Unnamed pond, Labyrinth	C ₈ -C ₃₂	64	C _{16u} (60), C _{18u} (29)
Lake Bonney, west lobe	C ₈ -C ₃₂	140	C _{18u} (30), C ₁₆ (27), C ₁₄ (19), C _{16u} (15)
Lake Joyce	C ₈ -C ₃₂	94	C ₁₆ (57), C _{18u} (13)
Soils		($\mu\text{g/g}$)	
Lake Vanda, east side	C ₁₀ -C ₃₂	3.0	C ₁₆ (21), C _{18u} (19), C _{16u} (13)
Lake Bonney, west lobe, west side	C ₁₀ -C ₃₇	0.72	C ₂₈ (18)
Epibenthic algae		($\mu\text{g/g}$)	
Coast Lake	C ₈ -C ₃₂	4100	C _{18u} (29), C _{16u} (24), C ₁₆ (23)
Onyx Pond	C ₁₂ -C ₃₂	180	C ₁₆ (39), C _{16u} (23), C _{18u} (21)
Lake Vanda, south-east side	C ₈ -C ₃₂	240	C ₁₈ (55), C ₁₆ (18), C _{16u} (18)

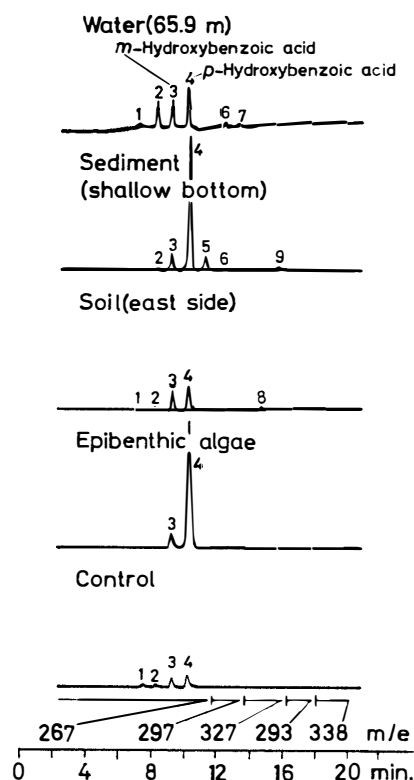
C_{16u} and C_{18u}: Unsaturated-C₁₆ and -C₁₈ fatty acids, respectively. nm: Not measured.

HANYA, 1978), where the range of the acids is usually $C_{8:0}$ to $C_{34:0}$. The narrow range of the acids in the McMurdo Sound region might reflect the absence of vascular plants because $C_{34:0}$ acid is present in epicuticular waxes of vascular plants (MATSUDA and KOYAMA, 1977).

The concentrations of fatty acids in the waters, sediments and soils are low except for Home Lake and dumping site at McMurdo Station where the concentrations are significantly high. Especially, the concentration of the acids of the soil collected at the west side of Lake Bonney is extremely low. It may be one of the features of the acids in polar deserts. In the waters of Lake Vanda, the highest value of the acids is obtained from a depth of 55.4 m. It is of interest to note that the acids may be associated with the vertical microbial community.

The major fatty acids of the waters, sediments and soils (except for the soil collected from the west side of Lake Bonney) are lower molecular weight ($<C_{20}$) ones such as saturated and unsaturated- C_{16} and - C_{18} acids as shown in Table 4. The major fatty acids are similar to those of algae and, therefore, it seems that the algae are one of the main sources of fatty acids. On the other hand, the wide range (C_{10} – C_{37}) and the dominance of higher molecular weight fatty acid (C_{28}) for soil at Lake Bonney are of interest, but their sources are not clear because the dominance of these acids in living organisms except for vascular plants is scarcely known.

Fig. 5. Mass fragmentograms of the phenol-carboxylic acid fractions obtained from water, sediment, soil, and epibenthic algae collected at Lake Vanda. Conditions: Same as in Fig. 3 except for column temperature, 100–200°C at 6°C/min and multiplier gain, 3.



It is, however, probable that they come from some microorganisms, although their fatty acid composition is not yet known.

3.4. Phenolcarboxylic acids

Fig. 5 shows the mass fragmentograms of the phenolcarboxylic acid fractions obtained from water, sediment, soil and epibenthic algae collected at Lake Vanda. The mass numbers at m/e 267, 297, 327, 293 and 338 correspond to molecular ion (M)–15 of *o*-, *m*- and *p*-hydroxybenzoic, vanillic, syringic and *p*-coumaric acids and M of ferulic acid TMS derivatives, respectively. The retention time of the peaks #2, #3, #4 and #6 correspond to *o*-, *m*- and *p*-hydroxybenzoic and vanillic acids, respectively. Furthermore, *m*- and *p*-hydroxybenzoic acids were confirmed by the direct comparison of their mass spectra with those of authentic compounds. However, other peaks were not ascertained by their mass spectra because of their small quantity and unresolved mixtures.

Table 5 summarizes the phenolcarboxylic acids found in the waters, sediments, soils and epibenthic algae. *m*- and *p*-Hydroxybenzoic and *o*- and *p*-hydroxyphenylacetic acids were identified and the presence of *o*-hydroxybenzoic and vanillic acids was suggested for the samples except for the water of the dumping site at McMurdo Station where *o*-, *m*- and *p*-hydroxybenzoic, vanillic, ferulic and *p*-hydroxyphenylacetic acids were identified and the presence of syringic and *p*-coumaric acids was suggested. These phenolic acids found in the water of the dumping site must be derived from sewage (MATSUMOTO, unpublished) and the degradation products of wood (SMITH, 1955; PEARL and BEYER, 1961), which was used for the construction and packings.

The phenolcarboxylic acids found in the McMurdo Sound region except for the water of the dumping site are remarkably different from those of river and pond waters (MATSUMOTO *et al.*, 1977; MATSUMOTO and HANYA, 1978) and river and lake sediments (MATSUMOTO, unpublished) of the Tokyo area and the Ogasawara Islands, where a series of phenolcarboxylic acids, *p*-hydroxybenzoic, vanillic, syringic, *p*-coumaric and ferulic acids are found, but *o*- and *p*-hydroxyphenylacetic acids are not detected in both areas. Therefore, the lack of syringic, *p*-coumaric and ferulic acids for the McMurdo Sound region must be attributed to the absence of vascular plants, since little is known on the wide occurrence of a series of phenolcarboxylic acids in living organisms except for vascular plants.

The concentrations of *p*-hydroxybenzoic acid in the lake waters are ranging from 0.02 to 12 $\mu\text{g/l}$ depending on the sampling depths and locations (Table 5). In the waters of Lakes Vanda and Bonney, the concentrations of *p*-hydroxybenzoic acid in the bottom waters are higher than those in the upper layers, as in the case of the TOC values. The highest concentration of *p*-hydroxybenzoic acid is found in the bottom water of the west lobe of Lake Bonney. The concentrations of *p*-hydroxybenzoic acid in the soils and sediments are extremely low. *o*-Hydroxy-

Table 5. Phenolcarboxylic acids found in waters, sediments, soils, and epibenthic algae collected from Ross Island and the Dry Valleys of the McMurdo Sound region.

Sample	OHA ¹		MHA ²		PHA ³	VA ⁴		OPA ⁵	PPA ⁶
Waters					($\mu\text{g/l}$)				
Blue Lake (surface)	0.01	B	—		0.05 B	—		—	—
Home Lake (surface)	—		0.3	B	3.7 A	—		—	+ A
McMurdo Station, dumping site (surface)*	3.4	A	7.4	A	9.1 A	5.9	A	—	+ A
Onyx River (surface)	0.03	B	—		0.02 B	—		—	—
Lake Vanda (5.4 m)	—		—		—	—		—	—
(30.4 m)	—		—		0.02 B	—		—	—
(50.4 m)	—		—		0.02 B	—		—	—
(55.4 m)	—		—		0.04 B	—		—	—
(60.4 m)	0.03	B	0.02	B	0.2 B	—		—	—
(65.9 m)	0.1	B	0.2	B	0.2 B	0.1	B	+ A	—
Unnamed pond, Labyrinth (surface)	—		—		—	—		—	—
Lake Bonney, east lobe (5.4 m)	—		—		0.07 B	—		—	—
(19.4 m)	0.2	B	0.2	B	2.9 A	0.5	B	—	—
(33.4 m)	—		0.1	B	6.1 A	0.4	B	—	—
Lake Bonney, west lobe (5.4 m)	—		—		0.06 B	—		—	—
(18.4 m)	—		—		0.05 B	—		—	—
(30.4 m)	—		—		12 A	—		—	—
Lake Joyce (30.4 m)	—		—		0.1 B	—		—	—
Sediments					($\mu\text{g/g}$)				
Home Lake	0.07	B	0.23	A	2.0 A	—		—	+ A
Lake Vanda, south-east side (shallow bottom)	0.001	B	0.003	B	0.024 A	0.001	B	—	+ A
Unnamed pond, Labyrinth	—		—		0.054 A	—		—	—
Lake Bonney, west lobe	0.012	B	0.038	A	0.12 A	0.008	B	—	—
Lake Joyce	0.011	B	—		0.24 A	0.009	B	—	+ A
Soils					($\mu\text{g/g}$)				
Lake Vanda, east side	0.003	B	0.018	A	0.035 A	0.003	B	—	—
Lake Bonney, west lobe west side	0.001	B	—		0.005 A	0.002	B	—	—
Epibenthic algae					($\mu\text{g/g}$)				
Coast Lake	0.2	B	0.90	A	3.9 A	—		—	+ A
Onyx Pond	0.022	B	0.046	B	0.33 A	0.029	B	—	—
Lake Vanda, south-east side	0.004	B	0.017	B	0.16 A	0.004	B	—	+ A

1: *o*-Hydroxybenzoic acid. 2: *m*-Hydroxybenzoic acid. 3: *p*-Hydroxybenzoic acid.
 4: Vanillic acid. 5: *o*-Hydroxyphenylacetic acid. 6: *p*-Hydroxyphenylacetic acid.
 *: Concentrations of syringic, *p*-coumaric, and ferulic acids were 2.0 B, 1.3 B, and 19
 $\mu\text{g/l}$ A, respectively. —: Not detected. +: Presence but not quantified. Identification:
 A, retention time and mass spectrum; B, retention time of fragment ion.

phenylacetic acid is found only in the bottom water of Lake Vanda, but *p*-hydroxyphenylacetic acid is detected in the surface water of Home Lake and in the sediments and epibenthic algae. The difference of the constituents of the phenolcarboxylic acids among the samples may be due to the difference of the kinds of source organisms.

There have been a few papers reporting the presence of phenolcarboxylic acids in organisms and their metabolites except for vascular plants. *o*-Hydroxybenzoic acid is produced by actinomycets (RATLEDGE, 1964; RATLEDGE and CHAUDHRY, 1971; RATLEDGE and HALL, 1971) and *Aerobacter aerogens* (RATLEDGE, 1964). *o*-, *m*- and *p*-Hydroxybenzoic acids are formed by *Penicillium griseofulvum* (SIMONART *et al.*, 1960). *p*-Hydroxybenzoic acid is also produced by *Penicillium* spp. (TANENBAUM and BASSETT, 1958; SIMONART and VERACHTERT, 1966), *Aspergillus fumigatus* (SIMONART and VERACHTERT, 1966), actinomycets, and *Aerobacter aerogens* (RATLEDGE, 1964). Furthermore, SHIVRINA *et al.* (1959) reported the presence of *p*-hydroxybenzoic and vanillic acids in bracket fungi (Polyporaceae). *o*-Hydroxyphenylacetic acid has been detected in mother liquors of *Penicillium* mould (HARBONE and SIMMONDS, 1964). *p*-Hydroxyphenylacetic acid has been found in the metabolites of *Penicillium* sp., *Aspergillus* sp. (SIMONART and VERACHTERT, 1966), and yeast (HARBONE and SIMMONDS, 1964).

Fungi including *Aspergillus* spp. and *Penicillium* spp., actinomycets and bacteria have been found by many workers in Ross Island and the Dry Valleys of the McMurdo Sound region (MEYER *et al.*, 1962; DI MENNA, 1966; SUGIYAMA *et al.*, 1967; BENOIT and HALL, 1970; CAMERON *et al.*, 1970; HOROWITZ *et al.*, 1972; WAGURI, 1976; KRYCE *et al.*, 1977). The major sources of the phenolcarboxylic acids must, therefore, be those organisms and epibenthic algae in the lakes and their environments.

4. Conclusion

The TOC and EOC values of lake waters showed a wide range of variation depending on the sampling depths and the environmental conditions. The low contents of TOC, total-N and EOC for the sediments and soils may reflect the low productivity of the lakes and their environments. Generally the low contents of hydrocarbons and fatty acids were found for lake waters, sediments and soils. The dominance of unsaturated hydrocarbons and the narrow range of carbon chain length for fatty acids are thought to be a feature of this cold desert area. The dominance of *p*-hydroxybenzoic acid among the phenolcarboxylic acids found and the lack of syringic, *p*-coumaric and ferulic acids of the lake waters, sediments and soils must reflect the absence of vascular plants. The sources of those organic compounds are algae and other organisms in the lakes and their environments.

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