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Acidic Nature of Dissolved Organic  
Matter in Coloured Natural Waters

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## MANAGEMENT PERSPECTIVE

Dissolved organic matter (DOM) is an important constituent in coloured waters from southwestern Nova Scotia. An improvement in our understanding of the distribution and chemical character of DOM in these waters is necessary if we are to learn how it affects water quality. Acidic fractions of DOM are responsible for the natural acidity of these waters, and the contribution of natural acids to the total acidity of these waters is a major concern of the LRTAP program. Complexation by DOM fractions is a possible mechanism for protecting local fish populations from the toxic effects of aluminum and other metals. To effectively address these concerns, the spatial and seasonal variations in the distribution of organic acids, their acid content, and acid strengths must be known. This preliminary report presents initial results from a continuing study. It shows that acidic fractions make up about half of the DOM at sites in Kejimikujik National Park, NS and in Barrington Township, NS. Variations in type of organic acid are found to occur when samples are grouped by location and season.

## PERSPECTIVE-GESTION

Les matières organiques dissoutes (MOD) sont une importante composante des eaux colorées que l'on retrouve au sud-ouest de la Nouvelle-Écosse. Il est nécessaire de mieux connaître la distribution et les caractéristiques chimiques des MOD dans ces eaux si nous voulons savoir comment leur présence influe sur la qualité de l'eau. Les fractions acides des MOD expliquent l'acidité naturelle de ces eaux et la contribution d'acides naturels à l'acidité totale de ces eaux est une question importante sur laquelle on se penche dans le cadre du programme TGDPA. La complexation par les fractions de MOD est un mécanisme possible de protection des populations locales de poissons contre les effets toxiques de l'aluminium et d'autres métaux. Pour qu'on puisse mieux comprendre ces questions, il est essentiel de connaître les variations spatiales et saisonnières de la distribution des acides organiques, leur teneur en acidité et la force des acides. Le présent rapport préliminaire fournit les premiers résultats obtenus dans le cadre d'une étude en cours. Les résultats montrent que les fractions acides composent environ la moitié des MOD à certains sites du parc national de Kejimikujik en Nouvelle-Écosse et du Canton de Barrington en Nouvelle-Écosse. On note des variations du type d'acide organique lorsque les échantillons sont regroupés par site et par saison.

## ABSTRACT

Dissolved organic matter (DOM) is an important constituent in coloured waters from southwestern Nova Scotia, influences their acidity<sup>1,2</sup>, and may be important in protecting local freshwater fish populations from the toxic effects of Al<sup>3-6</sup>. DOM was fractionated<sup>7-9</sup> from 71 samples of bog, creek, lake, and river waters. Recent studies have determined the acidic character of similar waters<sup>10-12</sup> and a model has been used to estimate the carboxylate (COO<sup>-</sup>) content of natural waters based on measurements of pH and dissolved organic carbon (DOC)<sup>10</sup>. In our samples only 53±16% of the DOC was found to be associated with acidic fractions, and on average about 10% of DOC is associated with the more hydrophilic acidic component of DOM, a fraction which likely contains stronger organic acids<sup>8,11-13</sup>, and which is ignored by the DOC model<sup>10</sup>. Variations in the relative proportions of acidic organic fractions occur when samples were grouped by sampling environment or by season. Little variation was found when hydrologic conditions were used to group samples. These results indicate that more information regarding the acidic nature of DOM, and its seasonal distribution, at a given site, is necessary to determine the COO<sup>-</sup> content of natural waters. Once known, COO<sup>-</sup> content can be used to model the complexation of metals, such as Al, and aid in prediction of fish toxicity.

## RESUME

Les matières organiques dissoutes (MOD) sont une importante composante des eaux colorées qu'on trouve au sud-ouest de la Nouvelle-Ecosse. Elles influencent l'acidité<sup>1,2</sup> de ces eaux et pourraient bien jouer un rôle important dans la protection des populations locales de poissons d'eau douce contre les effets toxiques de l'Al<sup>3-6</sup>. Les MOD ont été fractionnées<sup>7-9</sup> à partir de 71 échantillons provenant d'eau recueillie dans des tourbières, des ruisseaux, des lacs et des rivières. Des études récentes ont permis de déterminer le caractère acide d'eaux semblables<sup>10-12</sup> et un modèle a été utilisé pour estimer la teneur en carboxylate ( $\text{COO}^-$ ) des eaux naturelles en fonction de mesures du pH et de la teneur en carbone organique dissous (COD)<sup>10</sup>. Dans nos échantillons, seuls  $53 \pm 16$  % du COD était associé à la composante acide plus hydrophile des MOD, fraction qui probablement renferme des acides organiques plus forts<sup>8,11-13</sup> et dont ne tient pas compte le modèle du COD<sup>10</sup>. Des variations des proportions relatives des fractions organiques sont observées lorsque les échantillons sont groupés par environnement d'échantillonnage ou par saison. Peu de variation a été observée lorsque les groupements ont été faits en fonction des conditions hydrologiques. Ces résultats indiquent qu'il est nécessaire d'obtenir plus de renseignements concernant la nature acide des MOD et leur distribution saisonnière à un site donné afin de déterminer la teneur en  $\text{COO}^-$  des eaux naturelles. Lorsque cette teneur sera connue, elle pourra être utilisée pour modéliser la complexation des métaux, par exemple Al, et aider à prédire la toxicité pour les poissons.

Filtered water samples were obtained from several areas in southwestern Nova Scotia during the period of July, 1984 - August, 1985 at the specific sites described in Table 1. In this study the total DOM is considered to be humic matter and is fractionated into humic acid (HA) and fulvic acid (FA) fractions as usually defined in soil science<sup>14</sup>. The method of Leenheer<sup>7-9</sup>, slightly modified, was used to further separate the fulvic fraction based on physico-chemical characteristics. Thus a total of seven subfractions of DOM are isolated; HA, fulvic hydrophobic-acids (HPOA), -bases (HPOB), -neutrals (HPON), fulvic hydrophilic-acids (HPIA), -bases (HPIB), and -neutrals (HPIN). Determinations of the relative concentrations of the fractions are based on DOC analyses<sup>8</sup> and are expressed as percentages  $((\text{Fraction-C} / \text{DOC}) \times 100)$ .

The HPOA, HPON and HPIN fractions are the most abundant, comprising on average 28.2, 23.0, and 19.6% of the DOC respectively. Another 25.4% of DOC is associated with the remaining acidic fractions, 14.5% with the higher molecular weight HA and 10.9% resides in HPIA. On average only a small amount of the DOC fractionates into basic fractions, HPOB (3.1%) and HPIB (0.6%) (Figure 1). The total of acidic fractions (HA + HPOA + HPIA) comprises on average 53.6% of the DOC. Commonly DOC in natural waters is thought to be comprised of HA and FA and considered to be polymers of acidic monomers. Researchers who study the carboxylic acid content of these materials usually report it on the basis of DOC<sup>10-12</sup>. Considering that only about half of the DOC is from acidic fractions in these samples, obtained from predominantly acidic environments (average pH=4.6), the perception of the high acidic character of DOC requires moderation. Furthermore, the HA fraction could conceivably contain basic and neutral components as well as acidic ones. HA cannot be fractionated by the same procedures used for FA (because of solubility interferences), so here it is considered to be wholly acidic, "weakened" by its basic and neutral components. Thus 53.6% should be considered as a maximum average acidic fraction content in terms of DOC.

Recently, the total carboxyl (COOH) content of various fractions of DOM have been estimated by direct titration<sup>10,11</sup>. While this procedure provides only operationally-defined estimates<sup>15,16</sup>; it does allow comparisons among different samples and laboratories. Oliver *et al.*<sup>10</sup> studied the variability of COOH content of DOM fractions from a variety of lake, river, and bog waters and reported ranges of 5.1-9.9  $\mu\text{eq COOH/mg-C}$  for HA and 9.9-13.4  $\mu\text{eq COOH/mg-C}$  for FA. The difference in carboxylic content of HPOA and HPFA (10.1 and 13.2  $\mu\text{eq COOH/mg-C}$  respectively) from river water was reported by McKnight *et al.*<sup>11</sup>. Soil leachates, which are presumably more like HA, yielded 5.6-8.3  $\mu\text{eq COOH/mg-C}$ <sup>12</sup>. From these limited data it appears that HPFA can contain up to twice the content of COOH as HA on an equal carbon basis; HPOA is likely intermediate in COOH content. This study shows that the distribution of acidic fractions can vary widely even in samples from similar environments (Table 1 and Figure 1). Therefore, when possible, it is wise to consider the relative acidic contents of the fractions rather than estimating organic acidity empirically from DOC data alone. Further work on quantifying the COOH content of acidic fractions is ongoing and will be reported elsewhere.

The average content of acidic fractions for samples grouped according to sampling environment (Table 1) is compared in Figure 2. Bog interstitial water and water from bog drainage creeks give virtually identical distributions in terms of percentage of DOC. This result is expected considering the hydrological characteristics of a domed *Sphagnum* bog. There is a direct connection between the bog and its drainage creek with little influence from sources outside of the bog. Near the mouths of rivers in southwestern Nova Scotia, an increase in the relative amount of HA is evident compared to headwater streams. A corresponding decrease in HPOA content also occurs along the course of rivers. These observed changes suggest the diagenetic production of HA from FA fractions (especially HPOA) through condensation reactions. Pebblelogitch Lake is a headwater lake

which is flanked by a bog through which the main input stream flows. Consequently the distribution of acidic fractions is similar, on average, to that of headwater streams. In contrast, Beaverskin Lake contains the lowest proportions, on average, of HPOA and HPIA, and the highest relative proportion of HA. This clearwater lake probably receives most of its DOM from the degradation products of phytoplankton with little contribution from the thin soils in its watershed<sup>17</sup>.

Since the COOH contents of these acidic fractions are as yet unknown it is not possible to discuss quantitatively the importance of organic acid contribution to the total acidity of these waters. However, Beaverskin and Pebbleloggitch Lakes may be compared in a preliminary way. These two lakes are about one km apart, and except for the bog on the periphery of Pebbleloggitch Lake, they have similar bedrock, soils, and forest cover in their watersheds, and presumably receive the same atmospheric input. Average pH for Beaverskin Lake over the sampling period was 5.4, and 4.6 for Pebbleloggitch Lake. These two lakes exhibit essentially identical major ion chemistry<sup>18</sup>, but average DOC values were 7.1 and 18.9 mg/l for Beaverskin Lake and Pebbleloggitch Lake respectively. If we assume that the COOH contents of the acidic fractions from these lakes are similar to those determined by the other workers discussed above<sup>10-12</sup>, then the stronger HPOA and HPIA fractions contribute significantly to the lower pH observed in Pebbleloggitch Lake.

All samples described in Table 1 were re-grouped according to hydrological condition (Table 2). "Dry", "intermediate", and "wet" hydrological condition was assigned, in a semi-quantitative manner, on the basis of field observations of water level in lakes and rivers, rain and snow fall, snowmelt, and water table depth in bogs. DOC concentrations decrease on average from dry to wet periods, probably due to dilution by precipitation or snowmelt. However, in terms of average relative proportions of the acidic organic fractions, HPOA and HPIA do not vary greatly among the three hydrological conditions (Table 2). Only the HA fraction



exhibits a relative increase during dry periods. Increased HA contents were observed in the deeper interstitial waters from the bog studied here. As well increased HA content of the bog drainage creek in summer relative to bog surface interstitial water has been reported<sup>19</sup>. During dry periods the bog drainage creek draws a higher proportion of deeper water containing more humified (i.e. higher HA content) DOM.

Greater variation occurred among groups of samples arranged by season than groups arranged by hydrological condition (Table 2). Comparison of the DOC data by seasons with that of hydrological condition suggests that summers are dry and winter, spring, and autumn are wet, as expected given the maritime climate of southwestern Nova Scotia. The influence of temperature and associated changes in biological productivity must be considered in discussing seasonally grouped data. The lack of variation in the average relative content of HPOA regardless of season suggests that this fraction represents a conservative component of the DOM. In contrast, variations in the average HPIA contents may be explained in terms of summer production of soluble acidic components (e.g. Krebs Cycle acids). Autumn rains flush these soluble acids from bogs and soils and yield the highest average proportion of HPIA during this season. Minor thaws during winter mobilize the remainder of the summer production resulting in intermediate average proportion of HPIA. Minimum levels of HPIA are seen during spring following the period of lowest production in winter. Highest average proportions of HA occur during the summer probably due to drawdown as discussed above. In winter the opposite effect is seen with HA. DOM is trapped in the frozen layers of soils and bogs. Winter snowmelt and rainfall flow over saturated bogs and soils; entraining relatively little HA because this fraction is predominantly contained in the deeper layers. Increases in HPIA and HA relative proportions are reflected in higher total acidic fraction content during summer and autumn.

In summary, about half of the DOC in these waters resides in acidic fractions. Samples from different environments (bogs,

creeks, rivers, lakes) exhibit variations in relative proportions of acidic organic fractions. The relationship between the various acidic organic fractions in these waters is not affected by dilution, i.e. average concentrations of fractions track with average DOC, save for an increase in HA during dry periods likely caused by drawdown. Seasonal variations are seen in the relative proportions of HPIA and HA and may reflect changes in production and seasonal hydrology. These effects combined with the variation of DOC content and the possible differences in COOH content of fractions suggests that summer and autumn are likely periods when the organic contribution to total acidity is maximum.

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Table 1

## Descriptions of Sampling Areas in Southwestern Nova Scotia

Sample Type (Fig. 2 Designation)	No. of Samples	Location and Description
Bog Interstitial Water (BOG INT)	12	Water collected by infusion of 7.6 cm piezometers placed in a domed <u>Sphagnum</u> bog in Barrington Twp., NS, and from ponds in the same bog and another in Kejimikujik N.P., NS
Bog Drainage Creek (BOG DRN)	17	Water collected at six locations along the course of Judas Creek which drains the Barrington bog described above
Headwater Streams (HDW STR)	14	Water collected from streams in Kejimikujik N.P. and from Barrington which are located in watersheds containing thin acidic soils
River Mouths (RIV MTH)	15	Water collected from the Clyde, Roseway, Medway, and Mersey rivers at points near their mouths and upstream from the upper limit of tidal influence
Pebbleloggitch Lake (PEB LAK)	6	Surface water from the deepest part of this coloured lake in Kejimikujik N.P. which is flanked by a bog through which the lake's main input flows
Beaverskin Lake (BVS LAK)	7	Surface water from the deepest part of this clearwater lake one km from Pebbleloggitch L., and surrounded by thin soils

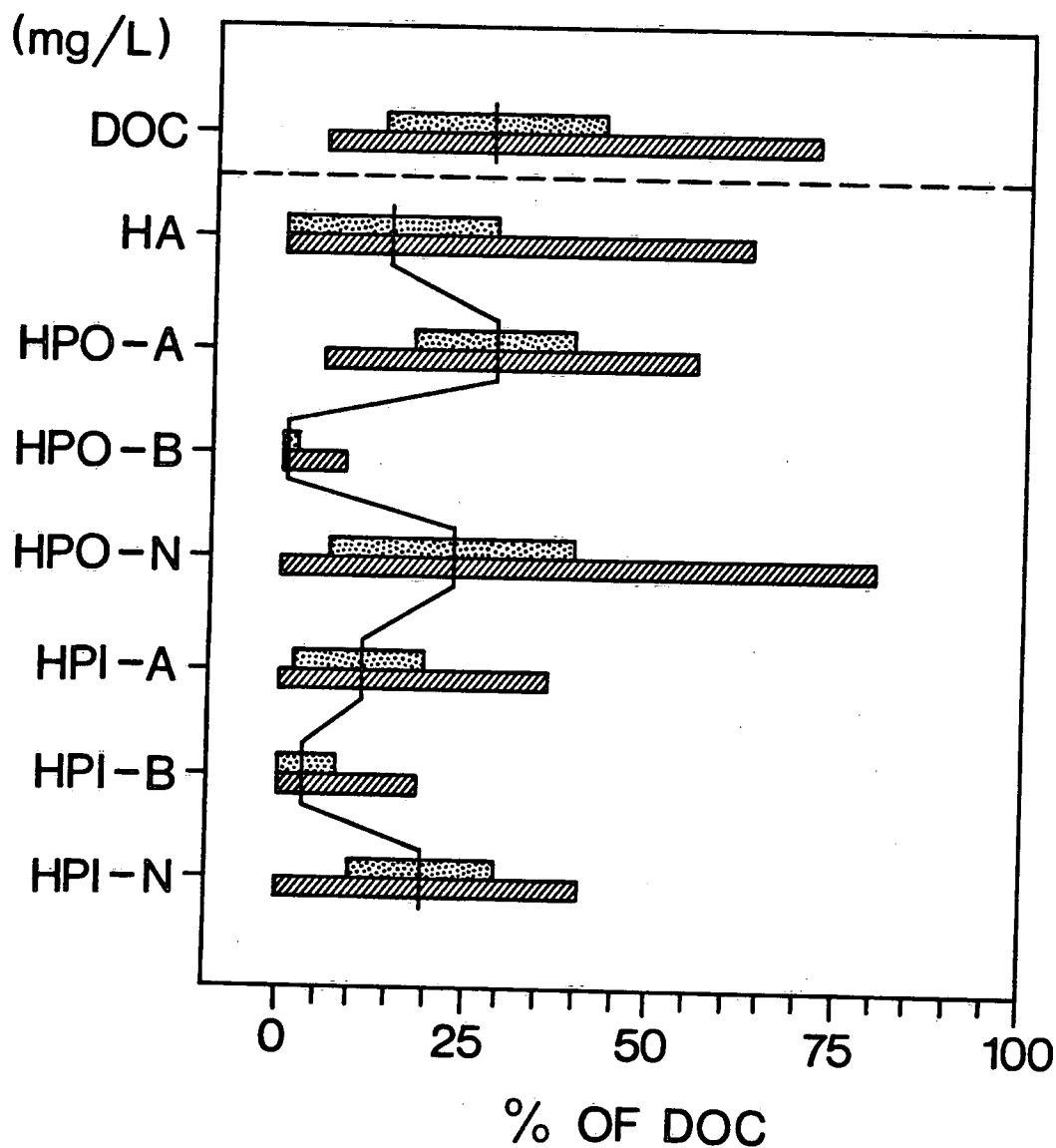


Figure 1

Plot of the total fractionation data set from 71 samples of bog, creek, river, and lake water from southwestern NS. Hatched bars represent the range of values for each fraction, vertical lines are placed at the mean value, and stippled bars represent the standard deviations about the mean.

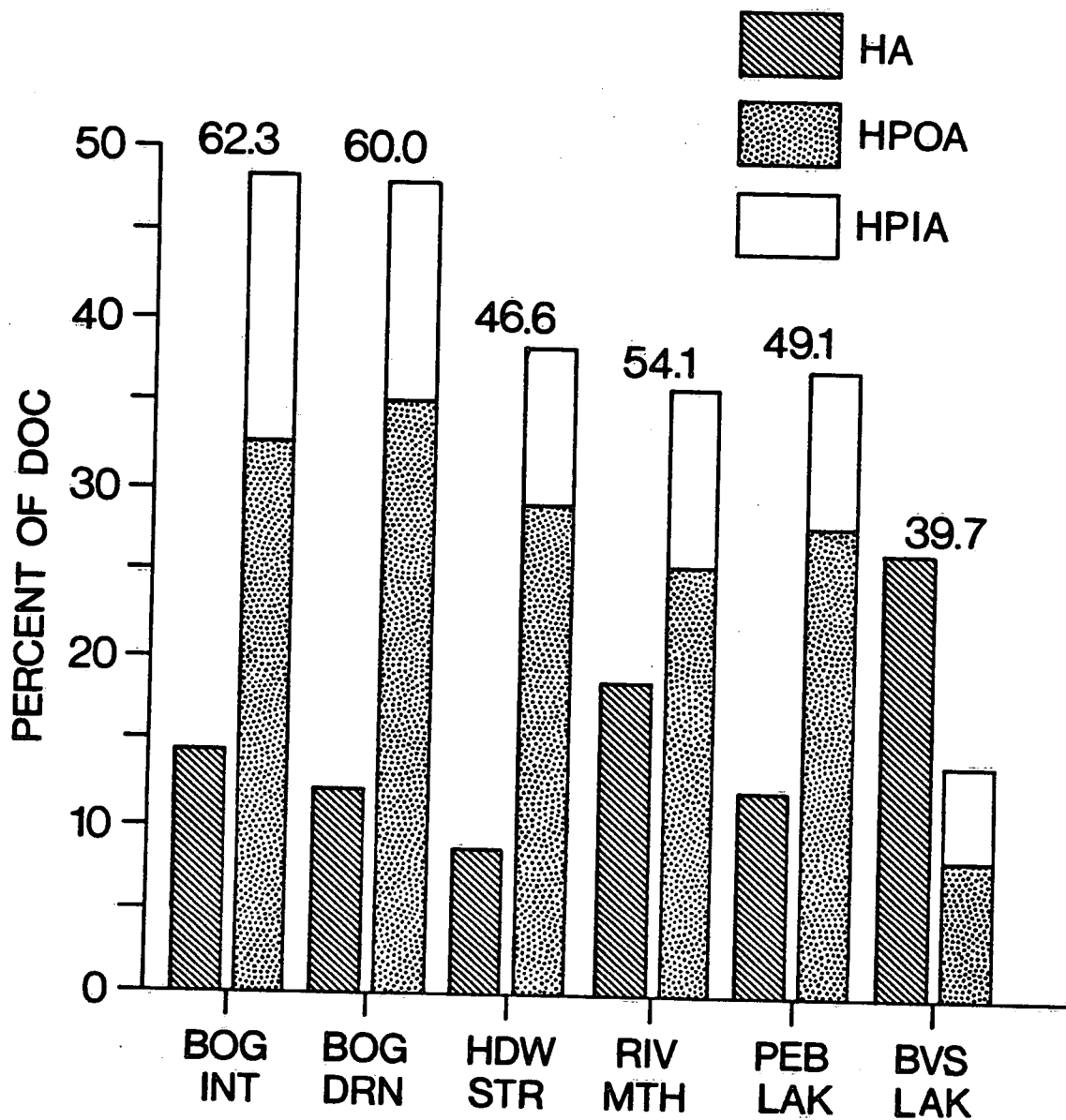


Figure 2

Average acidic organic fraction contents expressed as percentage of DOC. Groupings are by sample type and environment (see Table 1) and without regard to sampling date. Values above each pair of bars represent the sum of acidic fractions, on average, for the group.

Table 2  
Variation in Average DOC and Organic Fraction Composition  
with Hydrologic Regime and by Seasons (N=71)\*

Selection Criteria	No. Samp.	DOC mg/l	HPOA -----	HPIA Percent of DOC	HA	SUM AC -----
Dry Periods	23	33.7	27.1	10.7	18.5	56.3
Intermediate	22	29.4	27.1	12.1	13.1	52.3
Wet Periods	26	21.4	29.9	10.0	12.1	52.0
Winter	14	20.3	27.5	11.0	7.8	46.3
Spring	12	19.7	27.4	6.4	12.5	46.3
Summer	39	34.0	28.7	11.3	17.8	57.8
Autumn	6	22.2	27.4	16.6	12.7	56.7

\* Hydrologic regime assigned without regard to season or sample type (see text).

Winter: Dec, Jan, and Feb

Spring: Mar, Apr, and May

Summer: Jun, Jul, and Aug

Autumn: Sep, Oct, and Nov