RRB-87-66

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DISTRIBUTION PATTERNS OF DISSOLVED ORGANIC MATTER FRACTIONS IN NATURAL WATERS FROM EASTERN CANADA

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October 1987
NWRI Contribution #87-143

Submitted to: Organic Geochemistry, October 1987

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Keywords: DOM fractions, hydrophobic components, hydrophilic components, humic acid, fulvic acid, coloured waters, eastern Canada

Running Title: Distribution patterns of DOM fractions

MANAGEMENT PERSPECTIVE

Dissolved organic matter (DOM) is an important constituent of many natural waters in eastern Canada. Acidic constituents of DOM are responsible for the natural component of the total acidity of these waters. The relative importance of natural and anthropogenic acidity in these waters is a major concern of the LRTAP program. A deeper understanding of the character of DOM by methods used in the present work will enhance our ability to determine the impact of DOM on acidity, and metal complexation, a process which can protect aquatic biota from metal toxicity.

These issues are important to DOE participation in negotiations concerned with reducing the atmospheric loading of sulfur and nitrogen oxides from combustion sources. Opponents of reductions have argued that lake acidification is caused by natural processes including contributions from soil derived DOM, and point to eastern Canada as a prime area where this material is prominent. The results of this study set the scene for further characterization of the acidic strength of DOM fractions so that their contribution to total acidity may be determined on a spatial and seasonal basis.

PERSPECTIVES DE GESTION

Les matières organiques dissoutes (DOM) sont une composante importante de nombreuses eaux naturelles de l'est du Canada. Les composantes acides des MOD sont à l'origine de la part naturelle de l'acidité total de ces eaux. L'importance relative de l'acidité naturelle et de l'acidité anthropique dans les eaux de l'est du Canada est une des grandes préoccupations du programme TADPA. La meilleure compréhension des caractéristiques des MOD découlant des méthodes utilisées dans la présente étude nous permettra de mieux évaluer l'impact des MOD sur l'acidité et la complexation des métaux, processus qui peut protéger le biote aquatique de la toxicité des métaux.

Ces recherches sont importantes pour la participation du MDE aux négotiations portant sur la réduction des charges atmosphériques d'oxyde de soufre et d'azote découlant de la combustion. Les opposants à la réduction soutiennent que l'acidification des lacs est causeé par les processus naturels, parmi lesquels on compte l'apport des MOD provenant des sols, et considèrent l'est du Canada comme l'une des principales régions où ces matières prédominent. Les résultats de cette étude ouvrent la voie à une caractérisation plus poussée de la concentration acide des fractions de MOD, de façon à ce que leur apport à l'acidité totale puisse être déterminé dans le temps et dans l'espace.

ABSTRACT

Dissolved organic matter (DOM) in natural waters from eastern Canada, when fractionated into humic acid (HA) and six fulvic acid sub-fractions, hydrophobic acid, base and neutral (HPOA, HPOB, and HPON), and hydrophilic acid, base, and neutral (HPIA, HPIB, and HPIN), shows a high degree of variability in the distribution of fractions. On average the fractions are ranked by concentration (mgC/L): HPOA > HPON > HA > HPIN > HPIA > HPIB > HPOB, and 59.7% of the dissolved organic carbon (DOC) is contained in acidic fractions (HA + HPOA + HPIA). Localized conditions are more important in determining the character of DOM than are seasonal fluctuations. Evidence suggests that HA and HPOA can be formed, in part, from polycondensation reactions, and that the composition of HPIA and HPIN are influenced seasonally by microbial degradation. Fractionation of DOM assists in distinguishing distribution patterns which are not shown by DOC measurements alone, but further characterization is required to fully understand the influence of DOM character on natural acidity and metal complexation.

RÉSUMÉ

Les matières organiques dissoutes (MOD) des eaux naturelles de l'est du Canada présentent un fort degré de variabilité dans la distribution de leurs fractions lorsqu'elles sont fractionnées en acide humique (AH) et en six sous-fractions d'acide fulvique, soit les acides, les bases et les composés neutres hydrophobes (HPOA, HPOB, et HPON), et les acides, les bases et les composés neutres hydrophiles (HPIA, HPIB, et HPIN). En moyenne, les fractions sont classées par concentration (mgC/L): HPOA > HPON > HA > HPIN > HPIA > HPIB > HPOB, et 59.7 % du carbone organique dissous (COD) se trouvent dans les fractions acides (HA + HPOA + HPIA). Les conditions propres à l'endroit sont plus importantes pour déterminer ces caractéristiques des MOD que les fluctuations saisonnières. Selon les données recueillies, il semble que HA et HPOA peuvent se former, en partie, par des réactions de polycondensation, et que la composition de HPIA et HPIN est influencée saisonnièrement par la dégradation microbienne. Le fractionnement des MOD aide à distinguer des configurations de distribution que ne revèlement pas les seules mesures du COD, mais une caractérisation plus poussée est nécessaire pour bien comprendre l'influence des caractéristiques des MOD sur l'acidité naturelle et la complexation des métaux.

INTRODUCTION

For some time the acidity of natural waters has been the subject of much controversy, especially in connection with the global problem of "acid rain". One aspect of the controversy is the delineation of the role that natural acidity from dissolved organic matter (DOM) plays in terms of the total acidity. Some have proposed that acidification of soils by organic matter, and other natural processes are the most important sources of acidity to lake waters (Rosenqvist, 1978; Krug and Frink, 1983). Others (Henriksen, 1979, 1980; Wright et al., 1980; LaZerte and Dillon, 1984; Charles et al., 1986; Glass et al., 1986; Jeffries et al., 1986; Linthurst et al. 1986; Underwood et al., 1987) have shown that atmospheric deposition of strong acids caused by pollution from combustion sources is related to and likely responsible for large scale acidification of aquatic ecosystems. It is possible that both organic and inorganic acidity are important in some areas (Patrick et al., 1981), and this has been recently shown for Nova Scotia waters (Gorham et al., 1986; Kerekes et al., 1986) and in Finland (Kortelainen et al., 1986; Kortelainen and Mannio, 1987). The question of degree remains open for most areas. It appears that on a large scale organic acidity plays only a minor role in lake acidification (Jeffries et al., 1986; Linthurst et al., 1986) in North America.

To address this question properly, it is ultimately necessary to be concerned with the character of humic matter in aquatic systems. This is particularly true in areas with coloured natural waters

containing high concentrations of DOM; a situation common in eastern Canada. The acidic character of DOM is of most concern and has been studied previously in a number of areas (Perdue et al., 1980; Oliver et al., 1983; Cronan and Aiken, 1985; McKnight et al., 1985; Kortelainen et al., 1986). However it is also important to consider the character of all components of the DOM, especially when modelling acidification on the basis of dissolved organic carbon (DOC), which includes components other than acidic ones. Another reason to study the character of DOM is to aid in understanding the mechanisms of complexation of metals which may otherwise be toxic to aquatic organisms. These and other issues reflecting the complexities of the "DOM problem" are well documented in Jones et al. (1986).

Aquatic humic matter has been the focus of much study for the past two decades, and the subject has been reviewed comprehensively by Thurman (1985). Soil humic matter has been reviewed several times by various authors, for example Stevenson (1982). In many ways aquatic humic matter and soil humic matter are very similar (Thurman, 1985), and it can be said that they are really the same thing. Discussions concerning humic matter character frequently result in a debate over operational definitions. Here the connection between the soil and aquatic fields is made in a simple way. The DOM in the aquatic systems studied (bogs, streams, lakes, rivers, etc.) is considered to be entirely humic matter "extracted" from the surrounding soils by natural leaching processes at ambient pH. In this way the "natural extract" is analogous to the base extract commonly used to define soil

humic matter. Subsequent fractionation and characterization of the DOM utilizes techniques developed by both soil and aquatic chemists.

The purpose of this work is to determine the general character of DOM found in natural waters collected from a variety of sampling environments at three study areas in eastern Canada. This information will be used to evaluate the influence of DOM on organic acidity, metal complexation, fish toxicity, and the impact of peatland development. Preliminary reports are available for background information (Bourbonniere, 1985; Glooschenko et al., 1985; Bourbonniere, 1986a,b; Bourbonniere and Richmond, 1986; Bourbonniere et al., 1987; Richmond and Bourbonniere, 1987).

MATERIALS AND METHODS

Sampling Sites

Filtered water samples were obtained from three study areas in eastern Canada during the period of July, 1984 - March, 1986 (Fig. 1). At Sept-Iles, Que. samples were taken from six sites, three times each under different climatic conditions. These sites are in bogs or bog drainage representing different degrees of development for horticultural peat. In Kejimkujik N.P., and nearby areas, samples representing a broad range of DOM content were collected over a 20-month period from lakes, rivers, headwater streams, river mouths, and a bog. Barrington Bog, N.S. is an undeveloped, domed, Sphagnum bog with natural drainage occurring through Judas Creek to a salt marsh at the mouth of the Clyde River. Samples were taken at various times over a 21-month period along the course of Judas Creek, from the Clyde River, and from pore waters in the bog proper. Further details concerning the types of sampling sites appear in Table 1, and sampling methodology details can be found in Bourbonniere et al. (1987).

Fractionation of DOM

The DOM from 160 samples, "natural extracts", was fractionated into humic acid (HA) and fulvic acid (FA) fractions as usually defined in soil science (Stevenson, 1982). The method of Leenheer and co-workers (Leenheer, 1981, 1985; Leenheer et al., 1982; Leenheer and Noyes, 1983), slightly modified (Richmond and Bourbonniere, 1987), was used to further separate the fulvic fraction based on physico-chemical

characteristics. Thus a total of seven sub-fractions of DOM are isolated; HA, fulvic hydrophobic-acid (HPOA), -base (HPOB), and -neutral (HPON), and fulvic hydrophilic-acid (HPIA), -base (HPIB), and -neutral (HPIN). A brief description of this fractionation follows.

HA is precipitated from the filtered water by acidification to pH<2 using concentrated HCl. After standing at least eight hours, the HA is isolated by filtration (Whatman 934-AH glass fiber). The remaining DOM is defined as the FA fraction and is subjected to further fractionation. Hydrophobic sub-fractions are defined by their ability to adsorb onto Amberlite XAD-8 resin at pH=6 or pH=2, combined with their ability (or lack thereof in the case of HPON) to be eluted from the resin by dilute acid or base. Hydrophilic sub-fractions do not adsorb onto the XAD-8 resin at either pH. HPIB (at pH=2) is defined by complexation onto a strong acid cation exchange resin and elution with 1N NaOH. HPIA (at pH=2) exchanges onto a strong base anion exchange resin and elutes with 1N NaOH also. HPIN is not adsorbed by any of the three resins.

DOC determinations

All DOC determinations were performed on a Beckman Model 915-A Total Carbon Analyzer after acidification with 12N HCl and purging with nitrogen where necessary. Total DOC was determined on the glass fiber filtered sample and FA (mgC/L) on the filtered sample following HA precipitation. HA concentrations were determined by difference. Determinations of the relative concentrations of the other fractions are based on DOC analyses (Leenheer et al., 1982, Richmond and Bourbonniere, 1987). In this paper concentrations are expressed

either as mg-Fraction-C/L or as percentages of the total DOC: (Fraction-C / DOC) x 100.

RESULTS AND DISCUSSION

RESULTS FOR THE ENTIRE DATA SET

- DOM fractionations were completed on 160 of the samples collected for this study. Statistical data (in mgC/L) for this set appear in Table 2 as well as the calculated average distribution of DOC among the seven organic fractions. The HPOA, HPON and HA fractions are the most abundant, comprising on average 31.2, 20.0, and 17.7% of the DOC respectively. Another 10.8% of DOC is associated with the remaining acidic fraction, HPIA, and 16.3% in the HPIN fraction. On average only a small amount of the DOC fractionates into basic fractions, HPOB (0.59%) and HPIB (3.40%), and these will be ignored from here on. The total of acidic fractions (HA + HPOA + HPIA) comprises on average 59.7% of the DOC.

Commonly DOM in natural waters is thought to be comprised of HA and FA which are considered polymers of acidic monomers. Previously reported values of the acidic fraction content of DOM in coloured and clear waters from lakes, wetlands, rivers, and streams range from 75-89% of the DOC (Malcolm, 1985; Thurman, 1985). On average only about 60% of the DOC is from acidic fractions in the present samples obtained from predominantly acidic environments (average pH=4.6); the perception of the highly acidic character of DOM requires moderation. Furthermore, HA likely contains basic and neutral components as well as acidic ones, but cannot be fractionated by the same procedures used for FA (because of solubility interferences), so it is considered to be wholly acidic, "weakened" by its basic and neutral components.

Thus the average value of 59.7% of DOC residing in acidic fractions would be decreased if basic and neutral components of HA could be isolated.

For most of the parameters in Table 2 the ranges determined are rather broad and quite variable as indicated by relative standard deviation (RSD) values. To some extent this is attributable to the variety of sample types and seasonal fluctuations, as will be seen later; but variability can also arise from the derived nature of some of the data. HA, HPIA, HPIB, and HPON are determined by the difference of at least two DOC determinations; carbon measurements for DOC, HPOA, HPOB, and HPIN are direct (Richmond and Bourbonniere, 1987).

RESULTS FOR SAMPLES GROUPED BY TYPE

The average contents of acidic and neutral fractions, pH, and DOC for samples grouped according to sampling environment or "type" (see Table 1), and without regard for sampling date, are shown in Table 3. Such grouping leaves temporal effects as the only major source of data variability. In comparison to the variability of the fractions for the entire data set (Table 2), the grouped data exhibit lower RSD values for most cases showing that localized conditions can have an effect on the composition of DOM. Comparing RSD values in Tables 2 and 3, grouping results in a decrease in variability for most cases.

For example, DOC, HPOA and HPIN show reduced RSD values for all cases after grouping. HA variability decreased in only a few cases suggesting that seasonal fluctuations in HA content are important even

within the same sampling environment. HPIA variability is decreased by sample grouping except in those environments which might be considered as "integrated", RVM, BVS, and, to a lesser extent, PEB; these are recipients of DOM from multiple sources, all of which may have seasonal fluctuations. HPON, like HA, shows little change in variability between grouped and ungrouped data except for BUP and BLP which show two-fold greater variability and BSL which exhibits about half. The former may arise because of intimate contact between pore water and peat, therefore greater quantities of the more "hydrocarbon-like" components which constitute the HPON fraction. In the BSL case, HPON may be the first fraction to coagulate or adsorb onto particulates and be deposited in flowing environments, a process which should be enhanced by increased ionic strength (Mayer, 1985).

DISTRIBUTIONS OF DOC FOR SAMPLES GROUPED BY TYPE

Comparison of the average composition of the DOM in samples grouped by type is more easily made if the distribution of DOC among the fractions is plotted as in Fig. 2. The average relative concentrations of the fractions are expressed as percentages of the sample DOC.

Dissolved Organic Carbon

Bog related samples contain the highest average DOC concentrations (Fig. 2a), especially pore water samples (BUP and BLP), but also the samples from bog drainage (BND, BAD, and BSL). This is expected because of the highly organic (peaty) character of the watersheds in the bog areas. Samples from more integrated

environments, headwater streams (HWS), river mouths (RVM), and Pebbleloggitch Lake (PEB) generally contain less DOC, even though they are coloured. The clear water in Beaverskin Lake (BVS) averages lowest in DOC concentration. These watersheds contain some bogs, but also forested areas with thin organic layers overlying mineral soils (Freedman and Clair, 1987) except for Beaverskin Lake which is almost free of organic soils (Kerekes et al., 1982).

Humic Acid (HA)

Average relative concentrations of HA for the various sample types appear in Fig. 2b. The most integrated sample types, RVM, PEB, and BVS contain a higher proportion of this more highly polymerized fraction of the DOM. The difference in HA content between RVM samples and the less integrated HWS samples suggests that HA may be a diagenetic product of the polymerization of FA fractions, a process that should be favoured by the increased aeration experienced as water moves along a river system. Alternatively, the increased HA content at river mouths relative to headwater streams may be related to increased leaching of soil HA by extensive damming.

Pore water from the lower layers of bogs contain approximately twice the HA content as upper layers (Fig. 2b). In the deeper layers the DOM is representative of more highly decomposed plant material, which is preserved in the relatively anaerobic and immobile environment. Preservation of HA may be the primary reason for the higher average DOC concentration in BLP samples (Fig. 2a). Bog drainage samples contain higher relative proportions of HA than BUP samples but less than BLP samples. This suggests that some

polymerization may occur even in short watercourses, or it may be evidence that deeper contribution to bog drainage varies temporally.

Hydrophobic Acid (HPOA)

The average relative contribution of HPOA to the DOC is nearly invariant for most sample types and comprises the largest fraction of the DOM for all types except BVS (Fig. 2c). Beaverskin Lake and BLP samples show the lowest relative HPOA content, and it may be significant that these same two types were highest in average relative HA content (Fig. 2b). If polycondensation occurs in these environments, then it seems reasonable that HPOA, consistent with its physico-chemical definition, would be among the easiest fractions to polymerize. Beaverskin Lake receives much of its DOM from the degradation products of phytoplankton (Kerekes, 1984) with little contribution from the thin soils in its watershed (Kerekes et al., 1982), unlike all of the other sampling locations. This strongly suggests that HPOA is soil derived and a major source of the colour of DOM. This is corroborated by observations during DOM fractionation where most of the colour of the FA fraction is represented by the HPOA sub-fraction (Richmond and Bourbonniere, 1987).

Hydrophilic Acid (HPIA)

The HPIA fraction is more soluble and its concentrates are much less coloured than those of HPOA. It generally exhibits the lowest relative concentrations of the five DOM fractions discussed here (Fig. 2d), ranging on average, from 3.5-15.4% of the DOC. Higher relative proportions of the DOC appear in the HPIA fraction in bog related samples and somewhat lower proportions occur in integrated sample

types. Some evidence suggests that HPIA contains lower molecular weight (poly-) carboxylic acids and hydroxy acids (Leenheer, 1981; McKnight et al., 1985; Bourbonniere, 1986a). Metabolic intermediates of this type are common (see e.g. Karlson, 1968), and if they occur in HPIA, they represent strong and labile acids which are diagenetically close to biochemical sources. Among the sample types represented here, BUP and BLP are the nearest to their biochemical sources, and these sample types show the highest proportions of HPIA.

Hydrophobic Neutral (HPON)

This fraction probably contains hydrocarbons and longer chain length lipids containing carbonyls such as wax esters, (Leenheer, 1981). Amorphous polymers with little peripheral functionality, and moderate to high molecular weight would fit within the operational definition of HPON. All of these types of materials would be relatively unreactive and stable; or they could be stable products of diagenetic reactions. In either case they might be expected to accumulate in integrated systems and in the deeper layers of bogs. Thus the higher relative proportions of HPON which occur in HWS, PEB, BVS, and to a lesser extent RVM (Fig. 2e) may be explained by higher soil (as opposed to bog) influence. The higher HPON content in BLP, BND, and BAD relative to BUP suggests that some portion of HPON is diagenetic, and that natural and especially amended bog drainage contains a component of deeper pore water.

The very high HPON content of the BVS dissolved organic matter may be explained by the low level of DOC in this lake. The average concentration of HPON in the BVS samples is not too different from the

other sample types except BLP (Table 3), and it is diluted to a lesser extent by coloured, more acidic components of DOM. The lowest relative proportion of HPON occurs in the BSL samples. Mayer (1985) reviewed the effect of salinity on dissolved humic matter, and it is consistent with previous work that HPON, with the properties described above, would tend to coagulate and drop out of the dissolved fraction as salinity increases.

Hydrophilic Neutral (HPIN)

This fraction is nearly invariant with regard to sample type (Fig. 2f), and likely contains carbohydrates (Leenheer, 1981). Like the HPIA fraction, HPIN should be close to original biochemical sources, and labile molecules likely make up a significant portion of this fraction. Mechanical ditching of the amended drainage samples (BAD) extended from 2-3 m. This undoubtedly exposed anaerobic peat to oxidation resulting in breakdown of polymeric carbohydrates to more soluble forms, thus higher relative concentrations of HPIN. However, these same processes (oxidation and biodegradation of carbohydrates) could also produce HPIA, and this fraction is not enriched in the BAD samples (Fig. 2d).

RESULTS FOR SAMPLES GROUPED BY SEASON

An appreciation of the importance of seasonal variation in the data set can be obtained by comparing RSD values by class from the entire data set (Table 2) with those from the seasonally sorted data in Table 4. For the purpose of sorting by seasons sampling date was used regardless of the climatic conditions of any particular year.

Thus "spring" was defined as Mar.-May, "summer" as Jun.-Aug., "autumn" as Sep.-Nov., and "winter" as Dec.-Feb. Grouping by season leaves sample type as the major source of data variability.

The variability in DOC and HPOA is less for all seasons except autumn when it is the same as for the entire data set. The correspondence of these two parameters is a reflection of the dominance of the HPOA fraction and an indication that it is a conservative component of the DOM. The HA and HPIA fractions show lower variability in all seasons except winter when it is higher than for the entire data set. This may be a reflection of the importance of hydrology and microbial degradation in controlling the concentrations of these DOM fractions. Hydrology may also be important in determining the differences in seasonal concentrations of HPON. The variability for HPON is less in the spring and winter (high flow) and more than for the entire data set in summer and autumn, the lower flow seasons. In summer the HPIN data shows the same variability as for the entire data set, but this fraction is less variable in the other seasons, reflecting the importance of decomposition in controlling the concentration of HPIN.

DISTRIBUTIONS OF DOC FOR SAMPLES GROUPED BY SEASON

Comparison of the average composition of the DOM in seasonally grouped samples are more easily made if the distribution of DOC among the fractions is plotted as in Fig. 3. The average relative concentrations of the fractions are expressed as percentages of the sample DOC.

Dissolved Organic Carbon

Average DOC concentrations show seasonal differences (Fig. 3a) previously shown in this area and for other sites in eastern Canada (Kerekes et al., 1986; Clair and Freedman, 1986). Summer values average nearly twice those of the spring and winter, with autumn concentrations intermediate. Dilution by spring rains and snow melt explains this variation.

Humic Acid

Lower average relative proportions of HA as a fraction of DOC occur during the spring (Fig. 3b) probably due to the predominance of snowmelt and saturated surface flow during this season. In the drier seasons, DOM flushed from the deeper layers of bogs and soils, makes up a greater portion of the total DOM. As seen above HA can be more prominent in the deeper layers resulting in higher HA proportions during drier seasons.

Hydrophobic Acid

The lack of variation in the average relative content of HPOA regardless of season (Fig. 3c) suggests that it is a conservative component of the DOM. It may be considered as a diagenetic intermediate, and likely contains components exhibiting a wide range of molecular weights. Thus polycondensation of lower molecular weight components from other fractions which would increase the pool of HPOA carbon likely occurs simultaneously with polycondensation of higher molecular weight components of HPOA into HA; a process which would remove carbon from the HPOA pool. If these reactions do occur as expressed here, then they are apparently in steady state equilibrium.

Hydrophilic Acid

The influence of temperature and associated changes in microbial activity must be considered in discussing seasonally grouped HPIA data (Fig. 3d). Variations in average HPIA contents may be explained in terms of summer biochemical production of soluble acidic components related to the decomposition of biomass which is greatest in summer (Auclair et al., 1976a,b). Autumn and winter relative proportions are progressively less than those in summer, reflecting decreases in biochemical activity and flushing of the summer accumulation by autumn rains and minor winter thaws. Lowest average levels of HPIA are seen during spring, following the period of lowest microbial activity in winter.

Hydrophobic Neutral

The proportion of the DOC present as HPON shows some seasonal variation (Fig. 3e), but the average concentration of HPON carbon is more constant (Table 4). It appears that the lower relative proportion of HPON found in the summer and autumn are due to dilution by increased amounts of the other fractions of DOM which contain greater functionality. This means that the increases in DOC content during the warmer seasons is caused by increases in acidic (and HPIN) fractions, as shown by the concentration data in Table 4.

Hydrophilic Neutral

Relative proportions of HPIN show a sequential decrease from spring to winter (Fig. 3f). In wetlands much of the annual loss of biomass is "exported" during the spring (Auclair et al., 1976a,b; Bartsch and Moore, 1985). This export likely represents the sum of

dissolved and particulate forms of carbon released by various physical, chemical, and microbial processes over the winter and flushed out by snowmelt. Soluble carbohydrates (part of HPIN) are certainly part of this material and may have survived further decomposition to HPIA because of decreased microbial activity in winter. Thus the HPIN and HPIA data (Fig. 3d) are consistent.

RELATIVE IMPORTANCE OF SEASONAL VS. SAMPLE TYPE VARIABILITY

Previous comparisons of seasonal and sample type sorting with the unsorted data set showed that sorting by either method decreased the variability (Tables 2, 3, and 4), suggesting that both factors have some influence on the composition of DOM in these waters. To compare the relative influence of the two factors, analyses of variance were calculated according to the unbalanced one-way classification model of Graybill (1961). Results for seven parameters grouped by types and seasons appear in Table 5. When data for the selected parameters are sorted by seasons, the assumption is that the variability is caused primarily by differences in sample type or sampling environment, all sample types treated as replicates. Similarly, when sorting by sample type one asumes that variability is an expression of the influence of seasonal or other temporal fluctuations, all seasons treated as replicates.

Mean square values in Table 5 may be compared across columns for each parameter because they represent proportions of the same total variance. Thus the ratio of mean squares shown in Table 5 indicates the relative importance of these factors for each parameter. For DOC,

HPOA, HPIA, and HPIN, the ratio is near but higher than unity suggesting that sample type is a slightly more (for HPOA somewhat more) important contributor to the total variance than is season. For pH and HPON type is much more important than season, and for HA season is more important than type.

Values for the F statistic which appear in Table 5 may be compared down a single column across parameters because all values in a column represent the same degrees of freedom. Thus it can be said with a high degree of certainty that the classification of samples as belonging to certain types explains most of the total variance for pH, DOC, HPOA, HPIN, and HPIA, decreasing in certainty in the order given. For HA it is less certain, and for HPON much less certain that the total variance can be explained by such classification. Similarly the variance for DOC, HPOA, HPIN, and HPIA may be explained to a large degree by seasonal classification, with a high certainty. It is less certain that HA variance can be explained by seasonal classification, and that for pH and HPON cannot be explained at all by such sorting.

COMPARISON WITH DOM FRACTIONATIONS OF PREVIOUS WORKERS

The averaged data from this study are compared in Table 6 with results of other workers who have utilized the same fractionation procedures, or nearly so. Data for comparison are based on the proportion of the sample DOC in each fraction. None of the previous workers isolated an HA fraction prior to DOM fractionation on the various columns. Based on its expected hydrophobic nature, HA should

isolate with the HPOA fraction, so for comparison the sums of HA + HPOA for the present work are included in Table 6.

The range of HA + HPOA values found in the samples from this study compares well with the HPOA values found in the other studies. Beaverskin Lake is the only clearwater site studied here and it gives the lowest value of any sample type in this study. This compares fairly well with the clearwater (low DOC) sites by other workers; these tend to have the lowest reported proportion of HPOA.

Agreement between the present work with the results of previous workers is not so good for the other fractions shown in Table 6. The average proportion of HPIA isolated from the samples in this study are 2-4 times lower than all but two of the other sites reported. More HPON was isolated from the eastern Canadian samples than from all but three of the other sites; and these samples contain a significantly greater proportion of their DOC as HPIN than all of the sites studied by previous workers.

Part of the reason for the apparent discrepancies may be that data for the present study represent averages of many samples. Indeed, individual samples in the data base occur which contain no HPIN or HPON, as well as some which contain high amounts of HPIA (see Table 2). Also the characteristics of sites sampled in eastern Canada, though considered varied from the local viewpoint, are relatively consistent when compared to the variety of samples which appear in Table 6. The comparison sites cover a wide geographic area and a wide range of sample types, from a bog to large rivers representing

integrated systems on a much larger scale than those represented in the eastern Canadian sample set.

Sorting out the differences on a sample by sample basis awaits further data analysis which will be reported elsewhere along with appropriate comparisons to the results of previous workers. Further comparisons will require more comprehensive characterization of the isolated fractions on the molecular level such as that done by Leenheer et al. (1982).

SUMMARY AND CONCLUSIONS

The DOM in the aquatic systems studied (bogs, streams, lakes, rivers, etc.) is considered to be entirely humic matter "extracted" from the surrounding soils by natural leaching processes at ambient pH. In this way the "natural extract" is analogous to the base extract commonly used to define soil humic matter. Subsequent fractionation and characterization of the DOM utilizes techniques developed by both soil and aquatic chemists.

The composition of DOM from the study areas is quite variable and on average the seven fractions isolated are ranked by concentration: HPOA > HPON > HA > HPIN > HPIA > HPIB > HPOB. The total of acidic fractions (HA + HPOA + HPIA) comprises on average 59.7% of the DOC. Grouping of samples by type or by season helps to explain the total variance, more so for sample type for all fractions except HA. This suggests that localized conditions are more important in determining the overall character of DOM than are seasonal fluctuations.

Distribution patterns which result by sorting this data set, the chemical character implied in the fraction definitions, and consideration of the sites studied leads to suggestions of the source, composition, and fate of five of the DOM fractions:

1). Humic Acid (HA)

This hydrophobic fraction is more prominent in pore waters from the deeper layers of bogs and in water from the more integrated sampling sites suggesting its probable origin from diagenetic processes in bogs and soils, or its production from condensation

reactions along watercourses. HA is associated with drier, low flow conditions.

2). Hydrophobic Acid (HPOA)

HPOA represents a conservative component of the DOM in coloured waters because of its relative lack of variation among sample types and seasons. Its high concentrations in coloured waters and relatively low concentration in the only clearwater site studied suggests that this fraction is soil derived. HPOA likely contains intermediates formed by the polycondensation of low molecular weight materials to HA.

3). Hydrophilic Acid (HPIA)

The HPIA fraction is more soluble, less coloured and is likely composed of strong and labile acids which are diagenetically close to their biochemical sources such as bog flora. Its seasonal distribution suggests that HPIA is produced primarily by microbial degradation.

4). Hydrophobic Neutral (HPON)

This fraction likely consists of hydrocarbon-like materials or moderate to high molecular weight amorphous polymers with little peripheral functionality. HPON is relatively unreactive and stable and tends to accumulate in integrated systems.

5). Hydrophilic Neutral (HPIN)

This fraction is nearly invariant with regard to sample type, and like the HPIA fraction should be close to the original biochemical sources. Labile molecules resulting from microbial degradation

(e.g. soluble carbohydrates) should occur in this fraction which exhibits a strong seasonal trend.

Generally the coloured waters studied from eastern Canada contain about the same hydrophobic acid (HA + HPOA) content as has been determined from other sites in North America. Hydrophilic acid contents, on average, tend to be lower, HPON and HPIN contents higher than those found by other workers. DOM fractionation provides information on spatial and seasonal patterns of DOM character that are not discernable by DOC determinations alone. However, further characterization of these fractions is necessary to fully understand the implications of seasonal and spatial distributions with regard to organic acidity, metal complexation, and toxicity to aquatic biota.

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ACKNOWLEDGEMENTS

The assistance of M. Richmond, B. VanSickle, D. Piche, L. Bisutti, K. Lawrynuik, R. Tordon, S. Mazzei, E. Tozer, L. Parent, S. Smith, and L. Holloway with field and laboratory work is very much appreciated. This work was supported by the Federal LRTAP Program and the Federal Panel on Energy R&D (PERD).

CAPTIONS FOR TABLES AND FIGURES

Table 1. Description of types of samples collected in eastern Canada.

Table 2. Statistical data for all samples with complete DOC fractionation (n= 160)[a].

Table 3. Statistical data for all samples sorted by sample type[a].

Table 4. Statistical data for all samples sorted by season[a].

Table 5. Analysis of variance results for one-way unbalanced classification for seven parameters grouped by sample type or by seasons[a].

Table 6. Comparisons of DOM fractionation results from various environments[a].

Fig. 1. Map of eastern Canada showing the three study areas from which samples were obtained.

Fig. 2. Comparison of the average DOC and DOM fractions for samples sorted by sample type. See Table 1 for type designations.

Fig. 3. Comparison of average DOC and DOM fractions for samples sorted by season. SPRING = Mar., Apr., May; SUMMER = Jun., Jul., Aug.; AUTUMN = Sep., Oct., Nov; WINTER = Dec., Jan., Feb.

Table 1

Sample Type Description	[a]Designation	Number
BOG PORE WATERS (upper layers, 0-75cm)	BUP	12
Mostly from Barrington Bog, but a few from Sept-Iles		
BOG PORE WATERS (lower layers, 1.25-2m)	BLP	4
Three from Barrington Bog and one from a bog adjacent to Pebbleloggitch L. in Kejimkujik N.P.		
BOG NATURAL DRAINAGE	BND	36
Mostly from Judas Ck. which drains Barrington Bog, but some from undisturbed drainage at Sept-Iles		
BOG AMENDED DRAINAGE	BAD	11
All from ditches dug to drain bogs in Sept-Iles so that peat could be harvested for horticultural purposes		
BOG DRAINAGE WITH SALINE INFLUENCE	BSL	7
All from the lower reaches of Judas Ck. which experience tidal influence		
HEADWATER STREAMS	HWS	29
Collected from streams in Kejimkujik N.P. and Barrington Bog areas in smaller watersheds containing thin organic soils		
RIVER MOUTHS	RVM	32
Collected from the Clyde, Roseway, Medway and Mersey Rivers in southwest N.S. at points near their mouths and upstream from the upper limit of tidal influence		
PEBBLELOGGITCH LAKE	PEB	15
Surface water from the deepest part of this coloured lake in Kejimkujik N.P. which is flanked by a bog through which the lake's main input flows		
BEAVERSKIN LAKE	BVS	14
Surface water from the deepest part of this clearwater lake one km from Pebbleloggitch L. and surrounded by thin soils		

[a]Designation used in Table 3, Fig. 2, and in some parts of text

Table 2

	pH	DOC	HA	HPOA	HPIA	HPOB	HPIB	HPON	HPIN
Min	3.4	4.99	0.0	0.26	0.0	0.0	0.0	0.0	0.0
Max	6.2	71.9	25.6	31.2	14.4	2.02	11.4	18.2	15.8
Mean	4.64	25.3	4.48	7.90	2.72	0.15	0.86	5.06	4.12
S.D.	0.57	13.7	4.86	5.78	3.11	0.28	1.56	3.46	3.26
RSD	12.3%	54.2%	109%	73.2%	115%	194%	181%	68.4%	79.2%
Frac-C (% of DOC)			17.7	31.2	10.8	0.59	3.40	20.0	16.3
Cum (% of DOC)			17.7	48.9	59.7	60.3	63.7	83.7	100

[a]All concentrations given in mgC/L

S.D. = ± Sample standard deviation (n-1 d.f.)

RSD = (S.D. / Mean) x 100%

Frac-C = Mean fraction (mgC/L) / Mean DOC (mgC/L) x 100%

Cum-C = Cumulation of Frac-C

		pH	DOC	HA	HPOA	HPIA	HPON	HPIN
BUP	Mean	4.19	38.5	4.05	13.1	5.91	5.14	7.56
	[a]S.D.	0.50	15.3	4.30	5.32	4.59	5.55	4.45
	[b]RSD	12.0%	39.8%	106%	40.6%	77.6%	108%	58.8%
BLP	Mean	4.05	47.1	11.1	11.7	7.27	8.68	8.20
	S.D.	0.48	6.13	9.00	7.56	3.07	8.78	3.93
	RSD	11.8%	13.0%	81.1%	64.6%	42.2%	101%	47.9%
BND	Mean	4.30	34.5	5.69	12.4	3.98	6.02	5.13
	S.D.	0.40	13.2	5.74	6.18	3.76	3.49	3.36
	RSD	9.2%	38.3%	101%	49.8%	94.6%	57.9%	65.4%
BAD	Mean	4.34	29.0	3.92	8.43	2.83	6.49	6.62
	S.D.	0.59	8.70	3.23	4.00	1.95	3.66	2.95
	RSD	13.5%	29.9%	82.4%	47.5%	68.8%	56.4%	44.5%
BSL	Mean	5.71	32.1	6.00	10.6	3.26	4.57	6.03
	S.D.	0.53	13.8	5.91	5.37	2.17	1.25	3.43
	RSD	9.3%	43.0%	98.4%	50.8%	66.6%	27.5%	56.9%
HWS	Mean	4.88	17.9	2.97	5.36	1.68	4.74	2.57
	S.D.	0.28	8.14	2.99	3.25	1.62	2.84	1.62
	RSD	5.8%	45.6%	101%	60.6%	96.6%	60.0%	63.2%
RVM	Mean	4.66	21.7	4.89	6.25	2.01	4.29	3.20
	S.D.	0.42	8.56	5.03	4.18	2.50	2.45	2.41
	RSD	9.0%	39.4%	103%	66.9%	124%	57.2%	75.2%
PEB	Mean	4.45	19.7	4.42	5.54	1.40	4.67	2.85
	S.D.	0.33	5.32	4.97	1.70	1.41	2.94	1.44
	RSD	7.5%	27.0%	112%	30.7%	100%	63.0%	50.6%
BVS	Mean	5.44	7.18	1.76	0.55	0.25	3.47	1.15
	S.D.	0.21	2.20	1.83	0.22	0.41	2.22	0.82
	RSD	3.8%	30.7%	104%	39.4%	164%	64.1%	71.6%

[a]See Table 1 for type designations and number of samples, all concentrations in mgC/L

[b]See Table 2 for definitions of statistical measures

Table 4

	pH	DOC	HA	HPOA	HPIA	HPON	HPIN
SPRING, n= 27							
Mean	4.66	18.0	2.18	5.33	1.41	4.49	3.83
[a]S.D.	0.53	6.45	2.04	2.45	1.26	2.46	2.50
[b]RSD	11.5%	35.7%	93.9%	45.9%	89.5%	54.9%	65.3%
SUMMER, n= 59							
Mean	4.58	31.8	5.67	10.28	3.84	5.05	5.47
S.D.	0.59	15.5	5.44	6.87	3.78	4.32	4.27
RSD	12.9%	48.9%	95.8%	66.9%	98.3%	85.6%	78.1%
AUTUMN, n= 36							
Mean	4.72	25.7	4.94	8.37	2.70	5.25	3.84
S.D.	0.64	14.2	4.93	6.01	2.96	3.83	2.19
RSD	13.6%	55.2%	99.9%	71.7%	110%	73.0%	57.0%
WINTER, n= 38							
Mean	4.65	19.9	3.83	5.57	1.91	5.30	2.50
S.D.	0.51	8.62	4.76	3.40	2.45	1.93	1.57
RSD	11.0%	43.3%	124%	61.0%	128%	36.5%	62.6%

[a]All concentrations in mgC/L

[b]See Table 2 for definitions of statistical measures

TABLE 5

PARAMETER	Sorting by Sample Type: Mean Sq. Types	Mean Sq. Replic.	F	Sorting by Seasons: Mean Sq. Seasons	Mean Sq. Replic.	F	Ratio[b]
pH	3.5	0.2	22.3*	0.2	0.3	-	17.5
DOC	1823	101	18.0*	1669	159	10.5*	1.09
HA	55.1	22.1	2.4#	83.6	22.5	3.7#	0.66
HPOA	285	20.1	14.2*	242	29.4	8.2*	1.18
HPIA	52.9	7.4	7.1*	48.4	9.0	5.4*	1.09
HPON	21.2	11.5	1.8<	4.1	12.2	-	5.17
HPIN	73.1	7.3	10.0*	70.7	9.5	7.4*	1.03

[a] N = 160; Deg. Freedom: Types (8), Replic. (151), Seasons (3), Replic. (156)

[b] Ratio = Mean Sq. Types / Mean Sq. Seasons

Confidence level: * - 99%, # - 97%, < - <95%

Table 6

SAMPLING LOCATION OR TYPE	DOC	HA	HPOA	HPIA	HPON	HPIN	[b]SUM
Bog pore water, upper (BUP)	38.5	10	34(44)[c]	15	13	20	92
Bog pore water, lower (BLP)	47.1	24	25(49)	15	18	17	99
Bog natural drainage (BND)	34.5	16	36(52)	12	17	15	96
Bog amended drainage (BAD)	29	14	29(43)	10	22	23	98
Bog drainage, saline (BSL)	32.1	19	33(52)	10	14	19	95
Headwater streams (HWS)	17.9	17	30(47)	9	26	14	96
River mouths (RVM)	21.7	22	29(51)	9	20	15	95
Pebbleloggitch L. (PEB)	19.7	22	28(50)	7	24	14	95
Beaverskin L. (BVS)	7.2	24	8(32)	3	48	16	99
[d]South Platte R., CO.	7.5	[h]-	18	18	32	6	74
[e]Black L., NC.	8.3	[h]-	41	8	19	0	68
[e]Ohio R., OH.	3.7	[h]-	32	36	25	0	93
[e]Missouri R., IA.	3.4	[h]-	19	51	0	0	70
[e]Suwannee R., GA.	38.2	[h]-	42	50	2	1	95
[f]Thoreau's Bog, MA.	31	[h]-	67	20	10	3	[i]-
[g]Sagamore L., NY.	7.5	[h]-	40	45	[j](N+B: 15)		100
[g]Hardwood soil soln., NY.	47	[h]-	47	37	[j](N+B: 16)		100
[g]Conifer soil soln., NY.	54	[h]-	46	43	[j](N+B: 11)		100

[a]All values as % of DOC except DOC which is mgC/L

[b]Sum of acidic and neutral fractions

[c]Values in parentheses are: HA + HPOA

[d]Leenheer (1981)

[e]Aiken (1985)

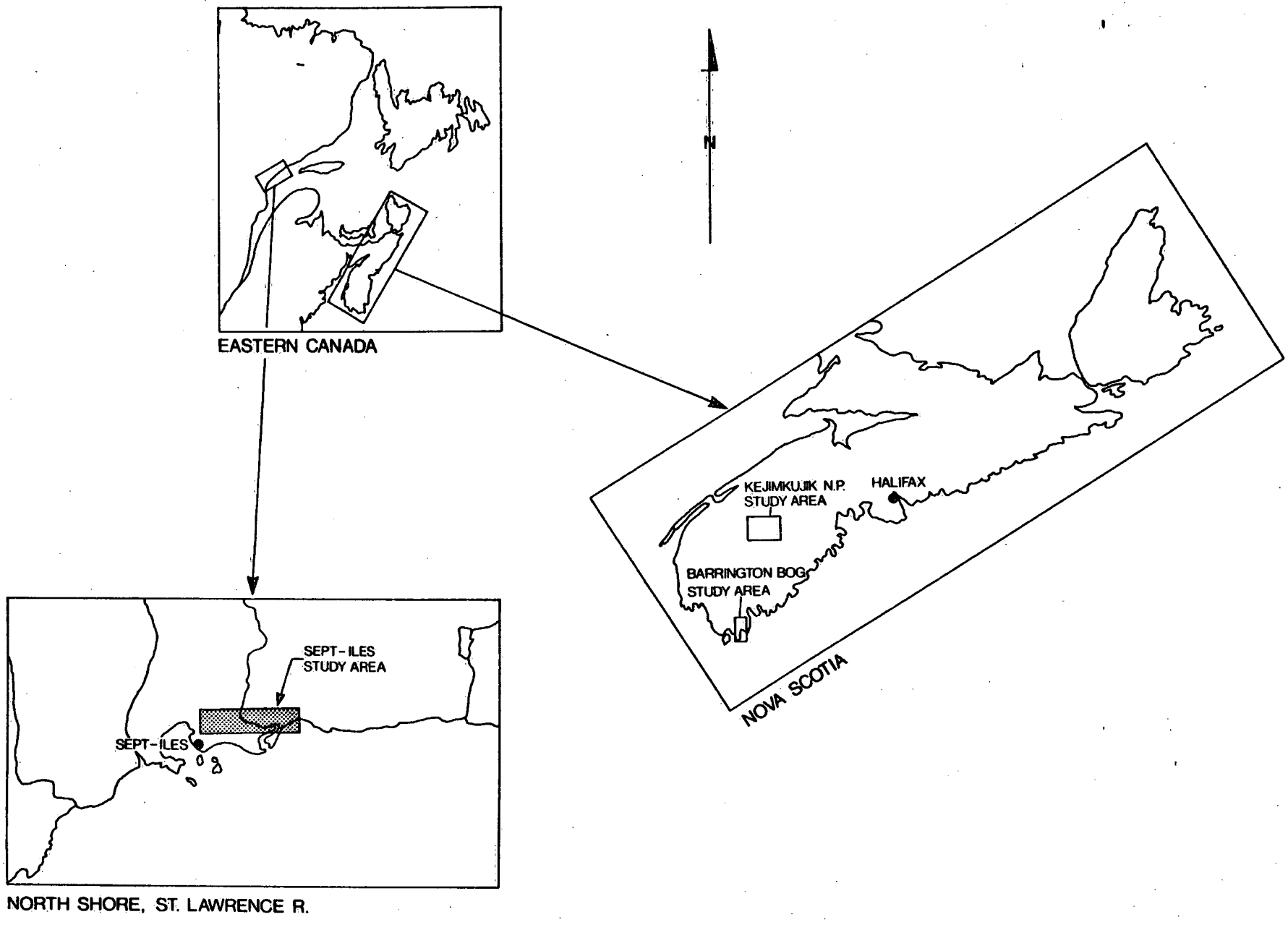
[f]McKnight et al. (1985)

[g]Cronan and Aiken (1985)

[h]HA not isolated from FA, should be included in HPOA

[i]Normalized data, only 78% of DOC accounted

[j]Reported as "neutrals + basics"


EASTERN CANADA
N
KEJIMKUJIK N.P.
STUDY AREA
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NORTH SHORE, ST. LAWRENCE R.

Figure 1

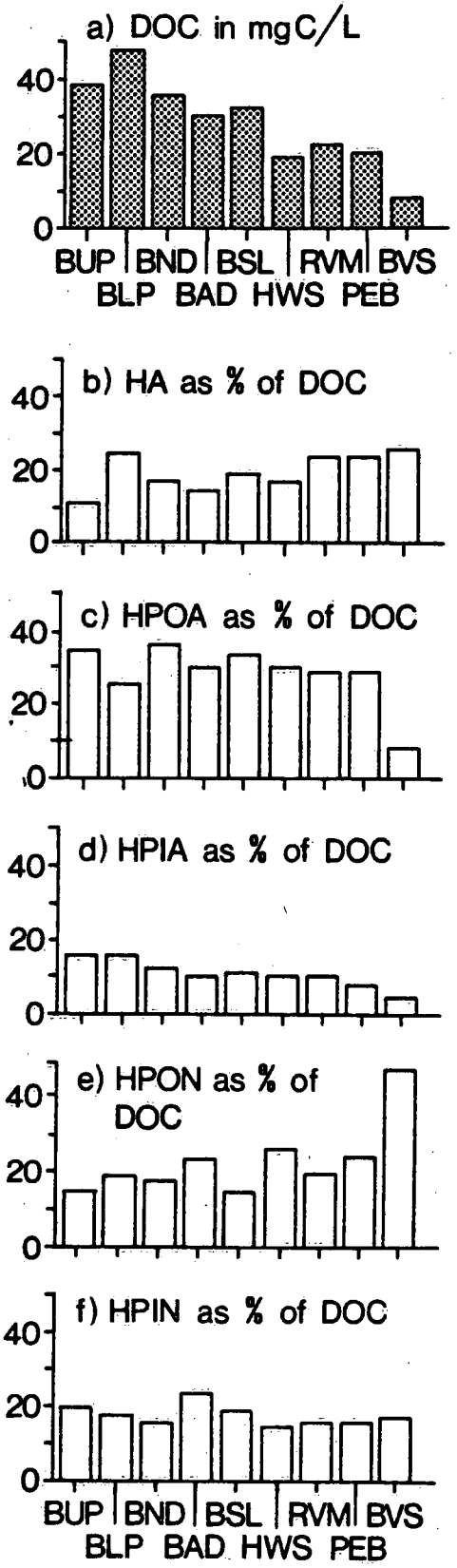
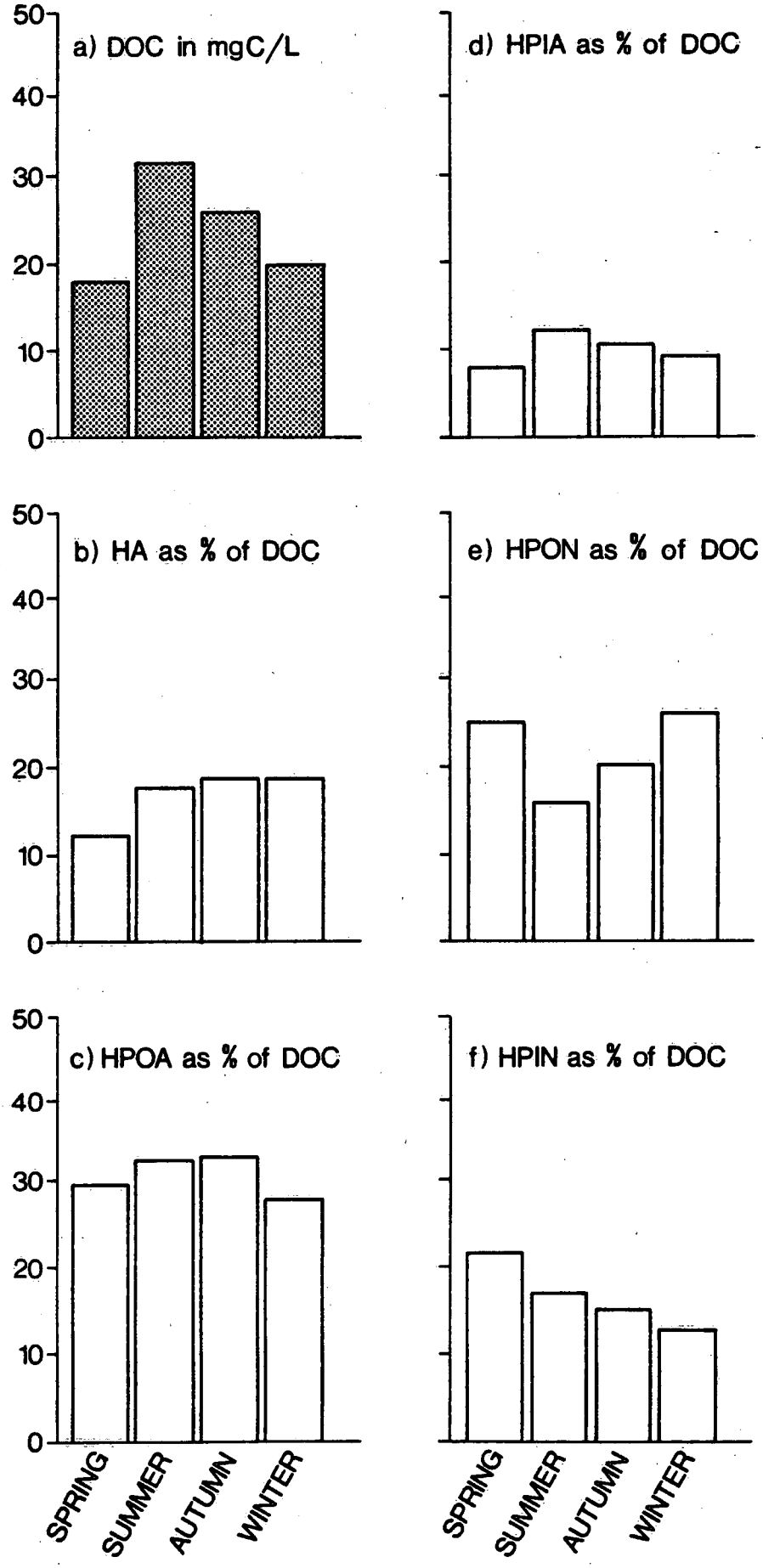

a) DOC in mgC/L
40
20
0
BUP
BND
BSL
RVM
BVS
BLP
BAD
HWS
PEB
b) HA as % of DOC
c) HPOA as % of DOC
d) HPIA as % of DOC
e) HPON as % of DOC
f) HPIN as % of DOC

Figure 3


a) DOC in mgC/L
d) HPIA as % of DOC
b) HA as % of DOC
e) HPON as % of DOC
c) HPOA as % of DOC
f) HPIN as % of DOC
50
40
30
20
10
0
SPRING
SUMMER
AUTUMN
WINTER