Water Quality

Ambient Water Quality Criteria for Organic Carbon in British Columbia

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Preface

The BC Ministry of Environment, Lands and Parks [BC Environment] (now called Ministry of Water, Land and Air Protection) develops province-wide ambient water quality criteria for substances and physical attributes of importance in both fresh and marine surface waters. These threshold values provide a basis

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for developing site-specific ambient objectives, set wastewater discharge limits and fees, and help identify areas with degraded conditions. The criteria are not legally binding but are intended as tools to provide policy direction to those making decisions affecting water quality issues (BC Environment 1995).

Anthropogenic activities such as forest management, road building, construction, dredging, gravel pit operations, and industrial waste management can cause marked changes in the physical, chemical, and biological characteristics of the watercourses located nearby and those located downstream. Changes in organic carbon levels can be used as an indicator of environmental impact arising from these anthropogenic activities. BC Environment has identified the need for the development of ambient water quality criteria for organic carbon in freshwater conditions. The guidelines will function as management tools, against which to assess whether a water use is adequately protected.

Summary of Recommended Criteria

Water Use	Parameter	Criterion
Raw drinking water	Total Organic Carbon	4 mg/L for source water, 2 mg/L for treated water
Freshwater aquatic life; Wildlife	Total Organic Carbon	The 30-day 50th percentile shall be within 20% above or below seasonally-adjusted median background levels as measured historically or at appropriate reference sites.
	Dissolved Organic Carbon	The 30-day 50th percentile shall be within 20% above or below seasonally-adjusted median background levels as measured historically or at appropriate reference sites.
Livestock watering; Irrigation; Recreation and aesthetics; and Industrial water supplies	Total and Dissolved Organic Carbon	None proposed

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Definitions, Concepts and Analytical Measurements

1.1 Key Concepts

Organic matter in aquatic systems is a complex mixture of molecules such as carbohydrates, amino acids, hydrocarbons, fatty acids and phenolics, natural macromolecules and colloids (e.g., humics), sewage and industrial particulates, soil organic matter, living phytoplankton and other plant material. These materials are of interest for several reasons. Their transport contributes significantly to the global carbon cycle. For example, the transport of soil-derived organic matter by rivers and its subsequent burial in marine sediments is an important global sink for carbon. The more reactive constituents of organic matter (e.g., carbohydrates) make a significant contribution to heterotrophic metabolism in streams, lakes, estuaries and coastal areas. Fulvic acids and other humic substances affect the behaviour and transport of metals by complexing them. These compounds also interact with organic pollutants and adsorb to the surfaces of mineral solids thus affecting surface chemistry and rates of aggregation.

Most waters contain organic matter that can be measured as total organic carbon (TOC). Sources of organic carbon in fresh and marine waters include living material and waste materials and effluents. Organic matter from living material may arise directly from plant photosynthesis or indirectly from terrestrial organic matter. An indication of the amount of organic matter present can be obtained by measuring related properties, principally the biochemical oxygen demand (BOD), chemical oxygen demand (COD), turbidity and colour. The COD usually includes the BOD as well as other chemical demands producing the relationship, COD greater than BOD greater than TOC. If the sample contains toxic substances, however, this relationship may not hold true. Turbidity is a function of light scattering by suspended particles, while colour is related to the quantity of dissolved (true colour) and particulate substances (apparent colour) present. As a result, both parameters are often highly correlated with organic carbon levels.

The total organic carbon in water can be a useful indication of the degree of pollution, particularly when concentrations can be compared upstream and downstream of potential sources of pollution. In surface waters, total organic carbon concentrations are generally less than 10 mg/L, and in ground water less than 2 mg/L, unless the water receives wastes or is highly coloured due to natural organic material (e.g., swamps, bogs). Total organic carbon consists of dissolved (DOC) and particulate organic carbon (POC) and is therefore affected by pronounced fluctuations in suspended solids in riverine systems. The DOC and POC levels are determined separately after filtering the sample through a filter approximately 0.4 to 0.7 micron pore diameter. Typically, DOC levels exceed POC levels in the range 6:1 to 10:1, except during river floods or in highly turbid waters where POC dominates (Wetzel 1975).

1.2 Particulate Organic Carbon

The particulate organic carbon fraction of total organic carbon has three major sources: allochthonous inputs from the drainage basin (e.g., leaf litter), and autochthonous inputs from the littoral and pelagic zones of carbon flux. Much of the metabolism and decomposition of particulate organic carbon takes place in the sediments or en route during sedimentation. The characteristics and rates of transport of organic carbon from the drainage basin depend on the composition of soils and parent materials, local climatic conditions, topography, hydrology, and vegetation of the watershed (Mitchell and McDonald 1995; Håkanson 1993; Heikkinen 1994; Midgley and Schafer 1992). In addition, some land use activities (e.g., animal husbandry) tend to accelerate soil erosion, thereby increasing the potential for problematic levels of particulate and total organic carbon in the water column, while other activities (e.g., clear

cutting) tend to decrease organic carbon inputs (Shields and Sanders 1986; Forsberg 1992; France 1995a,b).

1.3 Dissolved Organic Carbon

Dissolved organic carbon is composed primarily of two categories of substances: (i) non-humic substances, a class of compounds that includes carbohydrates, proteins, peptides, fats, pigments and other low molecular weight compounds, and (ii) humic substances which form most of the organic matter in waters, and consist of coloured hydrophilic and acidic complexes ranging in molecular weight from the hundreds to thousands (Wetzel 1975). Non-humic substances are easily utilized and degraded by microorganisms (i.e., substances are labile) and exhibit rapid flux rates in aquatic systems. Their instantaneous concentrations are usually very low as a result, although they may play an important role in system metabolism. Humic substances are formed largely as a result of microbial activity on plant and animal material and are more persistent than non-humic substances.

1.4 Analytical Methods

Total organic carbon (TOC) is determined without filtration of the sample. Samples for TOC determination should be stored in dark glass bottles, with minimum exposure to light or air, at 3 to 4 C for no more than seven days prior to analysis. Alternatively, samples can be acidified with nitric, phosphoric or sulphuric acid to pH 3 or less for longer term storage and to eliminate inorganic carbon. Samples for DOC determination follow a protocol similar to that for TOC, except that they are filtered (pore diameter = 0.4 to 0.7 micron, 0.45 micron being the most common) to remove particulate organic carbon.

There are several methods available for determining organic carbon depending on the type of sample to be analyzed. Methods are based on the principle of oxidation of the carbon in the sample to carbon dioxide (e.g., combustion, chemical reaction, ultraviolet radiation) which is then determined by one of several methods (e.g., volumetric determination, thermal conductivity, specific CO_2 electrode). The US EPA (1983) describes these methods in detail. Wet oxidation methods (e.g., UV persulphate) have been shown to underestimate total combustion techniques by 15 to 30 percent, most likely because of incomplete oxidation of organic carbon to CO_2 (Clair 1992).

Several specialized techniques are available to characterize the different forms of organic matter in water and wastewaters. For example, Thomas et al. (1993) and Huber and Frimmel (1992, 1994) describe a technique that involves separating out the organic matter fractions by molecular weight and other physical chemical properties using 3D low pressure gel chromatography, and characterizing the chromatographic fractions with high sensitivity DOC and UV detection. The detection limit for chromatographic techniques is in the range of several milligrams per liter and thus a pre-concentration step is necessary. Chromatographic techniques can be used to determine, for example, the fraction of humics that make up the DOC in the sample.

BC Environment (Water, Land and Air Protection) measures total organic carbon by converting it to CO_2 via catalytic combustion or wet chemical oxidation, and then measuring the CO_2 formed by infrared detector or converted to methane and measured by flame ionization (BC Environment 1994). Based on the findings of Clair (1992), the catalytic combustion technique is preferable to the wet chemical oxidation technique. The detection limit for TOC in drinking, surface, and waste waters is 1 mg/L. All samples are stored in cool (4 degrees Celcius), dark conditions in sealed containers. As with other jurisdictions, un-preserved samples must be analyzed within 72 hours. Preserved samples (i.e., pH adjusted to less than 2) must be analyzed within 28 days. Environment Canada (1995) uses a somewhat different approach to determining TOC and DOC levels in water. The analysis is comprised of two phases, the determination of total carbon or dissolved carbon and the determination of total inorganic carbon or dissolved inorganic carbon. TOC and DOC levels are then determined by difference. To do this, each sample is split into two. Total and dissolve carbon are determined by combusting the one split sample in the presence of a platinum catalyst at an elevated temperature with an oxygen gas carrier. Total and dissolved organic carbon are determined in the other split sample by combustion in a phosphoric acid solution through which the carrier gas is bubbled. An infrared detector is used to determine the CO_2 formed. The normal detection limit is 0.5 mg/L. Note that with this methodology, sample preservation by acidification to pH less than 2 is not recommended because it will result in the partial loss of the inorganic components.

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Occurrence

2.2 Natural Sources

Organic matter budgets of small streams in forested landscapes are dominated by inputs of terrestrial material (Bilby and Bisson 1992; Delong and Brusven 1994; France 1995a,b). This dominance is caused by high input rates of material from allochthonous sources (i.e., of terrestrial origin) combined with suppression of autochthonous production (i.e., of aquatic origin) by shading from riparian vegetation. As a result, streams are typically heterotrophic in the headwaters. The importance of direct allochthonous inputs decreases downstream as increasing stream size reduces the influence of the riparian vegetation (Delong and Brusven 1994).

The importance of allochthonous inputs to lakes varies with nearshore riparian slope, proximity of trees to the shoreline, extent of wetlands and peat lands in the drainage basin, proportional composition of deciduous leaf-fall, season, and the extent of bare ground surfaces exposed to precipitation (France and Peters 1995; France 1995b; Dillon and Molot 1997). The smaller the lake surface area, the less likely that fetch winds will develop that would remove leaf litter away from the water. Nevertheless, it is unlikely that lateral transport of leaf material will be as important for lakes as has been found for forested streams. France (1995b) found that the input rate for terrestrial leaf litter to small Canadian shield lakes was 2 g/m forested shoreline/year, an amount that represents 6% of the total annual allochthonous input of leaf-fall to these lakes. Other studies have suggested that terrestrial litter can contribute up to 15% of the total carbon supply to oligotrophic lakes (France and Peters 1995).

2.2 Anthropogenic Sources

Anthropogenic activities can have a profound effect on the organic carbon budgets of aquatic systems (Schepers and Francis 1982; France 1995a,b; France and Peters 1995). Snowmelt, runoff from agricultural lands, municipal and industrial wastewater discharges, and stormwater overflows can lead to substantial increases in the levels of total and dissolved organic carbon in surface waters. Schepers and Francis (1982), for example, found that grazing livestock increased total organic carbon by 11% in runoff waters as a result of increased soil erosion and production of animal wastes.

Of perhaps greatest concern in British Columbia, are forest management practices. Forest management practices can cause an initial increase in organic carbon as a result of increased soil erosion due to construction of infrastructure and harvesting of trees, discharge of coloured effluents, and leaching of wood debris, both in situ and from nearby storage sites (Butcher 1992; Taylor 1994; Nordin and Holmes 1992; Forsberg 1992). In the longer term, removal of riparian vegetation through timber harvesting reverses the relative importance of allochthonous organic sources by stimulating primary production (e.g., by removal of shading) and decreasing inputs of terrestrial organic matter (e.g., less leaf litter)(McLeod et al. 1983). In a comparison of two headwater tributaries to the Deschutes River, Washington, Bilby and Bisson (1992) found that allochthonous organic matter dominated inputs (300 g/m^2/year) in the tributary bordered by old-growth coniferous forest compared to autochthonous inputs (100 g/m^2/year). In the tributary in the clear-cut area, autochthonous inputs were 175 g/m^2/year and allochthonous inputs were only 60 g/m^2/year. Greater autochthonous production and decreased inputs of terrestrial materials have important consequences for consumer trophic levels in aquatic systems because autochthonous organic material (e.g., algae and algal-based detritus) generally has higher levels of primary amines, proteins, and carbohydrates and is more digestible than most incoming terrestrial material (McDowell and Likens 1988). Further, the food quality of the terrestrial organic material in areas that have been logged or turned over to agricultural crops is considered lower than in areas associated with mature riparian vegetation (Delong and Brusven 1994).

2.3 Concentrations

The existing data indicate that median total and dissolved organic carbon levels in British Columbia lakes and rivers are generally less than 5 mg/L except for waters that have high natural sources. For example, the median total organic carbon concentration ranged from 26-105 mg/L in Del Burns Bog. Similarly, sites that are located near anthropogenic sources such as Dawson Creek near the city discharge and dump (median range TOC=21-25.5 mg/L) may have elevated total organic carbon concentrations. Median total organic carbon levels in bogs and swamps or near anthropogenic sources are often greater than 20 mg/L. The data indicate that DOC is the dominate fraction of TOC in most British Columbia waters, and that organic carbon levels are generally correlated with true colour. The available data on total and dissolved organic carbon levels worldwide indicate that, as in British Columbia, the mean TOC and DOC levels are typically below 5 mg/L.

For some regularly sampled locations, there is evidence of considerable temporal variation. For example, in Adirondacks streams, mean seasonal DOC levels are typically between 1.5 and 5 mg/L; the annual ranges, however, indicate that DOC levels vary from lows of <0.7 mg/L to highs of >7.5 mg/L (Baldigo and Murdoch 1997). Numerous studies have noted that total and dissolved organic carbon levels can

exhibit short-term spikes following, for example, storms or litter-fall (e.g., Sugai and Burrell 1984; France 1995a,b). Figure 1 shows that levels in the Elk River and in two lakes in British Columbia (Kootenay Lake, Koocanusa Lake) vary greatly over time. Available data shows two to four-fold variations in organic carbon levels are frequent over time frames of several months (e.g., Gordon River at TR4, Flora Lake at Nitinat, Little Nitinat River at Rock Cut).

Figure 1. Total organic carbon levels in the Elk River at Phillips Canyon: 1972 to 1983.
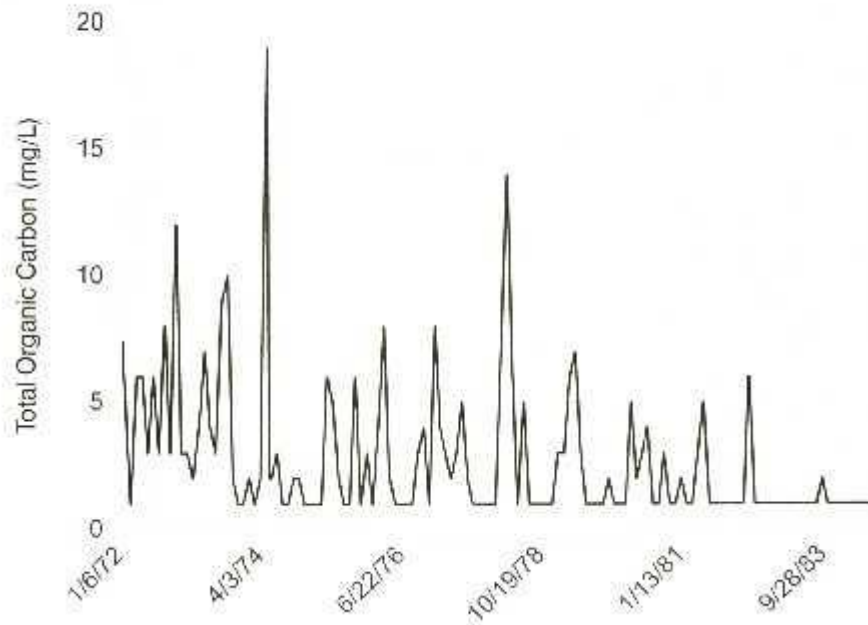
Several recent studies of receiving waters near pulp and paper mills in British Columbia indicate that many mills are not discharging the large quantities of total or dissolved organic carbon that had occurred in the past (see BC Environment 1998a). For example, concentrations of total organic carbon were similar (1.3 to 1.8 mg/L) in receiving waters from all near-field, far-field and reference sites in the Campbell River near the Elk Falls Pulp and Paper mill (Hatfield Consultants 1997a). Similar results were found for receiving waters near the Western Pulp, Port Alice operation (TOC = 1.8 to 4 mg/L, the highest level being observed at the reference site) (Hatfield Consultants 1997b), and near the Crofton Pulp and Paper Mill (Hatfield Consultants 1994). The observed improvement in effluent quality may be due to process changes that took place at many mills following enactment of the Canadian Pulp and Paper Effluent Regulations under the *Fisheries Act* in May 1992.

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Drinking Water

3.1 Water Treatment

Suspended particulates that contribute to total organic carbon are generally removed during the pre-treatment step usually by a combination of coarse and fine screens, micro-strainers and/or simple gravity settling (National Health and Welfare 1993).

The major mechanism for removal of dissolved substances such as humic and fulvic acids is the coagulation/sedimentation process (National Health and Welfare 1993). In British Columbia, very few water purveyors apply treatment beyond disinfection. Organics removal by coagulation has been found to be optimal at pH 4 to 6. Removal of organic material by aluminum and iron salts is effective with removal efficiencies varying from 55 to 90% between source waters (Reckhow and Singer 1990). Oxidation of organic carbon by chemical oxidants other than chlorine (e.g., hydrogen peroxide, ozone, UV radiation) are possible methods for removing organic carbon while also avoiding the formation of trihalomethanes. Removal of organic carbon compounds by activated carbon has had limited success because of early breakthrough problems (Symons et al. 1982).

3.2 Effects

Few human or animal toxicity studies of dissolved organic carbon compounds such as humic and fulvic acids have been undertaken. The limited studies that have been conducted indicate that these compounds are not toxic at the levels that could occur in drinking water. For example, male rats supplied with soil fulvic acid for up to 90 days at levels of 10, 100 and 1000 mg/L showed no significant changes in body weight, intake rates, organ/body weight ratios or tissue histology (Health Canada 1996). Little information is available on the toxicities of metals and their humate complexes (Health Canada 1996).

The primary reasons for reducing organic carbon in drinking water are not related to the toxicity of the organic carbon compounds themselves but rather to the desire to reduce the formation of trihalomethanes (THMs) following chlorination (Young and Singer 1979; Vogt and Regli 1981; Rathbun 1996; and numerous others), and avoid the objectionable colour that arises when humic and fulvic acids are present at high levels (Smith and Davies-Colley 1992; Smith et al. 1991).

Potential harm to humans can arise due to the reaction between humic and fulvic acids and chlorine to form THMs, trichloroacetic acid, dichloroacetic acid, haloketones and haloacetonitriles (Reckhow and Singer 1990; Rook 1977). The reaction of hypochlorous acid with the methyl ketone groups (acetyl groups) in humic acids to form trihalomethanes is shown in the equation below (Manahan 1984; Bunce 1990).

Equation 1.

$$R\text{-}CH_3O + 3\ HOCl = CO_2 + CHCl_3 + 2H_2O$$
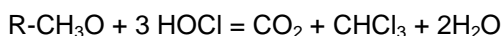
The haloform reaction shown in equation 1 is base-catalyzed and, as such, the rate is dependent on the pH of the reaction medium. The base-catalyzed reaction removes a proton from the carbon double bond causing the formation of the enolate ion. This is the rate determining step and the enolate ion will

subsequently undergo chlorine substitution at the carbon in the alpha position (the carbon next to the carbonyl carbon). The resulting trichloromethyl ketone then hydrolyzes, causing the cleavage of the carbonyl carbon and alpha carbon bond and yielding chloroform and a carboxylic acid. Although humic substances are likely the major source of trihalomethanes, other organic carbon substances can also be trihalomethane precursors. For example, with some alkenes, chlorine adds to an activated double bond, the byproduct of which may be oxidized to methyl ketones, and may then undergo the haloform reaction. Similarly, meta-hydroxy phenolic compounds and cyclohexanes containing a methylene group flanked by two carbonyls can yield trihalomethanes. Many of the compounds produced as a result of chlorination of organic carbon compounds are probable carcinogens to humans or have been shown to be mutagenic (Health Canada 1996; Reckhow and Singer 1990). Reckhow and Singer (1990) observed that the average yield of THMs in drinking waters of seven U.S. cities was 52.2 µg/mg total organic carbon. In cities with high organic carbon concentrations in the raw water (about 15 mg/L), concentrations of THMs were observed in the low mg/L range (Reckhow and Singer 1990).

3.3 Literature Guidelines

Health Canada has not established a drinking water quality guideline for either dissolved or total organic carbon (Health Canada 1996). Since 1978, a number of water quality parameters have been identified as not requiring a guideline, of which total organic carbon was one (Health Canada 1996). No rationale was given for total organic carbon specifically. In general, drinking water quality guidelines are not developed for parameters in which: (i) currently available data indicate no health risk or aesthetic problem, or (ii) the parameter is composed of several constituents for which individual guidelines exist or may be required. Guidelines do exist for several parameters related to dissolved and total organic carbon. For example, an aesthetic objective of 15 TCU has been established for true colour (Health Canada 1996), which obviates the need for a dissolved organic carbon guideline. Similarly, an aesthetic objective of 500 mg/L for total dissolved solids and a maximum acceptable concentration of 1 NTU have been established (Health Canada 1996), thus addressing some of this drinking water quality issues that would be associated with high levels of total organic carbon. No criteria for dissolved or organic carbon for protection of drinking water were found in the world literature or on the worldwide web.

The US EPA recently issued the Disinfectants and Disinfection By-Products Rule that specifies, amongst other things, maximum TOC levels of 2 mg/L in treated water and 4 mg/L in source water to ensure that disinfection byproducts such as trihalomethanes are present at acceptable levels (Pontius 1993).

3.4 Proposed Guidelines

The water quality criteria for total organic carbon are 2 mg/L for treated water and 4 mg/L for source water. The criteria should not be exceeded at any time in drinking water systems that use chlorination for disinfection. For systems that do not disinfect or which use other methods for disinfection (e.g., ozonation), the criteria do not apply. The appropriate methodology for determining total organic carbon is discussed in section 1.4 and in BC Environment (1994).

3.5 Rationale

The production of haloforms in drinking water as a result of the haloform reaction between organic carbon compounds and hypochlorous acid is a serious drinking water quality issue. The removal of excess organic carbon prior to chlorination will reduce the production of THMs and other substances that complex to humates at low levels. The interim maximum acceptable concentration for trihalomethanes derived by Health Canada (1996) for drinking water is 0.1 mg/L. A comparison of data from drinking water sources in the United States shows that, if TOC can be maintained below 2 mg/L in the drinking water effluent, there is a high probability that the THMs guideline of 0.1 mg/L will not be exceeded (Martin 1994).

Several studies have shown that dissolved and total organic carbon levels are strongly correlated with water colour (e.g., Effler et al. 1985; Gorham et al. 1986; Evans 1988). Concentrations of approximately 3 to 5 mg/L are associated with waters having a true colour of approximately 15 to 30 mg/L Pt (Hutchinson and Sprague 1987; Henriksen et al. 1988; Brakke et al. 1988; Matuszek and Beggs 1988; Welsh et al. 1993). This suggests that the drinking water quality criteria for both organic carbon parameters to address aesthetic concerns would be about 3 mg/L, thus further supporting the criteria proposed above.

Water Quality

Aquatic Life

4.1 Effects

Organic carbon plays a central role in lake and stream chemistry because it complexes metals and nutrients, affects pH and alkalinity, and acts as a substrate for microbial production (Dillon and Molot 1997). Dissolved organic carbon (DOC) can protect as well as harm aquatic life depending on concentration, chemical composition and system characteristics. For example, the humic fraction of DOC can form particulates that serve as a food source for filter and deposit feeders, while at the same time increasing exposure of these organisms to higher levels of non-polar toxic chemicals (Björk and Gilek 1996). Petersen and Persson (cited in Kullberg et al. 1993) observed that at pH 5, increasing humus concentrations improved survivorship and growth of Daphnia magna up to 10 mg/L after which survivorship declined. This section focuses on the role of organic carbon in the following key aquatic system processes:

- Bio-availability and toxicity of metals and organics,
- productivity and resulting impacts on food webs, and
- buffering and acidification.

Organic carbon also affects the optical properties of water which can have important consequences for protection of biota from the effects of ultraviolet radiation, depth of the euphotic zone, and algal species composition (see BC Environment 1998a). Because these effects were the focus of the recently

developed water quality criteria for true and apparent colour (BC Environment 1998a), they will not be dealt with here.

4.1.1 Bio-availability and Toxicity of Metals and Organics

Numerous studies have shown that the humics and other compounds that comprise dissolved organic carbon in water complex with cadmium (Stephenson and Mackie 1988), aluminum (Simonin et al. 1993), silver (Janes and Playle 1995), zinc (Starodub et al. 1987), lead (Starodub et al. 1987) and copper (Wilson 1972; Nilssen 1982; Winner 1985; Starodub et al. 1987; Meador 1991; Breault et al. 1996), thus reducing the toxicity of these metals (Winner 1985; Starodub et al. 1987; Hutchinson and Sprague 1987; Meador 1991; Welsh et al. 1993; Bresler et al. 1995). Similar relationships have been observed between organic carbon and bioavailability of organics such as PAHs and PCBs (Broman et al. 1996), chlorothalonil (Winkler et al. 1996), and cationic surfactants (Lewis 1992). Humic substances in dissolved organic carbon can bind with phosphorus or form iron-phosphate complexes, thus reducing the available phosphorus (Kullberg et al. 1993).

The proportion of metals complexed to humus is dependent on pH, ionic strength, and the relative concentrations of metals and humic material. At low pH, a larger portion of metals is released from the humic acid ligands, thus increasing bioavailability (Starodub et al. 1987; Spry and Wiener 1991; Meador 1991; Welsh et al. 1993). Hutchinson and Sprague (1987) showed the ameliorating effect of natural total organic carbon by exposing flagfish fry to a mixture of aluminum, copper and zinc at pH 5.8 in lake waters with natural TOC ranging from 1.9 to 8.5 mg/L. The LC50 in the highest TOC water was about 7-fold greater than that for the lowest TOC water. The following regression equation explained 84% of the variation in lethality of the metals mixture.

Equation 2.

$$\text{Log}_{10} \text{ LC}_{50} = -0.395 + 1.145 - \log_{10}\text{TOC}$$

When the LC_{50} was expressed in terms of dialyzable fraction of the metals (Molecular weight <1000), however, aluminum and copper concentrations were relatively constant, regardless of TOC, suggesting that toxicity was due to the free ionic forms of these metals. Welsh et al. (1993) also observed a strong relationship between copper toxicity to larval fathead minnows and dissolved organic carbon (mg/L). At pH 7.0, the following regression equation explained 92% of the variation in copper toxicity.

Equation 3.

$$\text{Log}_{10} \text{ LC}_{50} = 1.033 + 0.999 - \log_{10}\text{DOC}$$

The relationship between toxicity of metal mixtures and copper and organic carbon shown in laboratory studies has also been observed in in situ bioassays with brook trout exposed to elevated levels of

monomeric aluminum (Al_{im}) in Adirondack headwater streams (Simonin et al. 1993). This study indicated the following relationship between mortality of brook trout, duration of Al_{im} >100 mg/L (CONCDUR), and dissolved organic carbon (mg/L)(r^2 = 0.61).

Equation 4.

Percent Mortality = 49.7 + 0.01 - CONCDUR - 6.46 - DOC

If CONCDUR is held constant, the regression equation indicates that for every 1 mg/L reduction in DOC, mortality would increase 6.46% (until 100% mortality is reached). This study is consistent with the findings of several others (e.g., Effler et al. 1985; Baldigo and Murdoch 1997) that DOC complexes with inorganic Al to create organomonomeric aluminum (Al_{om}) species that are less toxic than Al_{im} to fish (Matuszek and Beggs 1988).

Several studies have shown that the relationship between mercury and organic carbon is different from that observed with other metals. Mercury availability, bioaccumulation, and hence toxicity increase as dissolved organic carbon increases in drainage lakes (Nilsson and Håkanson 1992; Driscoll et al. 1994; Mierle and Ingram 1991). Part of the reason for this relationship is that the mercury brought to an aquatic system from the surrounding catchment area is attached to humic substances (Nilsson and Håkanson 1992; Mierle and Ingram 1991). For deep lakes in Sweden, regression analyses indicated that an increase in water colour (a surrogate for dissolved organic carbon) from 10 to 50 mg/L Pt was associated with an increase in mercury tissue levels in fish of between 23.4 and 82.8%, depending on fish species, location, and depth of lake (Nilsson and Håkanson 1992). This suggests that DOC-mediated transport of mercury from the watershed may reduce tissue mercury levels more than the DOC-mediated inhibition of biomethylation which has been observed in several studies (e.g., Barkay et al. 1997).

The positive relationship between DOC and tissue mercury levels observed in drainage lakes does not exist for seepage lakes (Grieb et al. 1990). In the case of drainage lakes, much of the mercury is first complexed with humic material and then transported to the aquatic system from the surrounding catchment area (Driscoll et al. 1994; Richardson et al. 1995). Hence, the positive relationship between DOC and tissue mercury levels. In seepage lakes, however, most of the mercury arrives via atmospheric deposition (Grieb et al. 1990). DOC can inhibit bio-methylation of mercury by controlling the substrate for methylation. This can considerably reduce uptake in biota and thus the relationship between DOC and tissue mercury levels in seepage lakes is the reverse of that observed for drainage lakes.

4.1.2 Productivity and Food Web Effects

Several studies have noted that brown-water systems with high concentrations of dissolved organic carbon are associated with increased bacterial productivity and support denitrification (Hessen 1985; Tranvik et al. 1991; Weisner et al. 1994). For example, Hessen (1985) observed that the mean annual biomass of bacteria in holarctic oligotrophic lakes was 7.8-12.1 µg C/L in clear lakes, 10.5 µg C/L in slightly coloured lakes and 16.2-44.1 µg C/L in highly coloured humic lakes. Bacterial and zooplankton biomass were also high relative to algal biomass, strongly supporting the possibility that humics are an essential component of the carbon pool in these systems. Similar relationships between bacterial

biomass and organic carbon levels have been observed in organically polluted streams (Cazelles et al. 1991) and contaminated ground waters (Harvey and Barber 1992). Increases in bacterial biomass as a result of increases in organic carbon can cause oxygen depletion as has been observed in the central and eastern basins of Lake Erie (Charlton and Rao 1983).

The biological functions of many small lakes and headwater streams is controlled by the amount of externally produced allochthonous carbon, rather than the much smaller quantities of autochthonous carbon produced within the water. In such systems, plankton communities consume more carbon than the algae can themselves produce and are therefore reliant on external energy supplies. As a result, changes in input rates of allochthonous carbon would likely have profound effects on primary production and respiration. Indeed, France et al. (1996) observed that removal of riparian vegetation near boreal lakes resulted in reductions of DOC from 17.8 to 0.4 g/m shoreline/year which translated into an annual reduction in organic inputs to the lakes of 8 to 15%. The reductions in organic carbon inputs were associated with a 4-9% decrease in primary production and an 8-17% decline in respiration. Much of the reduction in external DOC input was due to the reduced transport of leaf litter to the lakes (France and Peters 1995), a factor that was not compensated for by increased soil erosion. Lakes and streams affected by clear cutting would likely shift from allotrophy (external energy reliance) to autotrophy (energy self reliance), a change that can have important effects on invertebrate and fish communities (Bilby and Bisson 1992).

Dissolved organic carbon in streams complexes with ferrous iron (FeII) and maintains it in this state until it reaches a lake or estuary where it can be utilized by phytoplankton. In the absence of DOC, most iron in flowing streams is oxidized to ferric hydroxide, which phytoplankton cannot assimilate (Kawaguchi et al. 1994). Thus, reductions in DOC from deforestation, agricultural disturbance to the riparian zone, or residential development can have important consequences on watershed productivity, in addition to the localized effects discussed above.

Allotrophic aquatic systems receiving large inputs of particulate organic carbon tend to have macroinvertebrate communities with high proportions of shredders and detritivores (Andersson and Danell 1982; Bilby and Bisson 1992; Delong and Brusven 1994). Delong and Brusven (1994) found that in sections of the Lapwai Creek in Idaho with reduced inputs of allochthonous carbon due to agricultural disturbances, shredders were rare and never made up more than 5% of the macroinvertebrate community. In other unaffected streams in the Lapwai Creek drainage basin, shredders were often abundant. Delong and Brusven (1994) also noted that gathering and filtering invertebrates, which are dependent on particulate organic matter, were never as abundant in Lapwai Creek as were grazing organisms utilizing the large biomass of algal matter found in the stream. Abelho and Craça (1996) also noted that not only does quantity of organic carbon inputs affect aquatic communities, so does quality. In their study, they found that replacement of deciduous forests with monocultures of Eucalyptus globulus resulted in reduced numbers and taxa of macroinvertebrates. The reasons for the low quality of eucalyptus detritus are the presence of oil glands and phenols in the leaves, and a superficial wax and a thick cuticle that delay conditioning of the leaves. Many conifer species share these leaf characteristics.

Bilby and Bisson (1992) observed that production of coho salmon and shorthead sculpin was elevated in a clear-cut site over that in a nearby old-growth site, despite a five-fold reduction in inputs of allochthonous carbon. In these sites, fish populations appeared to depend on food derived from autotrophic pathways during spring and summer, a hypothesis supported by stomach contents analysis and the similar ratios of autochthonous inputs and fish production between the two streams. In larger lakes and higher order streams, where shading by riparian vegetation has little impact on autotrophs, reductions in inputs of allochthonous organic carbon may lead to reductions in the macro-invertebrate

functional groups that depend on these sources as well as the fish species that feed on them (France 1995a).

4.1.3 Buffering and Acidification

Declines and losses of fish populations from acidified lakes and rivers have been observed by investigators in Canada, the United States and Scandinavia (Matuszek and Beggs 1988; Schindler 1988; Lien et al. 1996; and numerous others). In Canada, large acid-sensitive areas exist in the mountainous areas of the west, the Yukon, the Northwest Territories, as well as the well-known eastern sector of the country. Acid-sensitive aquatic systems are susceptible to the substantial increases in acidity of catchment soils and water that occurs following deforestation (Hedin et al. 1990). The available evidence suggests that most adult fishes can tolerate pH values of less than 5.5., but that juvenile fishes and many organisms lower in the food web cannot (Schindler 1988; Baldigo and Murdoch 1997). The early disappearance of biota at lower trophic levels may cause starvation to large predatory fish long before the direct toxic effects of the hydrogen ion are evident.

The reactive chemistry of dissolved organic matter is of great importance in determining the likely impacts of anthropogenic acid inputs to aquatic systems. Carboxylic acids comprise about 90% of the acid functional groups on humic compounds, and are the most important in the organic carbon pool because they possess reactive sites and contribute aqueous solubility and acidity to organic molecules (Eshleman and Hemond 1985; Kullberg et al. 1993). The presence of acid functional groups provides a pH buffer in aquatic systems, such that between pH 4 and 5, DOC is the principal buffer in surface waters (Kullberg et al. 1993; Roila et al. 1994). Brakke et al. (1988) showed that a large proportion of acidic lakes in the Adirondacks (acid neutralizing capacity or ANC = 0) were clear water lakes with DOC less than 2 mg/L. Hedin et al. (1990) and Roila et al. (1994) estimated that organic anions on humic compounds provide 1.8 to 2.0 meq acid-neutralizing capacity per mg C of DOC. The acid-base properties of DOC also mean that it is a natural background source of acidity, particularly in humus-rich waters, and that recovery of pH will be slowed by DOC buffering (Eshleman and Hemond 1985; Kullberg et al. 1993; Roila et al. 1994).

Aluminum is released to lakes and streams during acidification (Hedin et al. 1990). Only inorganic monomeric aluminum (Alim) is highly toxic to fish and present at low pH (Eshleman and Hemond 1985; Brakke et al. 1988; Cosby et al. 1996; Baldigo and Murdoch 1997). Dissolved organic carbon complexes with the Alim produced during acidification and thus if present at sufficiently high levels, DOC can protect fish species from aluminum toxicity (Matuszek and Beggs 1988; Lien et al. 1996; Baldigo and Murdoch 1997). Effler et al. (1985) observed that the removal of aluminum from the photic zone coincided with a depletion of DOC and a decrease in light attenuation; these observations support the notion that DOC can counteract the increased bioavailability of Alim resulting from acidification. The results of the study by Baldigo and Murdoch (1997) on moderately acidic streams (pH 5.2 to 5.6) in the Catskill Mountains, New York suggest that DOC concentrations greater than 2 to 3 mg/L significantly decrease monomeric inorganic aluminum and thus decrease toxicity to brook trout.

4.2 Literature Guidelines

Based on a review of the literature and the worldwide web, few, if any, jurisdictions have derived criteria for the protection of marine and freshwater aquatic life, for either dissolved or total dissolved carbon. The CCME (CCREM 1987 and updates) does not have organic carbon guidelines for the protection of freshwater or marine aquatic life.

4.3 Proposed Guidelines

4.3.1 Total Organic Carbon

The 30-day 50th percentile total organic carbon concentration shall be within 20% above or below seasonally-adjusted median background levels as measured historically or at appropriate reference sites. This criterion applies to freshwater aquatic systems only. The 30-day mean calculation should be based on a minimum of five weekly samples taken over a period of 30 days. The appropriate methodology for determining total organic carbon is discussed in section 1.4 and in BC Environment (1994).

4.3.2 Dissolved Organic Carbon

The 30-day 50th percentile dissolved organic carbon concentration shall be within 20% above or below seasonally-adjusted median background levels as measured historically or at appropriate reference sites. This criterion applies to freshwater aquatic systems only. The 30-day 50th percentile calculation should be based on a minimum of five weekly samples taken over a period of 30 days. The appropriate methodology for determining dissolved organic carbon is discussed in section 1.4 and in BC Environment (1994).

4.4 Rationale

The review of the literature on effects indicated that changes in concentrations of total and dissolved organic carbon can have a significant impacts on aquatic systems. Reductions in organic carbon, for example, can cause reductions in primary productivity, system metabolism, while increasing susceptibility to toxic metals and acidification. Increases in organic carbon can increase bacterial metabolism to the point of causing anoxia. Changes in the quality of organic carbon entering systems (e.g., allochthonous carbon versus autochthonous carbon) also can have dramatic impacts on the species composition of invertebrate and fish communities. Several of the studies reviewed above indicate that relatively small changes in average organic carbon levels above or below background (about 20%) can have measureable adverse impacts on aquatic systems (e.g., France et al. 1996), especially in areas where metals concentrations are elevated (Hutchinson and Sprague 1987; Simonin et al. 1993; Baldigo and Murdoch 1997) or there are nearby acid inputs (Brakke et al. 1988).

It is not useful to specify a single value as the ambient water quality criterion for total or dissolved organic carbon. A more useful approach is to determine whether a particular anthropogenic activity (e.g., road construction, harvesting of forests) is causing a change in total organic carbon levels compared to historical conditions or to background conditions in nearby aquatic systems. We selected a 20% change

in total and dissolved organic carbon for the criteria to ensure minimal impacts on aquatic biota. Smaller changes are not likely to be detected as significantly different from the stochastic variation often observed in British Columbia lakes and rivers (Figure 1).

4.5 Monitoring Considerations

The sampling design used to determine whether total or dissolved organic carbon has changed by about 20% as a result of an anthropogenic activity needs to be flexible. Some considerations include availability of historical data and/or reference sites, nature of the anthropogenic activity (e.g., point versus diffuse sources), natural seasonal variability, and various legal and economic issues. Short-term changes (e.g., <24 hours) can arise due to natural events (e.g., storms) and are unlikely to have serious impacts on aquatic communities. Therefore, when testing whether a particular anthropogenic activity has caused a failure to meet the organic carbon water quality guidelines, several samples (minimum n=5, preferably greater than 10) should be taken over a 30-day period and the 50th percentile calculated. The calculated 50th percentile for the site of interest should be compared to background data collected at similar times of the year and/or locations.

A substantial quantity of information has been collected on the levels of TOC and DOC in British Columbia. This information is useful for establishing background levels, although in some cases the necessary data will not be available or will not be sufficient to accurately determine reference conditions in the stream system under investigation. In both of these cases, it will be necessary to establish baseline conditions prior to the implementation of developmental activities or establish appropriate reference sites in upstream areas or nearby systems. It is recommended that several years of background data from the basin or site where management will occur and a similar set of data from comparable, unmanaged sites be obtained.

Water Quality

Wildlife

5.1 Effects

Wildlife can be directly or indirectly affected by changes in organic carbon levels in aquatic systems. For example, abundance of loons are negatively correlated with TOC and DOC levels because the latter are typically highly coloured and loons require clear water to sight their prey (Alvo et al. 1988; Heglund et al. 1994). Because effects due to the optical properties of water were the focus of the recently developed water quality criteria for true and apparent colour (BC Environment 1998a), they will not be dealt with here. Possible indirect effects arise because organic carbon plays an important role in aquatic system productivity and system response to acid inputs. These effects are discussed below.

Several studies have shown that the reproductive success and probability of presence of waterfowl are strongly related to pH levels (e.g., Blancher et al. 1992). Analyses of 212 lakes in central Ontario

revealed a positive relationship between DOC levels and presence of insectivorous waterfowl (i.e., black duck and ring-necked duck). Several factors could explain this relationship: (i) increased DOC is generally associated with increased system productivity and thus there may be more invertebrate prey available to waterfowl in lakes with high DOC, and/or (ii) DOC acts as a buffer and thus acid-sensitive invertebrates are available as prey in lakes with high DOC levels. Andersson and Danell (1982) found that addition of organic matter to man-made water-bodies was associated with an increase in macro-invertebrate predators (e.g., Hirudinea), an important food source for diving ducks (e.g., grebes). The increase in macro-invertebrate predators, however, decreased the abundance of their prey, detritivorous invertebrates (e.g., chironomids, Asellus), an important food source for dabbling ducks. Therefore, the relationship between DOC and waterfowl abundance is likely to be complicated because waterfowl are affected by a number of other variables (e.g., lake size, food web relationships, competition with insectivorous fish, etc) that are themselves positively or negatively correlated with DOC.

5.2 Literature Guidelines

No water quality criteria for the protection of wildlife were found in the literature for either total or dissolved organic carbon.

5.3 Proposed Guidelines

5.3.1 Total Organic Carbon

The 30-day 50th percentile percentile total organic carbon concentration shall be within 20% above or below seasonally-adjusted median background levels as measured historically or at appropriate reference sites. This criterion applies to freshwater aquatic systems only. The appropriate methodology for determining total organic carbon is discussed in section 1.4 and in BC Environment (1994).

5.3.2 Dissolved Organic Carbon

The 30-day 50th percentile dissolved organic carbon concentration shall be within 20% above or below seasonally-adjusted median background levels as measured historically or at appropriate reference sites. This criterion applies to freshwater aquatic systems only. The 30-day 50th percentile calculation should be based on a minimum of five weekly samples taken over a period of 30 days. The appropriate methodology for determining dissolved organic carbon is discussed in section 1.4 and in BC Environment (1994).

5.4 Rationale

The limited wildlife effects information indicates that changes in organic carbon are associated with possible impacts on abundance of waterfowl. The available information is, however, insufficient to define numerical criteria for the protection of wildlife that would be different from the aquatic life criteria. The aquatic life criteria should be protective of wildlife because the impacts of changes in organic carbon to

waterfowl are likely mediated through the aquatic food chain. Therefore, if aquatic life are protected, wildlife should also be protected.

Water Quality

Livestock

6.1 Effects

To our knowledge, no known effects of dissolved or total organic carbon to livestock have been documented at levels that are likely to occur in livestock water.

6.2 Literature Guidelines

There are no criteria specific to livestock watering available from any other jurisdiction.

6.3 Proposed Guidelines

There is insufficient information to derive water quality criteria for total and dissolved organic carbon for this water used.

6.4 Rationale

The limited information on the toxicity of humic and fulvic acids to mammals (see Section 3.2 of BC Environment 1998a) indicates that livestock are not likely to be adversely affected by waters with high levels of organic carbon. If the water was to impart a toxic effect to livestock, it would be due to other physical, biological and/or chemical parameters in the water. Existing criteria for these parameters should protect livestock from being harmed.

Water Quality

Irrigation

7.1 Effects

To our knowledge, no known effects of total or dissolved organic carbon in irrigation waters supplied to crops have been documented.

7.2 Literature Guidelines

There are no criteria for total and dissolved organic carbon specific to irrigation water available from any other jurisdiction.

7.3 Proposed Guidelines

There is insufficient information to derive water quality criteria for total and dissolved organic carbon for this water used.

7.4 Rationale

The effects to plants of water with high levels of organic carbon observed in aquatic systems are due to reductions in light quality and quantity (BC Environment 1998a). Such effects are highly unlikely for terrestrial plants exposed to irrigation waters with high levels of organic carbon. If the water were to impart a toxic effect to crops, it would be due to other physical, biological and/or chemical parameters in the water. Existing criteria for these parameters should protect crops from being harmed.

Water Quality

Recreation and Aesthetics

8.1 Effects

There are a number of publications indicating that people avoid highly coloured and/or turbid waters (see BC Environment 1998a). To our knowledge, no effects of total or dissolved organic carbon to the recreational quality of waters other than these visual aesthetics effects have been documented.

8.2 Literature Guidelines

There are no criteria for total and dissolved organic carbon specific to recreation and aesthetics available from any other jurisdiction.

8.3 Proposed Guidelines

No water quality criteria are proposed for total and dissolved organic carbon in waters used for recreation.

8.4 Rationale

The major requirements for recreational waters are that they contain low numbers of organisms posing health risks (e.g., fecal coliforms, pathogens), are free of nuisance organisms, and are aesthetically acceptable (i.e., low colour and turbidity, free from oil and grease). Dissolved organic carbon is often closely correlated with colour, while total organic carbon may be correlated with turbidity (e.g., Effler et al. 1985; Gorham et al. 1986; Evans 1988). However, water quality criteria for colour and turbidity have been developed (BC Environment 1998a,b) and these more directly address the issues posed by elevated levels of organic carbon in recreational waters.

Water Quality

Industrial Water Supplies

9.1 Effects

The colour-causing humic and fulvic acids that make up a large fraction of organic carbon in feedwaters may cause foaming in boilers and hinder other treatment processes such as iron removal and water softening (CCREM 1987 and updates). Colour-causing constituents and suspended particulates in organic carbon can also reduce paper brightness and sheet quality because cellulose fibers readily absorb these substances, and the colour may remain in the finished product. Organic compounds are difficult to remove from pulp fibers. For the same reason, organic carbon is undesirable in textile waters because it can cause staining. Several food and beverage industries (i.e., brewing, carbonate beverages, sugar manufacture) require water free from organic matter because it can cause spoilage, rings in bottles, and carbonation problems. Water used in the semiconductor industry must be ultrapure with TOC levels below 0.05 mg/L because TOC is directly correlated with defect density (George Varkey at www.exicom.org/cew/sep96/george.htm. Note: This link no longer works.)

9.2 Literature Guidelines

Water quality guidelines ranging from 0.2 to 1 mg/L TOC have been adopted by the CCME (CCREM 1987 and updates) for waters used in steam generators. The TOC guidelines are 0.2 mg/L when pressure is greater than or equal to 6.22 MPa, 0.5 mg/L when pressure is greater than or equal to 3.11 MPa and less than 6.21 MPa, and 1 mg/L when pressure is less than 3.1 MPa for industrial water tube boilers that include super heater, turbine drives or process restriction on steam purity. For steam industrial water tube boilers without super heater, turbine drives or process restriction on steam purity, the TOC guideline is 1 mg/L. For industrial fire tube boilers without super heater, turbine drives or process restrictions on steam purity, the TOC guideline is 10 mg/L.

9.3 Proposed Guidelines

No water quality criteria are proposed for total and dissolved organic carbon in industrial water supplies.

9.4 Rationale

Organic carbon for industrial water use are not likely necessary because industries requiring water free of colour-causing constituents or organic matter (e.g., production of fine paper) generally treat the water to remove organic carbon prior to use.

Water Quality

Research and Development Needs

The key to being able to apply the water quality criteria for total and dissolved organic carbon is the ability to distinguish changes due to anthropogenic sources against the background of strong and temporal variation that exists in many aquatic systems in British Columbia. The available data on levels of organic carbon in British Columbia aquatic systems indicates that many locations are sampled infrequently, or have not been sampled in recent years. For these systems, it will be difficult to detect whether a 20% change in organic carbon levels has occurred as the result of an anthropogenic activity. We therefore recommend that regular monitoring programs be carried out for aquatic systems that are or may become influenced by anthropogenic activities, as well as at appropriate reference sites.

Water Quality

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Glossary

Alim — inorganic monomeric aluminum

Alom — aluminum complexed with organic ligands forming organomonomeric aluminum.

Allochthonous organic matter — plant and organic matter transported into a water body from the surrounding terrestrial watershed.

Anoxia — lacking oxygen

Autochthonous organic matter — organic matter in a water body derived from primary producers or other autotrophic processes.

CONCDUR — concentration-duration factor defined as the median Alim concentration during an episode (period of daily median Alim greater than 100 mg/L) multiplied by the duration of the episode in days.

Detritivores — organisms that consume dead organic matter (detritus).

Dialyzable fraction — portion of a sample recovered after separation of substances in a solution by means of their unequal diffusion through a semi-permeable membrane.

Drainage lakes — lakes that receive the majority of their water from the surrounding watershed.

Euphotic zone — surface layer of water to the depth of light penetration where photosynthetic production equals respiration.

Filtering invertebrates — invertebrates that remove organic matter from the water column by filtering.

Gathering invertebrates — invertebrates that collect organic matter from their environment for consumption.

Heterotrophy — requiring a supply of organic matter or food from the environment.

Histology — a branch of anatomy that deals with the minute structure of animal and plant tissues as discernible with the microscope.

Holarctic oligotrophic lakes — northern lakes that are low in nutrients and in productivity.

Humic substances — high molecular weight substances formed from microbial degradation of plant material; persistent substances whose basic structure is aromatic rings variously bridged into condensed form by -O-, -NH, -CH2-, or -S- linkages with attached hydroxy groups that provide acidity, hydrophilic properties, base-exchange capacity, and tannin-like character.

Nonhumic substances — low molecular weight organic substances that are easily degraded and exhibit rapid flux rates; includes carbohydrates, proteins, peptides, fats, pigments, waxes, and amino acids.

Littoral zone — shallow water zone of lakes in which light penetrates to the bottom permitting vegetative growth; also zone between high and low water marks in tidal areas.

Oligotrophic — a water body low in nutrients and productivity.

Pelagic zone — free water zone generally populated by swimming and floating biota.

Photic zone — the depth of a water body through which light can penetrate.

Seepage lakes — lakes that receive the majority of their water from ground water sources.

Shredders — aquatic animals that feed on course particles of organic matter.

Temporal variation — change over time.

Trophic levels — functional classification of organisms in an ecosystem according to feeding relationships from first level autotrophs through succeeding levels of herbivores and carnivores.