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Extinction Coefficients and Dissolved Organic Carbon Content in Freshwater in Kenya

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Dissolved organic matter (DOM) in freshwaters has a number of important ecological and geochemical functions. Some of these functions have been discussed by various researchers based on findings from many years of research using different test methods and in most cases involving use of isolated humic substances i.e. fulvic (FA) and humic (HA) acids. The main functional properties of DOM in freshwaters include their ability to absorb light (which affects light penetration into surface waters and influences primary productivity), ability to bind protons (which affects the acidity and acid-base balance), ability to bind heavy metal and organic contaminants (which affects contaminant transport and bioavailability), ability to adsorb at surfaces (which affects the colloidal stability and ion binding of suspended particles, the soil particle chemistry and mineral dissolution) and their susceptibility to metabolism and ability to act as a metabolic substrate for micro-organisms (Abbt-Braun and Frimmel 1999; Kullberg et al. 1993; Perdue and Gjessing 1990; Ratnaweera et al. 1999; Tipping 1998; Tipping et al. 1988). These functions of DOM are dependent on its characteristic physical and chemical composition. The variability in DOM chemical composition and, consequently, in the mentioned functional properties, with time and origin, would make it difficult to directly compare DOM samples from different sources, especially when modelling chemical speciation in freshwaters. However, a number of studies have now shown that modelling, using DOC as input parameter, allows prediction of metal speciation in natural waters and soil solutions (Tipping 1998). By definition, DOM refers to the collection of organic compounds present in solution in surface waters, soil waters and ground waters which include humic substances (fulvic and humic acids and humin) together with minor components such as carbohydrates, amino acids, carboxylic acids and hydrocarbons (Thurman and Malcolm 1981). Aquatic DOM has been described as coloured polyelectrolytes of carboxylic, hydroxyl and phenolic functional groups which make up the major class of organic compounds, isolated from water by sorption onto XAD resin at pH 2 or by a comparable procedure (Thurman and Malcolm 1981). The aquatic DOM is also simply referred to as fulvic acid (FA) which is the major constituent of humic substances in freshwaters, unlike DOM extracted from soil which is mainly humic acid (HA). It has also been reported that 50-75% of aquatic DOM, depending on origin, consists of dissolved organic carbon (DOC) (Easthouse et al. 1992). DOC has often been used to quantify

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aquatic DOM by researchers and in most reports 59% is often taken to be the average % DOC content in freshwater DOM isolates (Tipping et al. 1988). The chemical structures of fulvic acids are described in literature (Easthouse et al. 1992; Perdue and Gjessing 1990). The aromatic structures account for between 20-60% of the organic carbon, depending on the origin. These various definitions of DOM only illustrate its chemical complexity. In addition, various types of DOM are expected to have different DOC contents and to absorb ultraviolet-visible (UV-VIS) light differently.

Compounds with loosely-bound Π-electrons or non-bonding n-electrons can absorb energy in the near-ultraviolet region (200-380 nm) of the electromagnetic spectrum. Within the molecules of DOM, specific segments or functional groups have this feature. Examples include functional groups containing un-bonded electrons and carbon-carbon multiple bonds (Stevenson 1982) and this is expressed by un-saturation and aromaticity of DOM molecules. Ultraviolet (UV) light absorbance characteristics of DOM have also been used quantitatively to estimate DOM concentrations in different freshwaters and coastal sea water (Mattson et al. 1974), lake water (Banoub 1973; De Haan et al. 1982; Tipping et al. 1988), river and stream water (Banoub 1973; Lewis and Cranfield 1977; Mrkva 1983; Tipping et al. 1988) treated and untreated waste water (MacCraith et al. 1993), in peat water (Moore 1985), precipitation (Bartels 1988), throughfall (Brandstetter et al. 1996) soil solution (Nunan et al. 1998). As the absorbance of light by DOM decreases with increasing wavelengths, most workers have used light in the range of 250-340 nm. At wavelengths below 235 nm nitrate contributes significantly to the total absorbance. Absorbance at 340 nm has been taken as a good estimate to quantify the amounts of humic substances in freshwaters by Tipping et al. (1988) who considered absorbance measurements at shorter wavelengths to be more sensitive but less accurate for quantifying DOM as they are more subject to interference by non-humic organic matter and by inorganic components, notably sulphate (Tipping et al. 1988). Qualitatively, the measurement of the UV absorbing characteristics of DOM has been used in environmental studies to assess the propensity of humic substances to bind to non-polar organic pollutants (Chin et al. 1997) and to evaluate DOM behaviour in sorption (Gu et al. 1996) or degradation experiments (Zsolnay and Steindl 1991). UV absorbance has also been used to identify the origin and assess the fate of DOM in lake waters (Andersen and Gjessing 2002; Sachse et al. 2001) and to characterize both total DOM and DOM fractions in waste water effluents (Imai et al. 2002). Variations in optical absorbance, photo-sensitivity, fluorescence, of various DOM isolates, especially based on the internationally accepted fulvic acid (FA) standard, the Suwannee River Fulvic Acid (SRFA), have been reported as a method of showing variability in DOM from different origins (Chin et al. 1997; Chiu et al. 1986; Cronan and Aiken 1985; Driscoll 1984; Faust and Hoigne 1987; Haitzer et al. 1999)

Although attempts have already been made in Kenya to monitor contaminant residues in aquatic environments no studies have been conducted to quantify

DOM and use it to evaluate the extent of freshwater pollution. In this paper, we report results of a study conducted to determine the DOC contents and UV-VIS absorbance properties of various freshwater samples taken from different regions in Kenya. The extinction coefficients expressed as the ratio of optical absorbances over the DOC contents of different water samples were compared. The use of the variability in extinction coefficients in characterizing DOM from different freshwater samples from different origins was considered. The results obtained can help in understanding the ecosystem characteristics within surface waters and the status of freshwater quality in Kenya as well as in understanding the potential influence of DOM on the transport and distribution of hydrophobic contaminants such as polynuclear aromatic hydrocarbons, PCB's, pesticides and heavy metals.

MATERIALS AND METHODS

A Shimadzu TOC 5050 Analyser operating at 680 °C was used to determine the dissolved organic carbon (DOC), the total organic carbon (TOC) and dissolved inorganic carbon (DIC) content in water samples. The limit of detection of DOC was 0.5 mg C/L. The UV-VIS absorbance was determined in a Hitachi U-2000 Spectrophotometer.

Water samples were taken from various locations in Nyanza, Western, Rift Valley and Nairobi provinces in Kenya in January 2004. This was a period of fairly dry weather throughout Kenya. In total eight sampling sites were covered, including three lake water samples of Lakes Naivasha (sample JA from Naivasha town), Nakuru (sample JH from Nakuru National Park) and Victoria (sample JE from Kisumu city pier), four river water samples of Athi River (sample JB from Athi River town), River Nzoia (sample JC from Imbaya, Siaya), River Yala (sample JF from Yala town) and Chiromo River (sample JG from Chiromo, Nairobi), and one spring water sample of Kong'wen Spring (sample JD from Nyabeda, Siaya). Suwannee River Fulvic Acid (SRFA) standard sample obtained from the International Humic Substances Society (IHSS), Minnesota, USA, was also used for comparison (see Table 1). The water samples were first filtered through Whatman GF/F 0.7 μm cellulose nitrate membrane filters to leave only the dissolved organic matter. The dissolved organic carbon (DOC), dissolved inorganic carbon (DIC) and total dissolved carbon (TDC) concentrations in the water samples were then determined in the TOC analyser (Table 1). In this analyser, total dissolved organic carbon was determined by the method of high temperature catalytic oxidation through which dissolved organic carbon was oxidized to CO_2 and quantified by a non-dispersive, infrared analyser. Dissolved inorganic carbon was analysed by quantifying the CO_2 generated following phosphoric acid addition. The DIC was subtracted from total dissolved carbon to give the dissolved organic carbon (DOC). The pH values of the water samples were also determined as recorded in table 1. Similar DOC and UV-VIS absorbance assays were performed, simultaneously, on the IHSS Suwannee River Fulvic Acid standard reference sample for comparison.

Before taking UV-VIS absorbance readings, filtered water samples were treated as follows to give a uniform electrolyte concentration of 0.1 M NaCl as follows and pH 7. In a 250-mL Erlemeyer flask, 26.7 mL of filtered water sample was mixed with 0.3 mL phosphate buffer (0.001M KH_2PO_4) to give a uniform pH 7 for all the samples and 3 mL of 1 M NaCl electrolyte to give a uniform 0.1 M NaCl electrolyte concentration. For standard SRFA sample, a 10 mg L^{-1} DOC solution was made with the same electrolyte concentration by mixing 14.02 mL de-ionized water, 2.68 mL of 1M NaCl (to give an electrolyte concentration of 0.1 M NaCl), 0.3 mL of 0.001M KH_2PO_4 buffer (to give pH 7) and 3 mL of stock solution of DOM isolate containing 100 mg L^{-1} DOC (to give a 10 mg L^{-1} DOC assay solution) giving a 30 DOM mL solution. Simultaneously, a control electrolyte solution was also prepared and used as blank water sample (i.e. containing no dissolved organic matter). This was prepared by taking 26.7 mL de-ionized water (filtered through the 0.7 μm cellulose nitrate membrane filter), 3 mL of 1M NaCl and 0.3 mL phosphate buffer to give an electrolyte solution of 0.1M NaCl ionic strength and pH 7. A UV-VIS absorbance scan in the wavelength range of 220-600 nm was performed on the blank (electrolyte) sample and on each water sample using 1 cm path length cell quartz cuvette. At sufficiently low concentration of electrolyte, Lambert-Beer's law [$A=\varepsilon lc$] can be applied, with absorbance A (dimensionless), concentration c (mg L^{-1}), path length l (in cm) and the quantity ε called extinction coefficient (cm^{-1} (g DOC)$^{-1}$). Based on this law, the respective extinction coefficients A_{340}/[DOC] and A_{254}/[DOC] at 340 and 254 nm, respectively, were calculated (Table 2).

RESULTS AND DISCUSSION

Table 1 shows the pH of the water samples determined at 22 °C, the dissolved organic carbon (DOC) content, the dissolved inorganic carbon (DIC) content and total dissolved carbon (TDC). The variations in these physical and chemical properties as shown in the table reflect the variations in geological characteristics of the sampling sites and their locations. Lake Nakuru and Lake Naivasha are both located in the Rift Valley and have no outlets. Both lakes are located adjacent to large industrial towns with high population densities and are recipients of treated industrial and municipal waste effluent. Lake Nakuru is also located in an area of extensive agricultural farming and therefore exposed to high levels of biomass and agrochemical residues. It is also a well known habitat for hundreds of thousands of birds, especially the flamingos, and bird droppings contribute a major portion of organic carbon entering the waters. Lake Naivasha is also close to the fluorspar and diatomite industries. Lake Victoria is the largest lake in Africa (covering an area of approximately 69,000 km^2) and has outlets but is located within an agricultural basin where it receives water from very many rivers and streams. The sampling site was in Kisumu City which is a large industrial city in Kenya which discharges large volumes of industrial and domestic effluent into the lake. The other samples were taken from small rivers i.e. Yala and Nzoia, both in the Lake Victoria basin, flowing through low-population and small-scale-farming regions and through vegetative swamps. Chiromo River is a small stream passing through the centre of Nairobi and is mainly exposed to domestic waste. The sampling site at Athi River was near a mineral processing factory and a cement factory.

Table 1. Water samples, sampling sites, pH and DOC contents.

Sample	pH (20 °C)	DOC (mg/L)	DIC (mg/L)
JA	7.71±0.13	16.21±0.26	31.97±0.57
JB	7.75±0.09	6.71±0.13	18.04±0.32
JC	7.51±0.21	4.9±0.24	13.11±0.13
JD	6.9±0.05	3.46±0.11	13.93±0.21
JE	7.3±0.22	6.97±0.21	17.71±0.11
JF	7.4±0.12	2.71±0.12	8.002±0.04
JG	7.2±0.14	4.09±0.06	19.08±0.14
JH	10.3±0.11	374±4.48	502±10.6
SRFA (10 mg/L)	6.9	10	0.41
Electrolyte	7	<1	nd

Note:'nd'denotes 'not determined'.

All the pH's of the water samples (except the Lake Nakuru sample) were comparable to those pH's of other waters in other tropical countries of Zimbabwe and India, respectively (Berg et al. 1995; Jain 2004). Tipping et al. 1988 reported similar pH ranges (ranging from 6.2-7.1 in lake water and 6.6-8.1 in stream and river waters) in various freshwaters in central part of UK (Tipping et al. 1988). Apart from Lake Nakuru, all the other sampling sites showed near neutral pH (ranging from 6.9-7.75). However the pH of the water sample taken from Lake Nakuru was very high (pH =10.30) indicating that the lake is very alkaline. In fact it is known that most rift valley lakes in Kenya including lakes Nakuru, Naivasha, Elementaita and Bogoria are very alkaline with pH ranges from 9.15-11.25 (Wandiga et al. 1983). The high pH detected in water samples of Lake Nakuru is therefore mainly as result of the geochemical processes in the rift valley region. This lake does not have any outlets and water evaporation losses can also leave high salt concentrations and can also influence the pH. The high DOC content (374 mg L^{-1}) of this lake can contribute to the water acid-base buffering and therefore also influence the pH. Besides being a well known habitat for a large population of bird species, part of the Lake Nakuru, from where the water samples were taken, is also located within Nakuru National Park, removed from agricultural and human activities of Nakuru town but still subjected to a large input of biomass waste from the wild animals which drink from the lake water and this also influences DOM composition. The Lake Nakuru water was very brown and this indicated high DOM. It is likely that eutrophication can occur as a result of high algal growth, decomposition of high concentrations of bird droppings and decarboxylation reactions within the water. The high pH was found to correspond with high DOC concentration (374 mg L^{-1}) in Lake Nakuru water compared to other freshwater sources investigated in this study (Table 2).

The L. Naivasha sample also showed slightly high pH (7.71) which corresponded with a high DOC content (16.21 mg L^{-1}) and indicated possible sources of algal growth and nutrients in the lake.

Apart from Lake Nakuru and Lake Naivasha, all the rest of the water samples had DOC concentrations <10 mg L^{-1}. Lake Nakuru and Lake Naivasha have often captured environmental attention due to concerns regarding high concentrations of residual concentrations of heavy metal contaminants in the water. The high DOC content detected in the water samples from these sites support these concerns. An extensive survey should be conducted to determine the extent of chemical pollution in these lakes as these high DOC contents can influence distribution of organic contaminants and trace metals. Lake Naivasha is very important especially for fish, second only to Lake Victoria in production of fish for local consumption, and export and presence of trace chemical residues in its water can pose a big threat to the people and the fish industry. Lake Victoria has also been known to experience environmental pollution problems originating from municipal and industrial effluent. The DOC level (6.97 mg L^{-1}) recorded in this study was also quite high for such a large lake (total surface area of approximately 68,000 km^2). The other sampling sites included fast flowing rivers Nzoia, Yala and Chiromo (stream) and Kong'wen Spring water and the DOC concentrations were lower, ranging from 2.71 mg L^{-1} (River Yala) to 4.90 mg L^{-1} (River Nzoia). River Nzoia is located in a gently sloping terrain and could be receiving more organic load than River Yala which passes through a plain topography in the lake basin. Kong'wen Spring is a small spring with water leaching through Savanna type of vegetation but at very fast flow and consequently with very low retention of water and DOM as shown by its relatively low DOC content of 3.46 mg L^{-1}.

Different water samples showed different UV-VIS absorbance readings (Table 2). Limited linear regression analysis was also attempted to correlate [DOC] and UV-VIS absorbance. It appeared, in general, that the absorbance increased with DOC content, with the [DOC] showing a linear correlation with UV-VIS absorbance, although this linearity could not be determined with certainty because of the large difference between the Lake Nakuru DOC content (almost 30× higher) and the other freshwater water samples. R^2 value for Abs_{254} and DOC was 0.999 and that for Abs_{340} and DOC was 0.963, considering all the eight samples that were taken. When the Lake Nakuru water sample was not considered, R^2 values were 0.326 (Abs 254) and 0.136 (Abs 340), indicating no relationship between DOC and UV-VIS absorbance. We expect that the DOM chemical composition in terms of DOC content and UV-VIS absorbance characteristics varies from region to region. However, the samples were taken from diverse regions in Kenya, representing different geochemical formations such as plain terrain savanna-type of vegetation (samples JC, JD, JF), volcanic rift valley lakes (samples JA, JH JB), proximity to large cities and differences in origins (lakes, rivers and springs) and these different characteristics are reflected in the differences in compositions of organic carbons in the water and consequently in the UV-VIS absorbance readings obtained. From these few data, correlation appeared between samples from the same type of source e.g. samples from Yala, Athi and Nzoia Rivers which showed linear relationship between Abs_{254} and [DOC] ($R^2=0.970$), Abs_{340} and [DOC] ($R^2=0.529$), and samples from Lake Naivasha, Nakuru and Lake Victoria which showed linear relationship between Abs_{254} and [DOC] ($R^2=0.999$) and Abs_{340} and [DOC] ($R^2=1.000$).

Table 2. DOC , absorbance (at 254 and 340 nm) and extinction coefficients.

Sample	[DOC]	Abs_{254}	Abs_{340}	E_{254}	E_{340}
JA	16.21±0.26	0.264±0.06	0.056±0.01	16.28	3.45
JB	6.71±0.13	0.396±07	0.116±0.03	58.98	17.28
JC	4.9±0.24	0.328±0.03	0.13±0.05	66.90	26.51
JD	3.46±0.11	0.046±0.00	0.032±0.00	13.30	9.25
JE	6.97±0.21	0.09±0.01	0.038±0.01	12.91	5.45
JF	2.71±0.12	0.168±0.02	0.082±0.02	61.99	30.26
JG	4.09±0.06	0.132±0.03	0.06±0.01	32.27	14.67
JH	374±4.48	21.40±0.44	0.6±0.05	57.22	1.60
SRFA	10	nd	0.68	nd	68.45

Note: Extinction coefficients (E_{254}, E_{340}) are expressed in $cm^{-1}(g\ DOC)^{-1}$. The absorbance readings shown in columns 3 and 4 are net values obtained after subtracting the blank readings.

For surface waters, many studies have obtained linear positive relationships between UV absorbance and DOM concentration as measured by DOC content (Tipping et al. 1988). A plot of extinction coefficient versus wavelength in the range 240-380 nm, for all the samples as shown in figure 1 was made to show variation in extinction coefficients in different water samples (Fig 1). The variation in extinction coefficients among different samples as shown in figure 1 (Fig 1) illustrates that different freshwaters have different DOM composition and different UV-VIS absorbance characteristics. Such variation in UV-VIS absorbance can be useful in characterizing DOM from different sources and to understand DOM functional attributes including hydrophobic/hydrophilic ratios, aromatic content and resonance structures of the DOC molecules.

Differences in values of pH, the dissolved organic carbon, dissolved inorganic carbon and total dissolved carbon were found among various water samples analysed in this study. These differences were expected because the water samples were taken from different sites in different regions in Kenya representing differences in geology, demography and agricultural activities. In addition, the sampling sites represented different ecosystems comprising of one spring, four rivers and three lakes. The DOC contents in the lake waters (ranging from 6.97 to 374 mg L^{-1}) were found to be higher than those reported elsewhere. It can be expected that the long sunshine hours throughout the year (daily average 12 sunshine hours in Kenya) and constantly high temperatures in these tropical lakes could contribute to greater primary activity and microbial decay compared to temperate lakes and this could contribute to the higher DOC. In addition, Lake

Nakuru water sample was taken from an area heavily inhabited by flamingos and therefore bird droppings were assumed to be some of the major contributors to its very high DOC. The pH of Lake Nakuru water was also very high (pH 10.3) indicating that the lake is eutrophic at the sampling site.

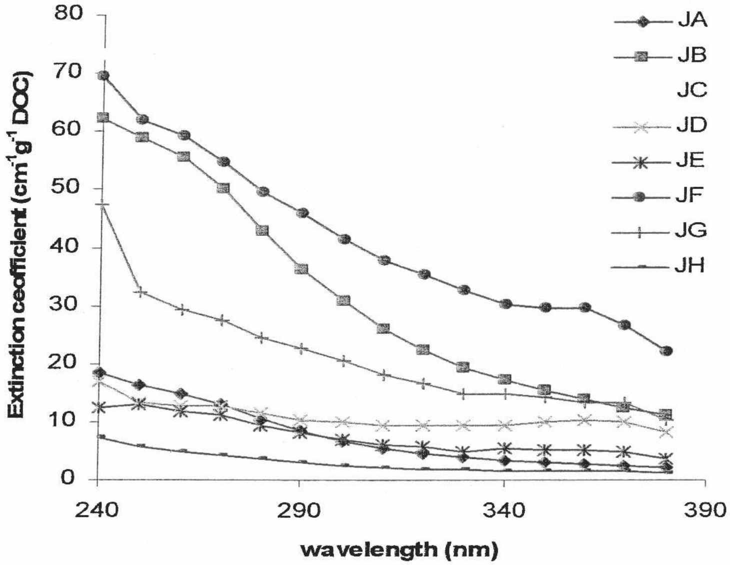

Figure 1. Variation in extinction coefficients among the samples. JA = Lake Naivasha, JB = Athi River, JC = Nzoia River, JD = Kong'wen Spring, JE = Lake Victoria, JF = Yala River, JG = Nairobi River, JH = Lake Nakuru

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