

UNIVERSITY OF JAFFNA, SRI LANKA



PROF. SIVAPATHASUNTHARAM
MAGESWARAN

MEMORIAL LECTURE - 2007



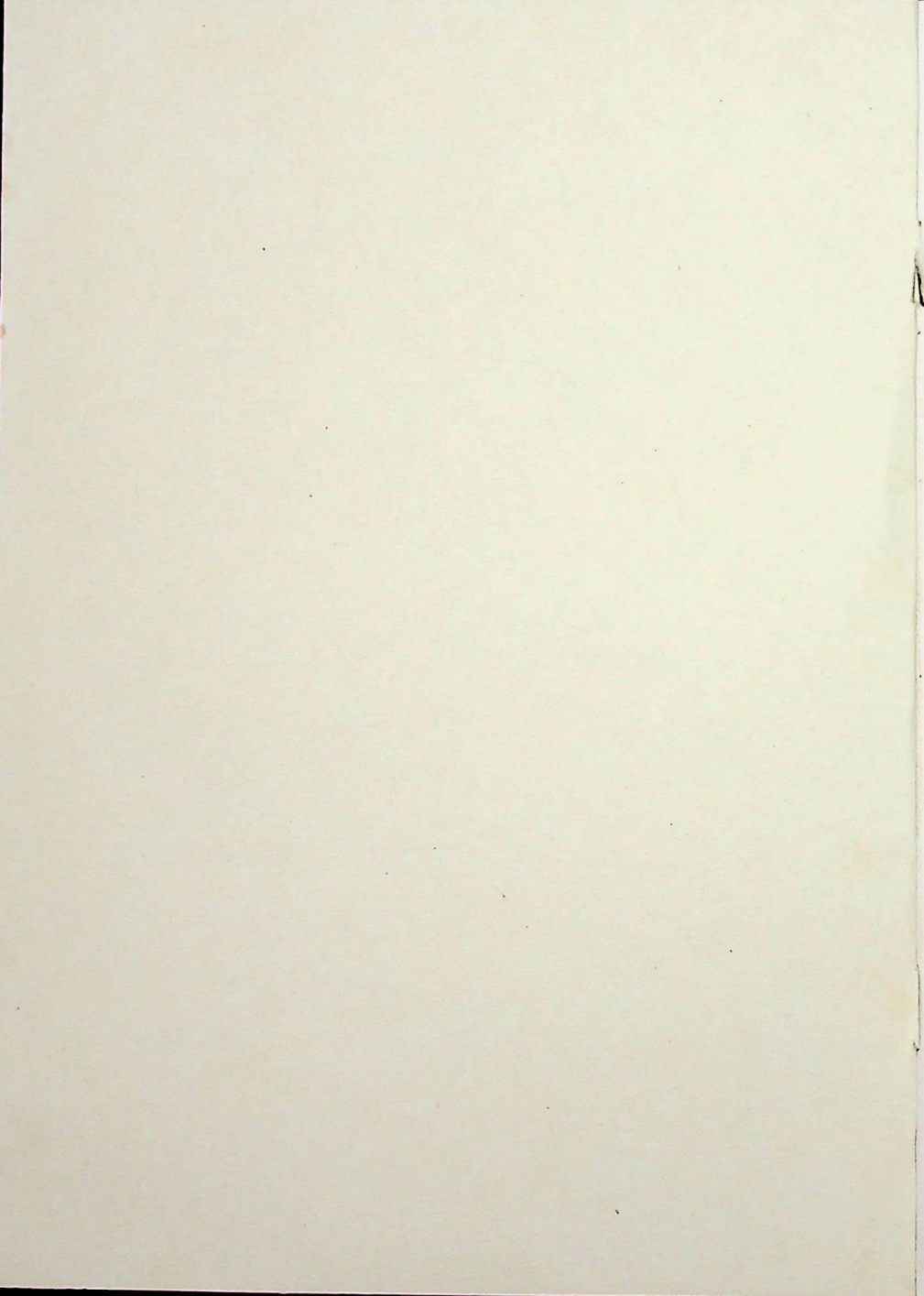
"ORGANIC MATTER IN WATER AND
WASTEWATER :
CONSTITUENTS AND ANALYSIS"

BY

Saravanamuthu Vigneswaran

*Faculty of Engineering, University of Technology, Sydney,
P. O. Box 123, Broadway, NSW 2007, Australia*

2007.05.15



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PROF. S. R. RATNAPARKARI

MADEIRA

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WASTEWATER

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BY

Saravananthi Virasawami

Department of Chemistry, Faculty of Science, University of Jaffna, Sri Lanka

2007.01.15

Prof. Sivapathasuntharam Mageswaran
Memorial Lecture – 2007

Forward

Late Professor Sivapathasuntharam Mageswaran was one of the most dedicated and dynamic pioneers who played a pivotal role in guiding the development of this University in general and the Faculty of Science in particular. He was also one of the finest synthetic organic chemists Sri Lanka produced. His students and well-wishers have graciously established a fund for conducting a memorial lecture annually to honour Prof. S. Mageswaran and to remember his yeoman services.

I am happy to see this year's lecture is delivered by Prof. Saravanamuthu Vigneswaran, a student of Prof. S. Mageswaran at the University of Peradeniya in mid-seventies and now the Professor of Environmental Engineering, Faculty of Engineering & Deputy Director of the Institute of Water and Environmental Resources Management, University of Technology Sydney, Australia on a topic that is very relevant to the development and economy of the North. Although stationed in Australia, Prof. Vigneswaran has shown a keen interest in the development of the Chemistry Department of the University of Jaffna and take lectures to our Honours Degree students in his field of specialization.

I wish Prof. Vigneswaran every success in his endeavors.

Prof. R. Kumaravadivel
Acting Vice-Chancellor
08th May 2007.

University of Jaffna.

Final Report on the
Investigation

Page

The following information was obtained from the records of the Department of the Interior, Bureau of Land Management, during the investigation of the lands in question. The lands in question are located in the State of California, County of Fresno, and are situated in the vicinity of the town of Hanford. The lands in question are situated in the vicinity of the town of Hanford, California, and are situated in the vicinity of the town of Hanford, California. The lands in question are situated in the vicinity of the town of Hanford, California, and are situated in the vicinity of the town of Hanford, California.

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Very truly yours,
Special Agent in Charge

ORGANIC MATTER IN WATER AND WASTEWATER: CONSTITUENTS AND ANALYSIS

Saravanamuthu Vigneswaran

Faculty of Engineering, University of Technology, Sydney,
Australia

ABSTRACT

The constituents and the characteristics of water and wastewater are becoming more complex each day due to the presence of many new emerging organic compounds. Organic matter plays a vital role in the water and wastewater treatment processes. Natural organic matter (NOM) should be carefully considered in terms of its constituent and effect because NOM is a complex substance that occurs in spatially and seasonally varying concentrations in natural waters. The first part of this paper presents the characteristics of natural organic matter present in water. These compounds mainly include humic substances, carbohydrates, proteins (amino acids), fats, oils, greases and trace organic compounds (endocrine disrupting chemicals and pharmaceuticals and personal care products). Correct characterization of organic matter is essential not only for the treatment purposes but also for further experimental research investigations in studying the constituents of organic matter. Of the many advanced analytical methods available for characterizing organic matter, spectroscopic analytical methods have distinct advantages over the conventional methods which were mostly used to obtain surrogate parameters. The second part of the paper presents a brief review of the applications of spectroscopic analytical methods such as high pressure size exclusion chromatography (HPSEC), nuclear magnetic resonance (NMR), Fourier transform infra red (FTIR), fluorescence spectroscopy, flow field flow fractionation (FFF)

and specific ultraviolet absorbance (SUVA) in characterizing organic matter in water and wastewater.

I. INTRODUCTION

With the technological advancement, people can enjoy the convenience and comfort of wide range of commercial and domestic products available in the market. These products can include components that are very complex chemically and unfortunately they are ultimately discharged into the aquatic environment in the form of wastewater. The composition of organic matter in wastewater is becoming more complex with the emergence of many new chemicals. Organic matter plays a very important role in the treatment of water and wastewater (Her et al., 2003; Shon et al., 2006). Natural organic matter (NOM) in water from decomposed plants and animals is responsible for the formation of disinfection by products (DBPs) (Weishaar et al., 2003; Kim and Yub, 2005; Lee et al., 2005). The effluent organic matter (EfOM) in wastewater has been found to include several trace organic contaminants, including endocrine-disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PCPs) and recently their presence has been a cause of increasing public concern due to their potential health risks (shon et al., 2006). Characterising organic matter (OM) in water and wastewater can give first hand information on the quality and quantity of the water and their treatment objectives.

BOD, COD and TOC have been used as surrogate parameters for describing the concentration of organic pollutants in water and wastewater for many years, but they do not provide a broad understanding of their true characteristics as they also contain numerous trace organic substances such as DBP, EDC, PCP, etc. Therefore correct characterization of organic matters in wastewater is essential as it provides a better understanding of the organic components present which would then be useful for

further interpretation of the experimental research results, determination of future research directions and evaluation of the progress of investigations (Shon et al., 2006). This characterization is also useful in the design optimisation of water and wastewater treatment facilities by identifying the performance of coagulation, granular activated carbon (GAC), ozonation, bio-treatment and membrane process by determining which DOM fractions can be preferentially removed by each process or which OM components are problematic for a given process (Her et al., 2003). Number of methods has been developed for characterising OM in natural water and wastewater. In general, these methods may be divided into those used to measure gross concentrations of organic matter (OM) greater than about 1 mg/L and those used to measure trace concentrations in the range of nano to micro sizes (Tchobanoglous and Burton, 1991). The characterization of OM can also be classified into two groups; traditional analyses and analytical methods (Her et al., 2002). Most chemical or physical characterization has been conducted on traditional analyses such as light absorptivity, DOC concentration, aromaticity, XAD fractionation and molecular weight (MW) due to the difficulty and higher cost associated when detailed structure analysis is taken (Shon et al., 2006). Analytical spectroscopic techniques are versatile because most of these techniques are non-destructive requiring small sample quantities, simple sample preparation procedures, applicable to both solid and liquid samples and also they provide valuable information on molecular structure and chemical or functional properties of OM (Stevenson, 1994; Chen et al., 2002). Analytical methods such as nuclear magnetic resonance (NMR), pyrolysis-GC/MS, IR and thermo-gravimetric methods provide detailed information for characterizing Organic Matter (Tanner, 1996). In this paper, applications of the spectral analysis such as High Pressure Size Exclusion Chromatography (HPSEC), Nuclear Magnetic Resonance (NMR), Fluorescence Spectroscopy, Fourier

Transform Infrared Spectroscopy (FTIR) and Specific Ultra Violet Absorbance (SUVA) in characterizing organic matter in water and wastewater are reviewed.

In fact there is no single analytical tool that can provide definitive structural or functional information of OM in water and wastewater because of its heterogeneous and ill-defined nature (Stevenson, 1994). Resolving the detailed components of dissolved organic matter (DOM) can be difficult and expensive (Leenheer and Philippecroue, 2003). Advanced analytical techniques, such as FTIR, solid-state ^{13}C -NMR and fluorescence spectroscopies, have been applied for the elucidation of structural features of size fractions from humic substances. FTIR and solid-state ^{13}C -NMR are very powerful techniques for determining functionality in humic substances, ultraviolet and fluorescence spectra can be used to estimate only the degree of aromaticity, the size of humic substances and the aquatic humus content (Duarte et al., 2003).

II. NATURAL ORGANIC MATTER

II.1. Overview of NOM in Natural Waters

Natural organic matter (NOM) originates from the contact of water with dead and living organic matter in the hydrologic cycle and is a fundamental component of aquatic ecosystems. NOM has important roles in water treatment processes since it produces harmful by-products with oxidants, increases chemical costs and deteriorates product water quality during distribution. Therefore, it is important to characterize NOM from many water supply systems in detail.

NOM present in natural waters is constituted of over 1000 organic compounds. Faced with this complexity, traditional analytical and assessment methods use bulk parameters, such as oxidant demand tests or even simpler surrogates like true colour. Indeed, simple methods are affordable and satisfactory in many

applications. However, it is increasingly important to better understand the origins, detailed characteristics and aquatic behaviour of individual NOM constituents to address water quality management and treatment needs more effectively.

NOM in natural water can be classified into two main groups by size: i) particulate organic carbon (POC) above $0.45 \mu\text{m}$ and ii) dissolved organic carbon (DOC) below that limit. Both groups include a wide variety of constituents (Figure 1).

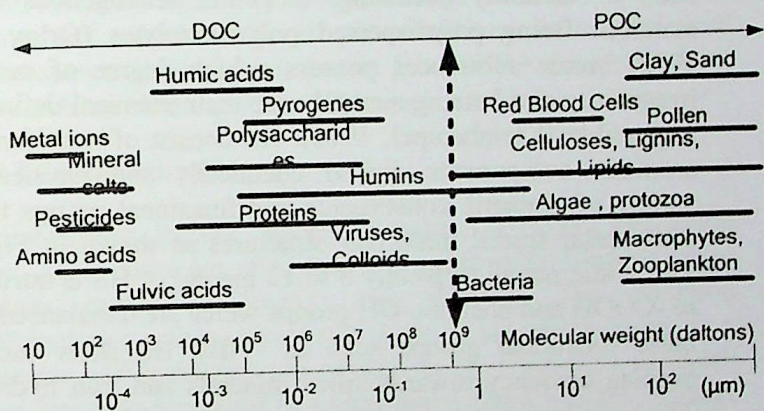


Figure 1: Typical constituents in water and their size ranges

POC includes zooplankton, algae, bacteria, and debris organic matter from soil and plants. Usually it represents less than 10% of total NOM and can be removed easily by solid-liquid separation processes.

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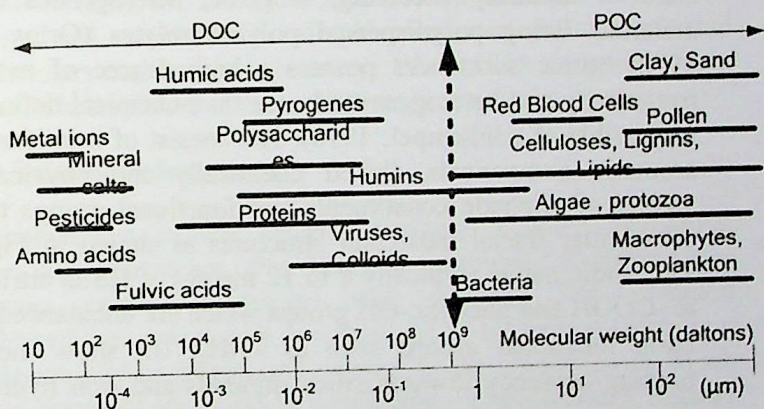


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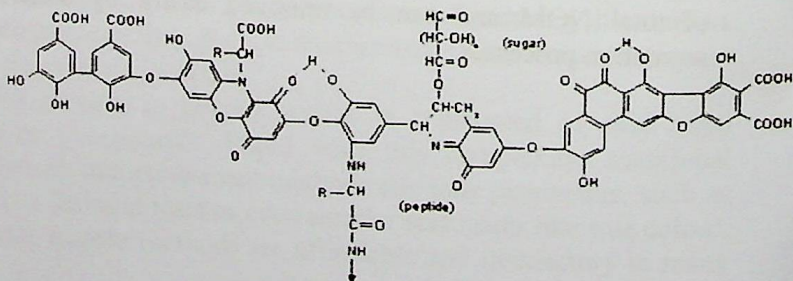
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II.2. Characteristics of NOM Components

II.2.1 Humic Substances (HS)

There are two major pathways by which humic substances can form in nature (Hatcher and Spiker, 1988). Macromolecules, chiefly plant biopolymers, such as lignin or cellulose partially decompose to HS, while the metabolic pathway involves condensation polymerisation reactions. HS represent a broad class of naturally occurring, biogenic, heterogeneous organic material. Being polydispersed polyelectrolytes (Orlov et al., 1972) humic substances possess a high degree of molecular irregularity and heterogeneity; hence their chemical definition is impossible (Kleinhempel, 1970). HS consist of multifunctional aromatic components, linked chemically and physically by variety of aliphatic constituents and functional groups to form self-similar fractal molecular structures as shown in Figure 2. The acidic nature (typically 8 to 12 meq/g) of HS is attributable to $-\text{COOH}$ and phenolic- OH groups which are unbalanced by the basic functional groups such as $-\text{NH}_2$. HS show molecular binding tendency towards silica minerals and iron hydroxides. The anionic macromolecular conformations of HS are analogous to those of flexible polyelectrolytes, adjusting to change in pH and ionic strength.

Figure 2: Generic structure of HS (Steinberg, 2003)



For operational definitions on the basis of solubility, the term HS represent three subclasses: 1) humins, 2) humic acids (HA) and 3) fulvic acids (FA). Humins are chiefly allochthonous in origin and washed into aquatic systems by runoff or percolating waters as fine, insoluble particles. HA are intermediates between humins and fulvic acids, soluble above pH 2. Their molecular weight (MW) ranges from 100 to about 100,000 daltons. They contain less aromatic rings and more carboxylic groups than humins. The dominant FA class has lower MW range (600 to 1,000 daltons), much less aromatic rings but more carboxylic groups and soluble under all pH conditions. In non-coloured freshwaters and humic-rich waters FA and HA comprise about 40 to 55% and DOC of 60 to 80% respectively.

II.2.2 Carbohydrates

Carbohydrates include sugars, starches, cellulose and wood fiber. All of these are often found in wastewater. Carbohydrates contain carbon, hydrogen and oxygen. The common carbohydrates contain six or a multiple of six carbon atoms in a molecule and hydrogen and oxygen in the proportion in which these elements are found in water. Some carbohydrates, notably the sugars, are soluble in water; others, i.e. the starches, are insoluble. Sugars tend to decompose; the enzymes of certain bacteria and yeasts set up fermentation producing alcohol and carbon dioxide. Starches, on the other hand, are more stable but are converted into sugars by microbial activity as well as by dilute mineral acids. From the standpoint of bulkiness and resistance to decomposition, cellulose is the most important carbohydrate observed in wastewater due to difficulty in decomposition. Wastewaters containing high-carbohydrate are also produced widely in industries such as food processing and fermentation. These wastewaters can cause serious pollution if released into the natural environment without proper treatment or disposal. Kumar et al. (1998) and Pawar et al. (1998)

discussed on the treatment of high-carbohydrate wastewater in detail.

Table 1 shows the distribution of different sugars in the influent wastewater and BTSE. Mannose is the carbohydrate that is less affected by the biological treatment. It could be either due to its protection or to the bacterial release of mannose during the treatment. Fucose is only decreased by 46% during the treatment. Rhamnose, ribose and glucose are also relatively concentrated in the hydrolysate of the BTSE. The presence of N-acetyl amino carbohydrates is revealed in the wastewater (total and soluble fractions) and BTSE. These compounds could contribute to the uncharacterized fraction of the EfOM and nitrogen. DNA, another nitrogen-containing compound, is present in the influent wastewater sample and activated sludge, but is not detected in the soluble fractions of the influent wastewater and BTSE. The EfOM percentage of monosaccharides follows the order of glucose > mannose > xylose > rhamnose.

Table 1: Comparison of the distributions of monosaccharides in the influent wastewater and their efficiencies (adapted from Dignac et al., 2000)

Monosaccharides	Total amino acids of the influent (%)	Removal efficiency (%)
Rhamnose	6	80
Fucose	3	50
Ribose	5	83
Arabinose	26	96
Xylose	42	96
Mannose	3	3
Galactose	7	93
Glucose	8	82

The carbohydrates as one of the EfOMs lead to operational problems in the biological treatment of activated sludge such as sludge bulking. Although some polysaccharides such as lignin are difficult to be degraded, in general carbohydrates provide a carbon source to micro and macroorganisms. As such, they also have an important role in biological treatment processes. Carbohydrates do not interfere significantly with traditional treatment technologies but are recognized as major foulants in membrane separation processes (Cho, 2005; Jarusutthirak, 2002; Shon et al., 2006).

II.2.3 Amino Acids and Proteins

Proteins are complex, high molecular weight organic compounds that consist of amino acids (AA) joined by peptide bonds. Protein is essential to the structure and function of all living cells and viruses. Thus, in natural waters the majority of AA and proteins come from living cells (extracellular enzyme) and dead cells (debris), either from animals or plants. Metabolism and catabolism of microorganisms in natural waters produce these materials and HS also consist of about 5-10% protein (Muller et al., 1986). The most definitive list on the origin of proteins and AA related to soluble microbial products is provided by Kuo (1993). While over 500 AA have been found in nature, research has been directed towards the 20 essential amino acids with available detailed measuring techniques (Table 2).

Sea and ground waters have the smallest concentrations of AA (around 50 $\mu\text{g/L}$), followed by oligotrophic lakes and rivers (100 to 300 $\mu\text{g/L}$) and eutrophic lakes and marshes (600 $\mu\text{g/L}$). These figures correspond to 2% to 3% of DOC in common drinking water supply sources. Generally, 0.5% is present as dissolved AA, 1% is bound to HS and the rest is bound to other substances. In humic substances, HA and FA contain relatively higher amounts of basic and acidic AA, respectively.

Table 2: Characteristic of essential amino acids

Name	Nature	IEP	Name	Nature	IEP
Alanine	HP	6.11	Glycine	HL	6.06
Cysteine	HL	5.05	Histidine	Basic	7.60
Aspartic acid	Acidic	2.85	Isoleucine	HP	6.05
Glutamic acid	Acidic	3.15	Lysine	Basic	9.60
Phenylalanine	HP	5.49	Leucine	HP	6.01
Asparagine	HL	5.41	Methionine	HP	5.74
Glutamine	HL	5.65	Proline	HP	6.30
Serine	HL	5.68	Arginine	Basic	10.76
Tryptophan	HP	5.89	Threonine	HL	5.60
Tyrosine	HL	5.64	Valine	HP	6.00

IEP = isoelectric point, HP = hydrophobic, HL= hydrophilic

II.2.4 Fats, Oils and Greases

Fats, oils and greases (FOG) can be classified into three main classes by origin: 1) vegetable FOG, 2) animal FOG and 3) mineral oils and derivatives from crude petroleum. Natural FOG consist of a wide variety of organic compounds such as fatty acids, n-alkyl hydrocarbons, n-alkyl alcohols, sterols, terpenes, polycyclic hydrocarbons, chlorophyll, fats, waxes and resins (Steinberg, 2003). Among these compounds, differentiation is possible in terms of structure as i) hydrocarbons (aliphatic and aromatic compounds), as detailed by Saliot (Saliot, 1981) or ii) triglycerides (fatty acid and glycerol). The majority of FOG in natural waters exist as fatty acids and glycerines, allowing further classification of FOG in terms of carboxylic acids.

Non-volatile fatty acids (such as steric and palmitic acids) are the degradation products of fats and triglycerides and are also important constituents of plants. Volatile fatty acids, like acetic or valeric acid, are short-chain molecules and result from anaerobic metabolism. Hydroxy acids are common intermediates

in biochemical pathways and excreted by algae during photorespiration. Dicarboxylic acids are common degradation products within soils and include oxalic acid and succinic acid. Lignin degradation products are aromatic acids and they occur in water extracts of leaf or conifer needle litter (Kaplan and Newbold, 2003). Their contribution to DOC is presented in Figure 3.

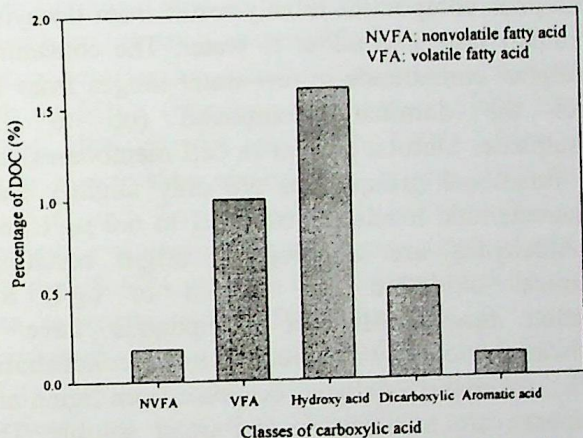


Figure 3: Monomeric carboxylic acids in surface water (Kaplan and Newbold, 2003)

The common man-made hydrocarbons entering natural waters include chlorinated aliphatic and aromatic hydrocarbons (from common solvent), polynuclear aromatic hydrocarbons (from combustion sources), saturated and unsaturated alkanes (from waste oil) and water.

FOG removal pathways using microorganisms have been investigated concerning natural waters (Nunn, 1986; Park et al., 1991), though a much larger body of knowledge exists for specific components, especially in relation to tertiary biological wastewater treatment processes (Tan and Gill, 1985; Han et al., 1988; Koh et al., 1992; Hur et al., 1999; Shimada et al., 1992).

II.2.5 Trace Organic Compounds

In natural water, there are many other different organic compounds usually present in very low or trace concentrations. Due to their large numbers, only few important groups as examples will be mentioned here, noting that details are available from Thurman (1985).

Organic sulphur compounds mostly result from decaying algae and can impart taste and odour to water. The concentration of volatile sulphur compounds in raw water ranges from 1 to 350 $\mu\text{g/L}$ and the dominant compound (up to 75%) is dimethylsulphide. Sterols, present in cell membranes, have one hydroxyl functional group, thus are only slightly soluble in water. Characteristic levels are from 0.1 to 6.0 $\mu\text{g/L}$ in natural waters. Aldehydes are of biogenic origin resulting from photochemical oxidation and present in ng/L to $\mu\text{g/L}$ concentration range. Aliphatic compounds have volatile characteristics; hence they are found in lower concentrations (10 to 50 ng/L). Aromatic aldehydes originate from lignin and other plant products, are non-volatile and water soluble. The most common compounds of organic bases are mononucleotides and nucleic acids. These are fundamental compounds of plant and animal cells and contribute to DOC concentrations from ng/L to $\mu\text{g/L}$ levels. Alcohols, ketones and ethers contribute a few $\mu\text{g/L}$ portion to DOC in natural waters. Alcohols and ketones can react with chlorine to form harmful compounds. In lake waters usually octanol and butanol are present, while in river water methanol and hexanol are typical. The majority of pigments originate from plants (chlorophyll, xanthophylls and carotenoids). These compounds degrade relatively fast, hence they usually represent less than 1% of DOC in natural waters.

Recently, endocrine disrupting chemicals (EDCs) and pharmaceuticals and personal care products (PCPs) have been

regarded as important emerging chemicals. EDCs refer to a class of toxicity in which an endogenous or exogenous chemical has the ability to mimic or block the natural action of endocrine system in animals (Ankley and Mihaich, 1998; Gillesby and Zacharewski, 1998). The ability of certain chemicals to mimic estrogen has been known for decades (Cook and Dodds, 1934; Stroud, 1940; Fisher and Keasling, 1952; Welch and Levin, 1969). However, the discovery of human hormones and a synthetic hormone used as a pharmaceutical for birth control may have been primarily responsible for reproductive impacts in fish below wastewater outfalls stimulated a plethora of new research on EDCs (Harries and Sheahan, 1997; Desbrow and Routledge, 1998; Snyder and Keith, 1999; Jobling and Coey, 2002). In response to amendments to the US Safe Drinking Water Act and Food Quality Protection Act mandating comprehensive screening of commercial chemicals for endocrine activity, the US EPA set forth to develop a screening program to evaluate approximately 87,000 chemicals in commerce for which minimal, if any, data are available regarding endocrine-related toxicity. The endocrine system of animals is vast and affects nearly all aspects of metabolism, growth, development and reproduction. However, the primary classes of EDCs are compounds which mimic or block the natural action of estrogen, androgen and/or thyroid. PCPs represent another group of emerging contaminants that can also be detected at ng/L concentrations in water. Most of the EDCs and PCPs are more polar than traditional contaminants and the majority have acidic or basic functional groups. These properties, coupled with occurrence at trace levels (i.e. $< 1 \mu\text{g/L}$), create unique challenges for both analytical detection and removal processes. Molecular structures of several EDC and PCP compounds can be found in Vanderford et al. (2003). Details of removal of EDC and PCP compounds in water can be found elsewhere (Alcock and Sweetman, 1999; Drewes and Heberer, 2002; Lindqvist and Tuhkanen, 2005; Shon et al., 2006). Table 3 presents general

classes of emerging contaminants. The majority of these contaminants are not currently regulated; however, they may be candidates for future regulation once environmental and human health relevance has been established. An interesting characteristic of these contaminants is that they need not persist in the environment to cause negative effects, since their high transformation/removal rates can be compensated by their continuous introduction into environment. For most of these emerging contaminants, occurrence, risk assessment and ecotoxicological data are not yet available and it is therefore difficult to predict their actual risk.

Table 3: Classes of emerging contaminants (adapted from Barceló, 2003)

Compound class	Examples
<u>Pharmaceuticals</u>	
Veterinary and human antibiotics	Trimethoprim, erythromycin
Analgesics and anti-inflammatory drugs	Codein, ibuprofen, acetaminophen, acetylsalicylic acid, diclofenac, fenoprofen
Psychiatric drug	Diazepam
Lipid regulators	Bezafibrate, clofibrac acid, fenofibrac acid
B-blockers	Metoprolol, propranolol, timolol
X-ray contrast media	Lopromide, iopamidol, diatrizoate
Steroids and hormones (contraceptives)	Estradiol, estrone, estriol, diethylstilbestrol
<u>Personal care products</u>	
Fragrances	Nitro-, polycyclic- and macrocyclic-musks
Sun-screen agents	Benzophenone, methylbenzylidene camphor
Insect repellents	N,N-dimethyltoluamide (DEET)

Compound class	Examples
Antiseptics	Triclosan, chlorophene
Surfactants and surfactant metabolites	Alkylphenol ethoxylates, alkylphenols (nonylphenol and octylphenol), alkylphenol carboxylates
Flame retardants	Polybrominated diphenyl ethers (PBDEs), Tetrabromo bisphenol A, Tris(2-chloroethyl)phosphate (TCEP)
Industrial additives and agents	Chelating agents (EDTA), aromatic sulphonates
Gasoline additives	Dialkyl ethers, methyl <i>tert</i> -butyl ether (MTBE)
Disinfection products	by- Iodo-THMs, bromoacids, bromoacetonitriles, bromoaldehydes, cyanoformaldehyde, bromate, NDMA

Some of these compounds are known to cause serious problems even when present in very low concentrations in water sources. For instance, some algal products are known as toxins. Pesticides are typically synthetic products, thus cannot be properly classified as NOM. However, it has been observed that NOM can associate with pesticides and many other organic compounds to form complex and toxic substances (Schnitzer, 1972). Pesticide concentrations vary according to regions, countries and locations, but may be present in the order of $\mu\text{g/L}$ in many waters.

III. SPECTROSCOPIC MEASUREMENT METHODS FOR ORGANIC MATTER

III.1. High Pressure Size Exclusion Chromatography (HPSEC)

High pressure size exclusion chromatography (HPSEC) (also known as High performance size exclusion chromatography) is an analytical tool used for measuring the MW distributions of aquatic OM/humic substance (Conte and Piccolo, 1999; Zhou et al., 2000; Matilainen et al., 2002; Irvine, 2003). It employs tightly pre-packed columns containing small and uniform particles of silica-based resulting in tens of thousands of theoretical plates per metre and are operated at high pressure to provide fast and high-resolution chromatograms (Pelekani et al., 1999; Irvine, 2003). HPSEC is a useful method with relatively simple technique and ease of application, requires modest equipment and has ability to generate both average and distributed size information (Pelekani et al., 1999; Her et al., 2002; Shon et al., 2006). Solute separation in terms of MW distribution is based on the different abilities of various solutes to enter the pores of the stationary phase via hydrodynamic molecular diffusion (Pelekani et al., 1999; Shon et al., 2006).

Different techniques are employed for detecting OM by HPSEC method; spectrophotometry, electrochemical detection, online light scattering detectors, electrospray ionisation mass spectrometry, etc (Irvine, 2003). Each type of detector has its own advantages and limitations and UV/Visible detection is the most commonly used detection method for HPSEC humic substance research (Zhou et al., 2000). HPSEC – UVA - DOC detection system can provide qualitative information in addition to quantitative information on size distribution but this system is not sufficient to identify the chemical and physical properties of the particular MW DOM components (Her et al., 2003).

HPSEC is calibrated using standard solutions of polystyrene sulphonate with known MW and the MW distribution is represented by UV response (mV intensity) with time (Her et al., 2002; Shon et al., 2006). The results can also be presented as normalized fraction percentages, obtained by dividing each incremental height of the chromatogram with a sum of the heights, when the chromatogram is divided into incremental mass intervals (Shon et al., 2006).

The MW distribution statistics by HPSEC include four average values of MW: i) M_n (number average MW), ii) M_w (weight average MW), iii) M_z (z-average MW) and iv) M_v (viscosity average MW) and the weight average MW (M_w) is commonly used (Shon et al., 2006). The definitions of all statistics are shown in Table 4.

However MW determination by HPSEC is influenced by factors such as: type of standard solutions used for calibration, detection methods and data processing of HPSEC chromatograms, degree and method of OM concentration and presence of polyvalent cations and ionic strength, eluent compositions, undesirable interaction among packing material, eluent and organic components and pH of the sample (Zhou et al., 2000; Her et al., 2002; Shon et al., 2006).

Table 4: Molecular weight statistics (adopted from Shon *et al.*, 2006)

Reference	Calculation method
Poole, 2003	<p>Suitable terms are the number average MW:</p> $M_n = \sum_{i=1}^n (N_i M_i) / \sum_{i=1}^n (N_i)$ <p>the weight average MW:</p> $M_w = \sum_{i=1}^n (N_i M_i^2) / \sum_{i=1}^n (N_i M_i)$ <p>or the z-average MW:</p> $M_z = \sum_{i=1}^n (N_i M_i^3) / \sum_{i=1}^n (N_i M_i^2)$ <p>where N_i is the number of molecules having the molecular weight M_i and i is an incrementing index over all molecular weight present.</p>
Beri <i>et al.</i> , 2001	<p>The viscosity average MW:</p> $M_v = \left[\sum_{i=1}^n (h_i M_i^{1+a}) / \sum_{i=1}^n (h_i M_i) \right]^{1/a}$ <p>where a is the Mark-Houwink exponent as defined by either prior knowledge of the Mark-Houwink constants or determination of a universal calibration curve with molecular weight standards and Peak maximum molecular weight (M_p), n is the number of chromatographic slices, h_i is the SEC curve height at the i^{th} volume increment, M_i is the molecular weight of the species eluted in the i^{th} retention volume increment.</p>

A typical chromatogram for MW distribution of DOC is shown in Figure 4. The MW of EfOM in BTSE ranged from 260 to

about 43,110 Da, with the highest fraction being 263 to 870 Da. The compound of 43110 Da may be polysaccharide; 580 Da and 865 Da - humic substances; 330 Da - building blocks; 250 Da - acids and less than 200 Da - amphiphilics (Huber, 1998; Shon et al., 2006).

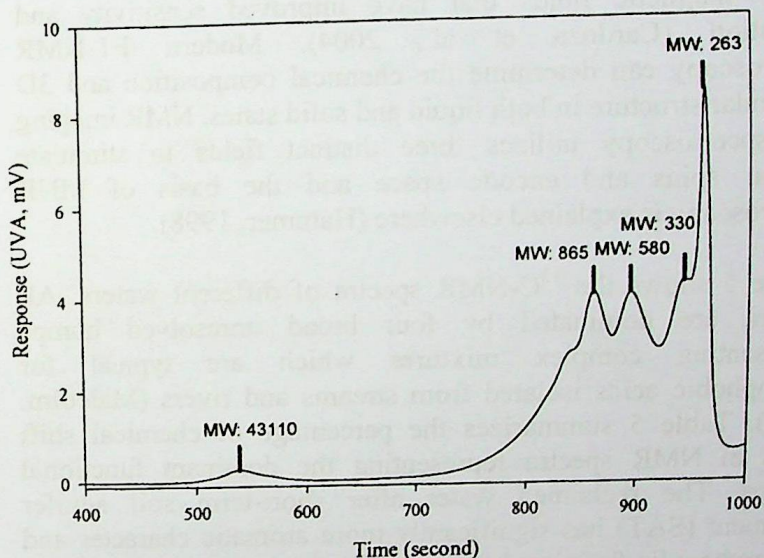


Figure 4: MW distribution of EfOM in BTSE by HPSEC technique (adapted from Shon *et al.*, 2006)

III.2. Nuclear magnetic resonance (NMR) spectroscopy

The phenomenon of nuclear magnetic resonance (MNR) was experimentally verified in 1946 by Blomenbergen, Pound and Purcell at Harvard and Bloch and Packer at Stanford (Andrew and Szczesniak, 1995; Hammer, 1998). Since then, this technology has been found application in variety of fields particularly analytical chemistry and medical imaging. NMR is one of the premier techniques for studying intermolecular

interactions and it has also been used extensively to investigate the environmental chemistry of humic substances (Cardoza et al., 2004). This technique can non-invasively and non-destructively examine the physical and chemical compositions of materials (Hammer, 1998). Interest in the use of NMR analyses for characterising organic matter has increased since the advent of pulsed Fourier Transform (FT) NMR spectrometers with higher magnetic fields that have improved sensitivity and resolution (Cardoza et al., 2004). Modern FT-NMR spectroscopy can determine the chemical composition and 3D molecular structure in both liquid and solid states. NMR imaging and spectroscopy utilizes three distinct fields to stimulate nuclear spins and encode space and the basis of MNR spectroscopy is explained elsewhere (Hammer, 1998).

Figure 5 shows the ^{13}C -NMR spectra of different waters. All spectra are dominated by four broad unresolved humps representing complex mixtures which are typical for hydrophobic acids isolated from streams and rivers (Malcolm, 1985). Table 5 summarizes the percentage of chemical shift areas in NMR spectra representing the dominant functional groups. The reclaimed water after short-term soil aquifer treatment (SAT) has significantly more aromatic character and less carboxylic functional groups as compared to drinking water NOM. However, during long-term SAT reclaimed water DOC is losing its aromatic and carboxylic character resulting in a relative increase in aliphatic compounds.

The results from NMR spectroscopy can be effected due to the presence of paramagnetic impurities such as iron and manganese and the generally low organic concentration (Chang et al., 2002; Conte et al., 2004). One approach is to quantify the paramagnetic effect by determining the effect of cation doping of model compounds and NOM while in another approach the

paramagnetic effect can be eliminated by chemical removal of the paramagnetic elements *via* extraction (Cardoza et al., 2004).

In NMR technology, the nuclei used as tags for monitoring the attenuation of the OM include ^1H , ^{13}C , ^{15}N , ^{19}F , ^{31}P , etc. Although ^1H -NMR spectroscopy has been used for humic substance functional group characterization, analysis by ^{13}C -NMR is generally preferred when sufficient quantities are available (Cardoza et al., 2004). ^{13}C -NMR has been used to determine a strong correlation between SUVA and the aromatic carbon contents of a large number of NOM fractions (Leenheer and Philippecroue, 2003). While NMR techniques alone can be used in characterising OM, they are often coupled directly with other analytical tools such as high performance liquid chromatography (HPLC) to provide even more sensitivity in obtaining information of the complex OM.

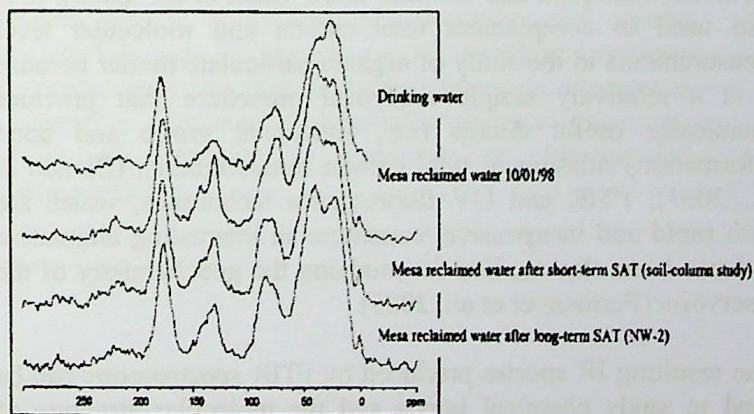


Figure 5: ^{13}C -NMR spectra of XAD-isolates of corresponding samples in Mesa, Arizona (adapted from Drewes and Fox, 1999)

Table 5: Percentage of chemical shift areas for ^{13}C -NMR spectra of XAD isolates (adapted from Drewes and Fox, 1999)

Chemical shift	Drinking water	Reclaimed water	Reclaimed after short-term SAT	Reclaimed after long-term SAT
Aliphatic	61.5	50.8	52.1	63.6
Carbohydrates	11.3	16.0	14.1	12.6
Aromatic	5.3	13.8	11.1	7.2
Carboxylic	15.9	13.2	14.1	12.9

III.3. FTIR: Fourier Transform Infrared Spectroscopy

Fourier Transform Infrared spectroscopy (FTIR) is a powerful non destructive analytical tool for determining and characterizing chemical compounds or their molecular functional groups in liquids, gases, powders and films (Duarte et al., 2003; Hallquist and Boman, 2004; Shon et al., 2006). It is also used to complement total carbon and molecular level measurements in the study of organic particulate matter because it is a relatively simple analytical procedure that provides chemically useful details (i.e., functional group and bond information) missing in total carbon measurements (Blando et al., 2001). FTIR and UV fluorescence techniques, which are both rapid and inexpensive, constitute an interesting alternative and has been also applied for studying the geochemistry of the reservoirs (Permanyer et al., 2005).

The resulting IR spectra produced by FTIR spectroscopy can be used to study chemical bonds and the molecular structure of organic compounds. Two new advances in FTIR, micro-beam technology and attenuated total reflection (ATR), allow analysing organic and inorganic functional groups. Internal reflection spectrometry or ATR/FTIR spectrometry can provide valuable information related to the chemical structure of OM.

Mid-infrared spectra are obtained against an internal reflection element (IRE), e.g. zinc selenide (ZnSe) or germanium (Ge), and the IR radiation is focused onto the end of the IRE. Light enters the IRE and reflects down the length of the crystal. At each internal reflection, the IR radiation actually penetrates a short distance (~ 1 mm) from the surface of the IRE (Figure 6). It is this unique physical phenomenon that enables one to obtain infrared spectra of samples placed in contact with the IRE. In the mid-infrared spectroscopy, absorption of radiation is related to fundamental vibrations of the chemical bonds. Internal reflection spectrometry provides information related to the presence or absence of specific functional groups, as well as the chemical structure of polymer membranes. Absorption bands are assigned to functional groups (e.g. C=O stretch and C-H bend). Shifts in the frequency of absorption bands and changes in relative band intensities indicate changes in the chemical structure or environment around the polymer membrane. The same analysis of vibrational spectra is applied to characterize the organic fouling layer that may be present on the membrane surface. ATR/IR spectrometry can also be used to determine changes in surface chemistry after special chemical or physical treatments are applied, e.g. exposure to surfactants or chlorine and temperature annealing.

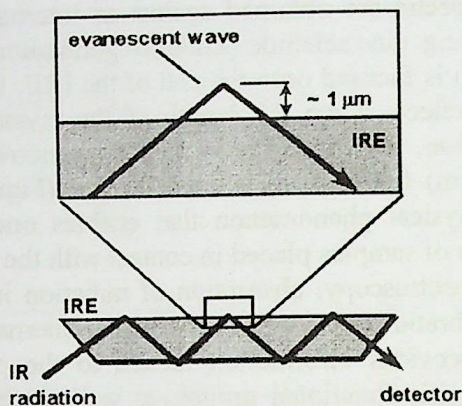


Figure 6: Total internal reflection at the interface of an internal reflection element.

Depth of penetration of the evanescent wave is approximately 1 mm.

A functional group of OM can be investigated both by extraction of organics and by attenuated total reflection-fourier transform infrared spectroscopic (ATR-FTIR) analysis (Weis et al., 2003). In ATR-FTIR spectroscopy, it is especially possible to confirm a detailed screen of the molecular functional groups consisted of OM. Some known compounds were also characterized for their functional groups using FTIR. They include polysaccharides, proteins and humic substances. The FTIR spectra of some of these compounds are shown in Table 6.

Table 6: FTIR spectra of known compounds (adapted from Skoog et al., 1998)

Compounds	Groups	Wave number (cm ⁻¹)	Functional group	Range (cm ⁻¹)
Sucrose	Polysaccharides	3400	Alcohol	3100-
Dextran		2940	(1,2,3,Ar)	3500
Blue dextran		1480	Alkane	2800-
Starch		1370	Alkane	3000

		1170	Alkane	1420-
		1120	Tertiary	1480
		1040	alcohol	1340-
		1000	Secondary	1400
		775	alcohol	1120-
			Aliphatic	1120
			ether	1050-
			Primary	1150
			alcohol	1040-
			Ethyl	1170
				1000-
				1080
				750-
				800
Glutamic acid	Proteins	3300	Alcohol	3100-
Lysozyme			(1,2,3,Ar)	3500
BSA			Amides	3200-
Bovine			Carboxylic	3500
pancrease		1640	acid	2900-
			1, 2 or 3	3300
		1540	amines	3200-
			Alkene in	3500
		1100	aromatic	1630-
			amides	1670
			Mono	1640-
			substituted	1720
			amide	1480-
			<i>Sec-, tert-</i>	1580
			amines (C-N)	1480-
			Ether	1581
			Esters	1040-
			Aldehydes	1170
			Ketones	1080-
				1150
				1020-
				1150
				1070-
				1220

Steric acids	Fatty acids	2950	Alkane	2800-
		2850	Carboxylic	3000
		1700	acids	1660-
		1470	Alkane	1740
		1430	-OH in	1420-
		1300	carboxylic	1480
PEG	Alcohols	2900	acid or	1260-
		1470	alcohol	1350
		1350	Alkane	2800-
		1280	Alkane	3000
		1240	Alcohol	1420-
		1150	Alcohol	1480
		1120	Ether	1330-
		960	Ether	1430
			Alcohol	1250-
			Aldehydes	1350
				1180-
		1300		
		1040-		
		1170		
		1050-		
		1160		
		830-		
		970		
SRHA, SRFA	Humic substances	3400	Alcohol	3100-
		2960	(1,2,3,Ar)	3500
		1720	Alkane	2800-
			Amides	3000
		1640	Carboxylic	1640-
			acids	1720
		1400	Alkene in	1660-
		1200	aromatic	1740
	amides	1630-		
	Alkane	1670		
	<i>tert</i> -alcohol	1640-		
	Ether	1720		
	Ketone	1340-		
		1400		

Jarusutthirak et al. (2002) studied the functional groups of different fractions in BTSE. In colloidal fraction, the peaks at wave numbers of 1540 and 1640 cm^{-1} reflect functional groups of primary and secondary amides. A peak at wave number of 1040 cm^{-1} indicates polysaccharides. These are indicative of proteins and N-acetyl aminosugars, possibly present in bacteria-related cell wall. In their study, hydrophobic and transphilic fractions included a peak of 1720 cm^{-1} , which is associated with carboxylic groups (HA and FA). The major difference between EfOM and NOM isolates is the series of distinct peaks at 1170, 1125 and 1040 cm^{-1} . Figure 7 shows the ATR-FTIR spectrum of BTSE.

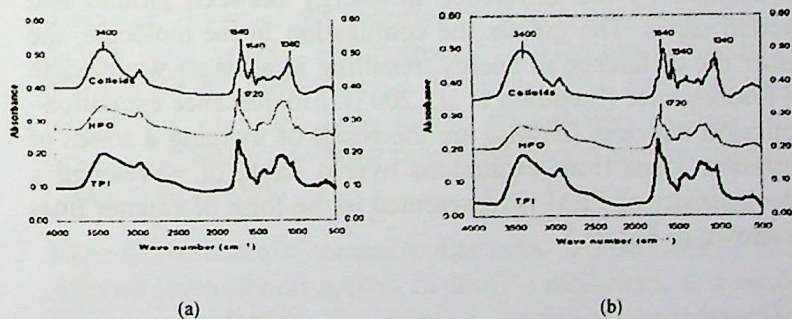


Figure 7: ATR-FTIR spectra of colloids, hydrophobic and transphilic acids in BTSE (a) Sain Julien L'Ars BTSE, b) Naintre BTSE in France (adapted from Jarusutthirak et al., 2002)

III.4. Fluorescence Spectroscopy

When a light is applied to water containing DOM, humic substances fluoresce with blue fluorescence and proteins fluoresce with UV fluorescence and therefore fluorescence spectroscopy has been utilized to probe the chemical composition of DOM (Stedmon et al., 2003; Shon et al., 2006). Moreover its experimental simplicity and ability to distinguish between certain classes of organic matter (Saadi et al., 2006) are some of the reasons why this technique is popular for characterising and monitoring DOM.

When a molecule absorbs light (energy), an electron is excited and promoted to an unoccupied orbital and the energy difference between the ground and excited states determines the wavelength at which light is absorbed (Stedmon et al., 2003). This absorption (excitation) can result in a range of molecular absorption spectra which are often seen to consist of broad peaks. The wavelength of the fluorescence emission is determined by the difference in energy between ground and excited states. The greater the conjugation in the molecule, the lesser the difference in energy, resulting in a longer wavelength of fluorescence (Stedmon et al., 2003). Fluorescence excitation–emission matrices (EEMs) are the result of merging a series of emission scans from excitations over a range of wavelengths. The intensity of EEM is represented in the form of counter lines as shown in Figure 8.

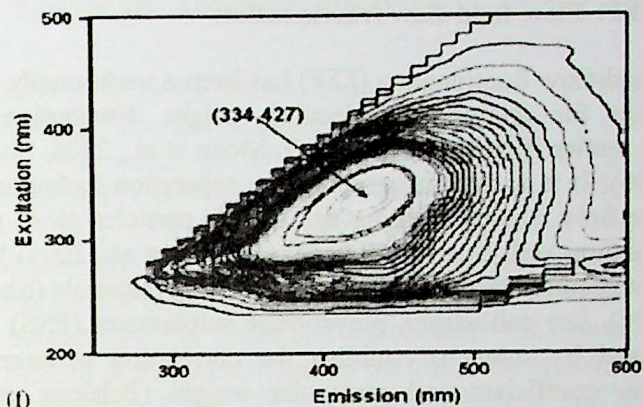


Figure 8: Fluorescence EEM of river water (Her *et al.*, 2003)

Numerous peak locations in EEM have been assigned to different DOM components. For example, the classification by Leenheer and Philippecroue (2003) suggests that fluorescence at 420–480/330–350 and 380–480/250–260 to be associated with humic-like material and 300–350/270–280 to protein-like structures. However the fluorescence results may be affected by factors such as pH, ionic strength and solution interactions between DOM molecules or between DOM and organic or inorganic co-species, both in the ground and excited states because of which one must be careful during the interpretation (Saadi *et al.*, 2006).

Since fluorescence spectrum results from the reactions of many different fluorophores present in the OM molecules, it would be difficult to identify the relevant structural and functional components responsible for fluorescence in these OM components without other complementary spectroscopic data, but the use of synchronous fluorescence can provide better sensitivity and improved peak resolution compared to the conventional emission fluorescence technique (Chen *et al.*, 2002).

III.5. FFF: Flow field-flow fractionation

Flow field-flow fractionation (FFF) has been a traditionally used technique for analysing molecular weight distributions of organic matter (Pelekani et al., 1999; Moon et al., 2006; Shon et al., 2006). It is a chromatography like separation technique, in which a field is used to bring the sample particles close to an accumulation wall in a thin channel (Assemi et al., 2004) but it does not require any chromatography packing materials (Shon et al., 2006). For calibration, polystyrene sulphonates (PSS) have been used by some to establish the correlation between the diffusion coefficient and molecular weight (Pelekani et al., 1999). However molecular size is estimated in terms of nanometer by converting molecular weight, using conversion equations between nm and Dalton (Giddings, 1997; Moon et al., 2006; shon et al., 2006).

There are two liquid flows in the FFF method: channel flow and cross flow at 90° and a semi-permeable membrane is placed on one side of the channel allowing cross flow to pass but not the compounds of interest (Shon et al., 2006). Figure 9 shows the FFF.

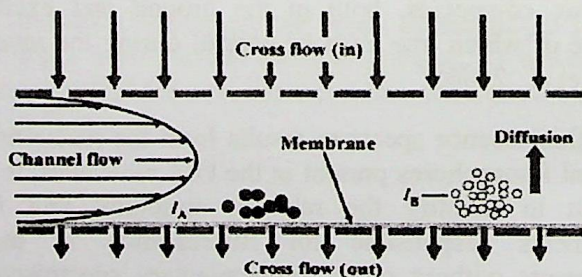


Figure 9: Exploded views of flow field-flow fractionation (FFF): Different distributions of two arbitrary components, A and B, across the parabolic flow profile (Moon et al., 2006)

III.6. Specific UV Absorbance (SUVA)

Natural organic matter (NOM) absorbs light over a wide range of wavelengths, whereas inorganic chemicals typically present in natural fresh waters do not absorb light significantly at 230nm (Matsche and Stumwohrer, 1996; Korshin et al., 1997; Vaillant et al., 2002). DOC concentration is proportional to the UV absorbance (Deflandre and Gagne, 2001) and therefore UV absorbance can be used as a semi-quantitative indicator for the OM concentration in water and wastewater. The absorbance of UV light by a molecule depends on the electronic structure of the molecule and the UV spectrum, therefore, indicates the presence of specific bonding arrangements in the molecule (Weishaar et al., 2003). The UV absorbance of an effluent may vary considerably according to its chemical composition. Each organic compound present in an effluent has a peak absorbance at a certain wavelength. For example, acetic acid has a peak at 204 nm, whereas phenol has a peak at 210 nm. Because effluents consist of many compounds in different proportions, the peak could vary according to the type of effluent and its pre-treatment (Brookman, 1997). Two phenomena are involved in the apparent absorption of UV light by the sample: the chemical absorption mechanism following the Beer-Lambert Law for dilute and homogenous solutions and the scattering effect due to the presence of heterogenous material, i.e. suspended solids and colloids (Vaillant et al., 2002).

The specific UV absorbance is defined as the ratio of UV absorbance at certain wave length (usually 254nm) to DOC ($SUVA = UVA/DOC$) and it has been applied in characterizing the aromaticity of the organic matter (Deflandre and Gagne, 2001; Jarusutthirak et al., 2002; Her et al., 2003; Weishaar et al., 2003; Lee et al., 2005). SUVA is shown to be a useful parameter for estimating the dissolved aromatic carbon content in aquatic systems (Weishaar et al., 2003). Its UV absorbance at 254 nm

represents both EfOM concentration and humic content (Edzwald et al., 1985; Owen et al., 1993; Cho 1998). Edzwald et al. (1985) compared the specific UVA ($SUVA = UVA_{254}/DOC$) of FA and natural bulk water.

The advantages of the use of SUVA in the characterization of organic matter are that it is non-destructive, only small quantities of samples are required and the test procedures are simple. While SUVA measurements are good predictors of general chemical characteristics of DOC, they do not provide information about reactivity of DOC derived from different types of source materials and their functional groups. The SUVA results are also affected by pH, presence of particles and inorganic species (such as iron and nitrate) that absorb light in the near UV and interfere (Deflandre and Gagne, 2001; Vaillant et al., 2002; Leenheer and Philippecroue, 2003; Weishaar et al., 2003).

IV. SUMMARY

In this paper, the different organic compounds present in water and the application of the spectrophotometric techniques (NMR, HPSEC, FFF, FTIR, SUVA and fluorescence) in characterising OM in water are reviewed. Some of these techniques are very powerful enough to provide a 3D molecular structure that can provide useful information in studying the chemical bonding of the molecular components of OM. While most of these techniques can be used alone in characterising OM, they provide even more information when coupled with other analytical techniques. Although there is no single analytical tool that can provide definitive structural or functional information of OM in water and wastewater because of its heterogenous and ill-defined nature, the results from some of these spectrophotometric

techniques can provide a wealth of information in characterising the OM. With further advancement in this field, the sensitivity of each technique could be improved through the discovery of new challenges and new coupling and detection devices. Nevertheless resolving the detailed components of DOM has still remained difficult and expensive.

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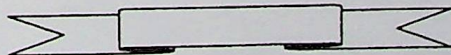
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