Natural Organic Matter and Its Significance in the Environment

Edited by Wu Fengchang and
Xing Baoshan

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Xing Baoshan is professor of environmental and soil chemistry (since, 2004) at Department of Plant, Soil and Insect Sciences, University of Massachusetts, Amherst, U.S.A., where he has been actively involved in teaching and research since 1996. Dr. Xing received his Ph.D. degree from University of Alberta, Canada in 1994. Dr. Xing's current research includes natural organic matter isolation and characterization, sorption and fate of organic chemicals in soils and sediments, environmental behaviour and ecotoxicity of engineered nanomaterials, interfacial processes in the environment, and application of spectroscopic techniques in environmental and soil sciences. Together with students and colleagues, he has published over 120 refereed articles, most of which are frequently cited by his peers. Currently, Dr. Xing is teaching 1) Environmental Soil Chemistry, 2) Advanced Soil Chemistry, 3) Inorganic Contaminants in Soil, Water, and Sediment, and 4) Environmental Impacts of Engineered Nanomaterials. He has been invited to present his research results at many universities and institutions. Dr. Xing is a technical editor of *Journal of Environmental Quality*, and an editorial board member of *Environmental Pollution, Chemosphere, International Journal of Phytoremediation, Communication in Soil Science and Plant Analysis, and Pedosphere*. He organized three special symposia related to natural organic matter and its environmental significances in the last two years. Dr. Xing won the outstanding research award of his college (Natural Resources and the Environment) in 2003 and of Soil Science Society of America and American Society of Agronomy (Northeast Branch) in 2006. He was early promoted to Associate Professor with tenure in 2000 and to Full professor in 2004. Together with his colleagues, Dr. Xing obtained research grants in total of over 2 million dollars (US) from various governmental agencies. His research program is recognized internationally.

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Preface

Natural organic matter (NOM) is ubiquitous in the environment and affects numerous environmental processes. Therefore, NOM attracts research attentions from a wide range of subject areas, such as biogeochemistry, chemistry, toxicology, soil science, global climate change, agriculture, environmental science, microbiology, and so on. In recent decades, we have witnessed the significance of NOM in the environment, and the rapid development in understanding the physical, chemical and biological characteristics and biogeochemical cycling of NOM. NOM strongly influences the environmental dynamics, toxicity and fate of contaminants (metals and organic compounds) in soils, sediments, water and air. NOM also has impacts on nutrient supplies (such as N and P), and is related to global carbon sequestration, human and public health and other eco-environmental impacts. Therefore, in the past years, several special symposia were convened, e.g., *Natural Organic Matter and Its Significance in the Environment* in the 15th Annual V.M. Goldschmidt Conference (2005), 7th International Conference of Environmental Geochemistry (2006), *Humic Substances as Environmental Sorbents* at the Annual Soil Science Society of America (2005), and Annual Humic Science and Technology Conference (Northeastern University, MA, USA).

The primary goal of this book is to bring together the latest research advancements for NOM and to stimulate and develop new directions of a variety of research areas. All authors in this book are experts in their subject areas, and were invited to contribute to the book.

The book consists of three parts. Part I is the characterization of NOM: its biogeochemical cycling of NOM in soil and natural waters, including analytical techniques, modeling, physical and chemical processes. Part II is the interaction between NOM and contaminants (trace metals and organic compounds): mechanisms and models. Part III is eco-environmental impacts on contaminants and public health, including its association with phosphorus, DNA-like material, and roles in mitigating greenhouse effect, and its sorption of antibiotics.

All chapters were subject to the peer reviewing and revision processes. We would like to thank the following reviewers for their many helpful comments and suggestions: Nicola Senesi, Universitate di Bari; EP Tipping, Centre for Ecology and Hydrology; Peter Campbell, University of Quebec; D. Di Toro, Princeton University; Wang Feiyue, University of Manitoba; He Zhongqi, USDA-ARS; B. Chefetz, The Hebrew University of Jerusalem; Zhang Chunlong (Carl), University of Houston-Clear Lake; Keith Goyne, University of Missouri-Columbia; R. Barnes, University of Massachusetts-Amherst; Z. Gerstl, The Agricultural Research Organization, Israel; Peter B. Woodbury , Cornell University; B.M. Sridhar, Bowling Green State University; Tan Zhengxi, USGS National Center for EROS; Mikhail Makarov, Moscow State University; Deng Baolin, University of Missouri-Columbia; Zachary Senwo, Alabama A&M University; Andrew Baker, University of Birmingham; Jonathan

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Contents

Part I

Characterization of Natural Organic Matter (NOM)

Chapter 1 *
Dissolved Organic Matter in the Aquatic Environment

1.1 Background

1.1.1 Dissolved organic matter (DOM)

Dissolved organic matter (DOM) is conventionally defined as any organic material that passes through a given filter (0.1–0.7 μm), termed "dissolved" and the organic material that is retained on the filter is termed "particulate". The organic substances in DOM, which can pass through filters, are fulvic acid, humic acid, carbohydrates, sugars, amino acids, proteins, lipids, organic acids, phenols, alcohols, acetylated amino sugars, and so on. The particulate organic materials are plant debris, detritus, living organisms, algae, corals, coral reefs, and so on. The DOM is a heterogeneous mixture of aromatic and aliphatic organic compounds, playing multiple functions in biogeochemical processes in natural waters which can be categorized as following:

(1) Important factors controlling drinking water quality include: ① balance in acidity and alkalinity in natural waters (Oliver et al., 1983; Pace and Cole, 2002; Hudson et al., 2003; Kopáćek et al., 2003), ② water transparency and thermal stratification due to protection of penetration of solar radiation by DOM (Laurion et al., 2000; Perez-Fuentetaja et al., 1999; Snicins and Gunn, 2000; Hudson et al., 2003), ③ redox (reduction-oxidation) reactions in water (Kwan and Voelker, 2002; Wu et al., 2005) as well as the photo-Fenton reactions accelerated by DOM in natural waters (Arakaki et al., 1999; Wu et al., 2005), ④ transport of metals, ions or organic contaminants through complex formation with DOM (Ittekkot et al., 1985; Mierle and Ingram, 1991; Kalbitz and Wennrich, 1998; Ohlenbusch et al., 2000), ⑤ acting as a precursor of a toxic by product e.g. trihalogen methane occurring during the treatment processes of drinking water (Palmstrom et al., 1988; Tao, 1996),

(2) DOM affects the character and function of the aquatic ecosystem (Wetzel, 1992; Hedges et al., 2000), including: ① photosynthesis as well as its efficiency are greatly dependent on the contents of DOM in waters, ② DOM provides a major source of energy, in the form of C and N, to drive aquatic ecosystems which are essential to all living organisms in the aquatic environment (Salonen et al., 1992; Wetzel, 1984, 1992; Tranvik, 1992; Hedges et al., 2000), and ③ thermal energy produced during photochemical redox reactions and photosynthesis is vital for natural water environments (Salonen et al., 1992; Komissarov,

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* Khan M. G. Mostofa, Wu Fengchang, Takahito Yoshioka, Hiroshi Sakugawa and Eiichiro Tanoue.

2003).

(3) Ecosystem maintenance through microbial loop, including: ① cycling of nutrients and dissolved inorganic carbon (DIC) through microbial and chemical degradation (Miller and Zepp, 1995; Wheeler et al., 1997; Guildford and Hecky, 2000; Ma and Green, 2004), ② food-chains for microorganisms (Salonen et al., 1992; Tranvik, 1992; Kirchman et al., 1995; Rosenstock et al., 2005), ③ production of bioavailable carbon substrates to enhance biological productivity (Norrman et al., 1995; Wetzel et al., 1995; Miller and Moran, 1997; Moran and Zepp, 1997), ④ attenuation of the penetration of solar harmful ultraviolet (UV) at deeper layers (Morris et al., 1995; Tranvik and Kokalj, 1998; Bertilsson and Tranvik, 2000) as well as the existence of chlorophyll a maxima at various water depths through restriction of penetration of solar radiation by DOM (Fennel and Boss, 2003; Hodges and Rudnick, 2004; Huisman et al., 2006; Yacobi, 2006).

(4) Global carbon cycle processes through production, distribution, transportation and decomposition of carbon compounds in natural water environments (Hedges, 1992; Amon and Benner, 1994; Ogawa and Tanoue, 2003), including: ① photodegradation of DOM in waters (Amon and Benner, 1996; Moran et al., 2000; Mostofa et al., 2005a, 2007b; Wu et al., 2005), ② production of low molecular-weight DOM, CO, CO_2 and DIC in waters (Jones and Amador, 1993; Kramer et al., 1996; Moran and Zepp, 1997; Ma and Green, 2004; Yoshioka et al., 2007), ③ production of hydrogen peroxide (H_2O_2) and organic peroxides (ROOHs) as a sign of photodegradation of DOM in waters (Moore et al., 1993; Mostofa et al., 2008), ④ autochthonous production of DOM which is photosynthetically produced in waters (Takahashi et al., 1995; Hamanaka et al., 2002; Marañòn et al., 2004; Medina-Sánchez et al., 2006), ⑤ control of photodegradation rate of DOM depending on the contents of DOM, exhibiting less photodegradation in waters having high DOM and high photodegradation having low DOM contents (Moran et al., 2000; Vähätalo et al., 2000; Ma and Green, 2004; Mostofa et al., 2007b) because the penetration of light depends on the contents of DOM in natural waters (Morris et al., 1995; Siegel and Michaels, 1996; Morris and Hargreaves, 1997).

1.1.2 Sources of DOM

DOM in freshwater environments is derived from two sources: one is allochthonous material which is the product of decomposition or disintegration of the terrestrial plant materials or sediments in soils, and the other is autochthonous material which is produced from freshwater ecosystem including water column (Malcolm, 1985; Nakane et al., 1997; Uchida et al., 1998, 2000; Mostofa et al., 2005a,b). Thus, DOM comprises a huge variety of organic substances including chromatographically unidentifiable humic substances (fulvic and humic acids) (Malcolm, 1985; Wu et al., 2003b, 2005) and chromatographically identifiable biomolecules such as carbohydrates, amino acids, fatty acids, etc (Hedges et al., 1994; Volk et al., 1997; Tânoue, 2000; Engelhaupt and Bianchi, 2001; Derbalah et al., 2003; Yamashita and Tanoue, 2003a, b). Allochthonous DOM also includes the anthropogenic source through fluxes of effluents from agricultural, industrial, and human activities in the surroundings of the catchment as well as airborn influx from vast areas. The influx of anthropogenic materials sometimes heavily influences the quality of local environments (Komaki and Yabe, 1982; Baker, 2001, 2002; Derbalah et al., 2003; Mostofa et al., 2005a, b). They include the fluorescence whitening agents (FWAs), components of detergents such as diaminostilbene (DASl) and distyryl biphenyl (DSBP), biphenyl, polycyclic aromatic hydrocarbons (PAHs), organo-chlorinated compounds, polychlorinated biphenyls (PCBs), hexachlorobenzene, octachlorostyrene, phenolic compounds or phenols, phthalates, alkyl and aromatic sulfonates, tryptophan, pesticides, herbicides, and amines (Matthiessen et al., 1992; Kramer et al., 1996; Opsahl and Benner, 1997; Derbalah et al., 2003; Managaki and Takada, 2005). Anthropogenic materials are quantitatively minor in DOM, for example, the average concentrations of DASl and DSBP in river waters were found to range from 0.04 to 0.7 μg/L and 0.04 to 0.6 μg/L, respectively in U. S. A. and Europe (Kramer et al., 1996 and references therein). In twelve Japanese rivers, they range from 0.9 to 17.5 μg/L (Komaki and Yabe, 1982). The major fractions of DOM are humic substances, composed of fulvic acid and humic acid both in rivers (Malcolm, 1985; Peuravuori and Pihlaja, 1999; Mostofa, 2005) and in lakes (Wang, 2007; Peuravuori and Pihlaja, 1999; Sugiyama et al., 2005). Due to universal solubility of fulvic acid in waters (soluble at all pH ranges) compared to humic acid (solid at pH $\leqslant$ 1), fulvic acid is present in all natural waters (Aiken, 1985; Malcolm, 1985). Due to the dominant presence of fulvic acid, it may play a significant role in controlling the photochemical, biological, biogeochemical processes in natural waters (Romankevich, 1984; Malcolm,1985; Kortelainen, 1999; Tanoue, 2000; Mostofa and Sakugawa, 2003).

A large amount of DOM in lakes and oceans is autochthonously produced in the waters of the epilimnetic layers (Tables 1.1 and 1.2). The major components, which are autochthonously produced, were various types of biochemical organic compounds, such as carbohydrates, amino acids, proteins, lipids or fatty acids, alcohols, alkenones, and pigments in natural waters. The major autochthonous components and their related organic substances detected till now in natural waters can be categorized as follows:

① Sugars which are comprised of arabinose, fucose, deoxyribose, rhamnose, arabinose, galactose, glucose, mannose, xylose, fructose and ribose in waters (Mopper et al., 1992; McCarthy et al., 1996; Kirchman et al., 2001; Skoog and Benner, 1997; Skoog et al., 1999; Panagiotopoulos and Sempéré, 2005).

② Dissolved carbohydrates that include monosaccharides, oligosaccharides and polysaccharides (including lipopoly-, exopoly-, homopoly-, and heteropoly-) in waters (Aluwihare et al., 1997; Opsahl and Benner, 1999; Repeta et al., 2002; Hayakawa, 2004; Van Oijen et al., 2005; Unger et al., 2005; Farjalla et al., 2006).

③ Nitrogen-containing compounds which consist of amino acids, proteins, amines, amides, peptides, polypeptides, pyrrole, and indole (McCarthy et al., 1997; Weiss and Simon, 1999; Rosenstock and Simon, 2001, 2003; Yamashita and Tanoue, 2003a, b; Rosenstock et al., 2005).

④ Lipids which are comprised of saturated, monounsaturated, polyunsaturated, branched-chain and odd-chain fatty acids. They mostly include oleic acid, arachidonic acid, eicosapentaenoic acid, linoleic acid, docosahexaenoic acid, cis-vaccenic acid, iso and anteiso-C_{15} and C_{17} fatty acids, polyunsaturated C_{22} and C_{20} fatty acids, high molecular-weight, straight-chain (C_{24} + C_{26} + C_{28} + C_{30}) fatty acids (Wakeham et al., 1997; Derieux et al., 1998; Hamanaka et al., 2002; Kainz et al., 2004; Ding and Sun, 2005).

⑤ Various steroidal alcohols (sterols) such as 24-methyl-cholesta-5,24(28)-dien-3*β*-ol, 24-ethylcholest-5-en-3*β*-ol,cholesta-5,22*E*-dien-3*β*-ol,cholest-5-en-3*β*-ol,cholesta-5, 22-dien-3*β*-ol,27-Nor-24-methylcholesta-5,22-dien-3*β*-ol,4α,23,24-trimethyl-5α-cholest-22*E*-en-3*β*-ol(dinosterol), 24-methylcholesta-5,22-dien-3*β*-ol, 24-ethylcholesta-5, 22*E*-dien-3*β*-ol, 24-ethylcholesta-5-en-3*β*-ol, 24-ethylcholesta-5,24 (28) *E*-dien-3*β*-ol, 24-n-propylcholesta-5,24(28)*E*-dien-3*β*-ol and 3-methyllidene-7,11,15-trimethylhexa decan-1,2-diol (phytyldiol) are widely distributed in natural water environments (Harvey et al., 1987; Wakeham et al., 1997; Volkman, 1986, 2003; Rontani et al., 2000; Marchand et al., 2005).

⑥ Bisnorhopane, and various alkenones such as four polyunsaturated C_{37} and C_{38} methyl-and ethyl-alkenones, 6, 10, 14-trimethylpentadecan-2-one (Wakeham et al., 1997; Hamanaka et al., 2000).

⑦ Acetylated amino sugars, N-acetyl amino polysaccharides, amines, amide, urea, purines and pyrimidines, chitin (a structural component of eukaryotic plankton species), Glucans (glucose polymer), galactans (galactose polymers), muramic acid and bacterial cell wall components such as mureins, peptidoglycan, pseud opeptodoglycan and lipopolysaccharides are a wide range of compounds usually observed in natural waters (Ittekkot et al., 1984; Romankevich, 1984; Liebezeit, 1993; Brock et al., 1994; McCarthy et al., 1997; Dauwe and Middelburg, 1998; Benner and Kaiser, 2003).

⑧ Organic acids including glycollate, tricarboxylic acids, hydroxamate, etc.

⑨ Pigments such as melanin, mycosporine-like amino acids which are mostly comprised of shinorine, palythine, porphyra-334, palythene and usujirene, and carotenoids which mostly include diadinoxanthin, zeaxanthin, myxoxanthophyll, and echinenone are a wide range of compounds usually observed in natural surface waters (Hessen and Sørensen, 1990; Laurion et al., 2002; Tartarotti and Sommaruga, 2006).

⑩ Vanillyl and syringyl phenols such as vanillin, acetovanillone, vanillic acid, syrin galdehyde, acetosyringone and syringic acid are the most abundant lignin derived oxidation products (Williams and Druffel, 1987; Opsahl and Benner, 1997; Opsahl et al., 1999; Mitra et al., 2000).