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Perspective

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Biological Formation of Organic Substances from Particulate Organic Matter

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Abstract: Biological degradation of terrestrially derived macromolecules including lignin and cellulose has been shown to produce a large number of environmentally relevant phenolic compounds. It has demonstrated that extracellular superoxide ($O_2^{-\bullet}$) is produced by heterotrophic bacteria that are common in lakes, soil, hydrothermal vents, marine sediments, estuaries and oceans. Rates of superoxide production normalized to the proportion of metabolically active cells vary between 0.02 ± 0.02 amol cell^{-1} hour^{-1} (mean ± standard error) and 19.4 ± 5.2 amol cell^{-1} hour^{-1}. Such findings provide insights into the mechanism of two key and yet unclear processes, including the biological degradation of particulate organic matter (POM) that can form dissolved organic substances, and the structural diversification of dissolved organic substances originated from POM such as plant material or algal biomass.

Keywords: Heterotrophic bacteria; extracellular superoxide; organic substances; biological degradation; particulate organic matter.

Various sources of superoxide by different organisms have been described in soils, sediments, freshwater and marine waters [1, 2]. Light-independent superoxide produced by heterotrophic bacteria can resolve some important issues such as the cycling of major and trace elements including mercury, carbon and nitrogen [1, 2], the oxidation of dissolved manganese to solid manganese oxides [2], as well as the degradation of dissolved organic matter (DOM) [3]. In particular, a key issue connected with superoxide of bacterial origin [1] is the degradation of organic matter (OM) in its dissolved and particulate forms. Biological formation of dissolved organic matter (DOM) including humic substances (allochthonous fulvic and humic acids) from particulate organic matter (POM: *e.g.* plant material) and autochthonous fulvic acid from aquatic POM (*e.g.* phytoplankton) is generally caused by biologically in soils, sediments and deeper natural water [3-6]. So the big question presently is: what is the mechanism for the formation of those DOM components from POM? Such important issue, which yet unclear processes, could be resolved by the extracellular superoxide ($O_2^{-\bullet}$) produced by heterotrophic bacteria

which are commonly detected in lakes, soil, hydrothermal vents, marine sediments, estuaries and oceans [1]. Such a finding provide insights into the mechanism of biological degradation of POM and the structural diversification of dissolved organic substances originated from plant material or algal biomass. DOM produced from POM is a fundamental phenomenon in soil, sediments and water which maintain the microbial food webs, photoinduced processes (e.g. $O_2^{-\bullet}$, H_2O_2 and $HO^{\bullet}$) along with reduction-oxidation (REDOX) reactions, global carbon cycle, nutrients cycle through degradation of its organic nitrogen or phosphorus , and finally a major source of energy to drive the aquatic ecosystem [4, 7, 8]. Allochthonous DOM originates from biological degradation of plant debris or root exudates and they includes fulvic and humic acids (humic substances), carbohydrates, phenols, organic acids, and so on [3-6]. Origin of allochthonous DOM from vascular plant materials is mostly regulated by the occurrence of three key factors [4]: (i) Physical functions (temperature and moisture); (ii) Chemical functions (nutrient availability, amount of available free oxygen and redox activity), and (iii) Microbial processes (microfloral succession patterns and availability of microorganisms (aerobic or anaerobic). Biological degradation of terrestrially derived macromolecules including lignin and cellulose has been shown to produce a large number of environmentally relevant phenolic compounds [3]. Allochthonous fulvic acid is composed of low aromaticity (17-30% of total C) and high aliphatic C (63%) with high C:N ratios (*ca*. 73-78 for Suwannee River Fulvic Acid, SRFA) whilst allochthothous humic acid includes relative high aromaticity (30-40% of total C) and low contents of aliphatic C (~30-47%) with relatively low C:N ratios (*ca*. 44-45 for Suwannee River Humic Acid, SRHA) [4, 9]. But autochthonous fulvic acid of algal origin is composed of highly aliphatic in nature, low contents of aromatic carbon (*ca*. 5–21 % of total carbon) and relatively high contents of dissolved organic N compared to organic C, i.e. significantly low C:N atomic ratios (ca. 8–36, but lower in surface waters and higher in deeper waters) [4, 9].

Allochthonous DOM in soils is partly discharged through hydrological processes directly into streams or riverbeds or surrounding water bodies, which ultimately flux to lake or oceanic environments as final water reservoir. It has been demonstrated that contribution of humic substances itself to total DOM is 20-80% in streams or rivers, 14-90% in lakes, and 11-75% in shelf seawater [4, 9]. On the other hand, autochthonous DOM originates from the respiration/degradation of algae or phytoplankton which produces through photosynthesis in water and they includes autochthonous fulvic acids, carbohydrates, amino acids, organic acids, lipids, fatty acids, alcohols, algal toxins, and so on [4, 9]. The fluorescence (excitation-emission matrix) properties of allochthonous fulvic acid or humic acid and autochthonous fulvic acid are characterized by differences in peak positions and intensities (Fig. 1a-c) [4, 10, 11].

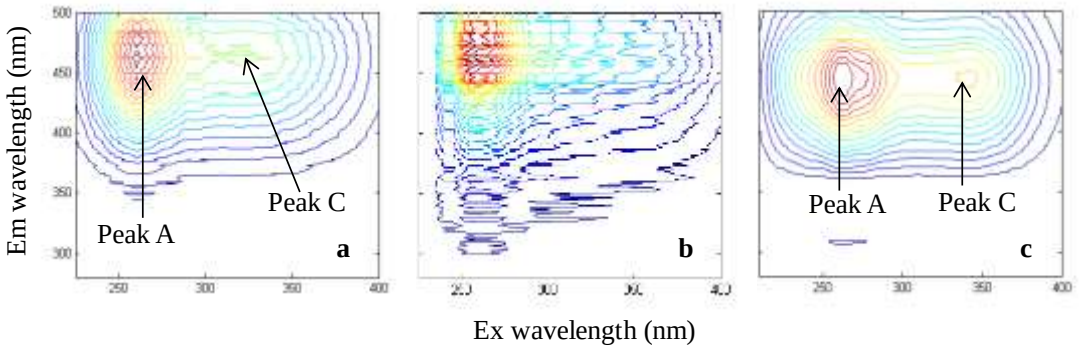

Figure 1. The fluorescent components of standard Suwannee River Fulvic Acids (C-like) (**a**), of standard Suwannee River Humic Acids (C-like) (**b**), and of autochthonous fulvic acid (C-like) (**c**) under microbial respiration or assimilation of lake algae, identified using PARAFAC modeling on their respective EEM spectra.

Studies revealed that the two fluorescence peaks (C and A) were typically observed for standard SRFA (Fig. 1a) and autochthonous fulvic acids (Fig. c) of algal origin whilst at least three fluorescence peaks were detected at peak C-region for standard SRHA, possibly the occurrence of high aromaticity in its molecular structure (Fig. 1b) [4, 10-12].

Light-independent superoxide produced by heterotrophic bacteria [1] can provide the mechanism for formation of DOM from plant debris in soils or algal biomass in waters and/or sediments. Note that rates of superoxide production normalized to the proportion of metabolically active cells is detected to vary between 0.02 ± 0.02 amol $cell^{-1}$ $hour^{-1}$ (mean ± standard error) and 19.4 ± 5.2 amol $cell^{-1}$ $hour^{-1}$ [1]. Such biological formation of H_2O_2 subsequently could be link with dark formation of hydroxyl radical ($HO^{\bullet}$) in Arctic soil and surface waters [13, 14].

The main mechanism behind the formation of DOM including allochthonous fulvic and humic acids from plant material in soils and sediments is most likely the reaction of superoxide and/or its related reactive oxygen species (ROS: H_2O_2 or $HO^{\bullet}$) with sugars, starch, proteins, lignin, cellulose and other carbon compounds of plant or animal origin. A similar process is susceptible to form various autochthonous DOM components including autochthonous fulvic acid from algal biomass or phytoplankton in deep seawater and sediments. Involvement of extracellular superoxide produced by heterotrophic bacteria can be justified by the observation that aerobic microorganisms can decompose POM at a faster rate than anaerobic ones, depending on the availability of free oxygen [15]. Besides, the increase in alkyl and carboxylic C with depth are the result of biodegradation of forest litter and oxidation of lignin side chains, respectively [16, 17]. Note also that in aqueous systems H_2O_2 can produce $HO^{\bullet}$ through the Fenton reaction ($H_2O_2 + M^{n+} \rightarrow HO^{\bullet} + HO^{-} + M^{n+1}$), which is also very effective toward the degradation of organic material [4, 18]. Actually, it is well known that the degradation of DOM including organic nitrogen and phosphorus in deep freshwater or seawater involves ROS, with eventual production of low molecular weight compounds, nitrate, phosphate, methane,CO_2 and dissolve inorganic carbon (DIC: dissolved CO_2, H_2CO_3, HCO_3^-, and CO_3^{2-}) [1, 2, 4, 7].

On the other hand, the diversification of supramolecular structures of allochthonous fulvic or humic acids and of autochthonous fulvic acids are familiar phenomena in the field of organic geochemistry. They are generally composed of a variety of functional groups such as OH (phenols, alcohols and carbohydrates), COOH (aromatic or aliphatic acids), as well as aldehydes (—CHO), ketones (C=O), ethers (R-O-R′), esters (COOR), methoxylates, and so on [4, 6, 9, 19]. Such functional groups may all be generated, at least in part, by the reaction of $O_2^{-\bullet}$ (and/or its related ROS) with the components of plants or algal biomass. These findings will give insight into the genesis and the molecular structure of allochthonous fulvic and humic acids, along with autochthonous fulvic acids. The discovery of an important biological source of superoxide [1] might pave the way for new research directions in the field of organic geochemistry in soil, sediments and deeper marine waters. Investigation on extracellular superoxide produced by heterotrophic bacteria along with the generation of specific DOM such as humic substances (fulvic and humic acids), organic acids, phenols and so on along with the autochthonous fulvic acids of algal origin in soils or sediments. These substances are very common and well understandable under biological processes (dark condition) for future research directions in this particular issue.

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The authors declare no conflict of interest

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