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## Autochthonous Dissolved Organic Matter from Algae in Lakes and its Biodegradability

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Dissolved organic matter (DOM) can play a major role as a source of carbon for heterotrophic bacteria in freshwater ecosystems. There are two major sources of DOM in lake waters: allochthonous origin from the catchment area and autochthonous origin produced within lakes. Allochthonous DOM is composed of primarily terrestrial humic substances which are recalcitrant to bacterial degradation, while autochthonous DOM is composed of more relatively labile compounds. As a result of this characteristic, in most lakes where allochthonous DOM is the dominant DOM source, most of the DOM pool is comprised of recalcitrant DOM. However, even in eutrophic lakes and oceanic waters, where autochthonous DOM is the major DOM source, much of the DOM pool is resistant to microbial degradation. Recent studies noted that autochthonous DOM could be transformed into recalcitrant forms without complete degradation to CO2 after UV radiation exposure, implying photoalteration is a chemical characteristic. However, there is little information on the changes in the chemical characteristics of autochthonous DOM by UV radiation. Therefore a relevant approach to evaluate photoalteration of algal DOM is needed. The first step may be to separate DOM into well-defined macro-fractions and to compare the fraction distribution before and after UV exposure. In pelagic waters, one of the most important sources of autochthonous DOM is extracellular organic matter (EOM) released from phytoplankton. The EOM may occuras a result of active excretion of photosynthetic products, leakage from senescent and dead algal cells, and its chemical composition varies with the physiological state of the algae. Therefore it seems reasonable to consider the physiological state of the algae in an estimation of photoalteration of algal DOM. The objective of this study was to examine the photoalteration of algal DOM produced from different growth phases of Microcystis aeruginosa by comparing the biodegradability and DOM-fraction distribution before and after UV exposure. The algal DOM was fractionated into five classes by using three kinds of resin adsorbents: hydrophobic acids, hydrophobic neutrals, hydrophilic acids, hydrophilic neutrals, and hydrophilic bases. To confirm the changes in DOM-fraction distribution after UV exposure, we also examined the fluorescent property and some organic acids of algal DOM. A bacterial degradation test was used as a measure of biodegradability of algal DOM. All algal DOM became recalcitrant toward bacterial degradation after UV exposure, without complete photodegradation. The decreased biodegradability after UV exposure was distinct in algal DOM from aged culture (stationary phase) as compared to the DOM from the exponential growth phase. The DOM-fraction distribution showed that two fractions, hydrophilic bases (HiB, protein-like DOM) and hydrophilic acids (HiA, carboxylic acid-like DOM), were abundant in all growth phases of M. aeruginosa. With aging of the algae the proportions of the HiB fraction increased, while the HiA fraction decreased. As was biodegradability, the DOM distribution was also significantly different after UV exposure, implying photoalteration in the chemical composition of algal DOM. After UV exposure, the proportions of the HiB fraction decreased (1.5-8.1% after UVA treatment and 5.3-15.8% after UVB treatment, respectively), whereas those of the HiA fraction increased by as much as the decrease of the HiB fraction. Analyses of the fluorescent property and some carboxylic acids further confirm the changes of the HiB and HiA fractions by UV radiation. However, the increased HiA fraction (probably produced as photo-product of HiB fraction) may not be linked to the recalcitrance of algal DOM by UV exposure because carboxylic acids are, in general, easily decomposable materials for bacteria. In this study, the proportions of the HiB fraction increased with aging of the algae, and the decreased biodegradability of algal DOM was distinct in aged phases. Furthermore, the initially labile HiB fraction became less available to the bacteria after UV exposure depending UV intensity. Thus, the HiB fraction may be linked to the recalcitrance of algal DOM by UV exposure. Our results indicate that algal DOM can be changed in its chemical composition as well as biodegradability by UV radiation, and suggest that the HiB fraction may be important in the formation of recalcitrant algal DOM.