Assessment of photo-oxidative alterations to natural organic matter in water using fluorescence excitation emission matrices and liquid chromatography-organic carbon detection techniques

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Abstract

Fluorescence excitation emission matrices (FEEMs) and liquid chromatography-organic carbon detection (LC-OCD) are relatively novel techniques currently used for analysing natural organic matter (NOM) in water. Regardless of the complexity of natural water matrices, LC-OCD is able to characterize and quantify NOM as five fractions: biopolymers, humic substances, building blocks, low molecular weight neutrals, and low molecular weight acids. FEEMs on the other hand characterize chromophoric dissolved organic matter and map out its emission and excitation spectral contours. In the current study, these techniques were used to characterize and quantify NOM fractions in raw water used for cooling at Eskom power stations, as well as monitor the changes in their composition when irradiated with different intensities of sunlight using a sun simulator. The effect of hydrogen peroxide ($H_2O_2$) (an oxidant) together with exposure to light on NOM was also investigated. Firstly, the results showed that humic substances decreased with increased sunlight intensities. Secondly, a similar trend was observed with the introduction of an oxidant such as $H_2O_2$. The dissolved organic carbon (DOC) in irradiated samples decreased from 9.100 ppm (in raw water) to 8.832, 8.838 and 8.175 ppm for 0.6 sun, 1.2 sun and 2.0 sun, respectively. At a constant sunlight intensity (of 1.2 sun), addition of increasing amounts of 30% $H_2O_2$ showed that the distribution of NOM fractions changed significantly. Generally, a decreasing trend in the molecular weight of NOM was observed with increased irradiation intensity as well as increased oxidant amounts. The fluorescence signature peaks showed that the humic substance (HS) contours changed but remained relatively stable with an increase in light intensity. The results of the peroxide effect on humic substances showed disappearing spectral signature peaks. No spectral contours in the HS region were formed for samples illuminated by near natural sunlight intensity in the presence of $H_2O_2$. These results are particularly important in understanding NOM in water used for cooling in power generation stations.