Supporting Information for:

Comparison of the Effects of Sonolysis and Gamma Radiolysis on Dissolved Organic Matter

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Experimental method of the application of the terephthalate •OH dosimeter in the sonolysis and radiolysis chambers. Terephthalate was chosen over other •OH dosimeters because it is non-volatile, specific to •OH and its chemical structure is similar to groups that exist in DOM. A 1L solution containing disodium terephthalate and IrCl$_6^{2-}$ (both 2.1 x 10$^{-4}$ M) was prepared in MQ-DI water. This terephthalate concentration was used because it had [DOC] = 20 mg/L, similar to typical initial [DOC] values for the experimental DOM solutions. Of this solution, 600 mL was placed in the sonolysis chamber and 15 20 mL aliquots (in 24 mL vials) were placed in the radiolysis chamber. The dosimeter solutions were sparged with O$_2$ (g) (sonolysis) or saturated with N$_2$O (g) (radiolysis) in the same manner as experimental DOM solutions. Aliquots of dosimeter solution were removed at 1-2 min intervals and the fluorescence of 2-hydroxyterephthalate measured (Photon Technology International) at excitation and emission wavelengths of 315 and 425 nm. For fluorescence measurements, samples were diluted by a factor of 1:25 in MQ-DI water and not further corrected for inner filter effects. Although the relationship between the emission intensity of 2-hydroxyterephthalate and its concentration can be calibrated using authentic standard (1), only relative rather than absolute rates of •OH scavenging by terephthalate were determined in this study. The plots of 2-hydroxyterephthalate fluorescence vs. reaction time are presented in Figure 1 of the supporting information. From the slopes of the initial linear regions of plots, the initial rate of •OH scavenging within the dosimeter solution was determined to be greater in the radiolysis reaction than in the sonolysis reaction by a factor of 2.6 ± 0.4.

The extrapolation of these results to the scavenging of •OH by DOM in the sonolysis and radiolysis reactions is likely subject to significant error, particularly for sonolysis. The validity of this result for sonolysis depends on the relation of the hydrophobicity of the terephthalate ion relative to the average hydrophobicity of the bulk of DOM molecules (35). An alternative approach to estimating the rate of •OH scavenging by DOM would be to determine the total rate of •OH production as the sum of scavenged •OH and •OH stored in H$_2$O$_2$, such as performed for sonolysis systems by Gutierrez and Henglein(2) and Mark et al. (3) and determining the rate of •OH scavenging by DOM indirectly via
measurement of the rate of H$_2$O$_2$ production. Such an approach was beyond the scope of the current work.

Figure 1. Production of 2-hydroxyterephthalate in the sonolysis and radiolysis chambers. 2-hydroxyterephthalate fluorescence intensity ($\lambda_{ex} = 315$ nm, $\lambda_{em} = 425$ nm), vs. irradiation time for solutions containing disodium terephthalate and Na$_2$IrCl$_6$(H$_2$O)$_6$ (both 2.1 x 10$^{-4}$ M) exposed to a) sonolysis (640 kHz, O$_2$ saturation), or b) $^{60}$Co $\gamma$–radiolysis (N$_2$O saturation). In this figure the error bars represent 3*$\sigma$, triplicate measurements.
Figure 2. 254 nm absorbance HPSEC chromatograms from DOM reacted by sonolysis (panel a) and radiolysis (panel b).
Figure 3. Fluorescence channel (excitation 350 nm, emission 450 nm) HPSEC chromatograms from DOM reacted by sonolysis (panel a) and radiolysis (panel b).
Figure 4. HPSEC chromatograms from continuous online dissolved organic carbon detection for DOM reacted by sonolysis (panel a) and radiolysis (panel b).
Figure 5. Weight average molecular weight ($M_w$) of DOM reacted by sonolysis (●) and radiolysis (□) as a function of reaction time, calculated from 254 nm absorbance channel.
Figure 6. RP-HPLC polarity (log $K_{ow}$) distributions for DOM reacted by sonolysis (panel a) and radiolysis (panel b).
Literature Cited

