Short and long term effects of X-ray synchrotron radiation on cotton paper

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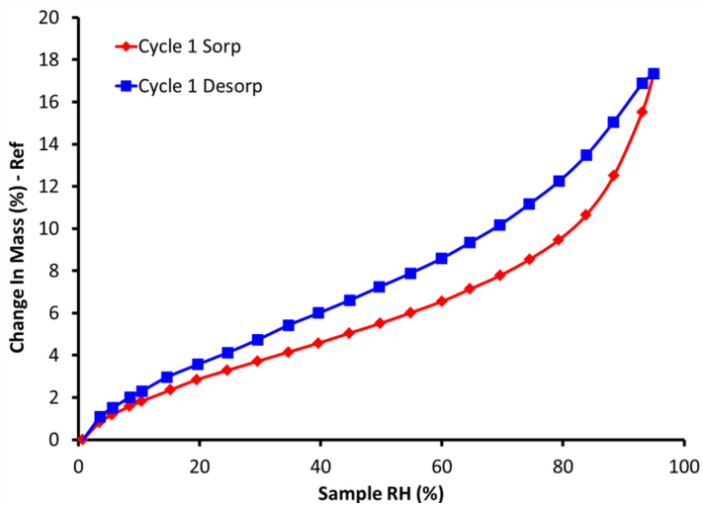

Figure S1. Water sorption isotherm of cotton paper Whatman n°1 paper at 23 °C measured with a Dynamic Vapor Sorption instrument (Advantage, Surface Measurement Systems). The reference mass was recorded after drying the sample for 5.5 hours. The relative humidity (RH) was increased stepwise from 3% to 97% RH (in 5% steps between 10% and 95% RH) until the sample mass stabilized. The isotherm (one adsorption and one desorption cycle) was completed in 116 hours.

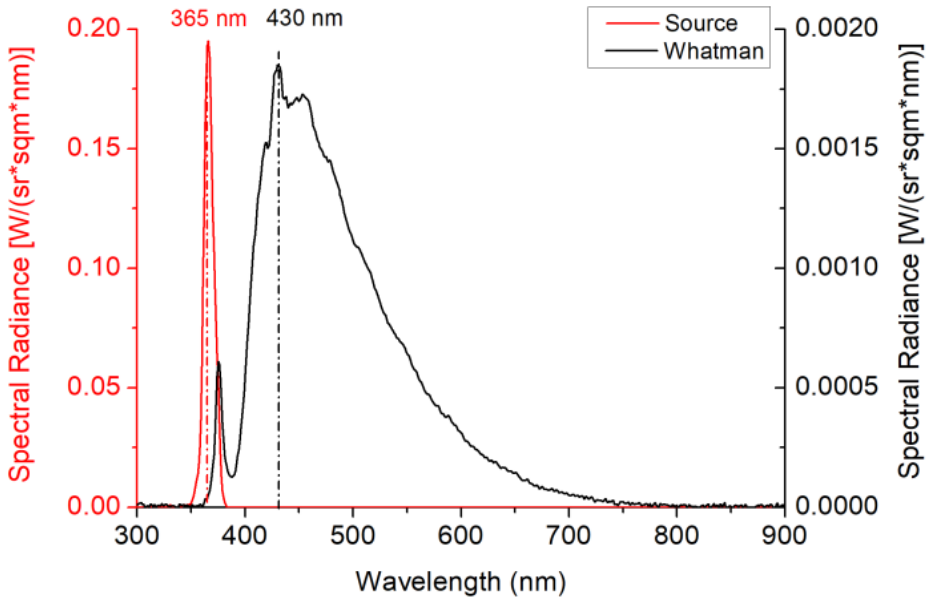

Figure S2. Whatman n°1 UV luminescence emission spectrum (black curve) and excitation spectrum at 365 nm (red curve) (λ_{max} = 430 nm)

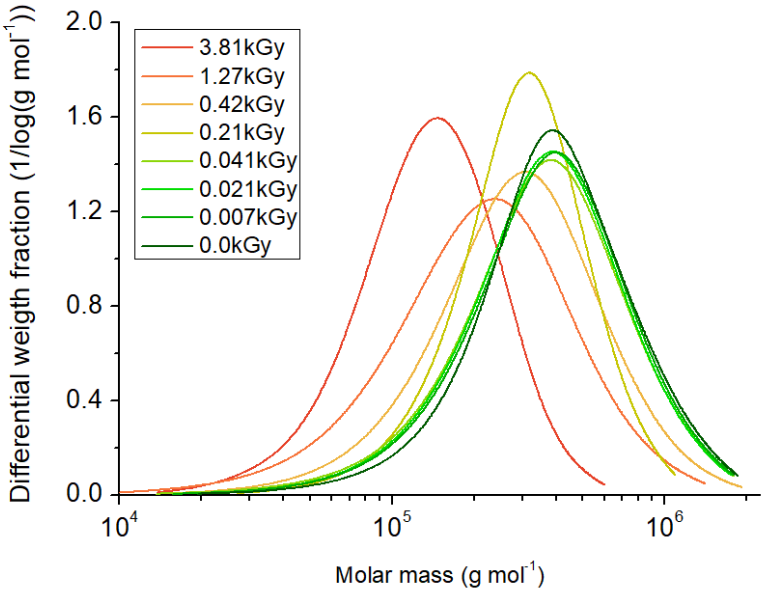

Figure S3. Differential weight fraction graph of W_0%RH_t_0 samples irradiated at 7.22 keV to various doses. The higher the dose, the larger the shift towards lower masses (color gradient from dark green to red). The lowest dose to which a shift to lower molar masses can be observed is 0.21 kGy (= $LOAED_s$).

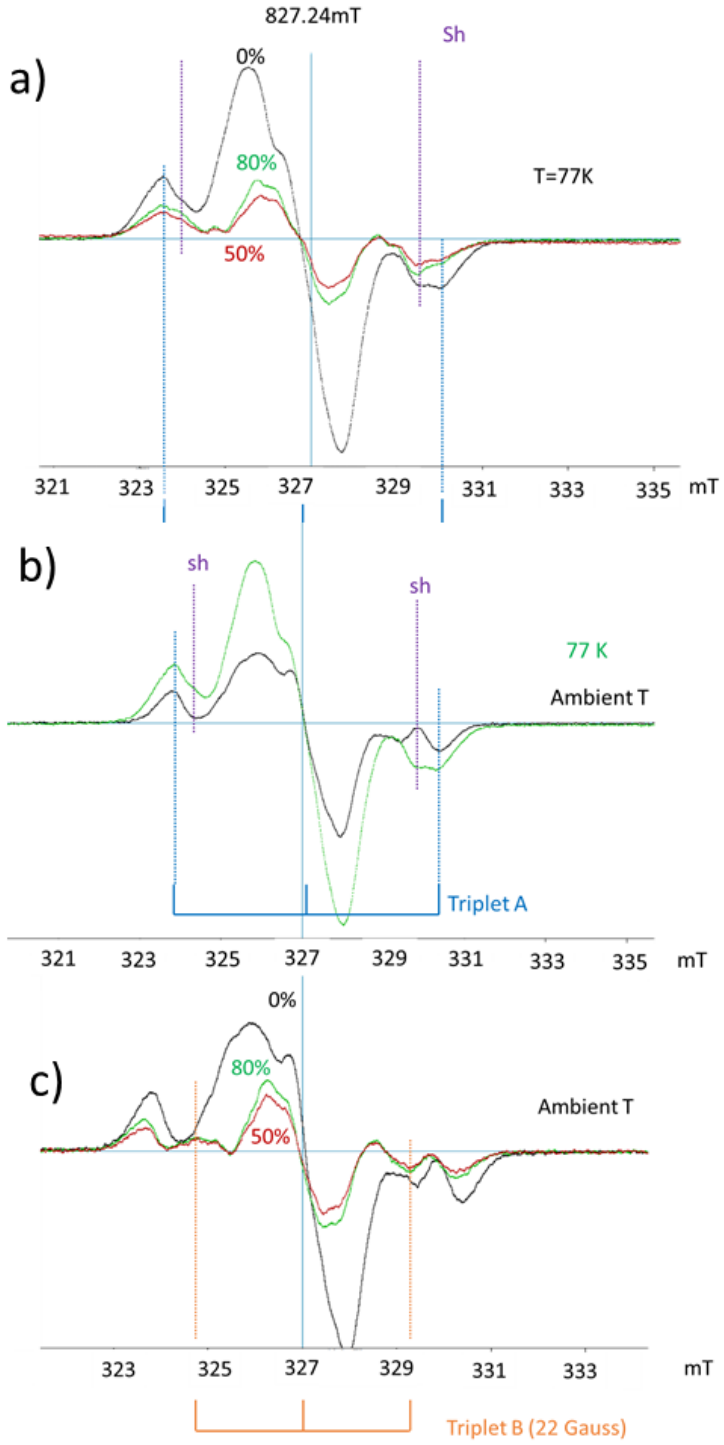

Figure S4. Electron paramagnetic resonance (EPR) of Whatman no. 1 paper exposed to SR X-rays to 20 kGy at 12.5 keV. (a) Spectra obtained at 77 K for W_0%RH (black), W_50%RH (red) and W_80%RH (green), (b) spectra of W_0%RH at 77 K (green) and ambient temperature (black), (c) spectra at ambient temperature for W_0%RH (black), W_50%RH (red) and W_80%RH (green).

EPR Experimental conditions. The empty EPR tubes were first analyzed by EPR spectroscopy to check for eventual impurities. After conditioning the tubes and the Whatman no. 1 papers at the desired relative humidity (RH), the tubes were filled with the samples prior to irradiation, and analyzed. The absence of EPR signal allowed assigning the signals obtained subsequently, after irradiation of the samples, exclusively to the SR X-ray exposure. Since free radicals have a very short lifetime, the SR X-ray radiation experiment was done with the paper directly inside the EPR quartz tube (about 10 mg of paper in small pieces). The exposure was done at 12.5 keV to 20 kGy (1040 s) instead of 7.22 keV, to lower the attenuation coefficient of quartz (25.3 cm^{-1} at 12.5keV and 126.5 cm^{-1} at 7.22 keV). The irradiation was carried out with the capped tube bottom up to avoid the formation of defects inside the quartz on the bottom part of the tube, as the latter is inserted inside the EPR instrument cavity. Working frequency was 9.14 GHz, with Gunn diode power of 0.02 mW, modulation width of 0.2 mT, sweep time of 8 min, and modulation frequency of 100MHz.

EPR results and discussion. Unambiguous interpretation of the EPR profiles is difficult. EPR spectra of irradiated cellulose by gamma rays[1–3], X-rays [4] or UV[2,5] have been reported but the differences in the dose, cellulose type, irradiation conditions and measurement conditions made it difficult to draw any correlation with the present measurements. A significant difference in the shape and intensity of the signal was observed between the driest sample (W_0%RH) and the wet samples (W_50%, W_80%RH) (a, c). This indicates a higher quantity of free radicals in W_0%RH. The intense centered signal could be attributed to an unresolved doublet, as expected for homolytic scissions of C1-H (cleavage of the glycosidic bond). It is also probably present in the wet samples but to a lower extent. A triplet with a splitting of about 32G was observed (a) and could be attributed to C5 radicals, the shoulders being due to the anisotropy of the signal, as previously reported[3]. Indeed, for W_0%HR, at 77 K the shoulders disappeared as the signal became more isotropic (b). Another triplet signal with a lower hyperfine splitting (≈ 22G) which could be attributed to C2 or C3 radicals was observed at room temperature (c) and was also probably present at 77 K.

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