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## Investigation of the photolytic fates of BPA analogues: BPF and BPS

### I. Introduction:

Bisphenol A [BPA; bis(4-hydroxyphenyl)propane] is a mass produced base chemical used in the manufacture of polycarbonate plastics and epoxy resins.<sup>1</sup> Leaching of BPA from consumer materials, along with the discharge of BPA via industrial and sewage effluent, has led to its ubiquitous presence as a contaminant in both environmental systems and in humans. A known endocrine disrupter, BPA has been found to elicit adverse biological responses in aquatic species and has gained serious attention for its toxicity to lab animals in low doses.<sup>2</sup> Controversy over its safety and the public demand for BPA-free products has prompted the use of alternative chemicals, including bisphenols similar in structure and function to BPA, in industrial applications.

Most widespread among these alternatives are the BPA analogues bisphenol F [BPF; bis(4-hydroxyphenyl)methane] and bisphenol S [BPS; bis(4-hydroxy-phenyl)sulfone]. Recent studies have reported the occurrence of BPF and BPS in indoor dust samples and lake sediments at concentrations similar to those of BPA (on the order of tens of micrograms per gram) in the U.S., Japan and Korea.<sup>3,4</sup> These concentrations are consistent with their increased applications in large-scale paper production in the U.S. as of 2006.<sup>5</sup> Research has demonstrated that both BPF and BPS test positive for estrogenic activity, though both were found to be lower in toxicity compared to BPA.<sup>6</sup> Nevertheless, recent studies also indicate that BPF and especially BPS are more resistant to biodegradation than BPA in river and seawater die-away tests.<sup>7,8</sup> Thus these compounds pose a risk of becoming ecologically burdensome, and investigations into other possible modes of degradation for these chemicals are needed.

Recent work in photochemistry has demonstrated the susceptibility of environmentally-relevant aromatic compounds to degradation via direct photochemistry or indirect photochemical pathways in a variety of environmental conditions.<sup>9</sup> In direct photolysis, photon absorption triggers the degradation of a compound, while with indirect photolysis, degradation only occurs through reaction with photolytically-excited compounds that are produced external to the molecule of interest. For example, some phytoestrogens that are otherwise stable in surface waters were found to degrade through reaction with photochemically produced reaction intermediates (PPRIs) formed in aquatic waters by the photolysis of natural organic matter (NOM).<sup>10</sup> Very recent studies have documented the direct

photodegradation kinetics of BPS.<sup>11</sup> However, complete kinetic and mechanistic studies have yet to be extended to BPS and BPF. Identification of relevant degradation pathways and kinetics is necessary in determining the persistence and overall ecological impact of these compounds. Thus this work was undertaken to experimentally identify the rate of direct photolysis of BPS as well as the PPRIs involved in the indirect photodegradation of BPF.

## II. Experimental:

**General.** Bisphenol S (**1**), bisphenol F (**2**), sorbic acid and isopropyl alcohol were purchased from Aldrich. Pony Lake fulvic acid (PLFA, a microbially-derived NOM) and Suwanee River fulvic acid (SRFA, a terrestrially-derived NOM) were purchased from the International Humic Substance Society. Solvents were of HPLC grade. Two types of quartz glass tubes were used for the photolysis experiments. Most experiments used open-topped quartz tubes (i.d.  $\approx$  1 cm, V  $\approx$  10 mL) purchased from Ace Glass. Sealable quartz tubes (i.d.  $\approx$  7 mm, V  $\approx$  7 mL) purchased from Technical Glass Products, Inc., were used in indirect photolysis experiments that tested for the effect of dissolved gases on degradation kinetics.

UV- vis absorption spectra for the bisphenols were recorded on a Perkin-Elmer Lambda 14 spectrophotometer. An Orion 5-star Plus portable multimeter equipped with a pH electrode was used for pH measurements. Buffer solutions were adjusted to the desired pH/pD values using NaOH, HCl, NaOD, or DCl solutions. Relative bisphenol concentrations were determined using reverse-phase HPLC with UV detection.

**HPLC Analysis.** An Agilent Technologies 1100 Series reverse phase HPLC coupled to an Agilent Tech. 1200 Series UV-vis detector was used to track the degradation of analytes. Samples were injected at a fixed volume of 10.0  $\mu$ L via an autosampler. For experiments with BPS, the mobile phase was composed of 35% MeOH and 55% pH 5 acetic acid:sodium acetate buffer, the flow rate set to 1.0 mL/min, and the run terminated after 15 min. For BPF experiments, the mobile phase consisted of 45% and 55% MeOH:buffer, with a flow rate of 1.0 mL/min and a run time of 10 min. An eclipse XDB C18 5 $\mu$ M packed column (4.6 x 150 mm) was used for chromatographic separation of both analytes. The column temperature was maintained at 30.0  $^{\circ}$ C and UV absorbance monitored at 258 and 280 nm for BPS and BPF, respectively.

**Photolysis Experiments.** Direct and indirect photolysis experiments were performed using an Atlas Suntest XLS+ solar simulator equipped with a Xe lamps and a UV glass filter to limit short wavelength irradiation. The simulator was operated at an intensity of 765 W/m<sup>2</sup>. The samples were kept at ambient temperature ( $\sim$ 25  $^{\circ}$ C) using an Atlas SunCool chiller unit. Test tubes were kept in a rack

and positioned at a 30° angle relative to the lamp. At given time points, small aliquots of sample (~300 µL) were withdrawn and transferred to HPLC vials for analysis. Direct photolysis experiments were carried out using solutions of BPF and BPS (2 µM) in buffers of either pH 6, 7, 8 (all phosphate buffers consisting of  $\text{KH}_2\text{PO}_4\text{:Na}_2\text{HPO}_4$ ) or 9 (boric acid:borax). Indirect photolysis experiments were also carried out in buffered D.I. water solutions, but with the addition of either PLFA or SRFA, at concentrations ranging from 5 to 30 mg/L. Additional indirect experiments were performed for pH 6, 7 and 8 buffered solutions of bisphenols with added quenchers of PPRIs. Sorbic acid was used for quenching excited state triplets (20 ppm) and isopropanol (1%) for  $\cdot\text{OH}$ .

**Dark and Outdoor Experiments.** Dark experiments were performed in pH7 buffered water to control for non-photolytic degradation of BPS. The same experiment was performed for BPF, but with the addition of varying amounts of SRFA (5 – 30 ppm) to test for degradation through reaction with ground state NOM. In order to verify that photodegradation rates in the solar simulator accurately represented rates in outdoor sunlight, photolysis experiments were performed on a rooftop on July 24<sup>th</sup> and 25<sup>th</sup>, both of which were clear-weather days. Test tubes were held in a rack at an angle 30° relative to the sun, and the rack moved at every time-point such that the test tubes were kept facing the sun. Aliquots were withdrawn and analyzed as described previously.

**Kinetic Solvent Isotope Effect and the Influence of Dissolved Gases.** Additional experiments were performed to assess the importance of  $^1\text{O}_2$  in the photolysis of BPF. One such method involved photolyzing samples in 90%  $\text{D}_2\text{O}$  solutions, rather than pure  $\text{H}_2\text{O}$  (90% was set as the upper limit of concentration because SRFA and PLFA, also present in solution, were prepared in  $\text{H}_2\text{O}$ ). This methodology takes advantage of the kinetic solvent isotope effect shown by singlet oxygen, as this PPRI is longer-lived in deuterated water. Thus experiments in which BPF was more rapidly degraded in  $\text{D}_2\text{O}$  would indicate that singlet oxygen was a key intermediate in photolysis. In order to further verify if the indirect photodegradation of BPF was mediated by singlet oxygen, or if  $^3\text{NOM}$  was instead a significant reaction intermediate, samples were purged of dissolved oxygen. Solutions were prepared in quartz test tubes with sealed screw caps that contained septum inserts for injection and sampling. The samples were sparged with  $\text{N}_2$  for at least ten minutes prior to photolysis. To limit the diffusion of ambient air into the samples, a 200 µL injection of  $\text{N}_2$  was delivered immediately prior to withdrawing a 200 µL aliquot for HPLC analysis at each time point.

### III. Results and Discussion:

**Direct photolysis.** Results of experiments performed without the addition of NOM or PPRI quenchers indicate that BPS follows first-order kinetics, where

$$-\frac{d[\text{substrate}]}{dt} = k_{\text{direct}} [\text{substrate}]$$

1

The half-lives for both bisphenols were calculated from the observed rate constants and are shown in Table 1. Figure 1 shows the linearized photodegradation kinetic profile for BPS and BPF at pH 6-8. Figure 2 suggests that BPS does not undergo any appreciable degradation in the dark, indicating that hydrolysis is not a significant mechanism for degradation of BPS at pH 8 and 9. Figures 3 and 4 verify that in dark experiments, BPF does not undergo any appreciable degradation through reaction with ground state SRFA or PLFA. UV absorption spectra for BPF (Figure 5) show increasing, red-shifted absorption with increasing pH, which is consistent with absorption changes that usually occur upon deprotonation of phenolic compounds. These data indicate that as BPS absorbs more light upon deprotonation, it is more readily degraded.

BPS in particular shows significant absorption in the wavelength region that coincides with emission by the solar simulator, while BPF absorbs very little of the simulated solar light (see Figure 6). This provides an explanation as to why BPS undergoes more rapid direct photolysis than BPF, a conclusion that is substantiated by recent literature.<sup>11</sup>

Further indication that BPS undergoes direct photolysis is provided by Figure 7, which shows that the addition of increasing concentrations of Suwannee River fulvic acid (SRFA) or Pony Lake fulvic acid (PLFA) hindered photodegradation of BPS. This suggests that in the direct photolysis of BPS, NOM is primarily serving to either screen light or quench excited state BPS, and that direct phototransformations of such compounds may be delayed or prevented at depth or in the presence of high concentrations of NOM, as has been suggested in recent literature.<sup>10</sup>

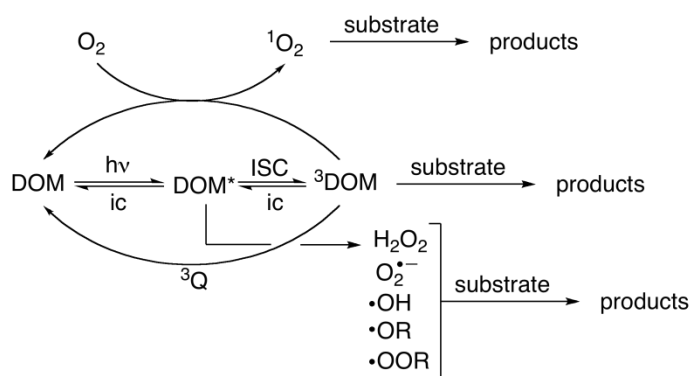
**Indirect photolysis.** Solutions of BPF (100  $\mu\text{M}$ ) were also photolyzed in the presence of PLFA and SRFA, at concentrations ranging from 5 to 30 mg/L. Unlike with BPS, addition of NOM to BPF solutions accelerated photodegradation rates. Figures 8 and 9 show that the rate of photolysis of BPF increases with increasing concentration of either PLFA or SRFA; however, rate enhancements were greater with PLFA than with SRFA.

Indirect photodegradation kinetics follow a bimolecular rate equation:

$$-\frac{d[\text{substrate}]}{dt} = (k_{\text{direct}} + \sum k_{\text{PPRI}}[\text{PPRI}])[\text{substrate}] \quad 2$$

where  $k_{\text{direct}}$ , the first order rate constant for direct photolysis, contributes only minimally to the overall rate of photodegradation of BPF. Scheme 1 depicts the direct and indirect phototransformation pathways under consideration for BPF, where NOM is natural organic matter,  $h\nu$  depicts light absorption by NOM,  $\text{NOM}^*$  is excited state singlet NOM,  ${}^3\text{NOM}$  is excited state triplet NOM,  $\text{O}_2$  is ground state oxygen,  ${}^1\text{O}_2$  is excited state singlet oxygen,  ${}^3\text{Q}$  refers to any excited state triplet quencher,  $\text{O}_2^{\cdot-}$  is superoxide radical anion,  $\cdot\text{OH}$  is hydroxyl radical,  $\cdot\text{OR}$  refers to alkoxy radicals, and  $\cdot\text{OOR}$  refers to peroxy radicals.

**Scheme 1. Kinetic Model Depicting Possible Reaction Pathways for the Indirect Phototransformation of Substrate.**



**Elucidating Indirect Photolysis Pathways of BPF.** In order to determine the extent of individual PPRI involvement in the degradation of BPF, experiments were conducted in the presence of certain quenchers of excited species. Addition of isopropanol, a radical quencher, had minimal effects on the degradation kinetics of BPF, indicating that radical species such as OR, OH, and  $\text{O}_2^{\cdot-}$  must not be significant intermediates in photolysis (Figure 10) Further studies on the indirect photodegradation mechanism of BPF were thus centered on determining the significance of the upper pathways of photolysis shown in scheme 1, namely reaction with  ${}^1\text{O}_2$  and  ${}^3\text{NOM}$ .

Experiments targeted at isolating the extent of  ${}^1\text{O}_2$  involvement were designed first using quenchers. Sodium azide, a scavenger of singlet oxygen, was first employed; however it was found that this compound reacted directly with BPF, greatly accelerating its degradation. DABCO [1,4-diazabicyclo octane] was also employed as a quencher of singlet oxygen, but it too reacted directly with BPF.

Another common experimental technique used in the determination of  $^1\text{O}_2$  involvement is the measurement of the kinetic solvent isotope effect (KSIE). Isotopes of  $\text{H}_2\text{O}$  are known to quench singlet oxygen to a greater extent than  $\text{H}_2\text{O}$ . Figure 9 shows that BPF degrades somewhat faster in experiments using deuterated solvent relative to pure water at both pH 7 and 8 and in the presence of NOM.

In order to further evaluate both the involvement of  $^1\text{O}_2$  and  $^3\text{NOM}$ , oxygen was removed from the solutions all together, and the reaction kinetics measured for solutions sparged with  $\text{N}_2$  relative to those containing air. As depicted in Scheme 2,  $\text{O}_2$  is necessary, predictably, for the production of  $^1\text{O}_2$ . In the process,  $\text{O}_2$  quenches  $^3\text{NOM}$ , thus decreasing the availability of this PPRI in solution. If  $^3\text{NOM}$  is a significant intermediate in the photolysis of BPF, removal of oxygen would increase the steady state concentration of  $^3\text{NOM}$  and consequently increase the rate of photolysis. If, on the other hand, photolysis is mediated by  $^1\text{O}_2$ , then removal of  $\text{O}_2$  would slow degradation. Photolytic processes that require both  $^1\text{O}_2$  and  $^3\text{NOM}$  would thus be simultaneously slowed and accelerated upon being sparged with  $\text{N}_2$ , and the kinetic data would reflect a balance of these processes. Results from these experiments (Figure 11) show that photolysis of BPF is accelerated both in the presence and the absence of oxygen; however, acceleration is greater with only nitrogen gas present. These results indicate that singlet oxygen cannot be singularly responsible for the degradation of BPF, and that  $^3\text{NOM}$  is a more significant reaction intermediate during photolysis.

To conclusively test for the involvement of  $^3\text{NOM}$  in the degradation of BPF, sorbic acid, a quencher of excited state triplet compounds, was added to the solutions. However, it is important to consider that sorbic acid, by removing  $^3\text{NOM}$  from solution, also decreases the production of PPRI that are produced downstream of  $^3\text{NOM}$  – namely  $^1\text{O}_2$ . Thus reactions that are mediated by either  $^3\text{NOM}$  or  $^1\text{O}_2$  will be slowed in the presence of sorbic acid. Results indicate that the addition of sorbic acid substantially decreased the rate of photolysis at pH 8 (Figure 12).

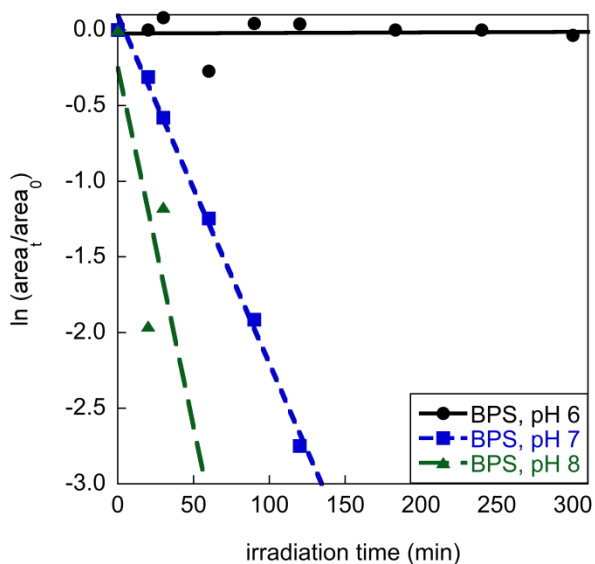
Overall, the results of mechanistic experiments implicate both  $^3\text{NOM}$  and  $^1\text{O}_2$  in the indirect photolysis of BPF. Experiments in deuterated solvent indicate that singlet oxygen plays only a modest role in the degradation of BPF, while experiments carried out with altered partial pressures of oxygen revealed a  $^3\text{NOM}$ -dominated pathway of degradation for BPF. Because BPS is not susceptible to indirect photolysis, it can be expected to degrade efficiently in relatively pristine waters above pH 6, but is likely to be persistent in the presence of higher concentrations of NOM. The indirect photolysis of BPF, on the other hand, is more difficult to extrapolate to field settings, and its near-surface half-life will likely vary with NOM concentration, NOM composition, and pH conditions.

Table and Figures:

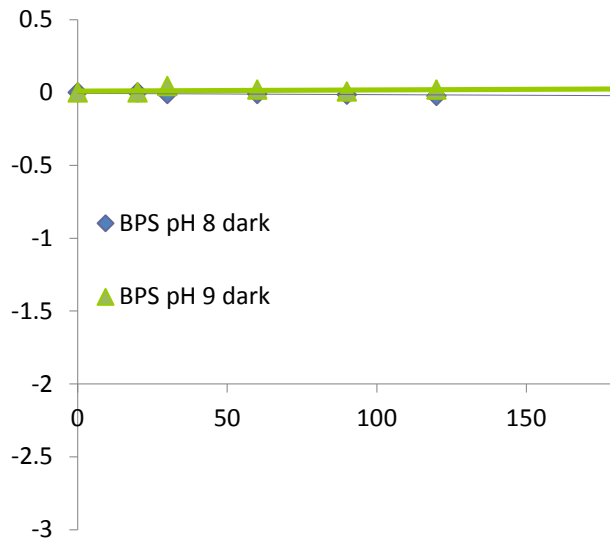
**Table 1.** Observed rate constants and half lives for the direct photolysis of BPS and BPF at various pH.<sup>a</sup>

Compound	pH 6		pH 7		pH 8		pH 9	
	$k_{\text{obs}}$ (1/s)	$t_{1/2}$ (h)	$k_{\text{obs}}$ (1/s)	$t_{1/2}$ (h)	$k_{\text{obs}}$ (1/s)	$t_{1/2}$ (h)	$k_{\text{obs}}$ (1/s)	$t_{1/2}$ (h)
BPS			0.000106	109	0.000388	30	0.000958	12
BPF								

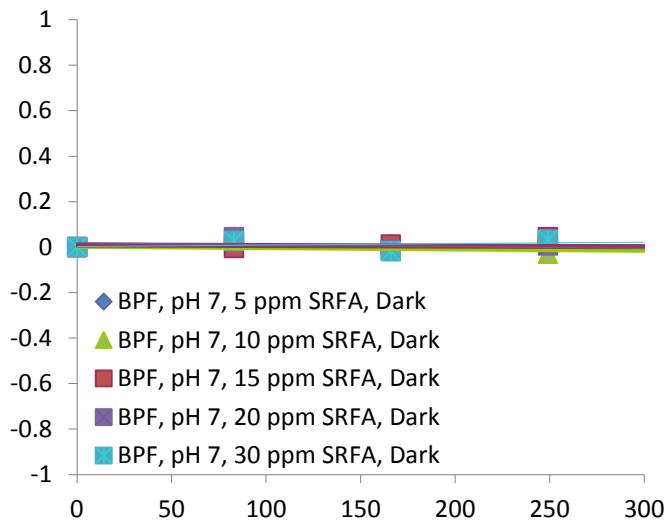
<sup>a</sup>Blank entries indicate negligible direct photolysis over the course of the experiment (5 h); half-lives could not accurately be determined for these compounds.



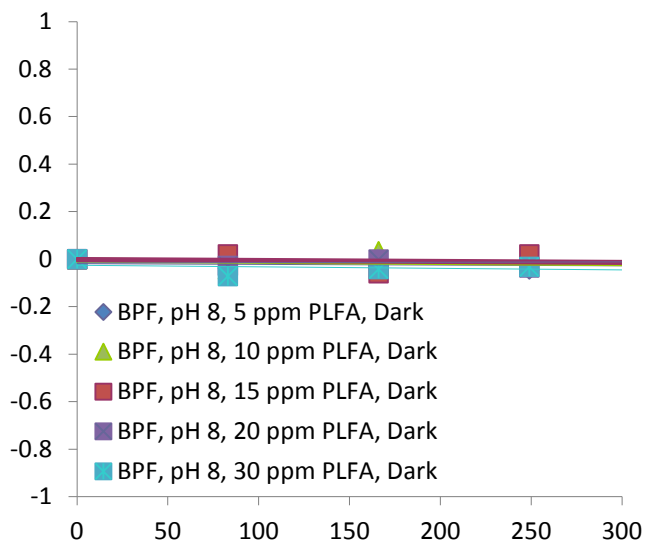
**Figure 1.** Rates of degradation of BPS increase with increasing pH.



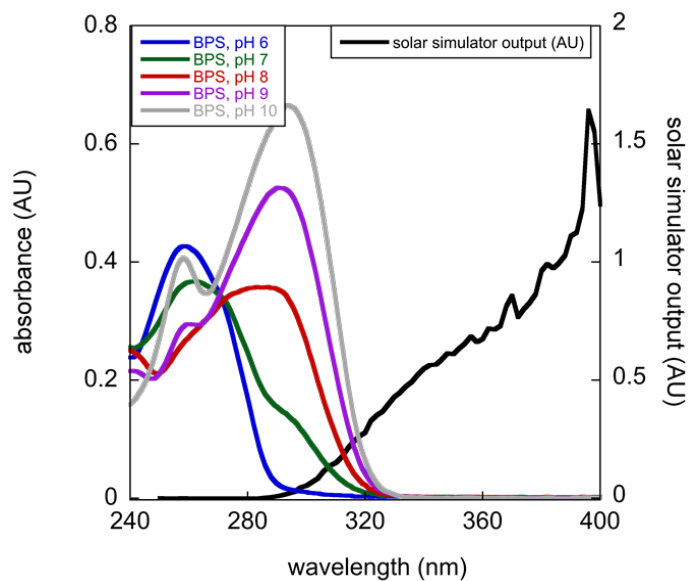
**Figure 2.** BPS shows no appreciable degradation in experiments carried out in the dark at pH 8 and 9.



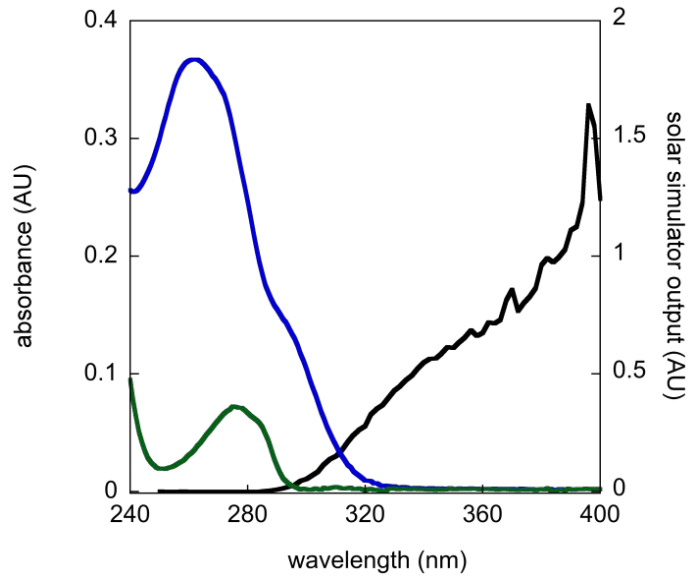




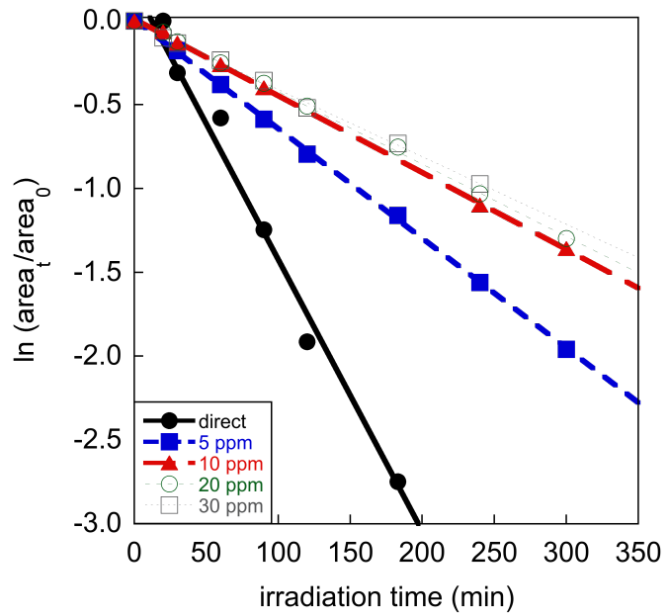
**Figures 3 and 4.** Degradation of BPF does not occur in the presence of varying concentrations of NOM when no light is present.



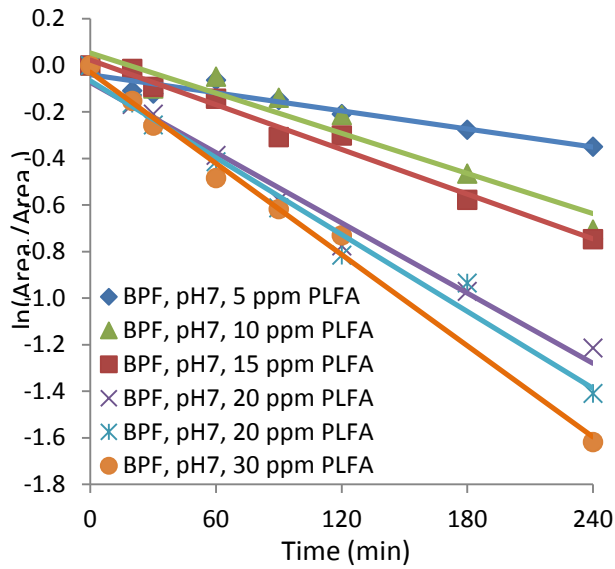
**Figure 5.** Absorption of light by BPS increases and becomes more red-shifted with increasing pH.



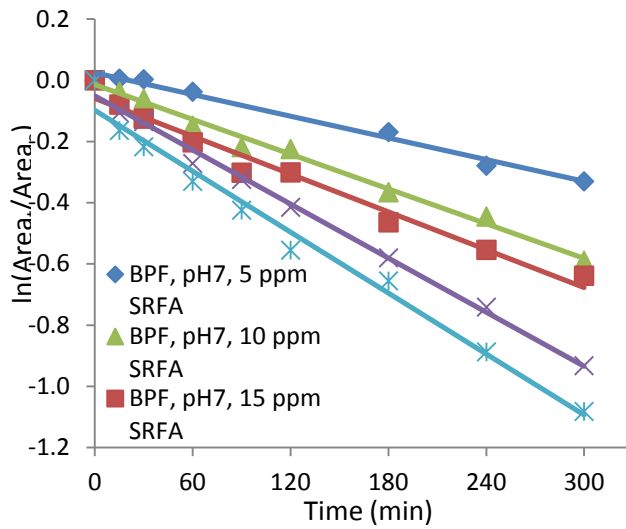
**Figure 6.** BPS absorbs more light in wavelength region emitted by the solar simulator than does BPF.



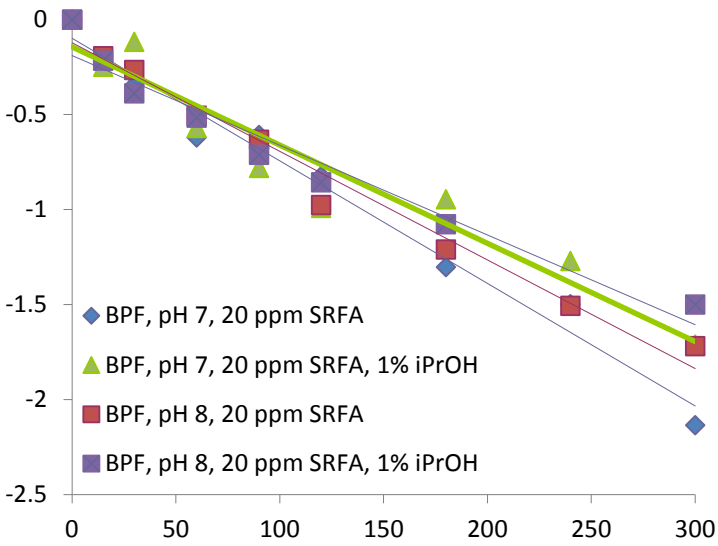
**Figure 7.** Rates of degradation of BPS are hindered with increasing concentrations of NOM.



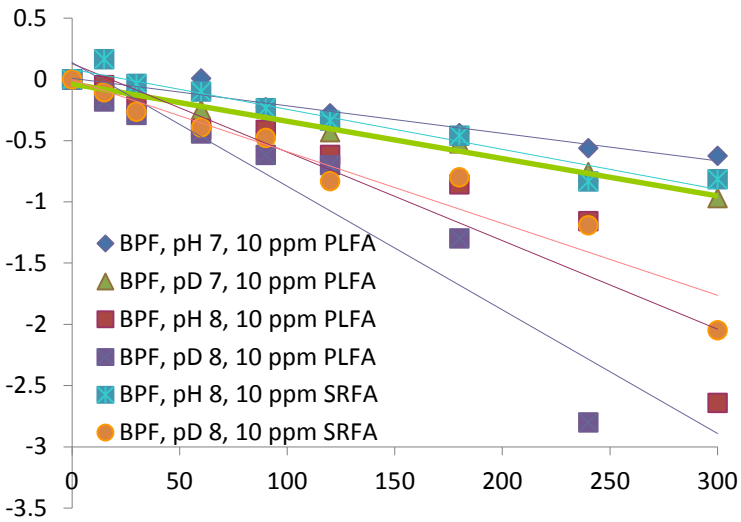
**Figure 8.** Rates of degradation of BPF increase with increasing concentrations of SRFA.



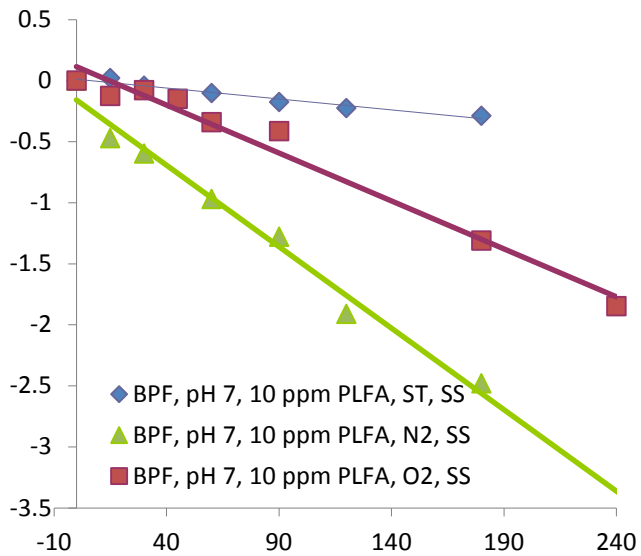
**Figure 9.** Rates of degradation of BPF increase with increasing concentrations of SRFA.



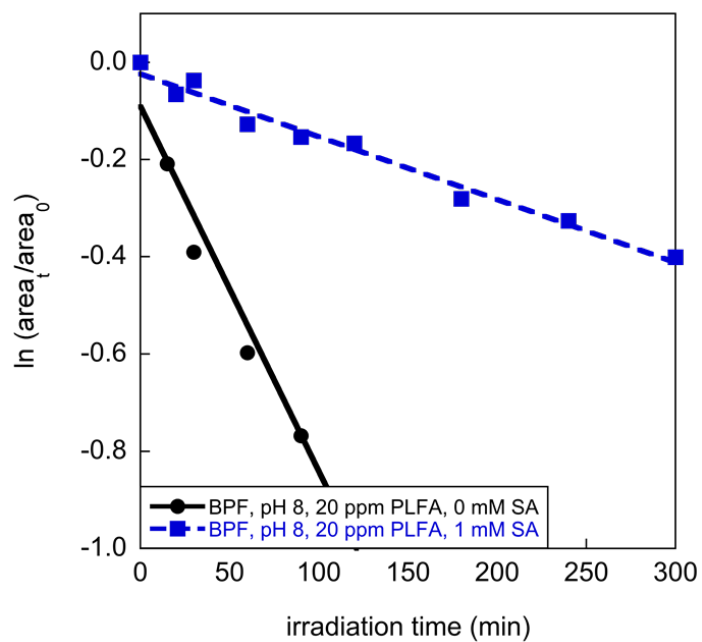
**Figure 10.** Rates of degradation of BPF are not appreciably altered with the addition of 1% isopropanol, a radical quencher.



**Figure 11.** Rates of degradation of BPF are modestly accelerated in deuterated water relative to pure water at both pH 7 and 8.



**Figure 12.** Degradation of BPF is accelerated in the presence and absence of O<sub>2</sub> relative to atmospheric conditions.



**Figure 13.** Rates of degradation of BPF are significantly delayed with the addition of 1 mM sorbic acid, a <sup>3</sup>NOM quencher.

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