Supplementary Information

Phototransformation of pesticides in prairie potholes: Effect of dissolved organic matter in triplet-induced oxidation

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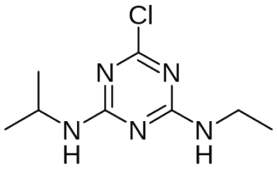
Summary: This file contains 28 pages, 22 Figures and 3 Tables.

1. Chemical Standards and Materials

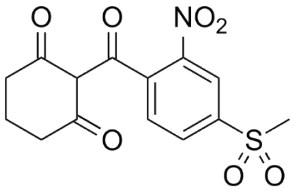
HPLC-grade solvents were purchased from Fisher Scientific (Waltham, MA) and Sigma Aldrich (St. Louis, MO). Pesticide standards for atrazine (6-chloro-N2-ethyl-N4-isopropyl-1,3,5-triazine-2,4-diamine; 99.8%), mesotrione (2-(4-(methylsulfonyl)-2-nitrobenzoyl)cyclohexane-1,3-dione; 99.9%), isoproturon (3-(4-isopropylphenyl)-1,1-dimethylurea; 99.9%), metolachlor (2-chloro-N-(2-ethyl-6-methylphenyl)-N-(1-methoxypropan-2-yl)acetamide; 97.6%) were purchased from Fluka. Ultrapure water was produced by a Milli-Q Academic system (EMD Millipore, Inc., Billerica, USA). Prior to use, all glassware was cleaned with Alconox detergent, triple rinsed with DI water, and baked at 550 °C for ≥4 hours. Stock solutions of target pesticides and benzophenone-4-carboxylate were prepared in acetonitrile. For the irradiation experiments, aqueous solutions of pesticides were prepared by adding stock solutions into volumetric flasks and subsequently evaporating the solvent phase by purging with N_2 gas and adding Milli-Q water. Iron(III) was measured following a slightly modified version of the ferrozine method of Viollier et al. (2000)[1]. Briefly, a 2.8 mL sample aliquot was amended with 0.2 mL of 10 mM

ferrozine. This mixture was allowed to react with 0.3 mL of 1.4 M hydroxylamine for 10 minutes. Finally, 0.1 mL of 10 M pH 9.5 ammonium acetate was added. The solution absorbance was measured at 562 nm. Standards were prepared with ferric chloride. The method detection limit was estimated to be 3 μM Fe(III).

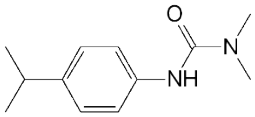
2. Pesticide Structures



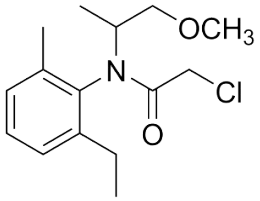
Atrazine



Mesotrione



Isoproturon



Metolachlor

3. HPLC Analysis

Concentrations of pesticides in aqueous samples were directly analyzed by an Agilent 1100 Series high-pressure liquid chromatography equipped with a micro degasser, a quaternary pump and an autosampler coupled to a multi-wavelength UV absorbance detector (MWD). Chromatographic separations were performed using a Supelco Discovery RP-Amide C16 column (15 cm × 4.6 mm; 5 μm) with an in-line Supelguard Discovery RP-Amide C16 cartridge (2 cm ×

2.1 mm; 5 μm). The mobile phase composition and the detection wavelengths are listed in the Table below. The flow rate was 1 mL/min and the injection volume was 35 μL.

Table S1 HPLC parameters for pesticide analysis

Compound	Mobile Phase Composition (v:v)	Detection Wavelength (nm)	Retention time (min)
Atrazine	0.1% (v/v) Phosphoric acid (pH 2.85) : ACN (50:50)	220	5.7
Isoproturon	0.1% (v/v) Phosphoric acid (pH 2.85) : ACN (50:50)	254	5.6
Mesotrione	0.1% (v/v) Phosphoric acid (pH 2.85) : ACN (55:45)	254	5.1
Metolachlor	0.1% (v/v) Phosphoric acid (pH 2.85) : ACN (35:65)	220	5.2

4. Light Screening Corrections

Screening factors are calculated as a ratio of the rates of light absorption in the presence and absence of the species responsible for screening:

$$R_{a,i_\lambda} = W_\lambda \frac{(1 - 10^{-a_\lambda l})}{l} \quad \textbf{(1)}$$

$$R_{a,i\,j_\lambda} = W_\lambda \frac{(1 - 10^{-(a_{i_\lambda} + a_{j_\lambda})l})}{l} \times \frac{a_{i_\lambda}}{a_{i_\lambda} + a_{j_\lambda}} \quad \textbf{(2)}$$

$$S_{i,j} = \frac{\int_{\lambda_{low}}^{\lambda_{high}} R_{a,i\_j_\lambda}}{\int_{\lambda_{low}}^{\lambda_{high}} R_{a,i_\lambda}} \quad \textbf{(3)}$$

$$a_{j_\lambda} = a_{CB,_\lambda} = \varepsilon_{\lambda,CB} \times C_{CB} \quad \textbf{(4)}$$

$$a_{j_\lambda} = a_{DOM,_\lambda} \quad \textbf{(5)}$$

where $R_{a,i}(\lambda)$ is the rate of light absorption in the presence of constituent i, $R_{a,i\,j}(\lambda)$) is the rate of light absorption in the presence of constituents i and j, W_λ is spectral photon fluence rate (mEs cm^{-2} s^{-1}), a_λ is the light attenuation coefficient for natural water constituents (the measured absorbance for a given wavelength when the cuvette path length is 1.0 cm), $\varepsilon_{\lambda,CB}$ is molar extinction coefficient for CBBP (cm^{-1} M^{-1}), C_{CB} is the concentration of CBBP (M), and l is the path length of the test tubes used for the experiments [1.12 cm][2].

Integrals were estimated by summing average rates of light absorption over 1-nm intervals. It should be noted that $S_{i,j}$ is the screening factor for the screening of i by j. For example, $S_{DOM,CB}$ is the screening factor for the screening of DOM by CBBP.

References

[1]Viollier, Applied Geochemistry, 15 (2000) pp. 785-790.

[2]Leifer, A. The Kinetics of Environmental Aquatic Photochemistry: Theory and Practice; American Chemical Society: York, PA, 1988.

Table S2 Light Screening Correction Factors

DOM Source	S_{DOM}	S_{CB}	$S_{DOM,CB}$	$S_{CB,DOM}$
T9 Summer	0.949	0.926	0.996	0.616
T9 Fall	0.951	0.926	0.995	0.793
P7 Summer	0.953	0.926	0.995	0.848
P7 Fall	0.954	0.926	0.995	0.844
P1 Summer	0.939	0.926	0.992	0.838
P1 Fall	0.937	0.926	0.991	0.853
P8 Summer	0.946	0.926	0.994	0.808
P8 Fall	0.948	0.926	0.994	0.844

Table S3 Phototransformation Kinetics of Pesticides in PPL waters. Rate constants are given as mean (± standard error of the mean).

Compound	Site	Season					
		Summer			Fall		
		k_{PPL} (s^{-1})	$k_{CB,PPL}$ (s^{-1})	k_{CB} (s^{-1})	k_{PPL} (s^{-1})	$k_{CB,PPL}$ (s^{-1})	k_{CB} (s^{-1})
Atrazine	T9	**$1.78(\pm0.15) \times10^{-5}$**	**$1.78(\pm0.05) \times10^{-4}$**	**$3.12(\pm0.04) \times10^{-4}$**	**$1.11(\pm0.12) \times10^{-5}$**	**$1.95(\pm0.01) \times10^{-4}$**	**$2.95(\pm0.02) \times10^{-4}$**
	P7	**$2.69(\pm0.16) \times10^{-5}$**	**$2.32(\pm0.05) \times10^{-4}$**	**$3.61(\pm0.26) \times10^{-4}$**	**$1.57(\pm0.41) \times10^{-5}$**	**$1.88(\pm0.01) \times10^{-4}$**	**$2.95(\pm0.03) \times10^{-4}$**
	P1	**$5.81(\pm0.14) \times10^{-6}$**	**$2.15(\pm0.07) \times10^{-4}$**	**$3.16(\pm0.02) \times10^{-4}$**	**$2.22(\pm0.76) \times10^{-6}$**	**$1.31(\pm0.27) \times10^{-4}$**	**$2.54(\pm0.12) \times10^{-4}$**
	P8	**$8.06(\pm0.31) \times10^{-6}$**	**$2.14(\pm0.06) \times10^{-4}$**	**$3.34(\pm0.02) \times10^{-4}$**	**$5.56(\pm0.32) \times10^{-6}$**	**$1.76(\pm0.04) \times10^{-4}$**	**$2.84(\pm0.04) \times10^{-4}$**
Isoproturon	T9	**$9.92(\pm0.35) \times10^{-5}$**	**$3.14(\pm0.10) \times10^{-4}$**	**$2.52(\pm0.07) \times10^{-4}$**	**$8.94(\pm0.19) \times10^{-5}$**	**$3.14(\pm0.04) \times10^{-4}$**	**$2.61(\pm0.01) \times10^{-4}$**
	P7	**$1.32(\pm0.20) \times10^{-4}$**	**$3.77(\pm0.16) \times10^{-4}$**	**$2.74(\pm0.10) \times10^{-4}$**	**$9.16(\pm0.05) \times10^{-5}$**	**$4.24(\pm0.05) \times10^{-4}$**	**$2.54(\pm0.05) \times10^{-4}$**
	P1	**$9.56(\pm0.22) \times10^{-5}$**	**$3.04(\pm0.02) \times10^{-4}$**	**$2.41(\pm0.07) \times10^{-4}$**	**$7.21(\pm0.52) \times10^{-5}$**	**$4.42(\pm0.04) \times10^{-4}$**	**$2.51(\pm0.04) \times10^{-4}$**
	P8	**$8.12(\pm0.23) \times10^{-5}$**	**$2.95(\pm0.04) \times10^{-4}$**	**$2.62(\pm0.05) \times10^{-4}$**	**$7.03(\pm0.01) \times10^{-5}$**	**$3.33(\pm0.07) \times10^{-4}$**	**$2.58(\pm0.02) \times10^{-4}$**
Mesotrione	T9	**$1.06(\pm0.01) \times10^{-5}$**	**$2.16(\pm0.02) \times10^{-5}$**	**$2.05(\pm0.01) \times10^{-5}$**	**$9.72(\pm0.25) \times10^{-6}$**	**$2.67(\pm0.06) \times10^{-5}$**	**$1.92(\pm0.04) \times10^{-5}$**
	P7	**$6.67(\pm0.32) \times10^{-6}$**	**$2.39(\pm0.06) \times10^{-5}$**	**$1.83(\pm0.01) \times10^{-5}$**	**$1.14(\pm0.01) \times10^{-5}$**	**$2.49(\pm0.10) \times10^{-5}$**	**$2.25(\pm0.01) \times10^{-5}$**
	P1	**$1.14(\pm0.01) \times10^{-5}$**	**$2.85(\pm0.10) \times10^{-5}$**	**$1.96(\pm0.01) \times10^{-5}$**	**$9.44(\pm0.27) \times10^{-6}$**	**$2.69(\pm0.10) \times10^{-5}$**	**$2.08(\pm0.01) \times10^{-5}$**
	P8	**$1.17(\pm0.06) \times10^{-5}$**	**$2.65(\pm0.07) \times10^{-5}$**	**$2.03(\pm0.01) \times10^{-5}$**	**$1.22(\pm0.03) \times10^{-5}$**	**$2.89(\pm0.12) \times10^{-5}$**	**$2.36(\pm0.01) \times10^{-5}$**
Metolachlor	T9	**$1.14(\pm0.03) \times10^{-5}$**	**$3.81(\pm0.06) \times10^{-5}$**	**$2.58(\pm0.04) \times10^{-5}$**	**$1.06(\pm0.04) \times10^{-5}$**	**$3.83(\pm0.05) \times10^{-5}$**	**$3.46(\pm0.15) \times10^{-5}$**
	P7	**$6.94(\pm0.10) \times10^{-6}$**	**$3.99(\pm0.22) \times10^{-5}$**	**$2.54(\pm0.32) \times10^{-5}$**	**$1.22(\pm0.01) \times10^{-5}$**	**$4.05(\pm0.01) \times10^{-5}$**	**$3.15(\pm0.14) \times10^{-5}$**
	P1	**$6.81(\pm0.06) \times10^{-6}$**	**$3.39(\pm0.05) \times10^{-5}$**	**$2.61(\pm0.02) \times10^{-5}$**	**$6.78(\pm0.07) \times10^{-6}$**	**$4.33(\pm0.02) \times10^{-5}$**	**$3.75(\pm0.14) \times10^{-5}$**
	P8	**$5.06(\pm0.11) \times10^{-6}$**	**$3.10(\pm0.05) \times10^{-5}$**	**$2.75(\pm0.02) \times10^{-5}$**	**$8.42(\pm0.03) \times10^{-6}$**	**$3.65(\pm0.01) \times10^{-5}$**	**$3.23(\pm0.11) \times10^{-5}$**

Fig S1 Phototransformation Kinetics of Atrazine in T9 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

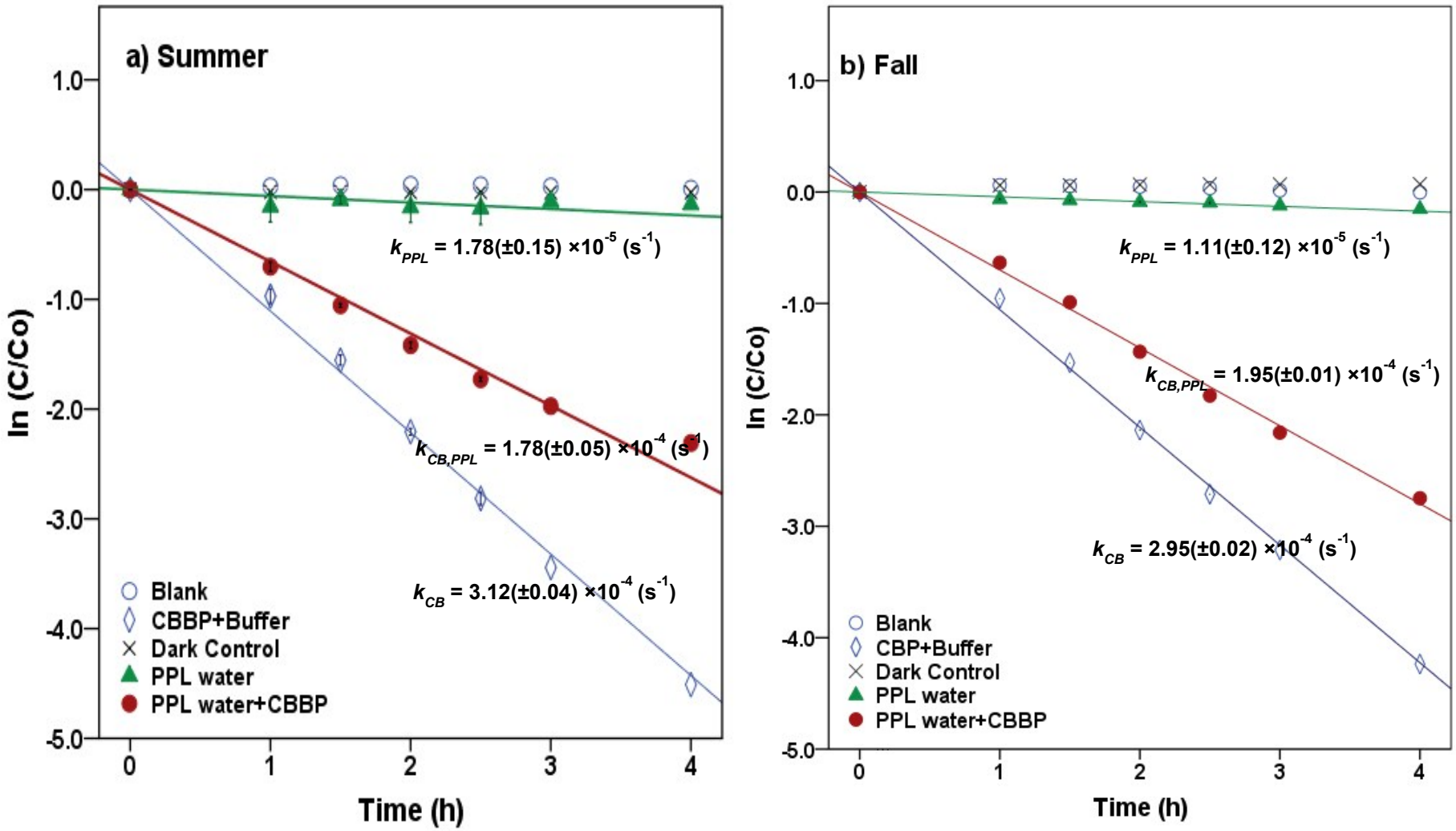


Fig S2 Phototransformation Kinetics of Atrazine in P7 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

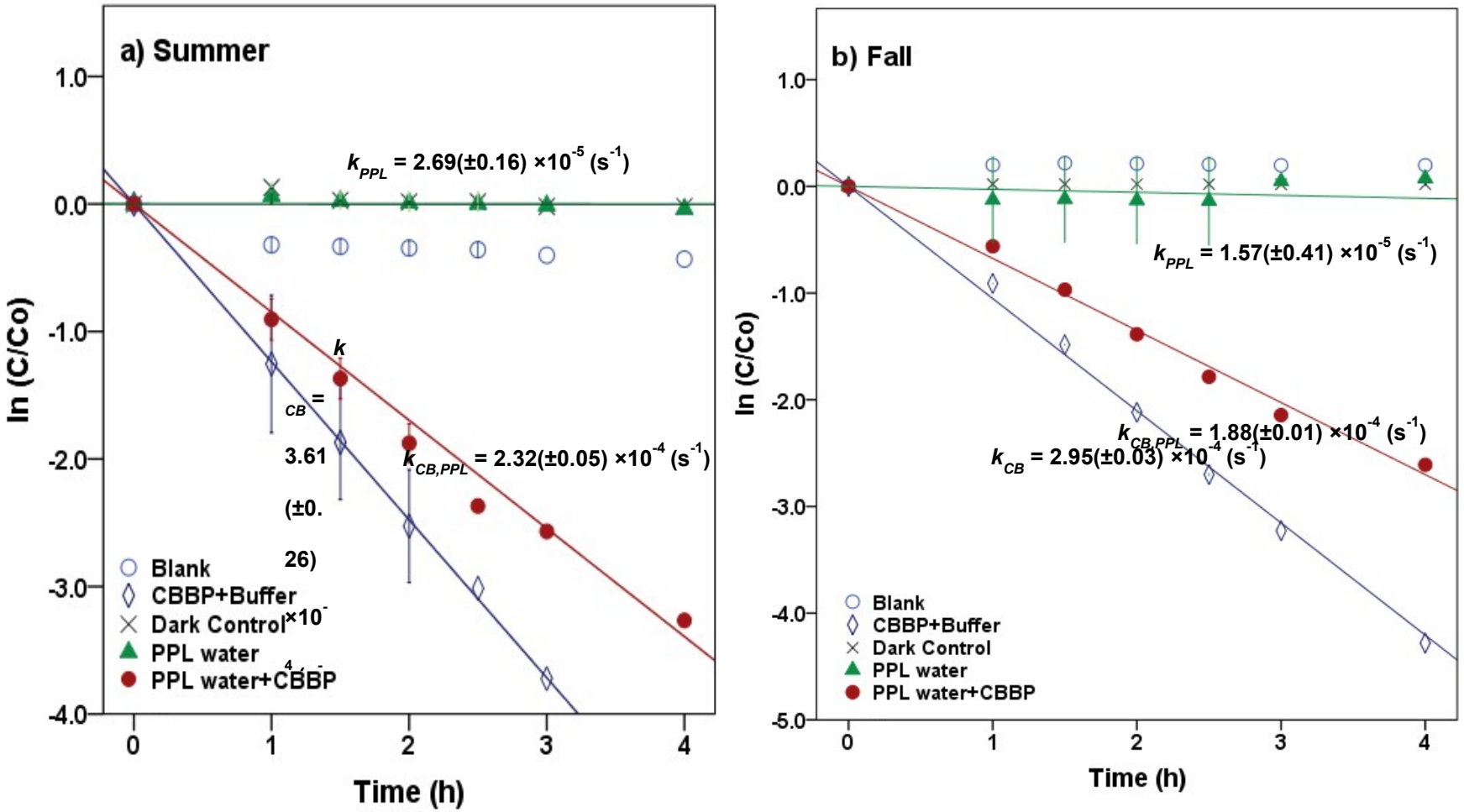


Fig S3 Phototransformation Kinetics of Atrazine in P1 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

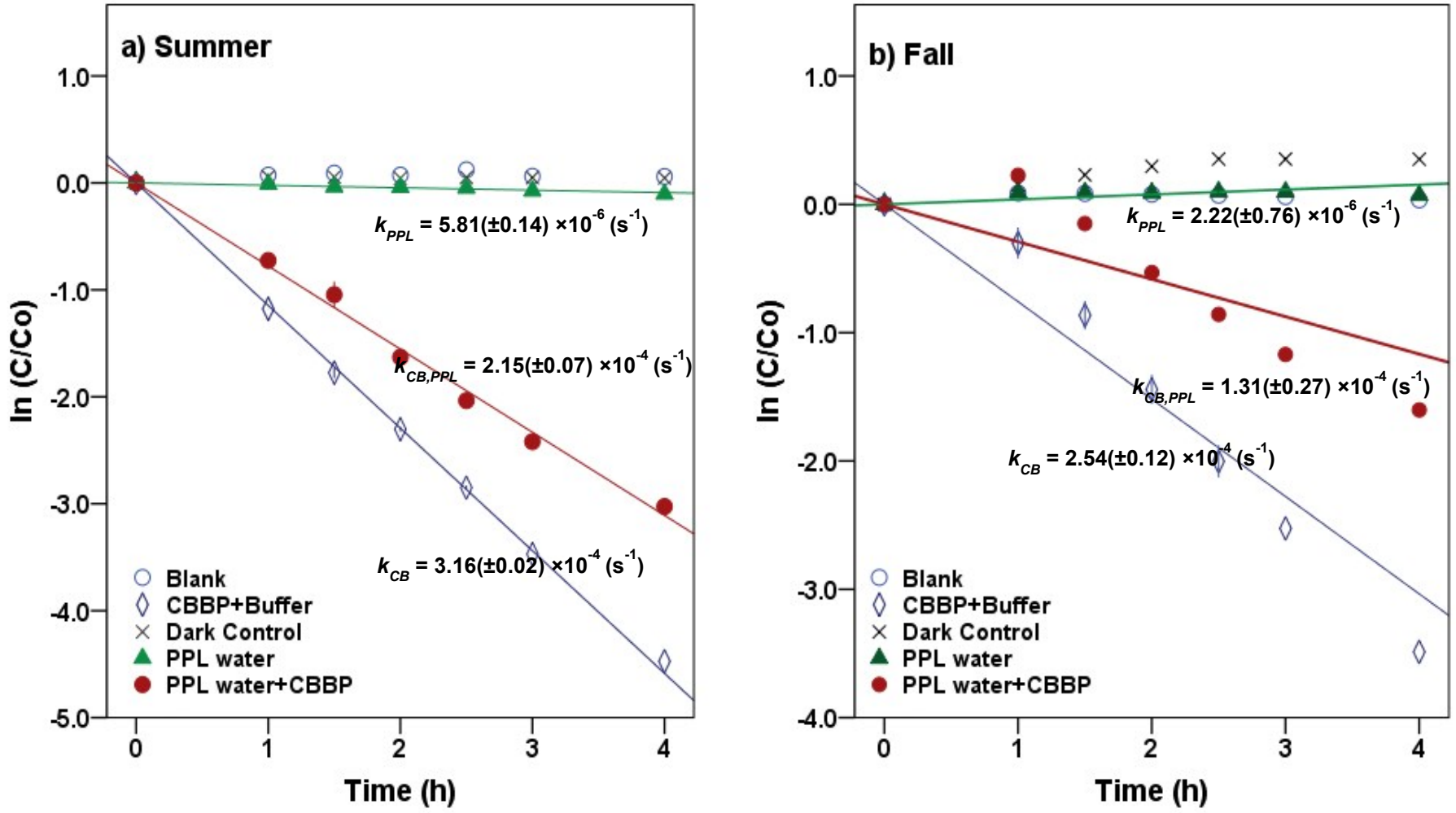


Fig S4 Phototransformation Kinetics of Atrazine in P8 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

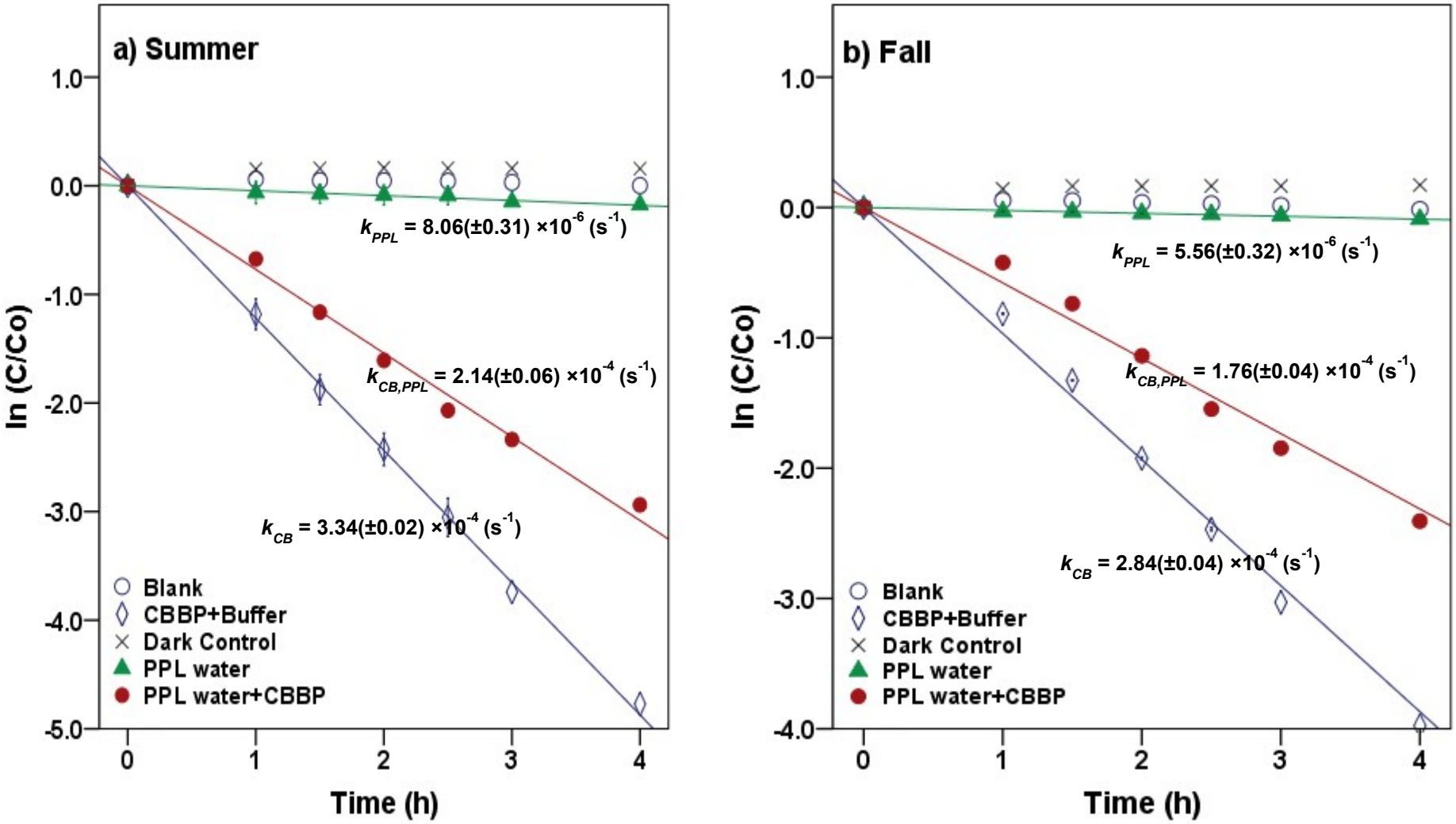


Fig S5 Phototransformation Kinetics of Isoproturon in T9 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

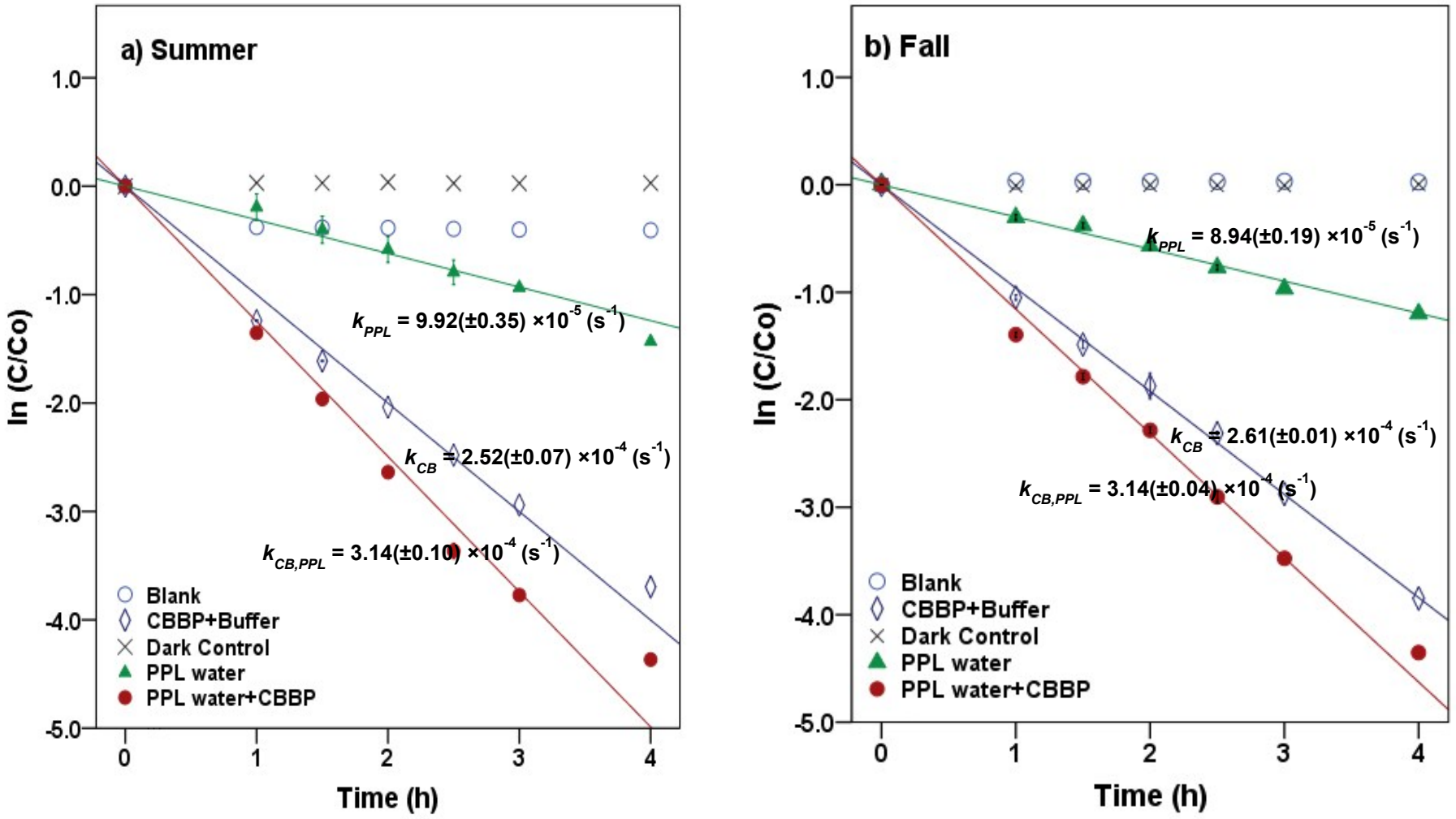
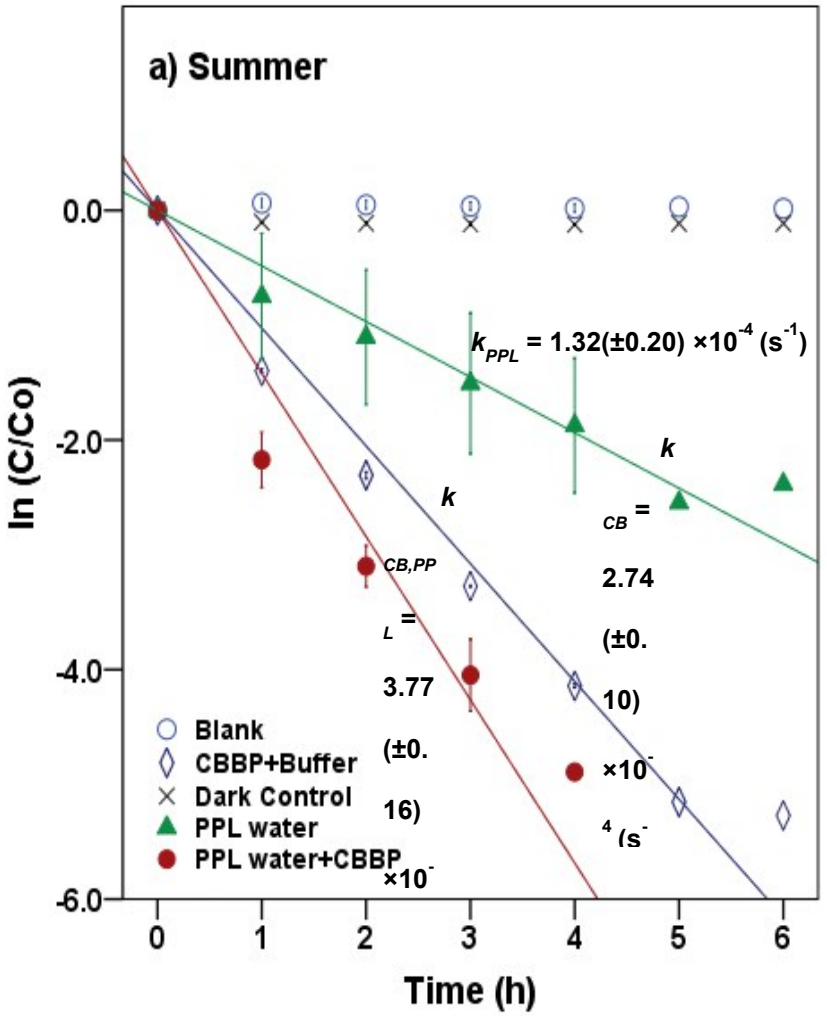


Fig S6 Phototransformation Kinetics of Isoproturon in P7 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.



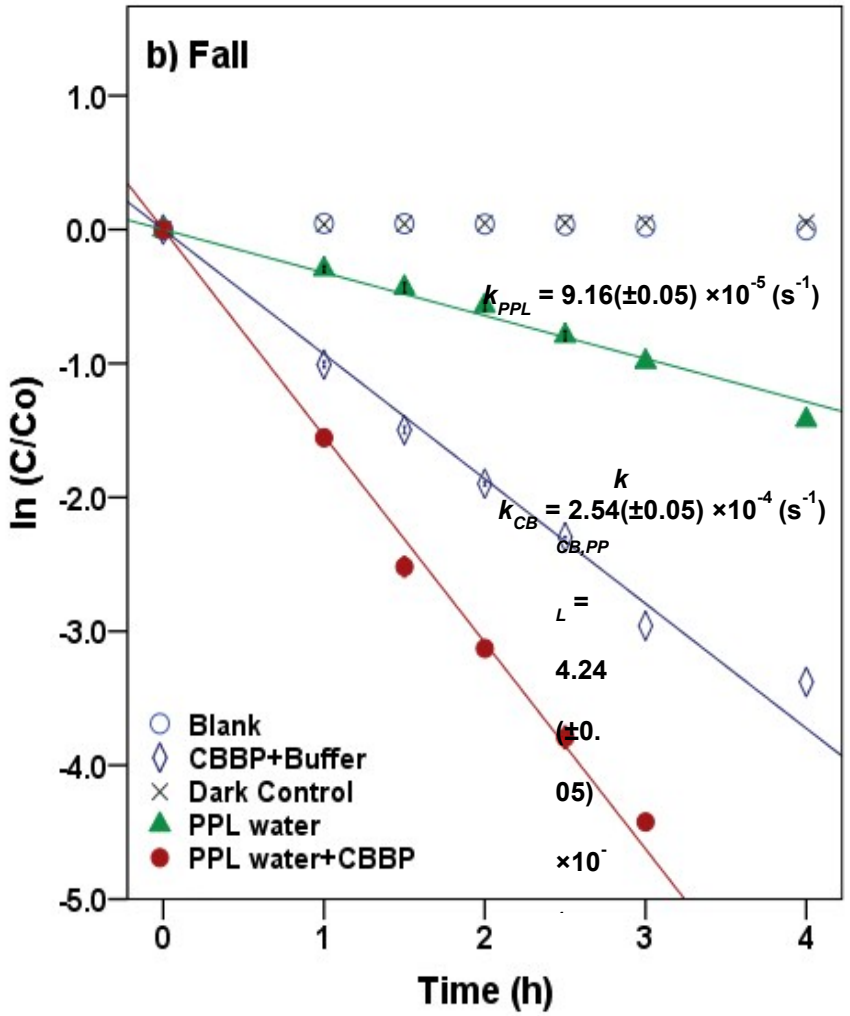


Fig S7 Phototransformation Kinetics of Isoproturon in P1 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

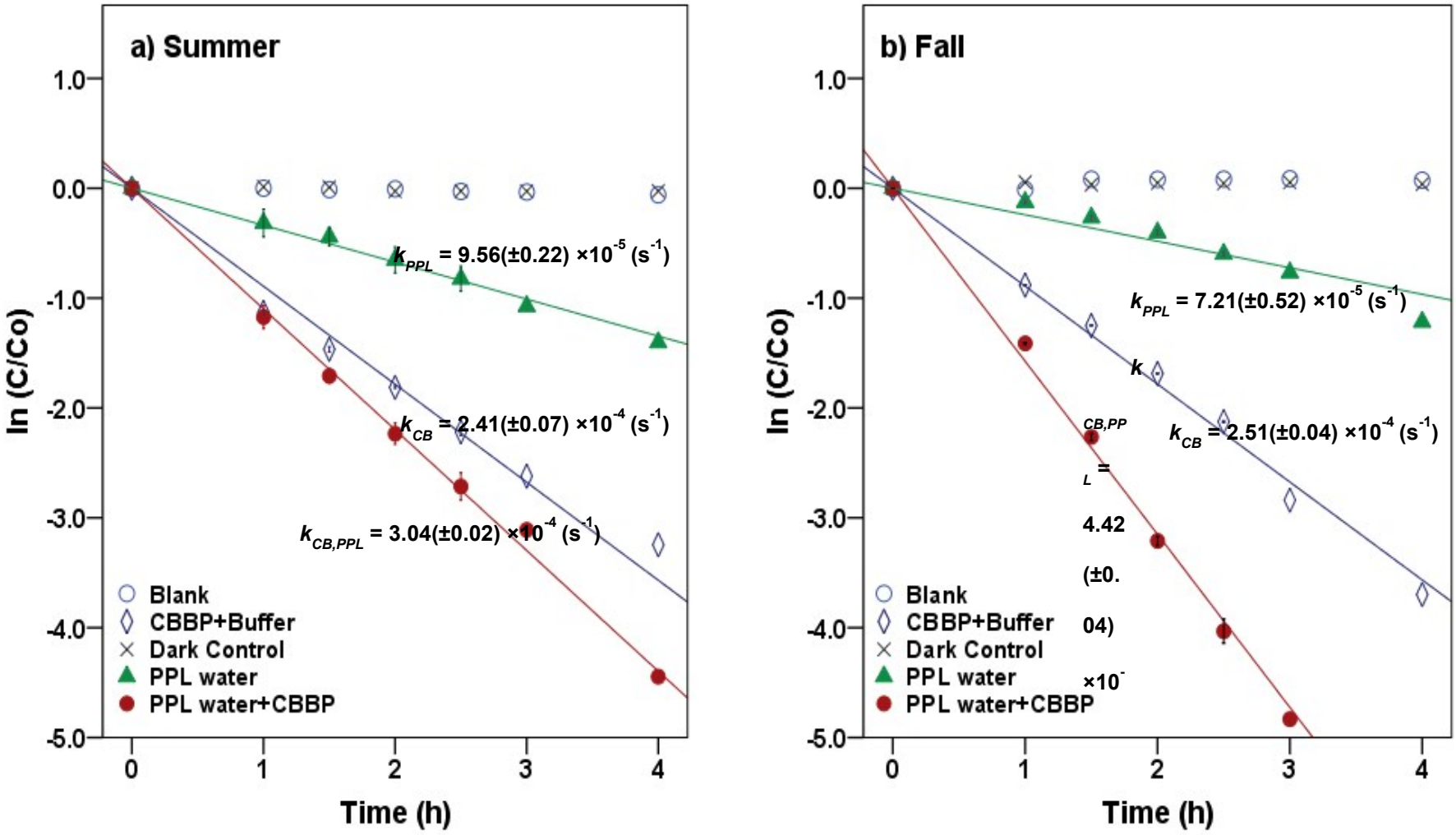


Fig S8 Phototransformation Kinetics of Isoproturon in P8 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

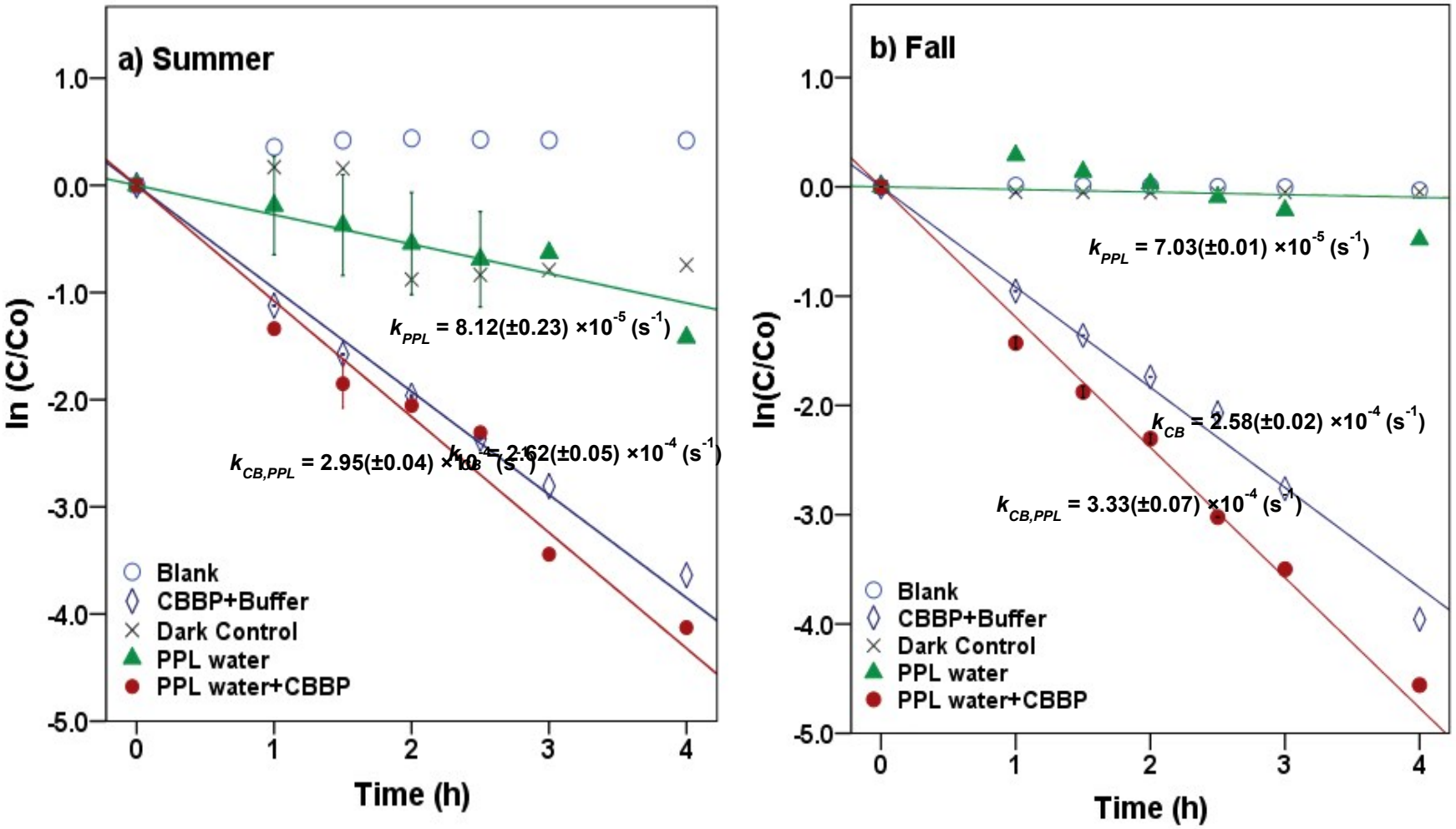


Fig S9 Phototransformation Kinetics of Mesotrione in T9 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

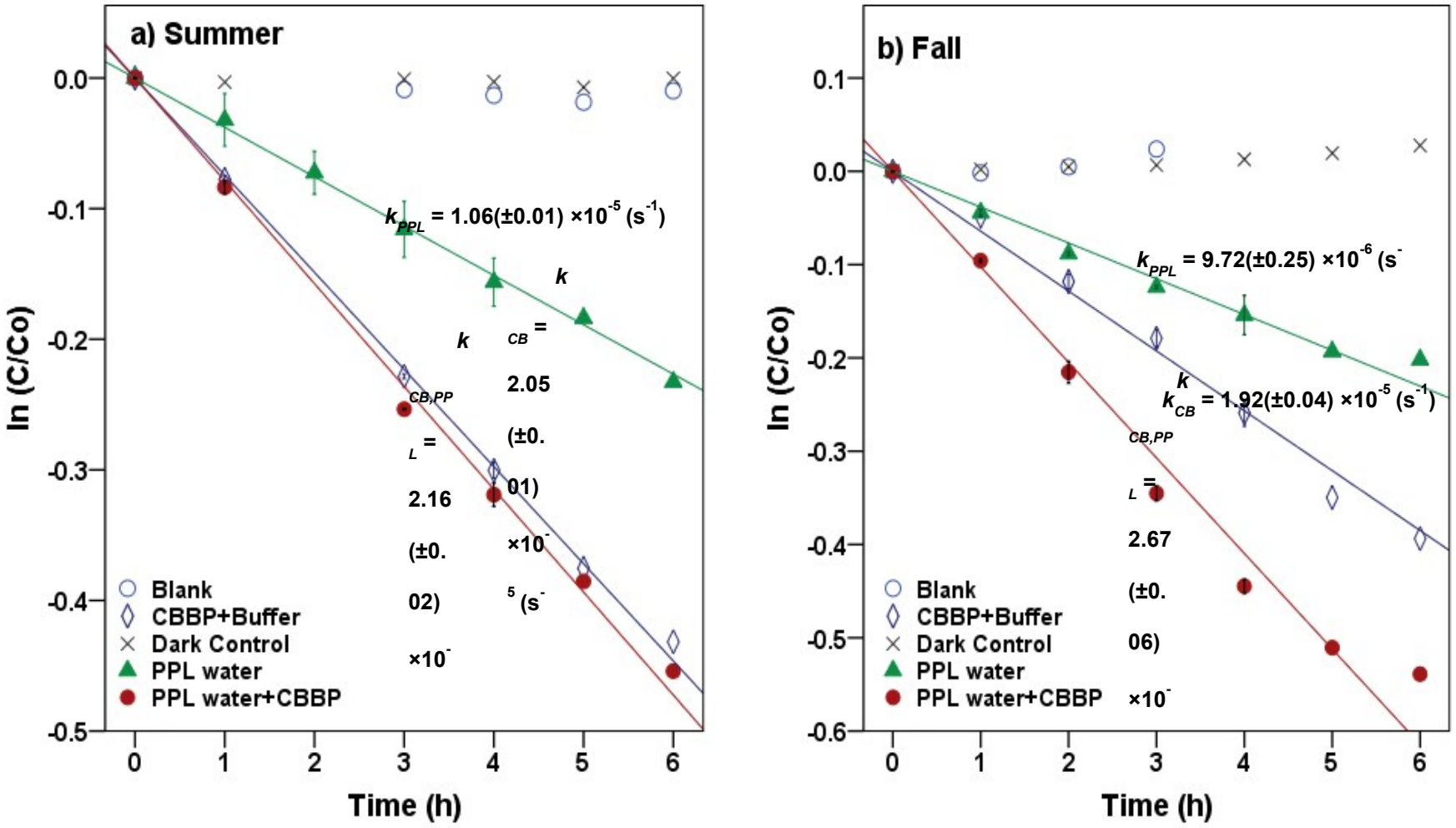


Fig S10 Phototransformation Kinetics of Mesotrione in P7 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

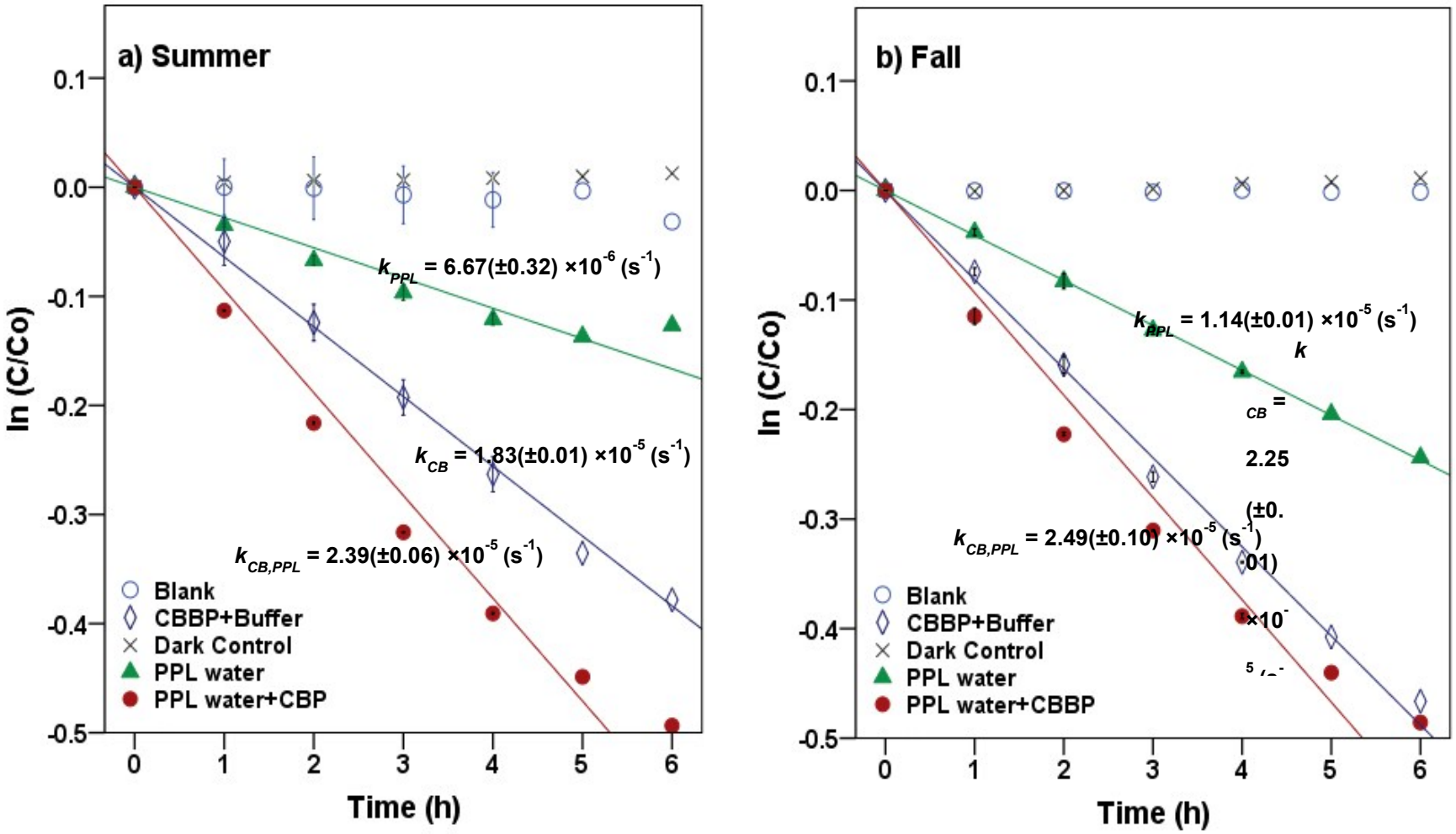


Fig S11 Phototransformation Kinetics of Mesotrione in P1 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

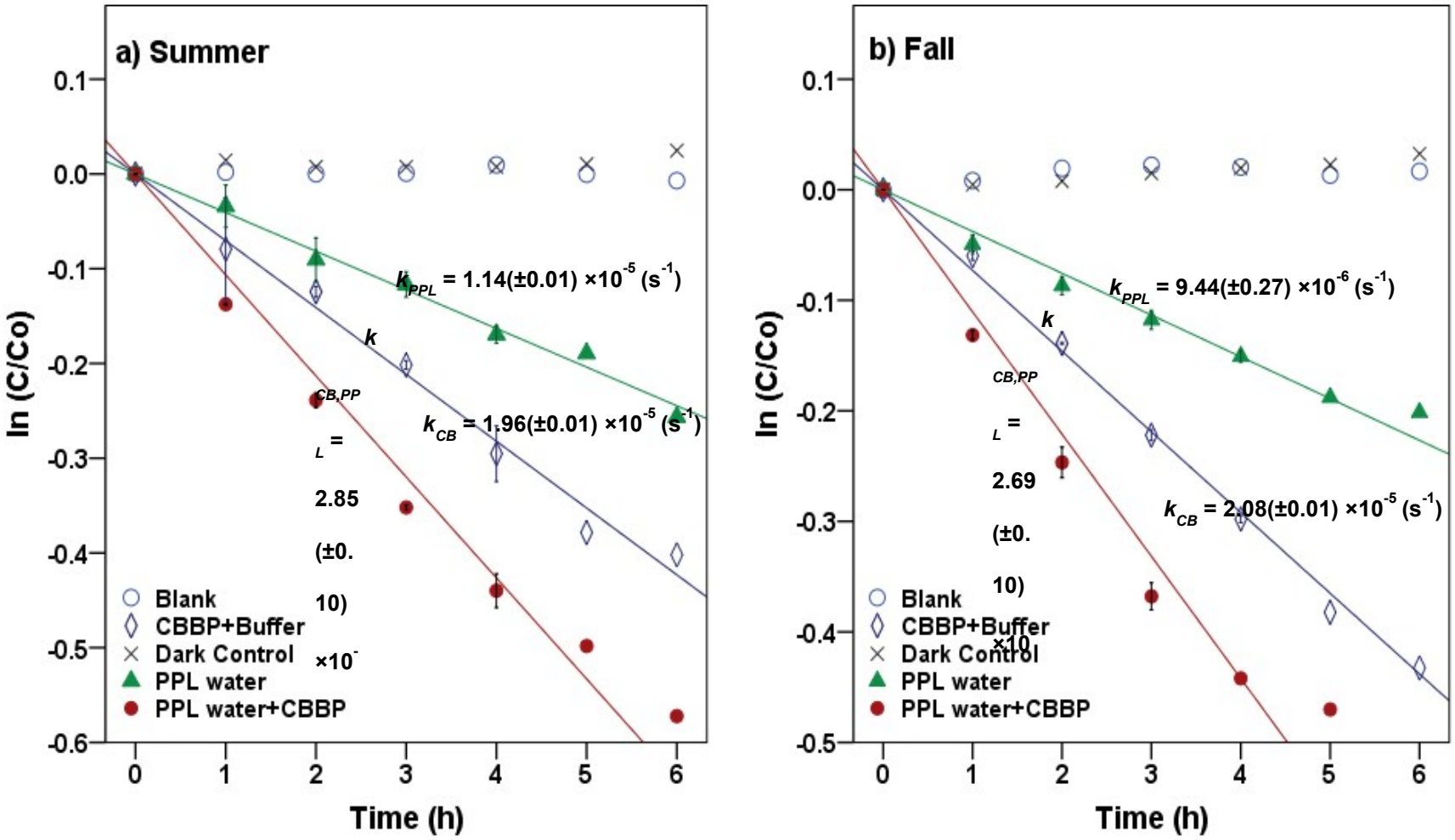


Fig S12 Phototransformation Kinetics of Mesotrione in P8 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

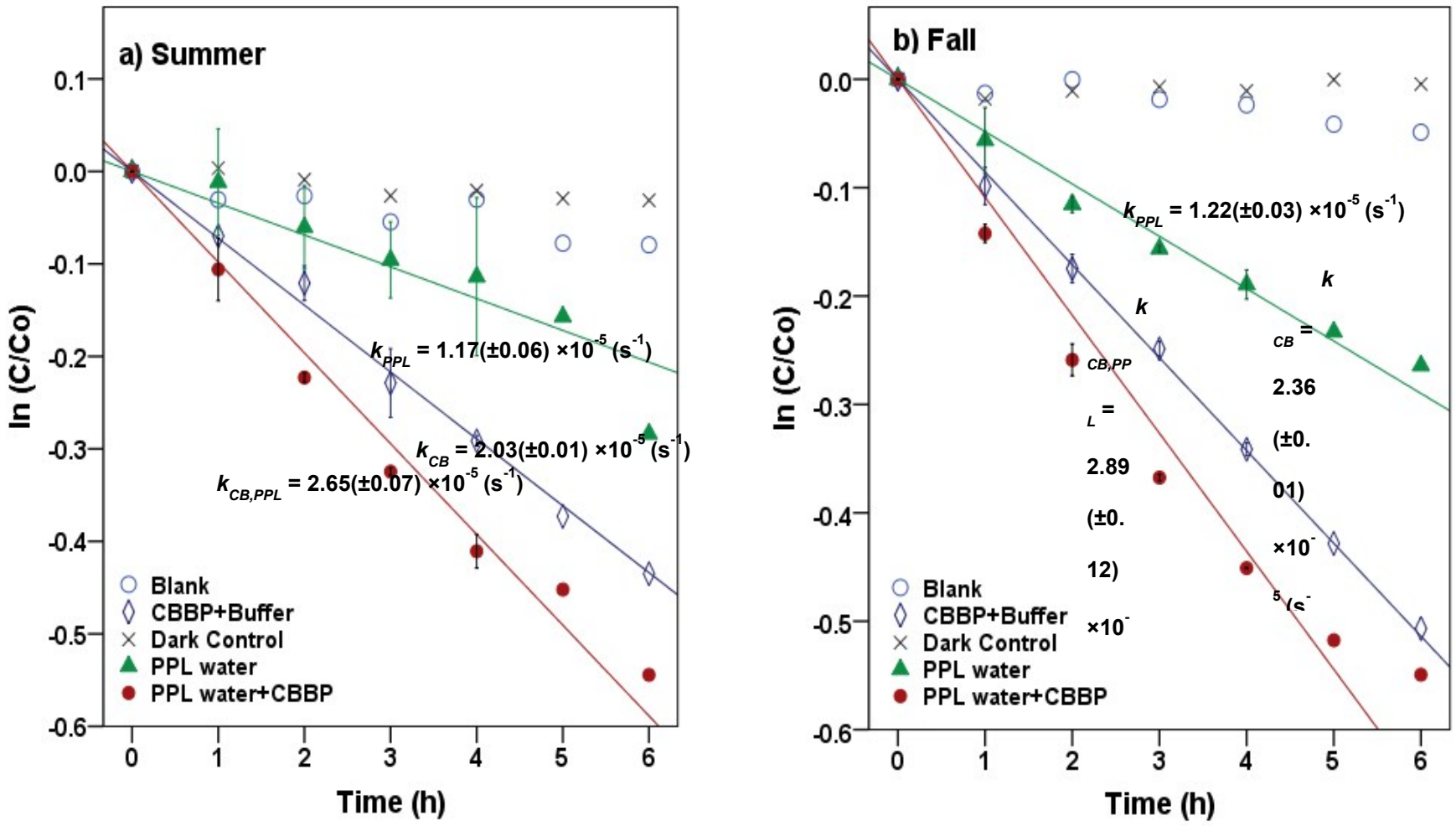


Fig S13 Phototransformation Kinetics of Metolachlor in T9 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

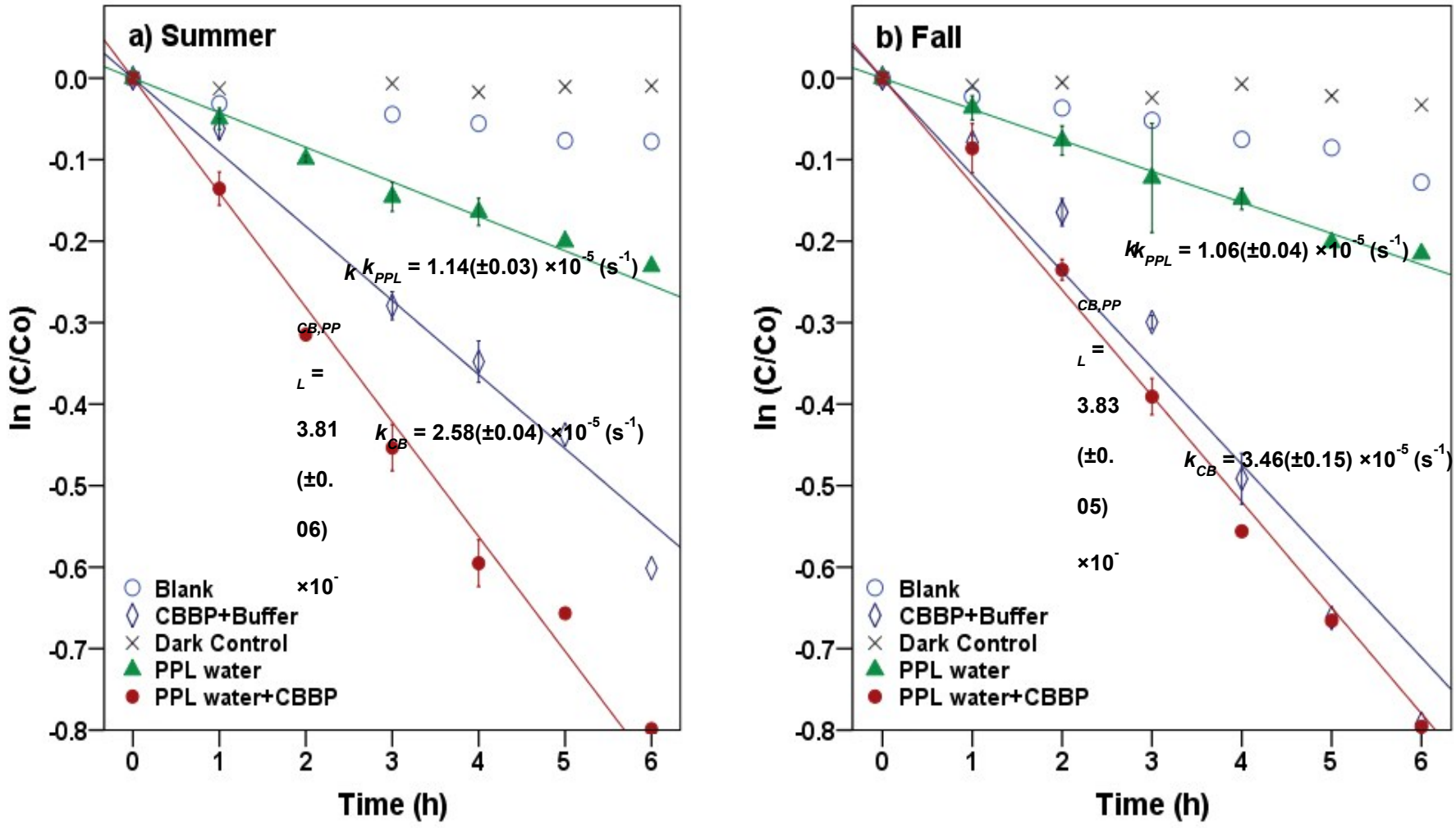


Fig S14 Phototransformation Kinetics of Metolachlor in P7 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

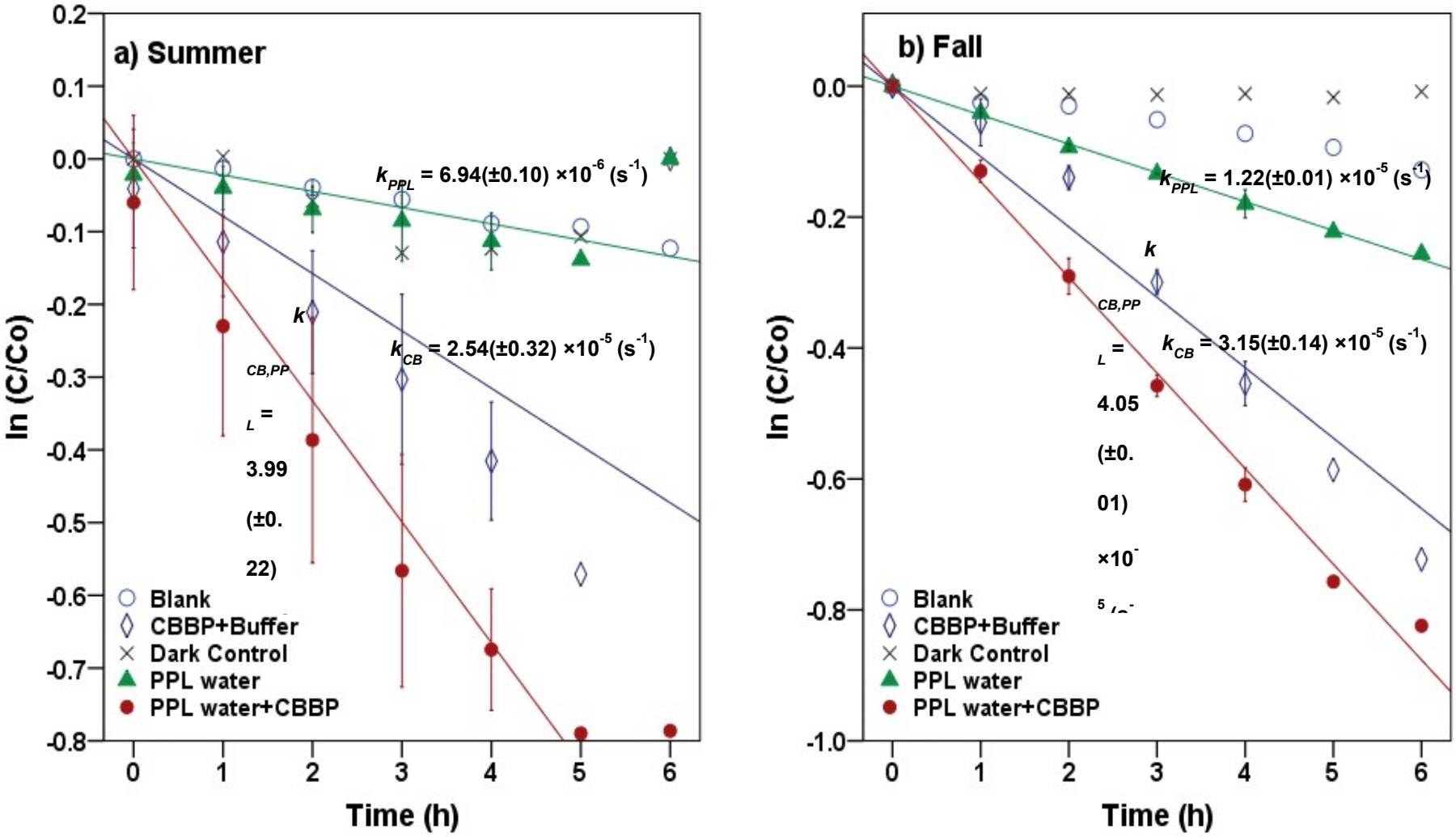


Fig S15 Phototransformation Kinetics of Metolachlor in P1 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

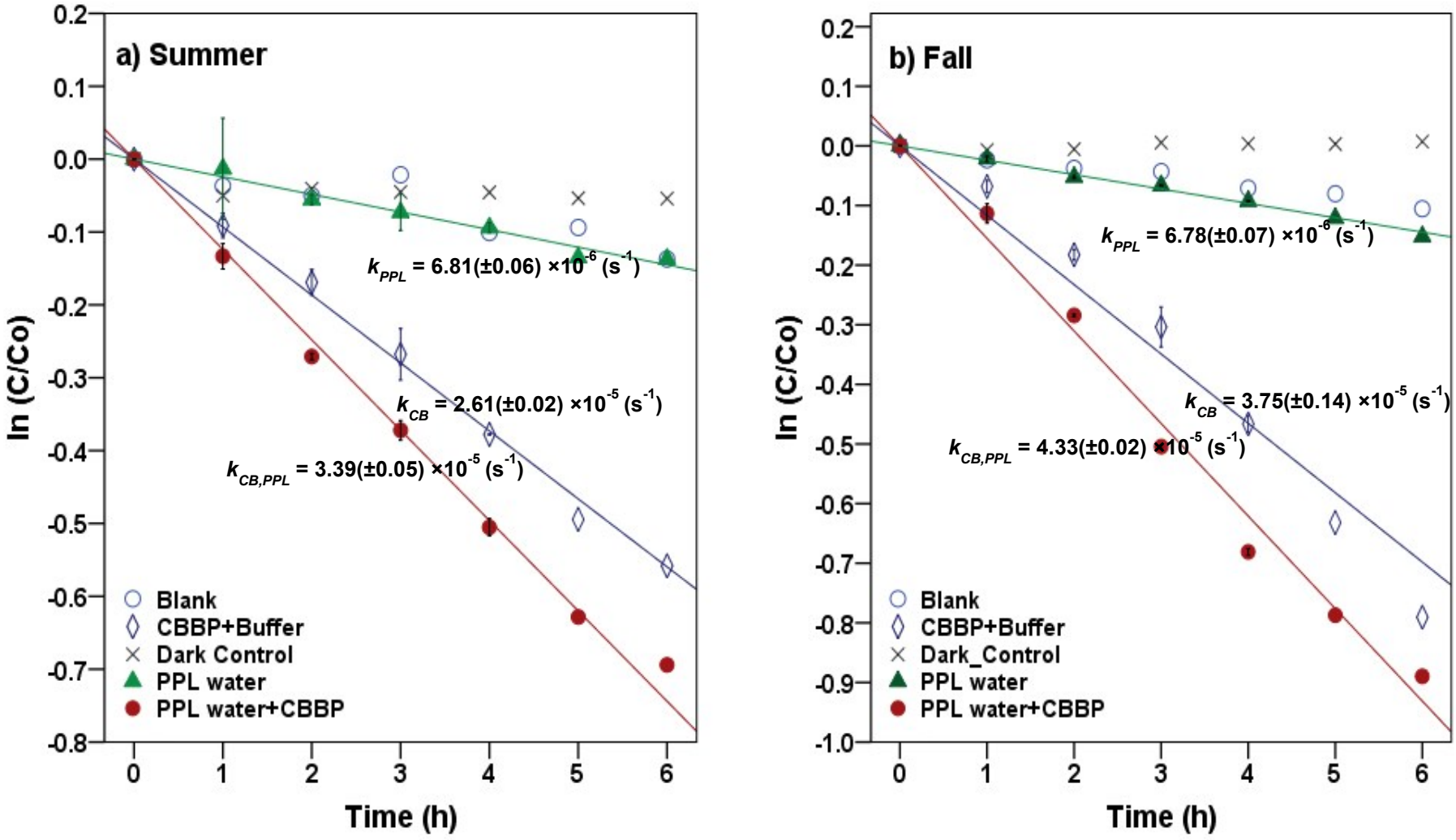


Fig S16 Phototransformation Kinetics of Metolachlor in P8 Water: a) In Summer, b) In Fall. Error bars represent 95% confidence intervals.

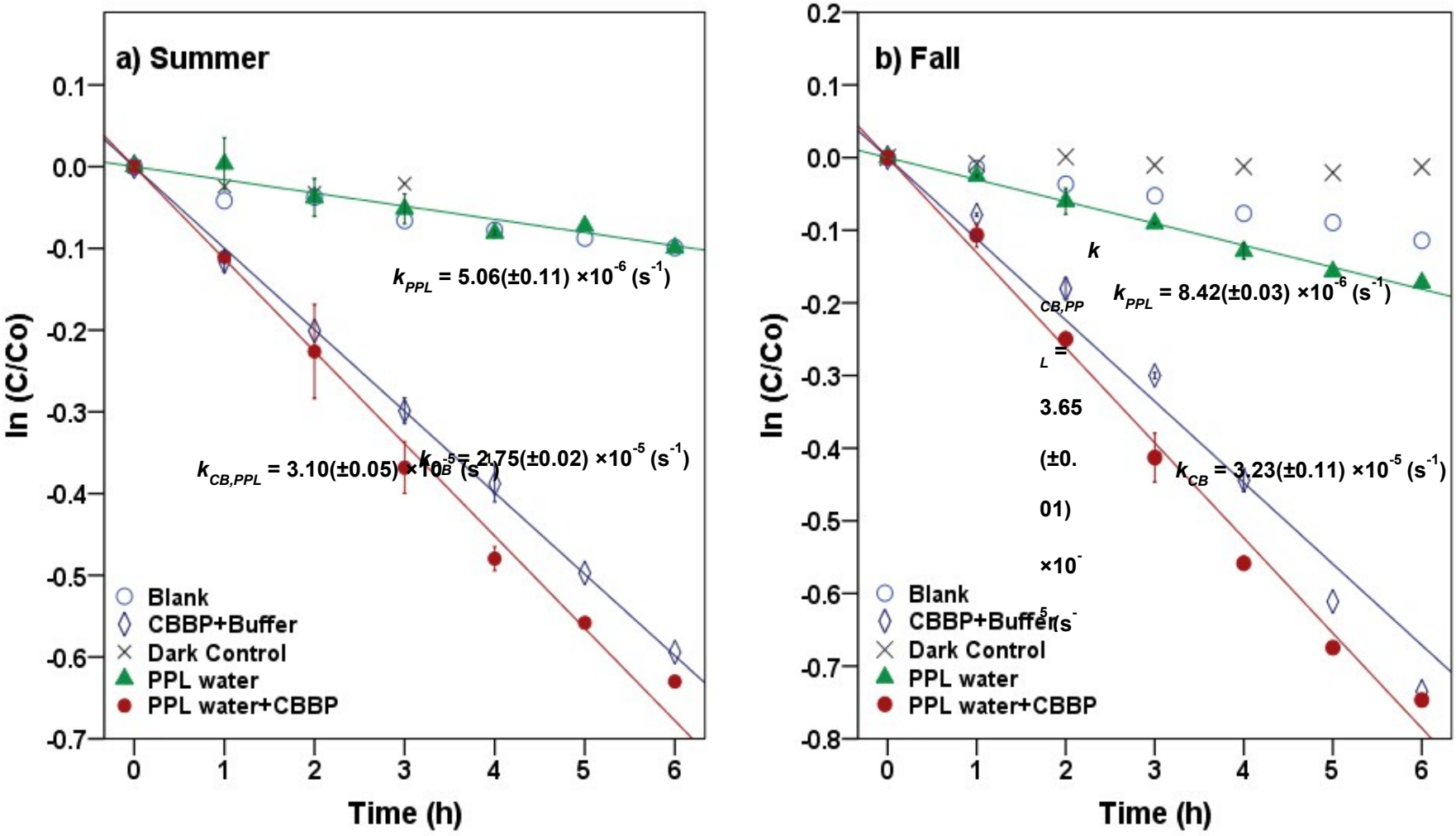
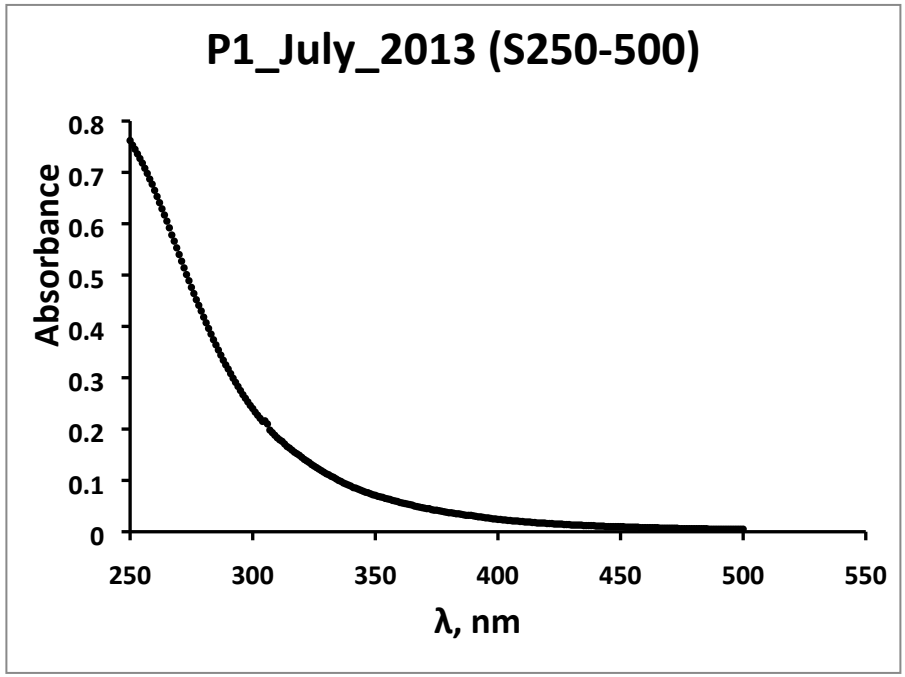


Fig S17 Absorption Spectra for P1 water.



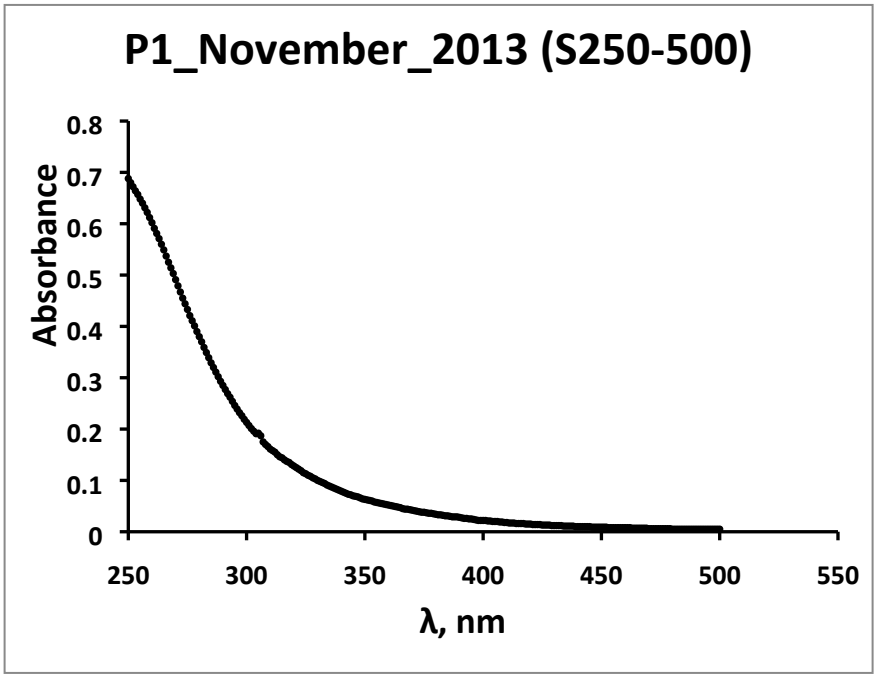
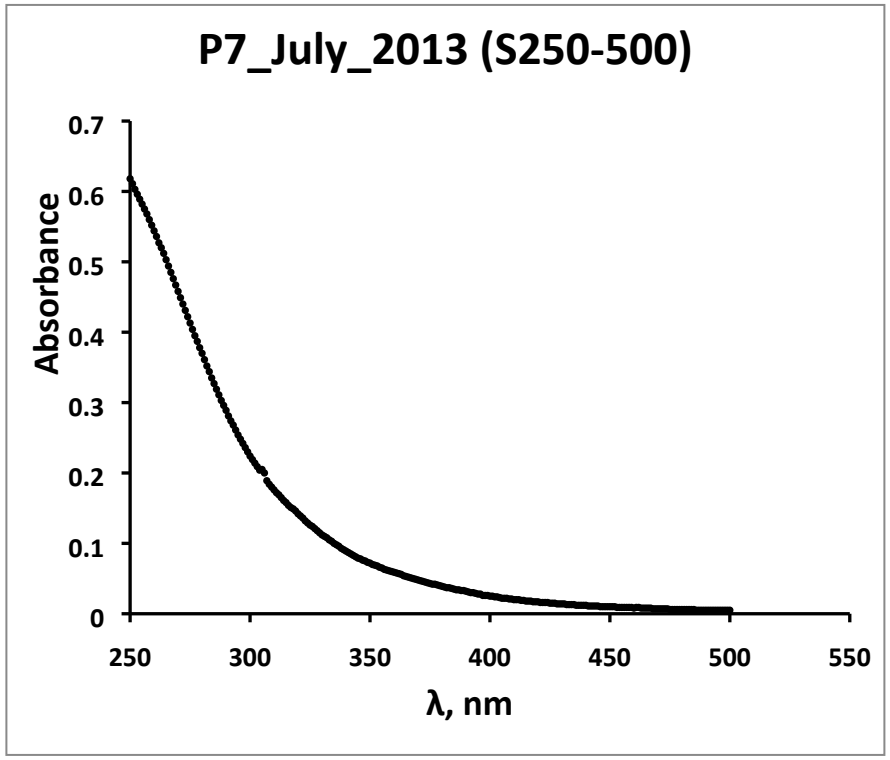


Fig S18 Absorption Spectra for P7 water.



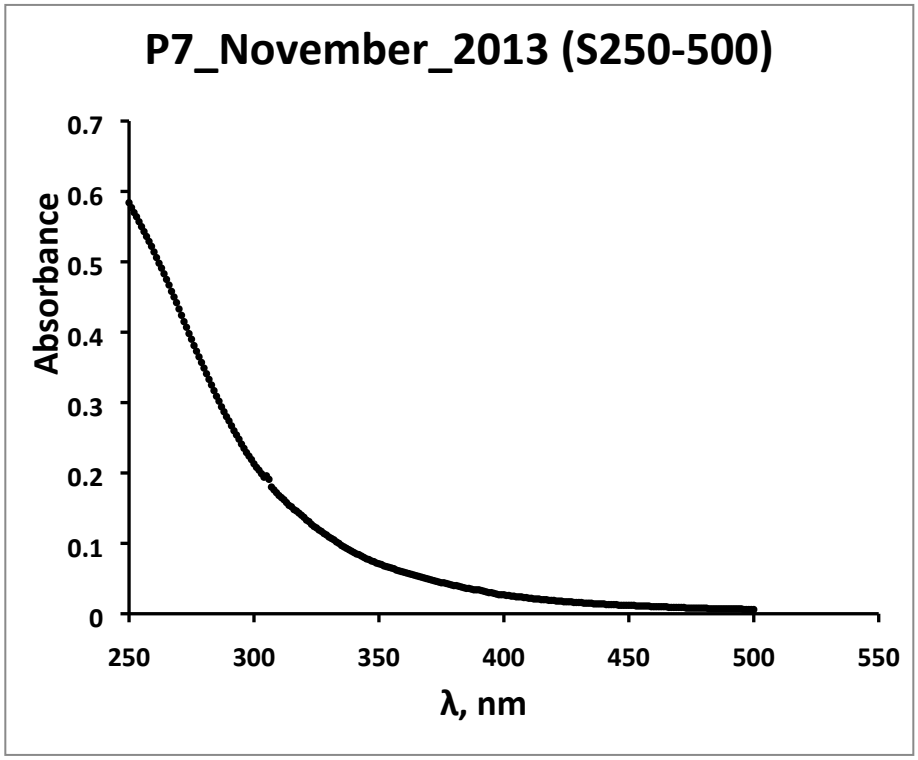
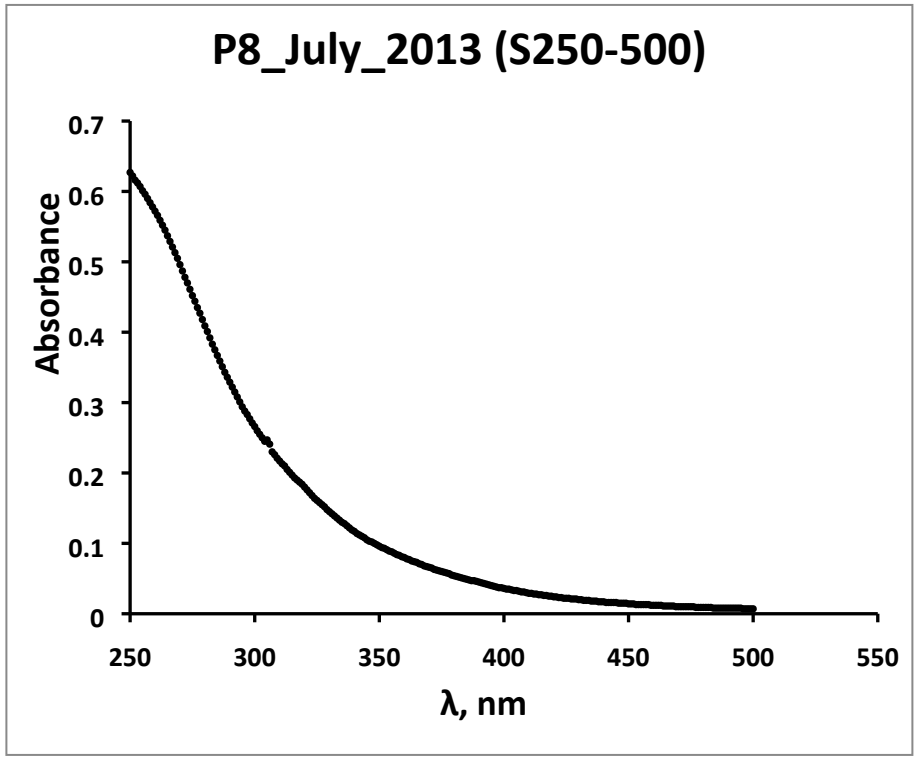


Fig S19 Absorption Spectra for P8 water.



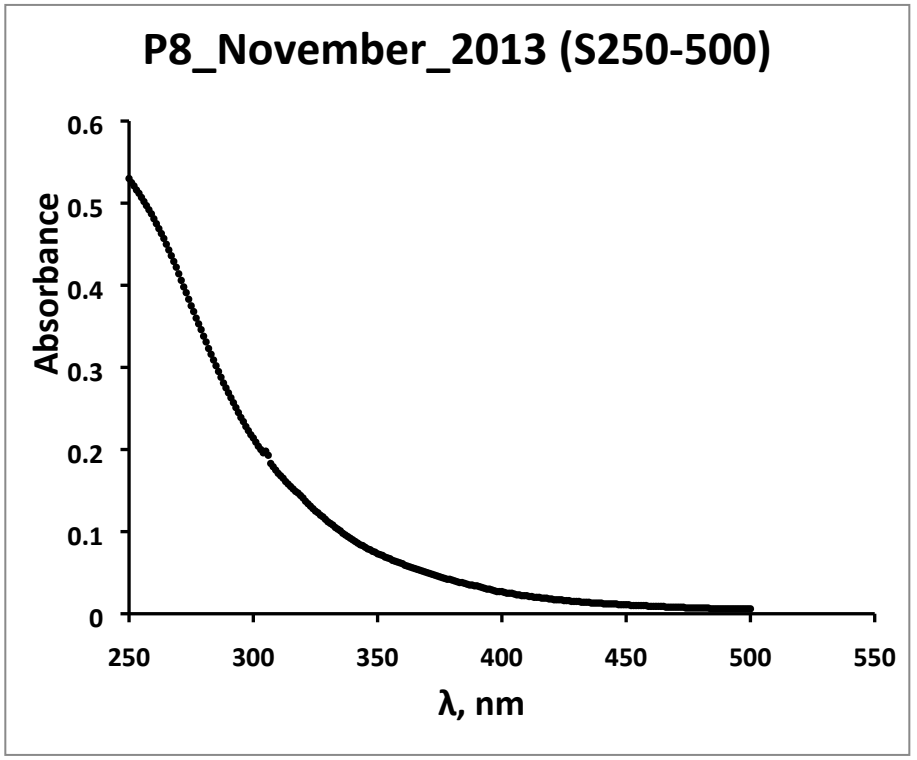


Fig S20 Absorption Spectra for T9 water.

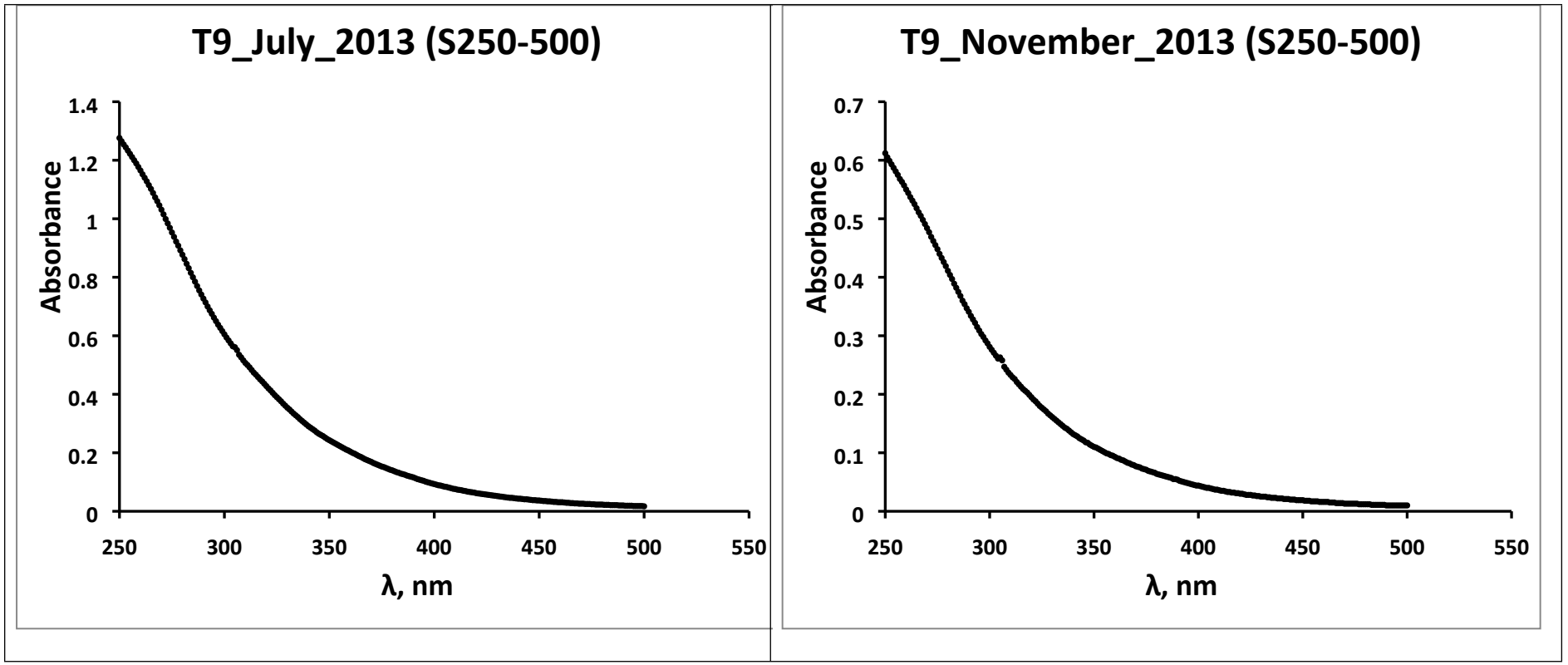


Fig S21 Molar absorptivities of the target pesticides and benzophenone-4-carboxylate (CBBP).

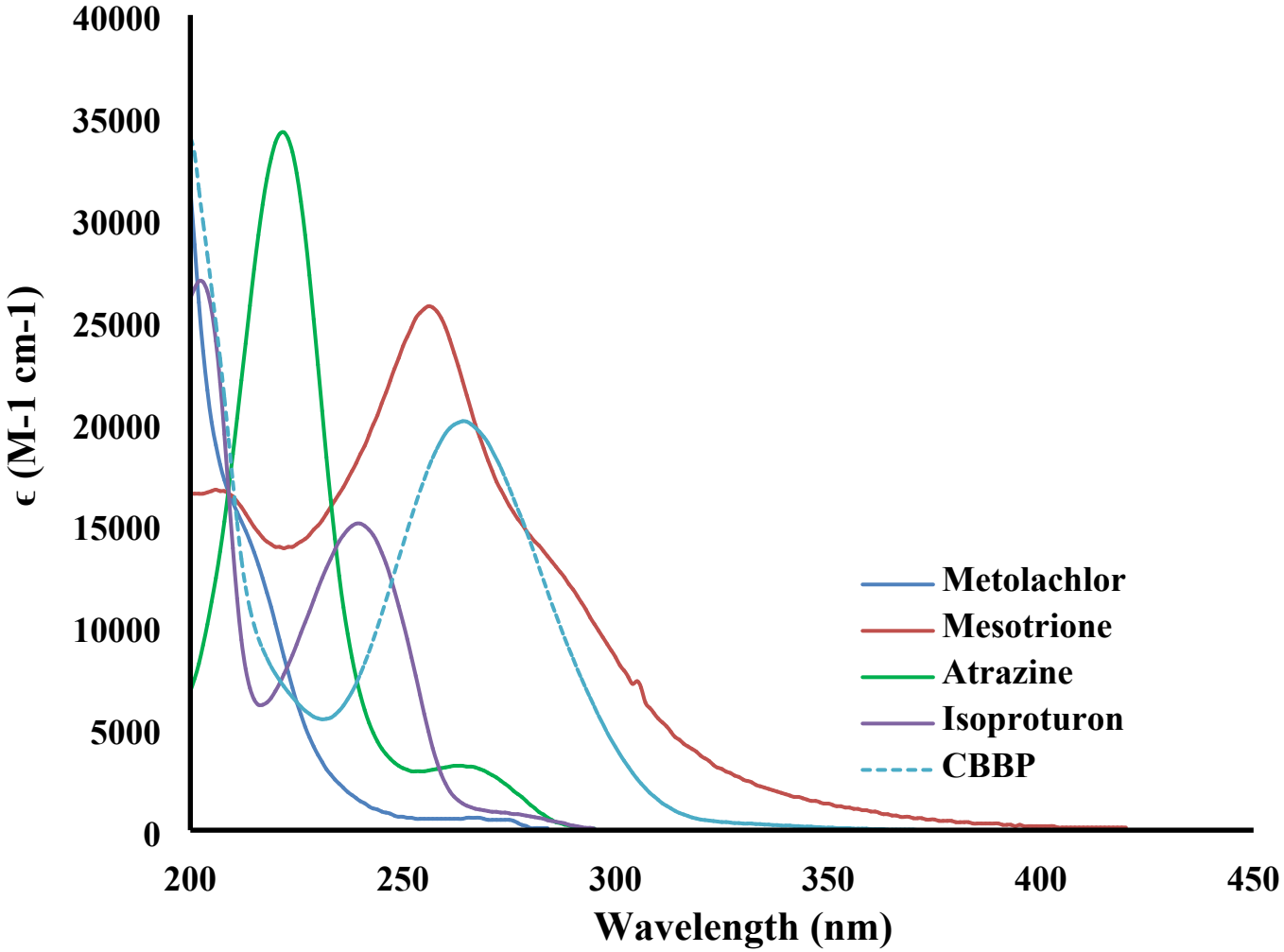


Fig S22 Lamp Spectra.