Transformation of Chlorpyrifos and Chlorpyrifos-Methyl in Prairie Pothole Pore Waters

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Electronic Supporting Information

HPLC Analysis

Samples were analyzed using a Waters high performance liquid chromatograph (HPLC) equipped with a Waters 2487 dual λ absorbance detector. The following conditions were used: Allure C18 column (pore size 60 Å; diameter 5 μm, 3.2mm x 150 mm), 65% methanol and 35% 1 mM phosphoric acid buffer for 10 minutes, flow rate 0.7 mL/min, injection volume 10 μL (24). A wavelength of 289 nm was used to analyze CPM and its product Trichloro-2-pyridinol (TCP).

Filter-Sterilization of Pore Water Samples

To assess the role of microbially mediated CPM transformation a subset of pore water samples were filter-sterilized (pore size 0.2 μM) prior to reaction. Filter-sterilization slightly increased pH and decreased $[H_2S]_T$ in pore water samples, possibly due to the removal of mineralized sulfur species. Other reactive species that could be altered through filter-sterilization include dissolved organic matter and thiols produced by the addition of H_2S to DOM (54). The DOC content of native relative to filter-sterilized samples ranged from 0.97 to 1.08, suggesting the DOC content did not significantly change due to filter-sterilization.

Bulk Product Analysis

A subset of pore water samples were spiked to an initial concentration of 20 μM CPM for bulk product analysis (Figure S.3). Reacted pore waters were processed as described above and extracted with a 3:1 sample to solvent ratio after approximately 2-3 half-lives. Extracts were analyzed by high performance liquid chromatography (HPLC) as described below.

Figure Captions:

Figure S.1. Depth profiles of $[H_2S]_T$, dissolved organic carbon, and conductivity. Measurements from lakes P7 and P8 sampled May 2014. Note depth profiles were conducted in squeezed pore water samples. No hydrogen sulfide was detected in P7

sediment cores. Insufficient volume was extracted from lake P7 for conductivity measurements.

Figure S.2. Apparent rate constants of CPM hydrolysis in P7 pore water. Samples collected (●) May 2014, (▲) November 2014, and (■) filter-sterilized samples. Error bars represent 95% confidence interval. (✕) Hydrolysis in estuarine water (Lacorte, 1995). (+) Hydrolysis in buffered reaction solution (44). (O) Hydrolysis in buffered reaction solution (23). Dashed line represents average k'_{obs} (0.052 day^{1}).

Figure S.3. Chlorpyrifos-methyl product formation. A) Chromatogram of trichloro-2-pyridinol (TCP, ~ 5 μM) and chlorpyrifos-methyl (CPM, ~ 5μM). EA (ethyl acetate) represents solvent front. B) TCP formation due to hydrolysis after approximately 2 half-lives. C) TCP formation in pore water with reduced sulfur species ($[H_2S]_T$ ~ 3 mM) after approximately 3 half-lives (CPM below detection limit). Hydrolysis and reduced sulfur reactions were extracted at a 3:1 sample to solvent ratio.

Figure S.4. Fraction of CP and CPM bound to dissolved organic matter in PPR pore water.

Table S1. CPM rate constants in native and filter-sterilized pore waters

Wetland	Native			Filter-sterilized			$k'_{obs,native}/k'_{obs,filtered}$
	pH	$[H_2S]_T$ (mM)	k'_{obs} (day^{-1})[a]	pH	$[H_2S]_T$ (mM)	k'_{obs} (day^{-1})[a]	
P7	7.66	0.57	0.067 ± 0.008	7.83	0.53	0.065 ± 0.007	1.03
P8	7.63	1.97	0.187 ± 0.012	7.71	1.64	0.203 ± 0.022	0.92
P8	7.84	1.97	0.156 ± 0.017	7.85	1.79	0.137 ± 0.016	1.14

[a]Uncertainties reflect 95% confidence interval.

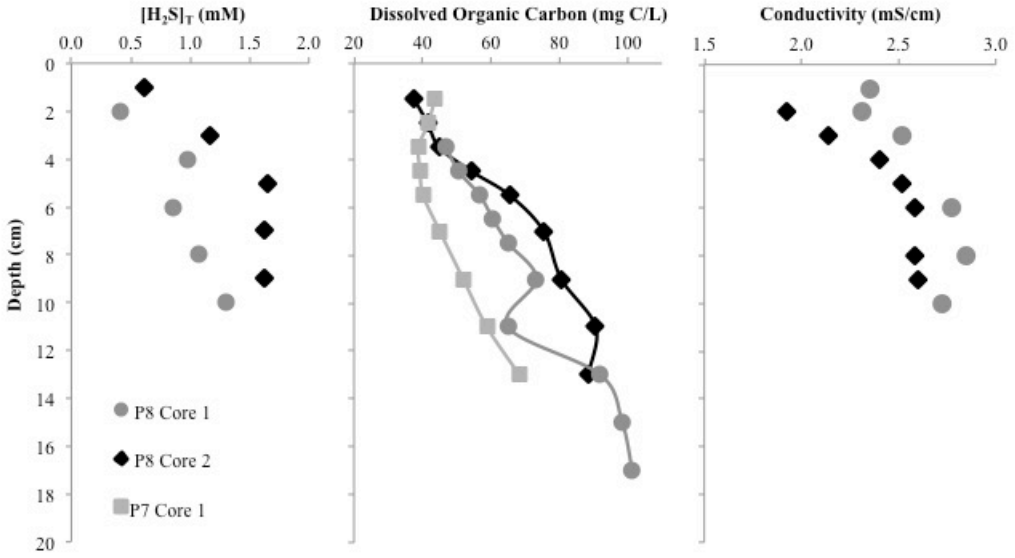

Figure S.1.

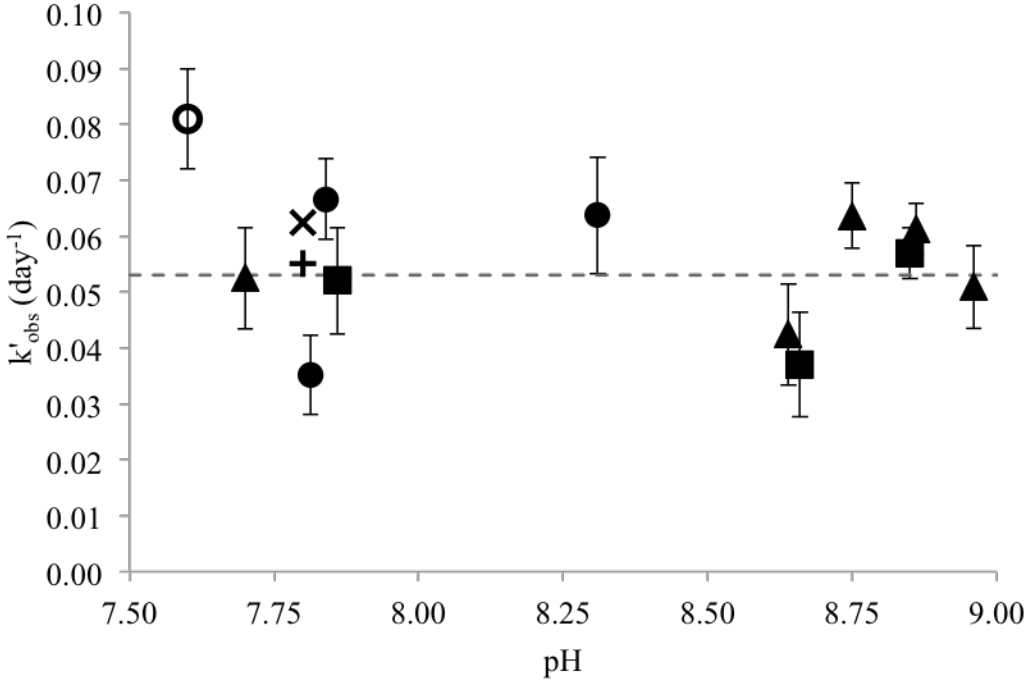

Figure S.2

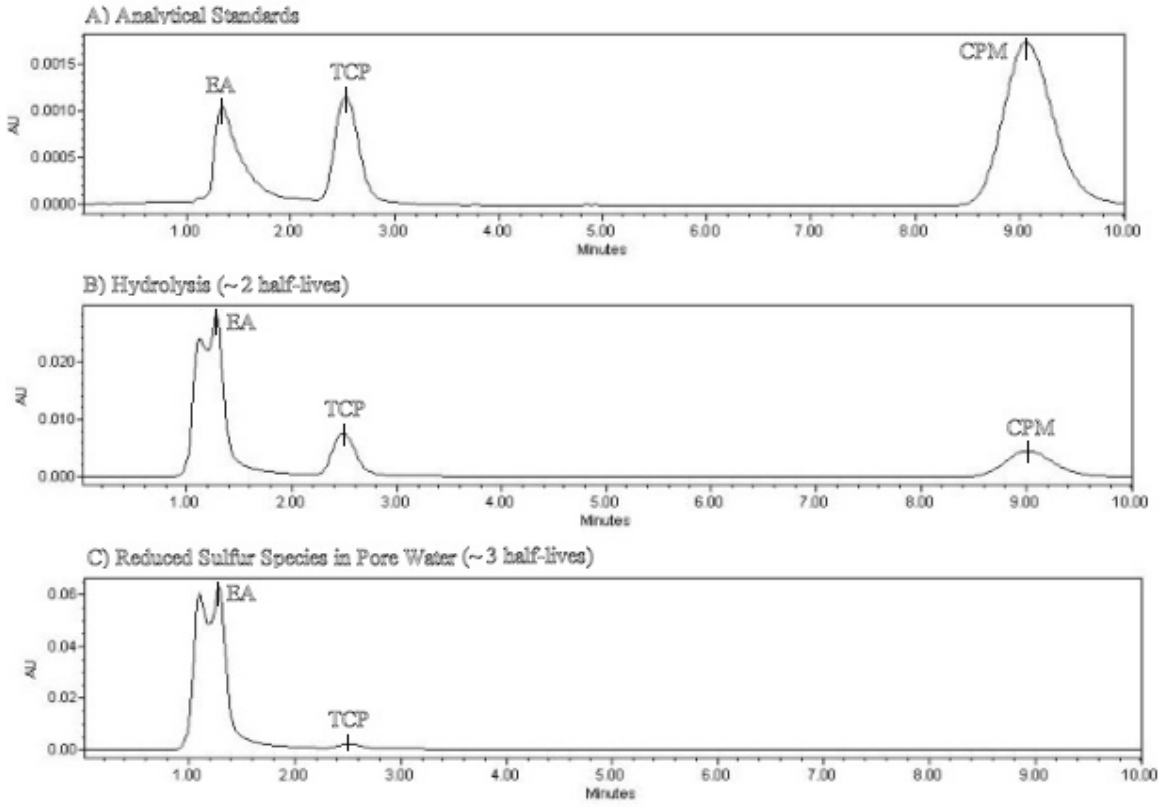
A) Analytical Standards
EA
TCP
CPM
AU
Minutes
B) Hydrolysis (~2 half-lives)
EA
TCP
CPM
AU
Minutes
C) Reduced Sulfur Species in Pore Water (~3 half-lives)
EA
TCP
AU
Minutes

Figure S.3