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Using slow-release permanganate candles to remediate PAH-contaminated water

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Highlights:

- We quantified the efficacy of slow-release permanganate-paraffin candles to degrade and mineralize PAHs.
- ¹⁴C-labeled PAHs were used to quantify both adsorption and transformation.
- Permanganate-treated PAHs were more biodegradable in soil microcosms.
- A flow-through candle system was used to quantify PAH removal in urban runoff.

Abstract

Surface waters impacted by urban runoff in metropolitan areas are becoming increasingly contaminated with polycyclic aromatic hydrocarbons (PAHs). Slow-release oxidant candles (paraffin-KMnO₄) are a relatively new technology being used to treat contaminated groundwater and could potentially be used to treat urban runoff. Given that these candles only release permanganate when submerged, the ephemeral nature of runoff events would influence when the permanganate is released for treating PAHs. Our objective was to determine if slow-release permanganate candles could be used to degrade and mineralize PAHs. Batch experiments quantified PAH degradation rates in the presence of the oxidant candles. Results showed most of the 16 PAHs tested were degraded within 2–4 h. Using ¹⁴C-labeled phenanthrene and benzo(a)pyrene, we demonstrated that the wax matrix of the candle initially adsorbs the PAH, but then releases the PAH back into solution as transformed, more water soluble products. While permanganate was unable to mineralize the PAHs (i.e., convert to CO₂), we found that the permanganate-treated PAHs were much more biodegradable in soil microcosms. To test the concept of using candles to treat PAHs in multiple runoff events, we used a flow-through system where urban runoff water was pumped over a miniature candle in repetitive wet-dry, 24-h cycles. Results showed that the candle was robust in removing PAHs by repeatedly releasing permanganate and degrading the PAHs. These results provide proof-of-concept that permanganate candles could potentially provide a low-cost, low-maintenance approach to remediating PAH-contaminated water.

Keywords: permanganate, slow-release oxidants, polycyclic aromatic hydrocarbons

1. Introduction

The water quality of lakes and streams associated with metropolitan centers is on the decline and reversing that trend presents a significant challenge. One class of chemicals negatively impacting surface waters is polycyclic aromatic hydrocarbons (PAHs). Sources of PAHs are both natural and anthropogenic. PAHs are constituents of petroleum-based products, like oil, gasoline, automobile tires, and asphalt. These products are more frequently concentrated in urban areas. Likewise, emissions from automobiles and power plants, which increase with urbanization, also contribute to the PAH load to

the environment. For these reasons, the PAH concentrations of many urban lakes and streams have been increasing, especially in areas with rapid population growth [1–3].

Because PAHs are hydrophobic, they tend to adsorb and accumulate with dust, debris, and sediment. PAHs emitted to the atmosphere will also sorb to particulates where most of these PAHs will either photodegrade or be deposited back to land. When rain and snow fall on impervious surfaces (e.g., roads, pavements, parking lots, sidewalks), these waters ultimately dissolve, accumulate, and transport PAHs to sewers and streams [4]. Consequently, a primary route of water contamination is through urban runoff. Although various storm

water filtration systems have been developed, reducing PAHs from urban runoff to safe water quality concentrations is still challenging.

Because of the carcinogenic and mutagenic potential of PAHs [5,6], the United States Environmental Protection Agency has listed PAHs as Priority Chemicals [7]. As such, remediating PAH-contaminated water is necessary to prevent exposure. Past wastewater, drinking water and ground water treatment schemes have shown that remediation can be accomplished in several ways [8–12]. Chemical oxidative processes are capable of degrading persistent and sorbed compounds and include treatments such as Fenton's reagent [13,14], modified Fenton's reagent [15], ozone [16,17], persulfate [15,18], or permanganate [15,19–21]. Permanganate is a favored oxidative treatment because it has a high standard oxidation potential (1.7 V) [22], is effective across a wide pH range, and is efficient in attacking the carbon-carbon double bonds of the PAH structure [23]. Ferrarese et al. [15] compared several oxidation methods to treat PAH contaminated soil and found that modified Fenton's reagent, hydrogen peroxide and potassium permanganate were very effective in degrading PAHs.

Slow-release chemical oxidants are a relatively new technology proposed for sub-surface remediation [24–28] but examples of field-scale applications are limited. Christenson et al. [28] was one of the first to field test the use of slow-release permanganate candles (paraffin-KMnO₄ mixtures). These slow-release permanganate candles (91.4 cm length, 5.1 or 7.6 cm diameter) were inserted into a contaminated aquifer by placing the candles in carriers and dropping them down designated wells or inserting them directly into the formation with direct push equipment (e.g., GeoProbe). Advantages to formulating slow-release oxidants as "candles" are that they negate the need for specialized equipment (mixing trailer, pumps, hoses, etc.), curtail health and safety issues associated with handling liquid oxidants, and greatly simplify the application process. In theory, these candles could also be placed in urban conduits that handle urban runoff, wastewater discharges, or holding tanks designed to contain runoff water. Because these candles only release permanganate when submerged, the ephemeral nature of runoff events would dictate when the permanganate is released from the candle and potentially offer a low-maintenance treatment.

Given that the majority of PAH contamination of many surface waters originate from urban runoff, our objective was to determine if the slow-release permanganate candles could be used to degrade PAHs. This was accomplished by quantifying the efficacy of permanganate candles to transform and mineralize PAHs and then testing their effectiveness in removing PAHs from urban runoff in a flow-through system.

2. Materials and methods

2.1. Chemicals and chemical analysis

Chemicals used in experiments were purchased from a variety of vendors and used as received. These chemicals included: potassium permanganate and manganese sulfate (Sigma-Aldrich, St. Louis, MO); HPLC-grade methanol and acetonitrile (EMD Chemicals, Gibbstown, NJ); phenanthrene and benzo(a)pyrene (Sigma-Aldrich, St. Louis, MO); PAH calibration mix (Supelco, Bellefonte, PA); ring-labeled ¹⁴C-phenanthrene (52 mCi mmol⁻¹, Moravek Biochemicals and Radiochemicals, Brea, CA); ¹⁴C-benzo(a)pyrene (25 mCi mmol⁻¹, American Radiolabeled Chemicals, St. Louis, MO); and straight paraffin wax (IGI 1343A, Peak Candle Supply, Denver, CO).

Details of chemical analysis procedures used for quantifying single and multiple PAH as well as ¹⁴C-activity and permanganate are provided in Supplementary material (SM) section.

2.2. Candle preparation

Slow-release permanganate candles were manufactured for laboratory experiments and produced in batches by mixing potassium permanganate and paraffin in a 4.6:1 ratio (23 g KMnO₄ and 5 g paraffin wax). The paraffin wax was melted in an aluminum weighing tin that was placed on top of a Fisher Scientific Isotemp hot plate at 95 °C. Potassium permanganate (grain size <300 μm) was then added to the melted wax to create a slurry, which had a milkshake consistency. The wax mixture was then poured into a plastic mold and tapped gently to eliminate any air pockets. The candles were allowed to cool and then removed from the mold. Candles shaped as cylinders were 0.8 cm in diameter and 2.7 cm in length. Individual permanganate candle weights were ~1.5 g.

When plain paraffin wax candles were needed (i.e., control candles) to quantify PAH adsorption properties, the potassium permanganate was omitted. The plain wax candles were made in the same mold and contained more wax on a mass basis than the permanganate candles but had the same dimensions (volume and surface area) as the permanganate candle. Individual control candle weights were ~0.72 g. A second type of control candle was also used where KCl replaced the KMnO₄ and the procedures used to make the permanganate candles were followed.

2.3. Batch experiments with phenanthrene

Initial batch experiments quantified phenanthrene degradation kinetics in permanganate solutions. Three permanganate concentrations (100, 250, and 500 mg L⁻¹) were used to treat 1 mg L⁻¹ phenanthrene. This initial experiment and all subsequent batch experiments were run in triplicate. Experimental units were 250-mL flasks where each flask received 150 mL of 1 mg L⁻¹ phenanthrene solution. The flasks were placed on a gyrotory shaker to provide continuous mixing and covered with paraffin film to prevent sample loss.

Samples were collected for HPLC analysis at *T* = 0 min, and then at 10, 20, 40, 60, 90, 120 min, and 24 h after spiking permanganate into the flasks. To prevent PAH volatilization during centrifugation and analysis, sample collection protocol maintained a ratio of 50% aqueous sample to 50% organic solvent (methanol for phenanthrene; acetonitrile for PAH syringe experiments). At each sampling, 0.7 mL of sample was placed into a 1.5-mL centrifuge vial and then mixed with 0.7 mL methanol or acetonitrile and 20 μL manganese sulfate solution (0.1 g mL⁻¹) to quench the reaction [30]. For control samples, 20 μL H₂O was used in place of manganese sulfate to maintain the dilution factor across all samples. The samples were centrifuged for 5 min at 14,000 rpm. The clearcolored supernatant was placed in an HPLC vial and sealed for HPLC analysis.

2.4. Effect of washed and unwashed candles on phenanthrene degradation

Previous research has established that the permanganate candles used in our experiments had two phases to their dissolution pattern [28,31]. Specifically, large fluxes of permanganate are initially observed from the candles as the permanganate located on the surface of the candle dissolved. With time, the mass of permanganate released is more linear and diffusion controlled. For this reason, we determined differences in phenanthrene degradation between freshly prepared permanganate candles versus washed (i.e., aged) candles. 150 mL of

phenanthrene (1 mg L^{-1}) was prepared from stock and placed in 250-mL Erlenmeyer flasks. Permanganate candles were prepared by placing three freshly prepared candles into 100 mL of H_2O for 24 h to "wash" the permanganate ions away from the outer surfaces of the candles. Individual candles were then added to the phenanthrene solution and placed on a gyrotory shaker and covered with paraffin film.

Samples were collected at $T = 0$ min for HPLC analysis for each treatment prior to adding the washed and unwashed permanganate candles to the phenanthrene solution. A sampling sequence and procedure matching the previous batch experiment was followed. To quantify permanganate concentration, 0.1 mL samples were collected and placed in a vial with 9.9 mL H_2O and analyzed with a UV spectrophotometer at 525 nm.

2.5. PAH adsorption to permanganate candles

Because phenanthrene and PAHs in general are hydrophobic and nonpolar, we determined the extent phenanthrene adsorbed to the wax matrix. ^{14}C -labeled phenanthrene was used in this batch experiment to differentiate between adsorption and degradation or mineralization. ^{14}C -labeled phenanthrene was spiked into $500 \mu\text{g L}^{-1}$ unlabeled phenanthrene; ^{14}C -activity of the test solution was $\sim 1000 \text{ dpms mL}^{-1}$. Treatments included a control (no candles), a plain wax candle, and a permanganate candle. Initial samples were collected for HPLC, liquid scintillation counting, and spectrophotometer analysis at $T = 0$ min. The plain wax and washed permanganate candles were then added to the flasks. Samples were then collected at 30, 60, 120 min, 4, 6, 24, and 48 h. Sample volume removed for HPLC analysis was 0.65 mL, which was added to 0.65 mL acetonitrile and 20 μL manganese sulfate solution (0.1 g mL^{-1}). Samples were centrifuged at 14,000 rpm for 5 min until a clear supernatant formed and transferred to HPLC vials for analysis. To quantify ^{14}C -activity in solution, 1 mL samples were collected and analyzed by liquid scintillation counting (LSC). Permanganate concentrations were collected at each sampling time and analyzed in the same manner as previously described.

2.6. Syringe experiments with mixed PAH solution

Permanganate candles were used to treat a mixture of 16 PAHs. The commercially purchased PAHs mixture included: acenaphthene, acenaphthylene, anthracene, benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(g,h,i)perylene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, fluoranthene, fluorene, indeno(1,2,3-cd)pyrene, naphthalene, phenanthrene, and pyrene. The ability of the permanganate candles to degrade the PAHs was tested in 100-mL gas-tight syringes equipped with septum valves (SGE, Austin, TX) in a manner similar to that described by Huang et al. [32]. In these experiments, each 100-mL glass syringe received 100 mL of the $50 \mu\text{g L}^{-1}$ PAH solution and a small magnetic stir bar. The PAH solution was prepared from the commercial standard by diluting 0.5 mL of the standard ($10,000 \mu\text{g L}^{-1}$ in CH_3CN) to 100 mL (H_2O) in a volumetric flask. Samples were collected for HPLC and spectrophotometer analysis at $T = 0$ min. A washed permanganate candle was then added to the syringe, and any trapped air inside the syringe was pushed out before placing the syringe on a magnetic stirrer (Barnstead, Thermolyne Cimarec 2 Stirrer, S46725, Dubuque, IA).

Samples were then collected by pushing samples out of the larger syringe into a 1-mL glass syringe to prevent the introduction of head-space. Temporal samples were taken at 30, 60, 90, 120, 240 min, 24, and 48 h. PAH concentrations were measured by HPLC. To quantify adsorption to the paraffin wax, the experiment was carried out in the same manner as

the PAH degradation experiment, except that a plain wax candle was used instead of a permanganate candle. Sampling and analysis followed the same time sequence and procedure.

2.7. Microcosm experiment

Once we determined that permanganate was unable to mineralize phenanthrene and benzo(a)pyrene, we quantified differences in biodegradability between the parent structures and degradation products produced from the permanganate treatment. This was accomplished by treating separate 100 mL-batches of ^{14}C -labeled phenanthrene and benzo(a)pyrene ($\sim 2500 \text{ dpms mL}^{-1}$ spiked into 1 mg L^{-1} unlabeled parent compounds) with $2500 \text{ mg L}^{-1} \text{ MnO}_4^-$ for 24 h. After confirming (via HPLC) that the parent compounds were completely transformed, and the ^{14}C -activity was unchanged (via LSC), we quenched the permanganate with 1 mL of manganese sulfate solution (0.1 g mL^{-1}). We divided each batch into 3 replicates and centrifuged the solutions at 5000 rpm for 15 min until a clear supernatant formed. Equal activities (dpms) of permanganate-treated ^{14}C -labeled phenanthrene and benzo(a)pyrene were then added to 150 g of air-dried soil. Additional H_2O was added to the microcosm to bring the soil gravimetric water content (θ_g) to 20.3%. Controls included untreated ^{14}C -labeled phenanthrene and ^{14}C -labeled benzo(a)pyrene.

To quantify mineralization, open vials of 0.5 N NaOH (5 mL) were placed inside the sealed microcosm to trap released $^{14}\text{CO}_2$. Each week, the $^{14}\text{CO}_2$ traps were replaced and sample volumes of 1 mL were removed and analyzed by LSC. Cumulative mineralization was quantified for 42 d.

2.8. Treatment of PAHs in urban runoff by flow-through candle system

To quantify the ability of the permanganate candles to treat PAHs in urban runoff, we collected urban runoff from an automated monitoring station located in Lincoln, NE (USA). Chemical characteristics of the runoff water were performed by standard methods (Table 1). The urban runoff collected consisted primarily of water, with some suspended solids and dissolved organic material (Table 1). To this matrix, we spiked in the 16 PAH mixture (previously listed) at an initial concentration of $\sim 1.5 \mu\text{g L}^{-1}$.

Runoff experiments were conducted in a flow-through candle system that consisted of: (i) a runoff reservoir (250-mL), (ii) piston pump (FMI lab pump, model QSY-2, Syosset, NY), (iii) Viton® tubing (Masterflex, Coleparmer, Vernon Hills, IL), (iv) a 116-mL chromatographic column equipped with a fritted disc (porosity of 70–100 μm) (Ace Glass, Vineland, NJ), and (v) a 250-mL beaker for collecting treated runoff water.

PAH concentrations in the reservoir were initially quantified ($T = 0$ min). Then 200 mL of PAH-spiked urban runoff was pumped at flow rate of 12.5 mL min^{-1} onto a previously washed permanganate candle. The fritted disk prevented the runoff water from immediately passing through the reactor and for the 16 min it took to pump the runoff water into the reactor, ~ 30 -mL of runoff water accumulated above the fritted disk. Once pumping ceased, it took an additional 4 min before the accumulated runoff water drained. Hence, cycling 200 mL of runoff water through the flow-through system took ~ 20 min.

To determine if the candle could treat multiple runoff events, fresh batches of spiked runoff water were prepared (concentrations labeled, 2nd and 3rd run, Table 2) and pumped over the same candle approximately 24 h after the previous runoff event. This wet-dry cycling was repeated a total of three times and the resulting PAH concentrations determined after each runoff event are labeled 1st, 2nd, and 3rd cycle (Table 2).

Table 1. Chemical characteristics of runoff water and analytical methods.

Chemical parameter	Units	Value	Method	Reference
Ammonia (NH ₃)	mg NH ₃ -N L ⁻¹	0.22	EPA 350.1	[37]
Nitrate plus nitrite	mg (NO ₃ ⁻ + NO ₂ ⁻ - N) L ⁻¹	0.84	EPA 353.2	[37]
Total Nitrogen	mg N L ⁻¹	2.74	4500-N _{org}	[38]
Total organic carbon (TOC)	mg C L ⁻¹	7.62	5310	[38]
Conductivity µS	cm ⁻¹	221	2510	[38]
pH	pH units	7.59	4500-H ⁺	[38]
Total suspended solids (TSS)	mg L ⁻¹	22.70	2540D	[38]
Turbidity	NTU	33.58	2130	[38]
Soluble reactivity phosphorous	mg PO ₃ ³⁻ -P L ⁻¹	0.53	Hach10209	[39]
Total phosphorous (TP)	mg PO ₄ ³⁻ -P L ⁻¹	1.26	Hach10210	[39]
Chemical oxygen demand (COD)	mg COD L ⁻¹	35.00	Hach8000	[39]
Chloride (Cl ⁻)	mg Cl ⁻ L ⁻¹	14.50	Hach8113	[39]

Table 2. Temporal changes in PAH concentrations in urban runoff following treatment with flow-through candle system.

PAHs	Initial PAH concentrations in urban runoff water					
	Conc. (µg L ⁻¹)					
	1st cycle		2nd cycle		3rd cycle	
Anthracene	1.45		1.16		1.65	
Pyrene	1.78		1.25		1.70	
Benzo(a)anthracene	1.49		1.31		1.58	
Benzo(k)fluoranthrene	1.45		1.30		1.77	
Benzo(a)pyrene	1.41		1.37		1.73	
PAHs	PAH Concentrations and % removals after running through flow-through system with permanganate candle					
	1st cycle		2nd cycle		3rd cycle	
	Conc. (µg L ⁻¹)	% removal	Conc. (µg L ⁻¹)	% removal	Conc. (µg L ⁻¹)	% removal
	(T = 20 min)					
Anthracene	nd [†]	100.00	nd	100.00	0.98	40.61
Pyrene	nd	100.00	nd	100.00	1.63	4.12
Benzo(a)anthracene	nd	100.00	nd	100.00	1.33	15.82
Benzo(k)fluoranthrene	0.40	72.41	0.97	25.38	1.64	7.34
Benzo(a)pyrene	nd	100.00	nd	100.00	1.29	25.43
	(T = 2 h)					
Anthracene	nd	100.00	nd	100.00	nd	100.00
Pyrene	nd	100.00	nd	100.00	0.35	79.41
Benzo(a)anthracene	nd	100.00	nd	100.00	0.69	56.32
Benzo(k)fluoranthrene	0.25	82.75	0.62	52.30	1.45	18.08
Benzo(a)pyrene	nd	100.00	nd	100.00	0.53	69.36
	(T = 24 h)					
Anthracene	nd	100.00	nd	100.00	nd	100.00
Pyrene	nd	100.00	nd	100.00	nd	100.00
Benzo(a)anthracene	nd	100.00	nd	100.00	nd	100.00
Benzo(k)fluoranthrene	nd	100.00	0.37	71.53	0.92	48.02
Benzo(a)pyrene	nd	100.00	nd	100.00	nd	100.00

† Detection limit of PAHs = 0.25 µg L⁻¹.

Once all the runoff water had drained from the reactor ($T = 20$ min) we sampled for PAH and permanganate concentrations from the collection beaker. We then sampled again from the same beaker at $T = 2$, and 24 h. To verify that the flow-through system was not causing significant decreases in the PAH concentrations by itself, a control experiment was also performed where 200 mL of spiked PAH solution was passed through the reactor without a permanganate candle and concentrations determined at $T = 20$ min, 2 h and 24 h.

We determined PAH concentrations in the runoff water that had passed through the flow-through candle system by removing 10 mL from the collection beaker and adding 20 µL manganese sulfate solution (0.1 g mL⁻¹) to quench the reaction. Solid-phase extraction cartridges were then used to extract and concentrate the PAHs. The Sep-Pak® Plus tC18 Environmental cartridges (Waters, Milford, MA, USA) were first washed with 5 mL methanol and 5 mL water. Then the 10-mL samples were applied to the cartridges and eluted with 5 mL

ethyl acetate into glass test tubes containing 0.5 g sodium sulfate to remove water. The solutions were then transferred to vials for HPLC analysis.

3. Results and discussion

3.1. Batch experiments with phenanthrene

Treating phenanthrene with varying permanganate concentrations showed a nearly linear increase in first-order degradation rates with increasing permanganate concentrations ($k = 0.50$ h⁻¹, 100 mg L⁻¹ MnO₄⁻; $k = 1.31$ h⁻¹, 250 mg L⁻¹ MnO₄⁻; $k = 2.78$ h⁻¹, 500 mg L⁻¹ MnO₄⁻). Using an initial MnO₄⁻ concentration of 500 mg L⁻¹, phenanthrene degradation was completed within 2 h (Figure 1). These results confirmed that if permanganate candles generate and sustain permanganate concentrations ≥ 100 mg L⁻¹, PAH degradation would be possible within a few hours.

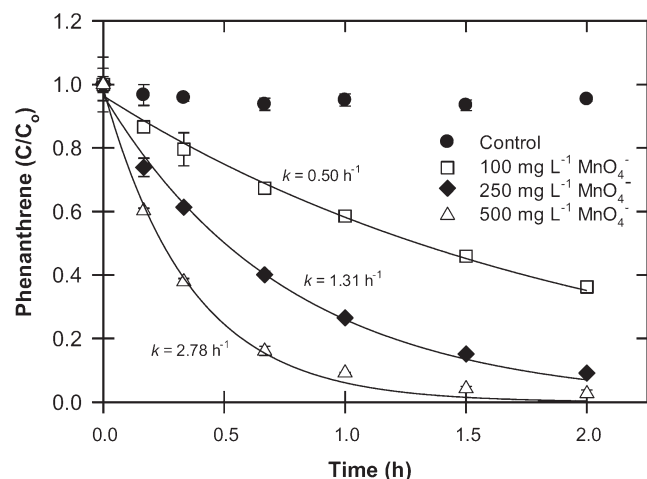


Figure 1. Temporal changes in phenanthrene concentrations following treatment with varying permanganate (solution) concentrations.

Earlier work by Christenson et al. [28] and Kambu et al. [27] using similar sized slow-release oxidant candles showed that contaminant degradation kinetics mimicked the dissolution patterns of the candles. Specifically, freshly prepared candles initially produced first-order contaminant degradation rates as the permanganate on the surface of the candle dissolved. With time, degradation kinetics followed a more linear (zero-order) decline as the candle aged and the dissolution front moved into the wax matrix. With time, the release rate does decrease as the mass of permanganate becomes limiting.

Treating phenanthrene with washed (aged) and freshly prepared (i.e., unwashed) permanganate candles showed, as expected, that the fresh permanganate candle was able to degrade phenanthrene considerably faster than the washed candle. The unwashed candle degraded phenanthrene within 90 min, while the washed candle was unable to completely degrade phenanthrene within 2 h (Figure 2A). Corresponding permanganate concentrations generated by the dissolution of the washed and unwashed candles showed distinct differences in permanganate release rates (Figure 2B). The permanganate on the outer surfaces of the freshly prepared candle quickly dissolved into solution, which resulted in an approximately 10-fold higher permanganate concentration over the washed candle (Figure 2B). The permanganate in the washed candle must diffuse through the wax matrix that developed during the 24-h washing. This in turn produced lower permanganate concentrations and slower degradation kinetics (Figure 2). Given that the initial release rate from the fresh candles is short lived and does not represent the oxidant release rate observed for most of the candle's lifespan, washed candles were used for all subsequent experiments. This ensured a more constant, slow release of permanganate rather than the immediate loading of the experimental units with permanganate.

When we treated phenanthrene ($500 \mu\text{g L}^{-1}$) with permanganate (150mg L^{-1}) versus a washed permanganate candle, we observed a slightly faster removal rate with the permanganate candle (data not shown). While the faster removal rate is in part due to the permanganate candle producing a higher permanganate concentration in solution, we also recognized that the wax matrix could serve as a sink (i.e., adsorption). Consequently, we compared phenanthrene removal from washed permanganate candles versus plain wax candles (control candle) using ^{14}C -labeled phenanthrene. Results from this test showed that the wax matrix can adsorb phenanthrene at a rate of $k = 0.37 \text{h}^{-1}$; while the permanganate

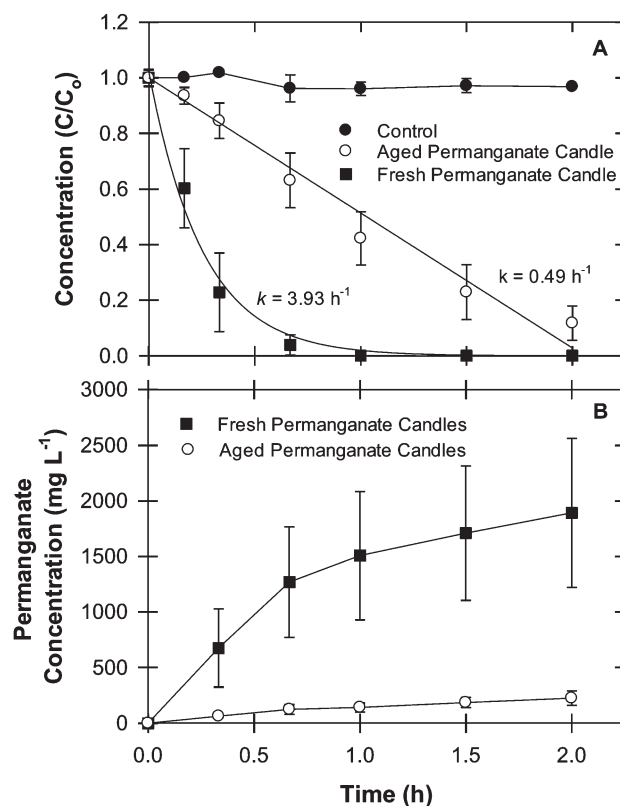


Figure 2. (A) Temporal changes in phenanthrene concentrations ($C_0 = 1000 \mu\text{g L}^{-1}$) following treatment with freshly prepared and washed (i.e., aged) permanganate candles. Data from the fresh candle was fit to a first-order equation ($C/C_0 = e^{-kt}$); while data from washed candle was fit to a zero-order equation ($C/C_0 = -kt + 1$). (B) Temporal permanganate concentrations released from fresh and aged permanganate candle.

candle removed phenanthrene at a rate of $k = 2.48 \text{h}^{-1}$ (Figure 3). Changes in ^{14}C -concentrations provided further evidence that the plain wax adsorbs ^{14}C -phenanthrene ($k = 0.35 \text{h}^{-1}$). However, tracking ^{14}C -activity in the permanganate candle treatment indicated that ^{14}C -phenanthrene was initially adsorbed to the wax matrix, but then released back into solution following transformation to more soluble intermediates (Figure 3). Given that the mass of wax in the control candle was greater than what was present in the permanganate candle, a second control candle consisting of KCl and wax was prepared. Results showed the KCl candle adsorbed less ^{14}C -phenanthrene from solution than the plain wax candle (see Supplementary material, Figure SM-1). Collectively, differences in removal kinetics of phenanthrene and ^{14}C -activity between the permanganate candle and two control candles indicate that oxidation was the primary mechanism responsible for PAH loss by the permanganate candles.

3.2. Syringe experiments with mixed PAH solution

To expand upon the results obtained with phenanthrene, we determined whether the permanganate candles could treat multiple PAHs. This was accomplished by treating a mixed solution of 16 PAHs in zero headspace reactors with slow-release permanganate candles. Based on the initial concentration of the PAHs ($50 \mu\text{g L}^{-1}$), and the detection limits of our HPLC (with fluorescence detection), we were able to identify 11 of the 16 PAHs in the mixture. A time sequence of PAH chromatographs ($T = 0, 2, 4 \text{h}$) showed that all of these peaks decreased in area with time (Figure 4). To quantify the extent of

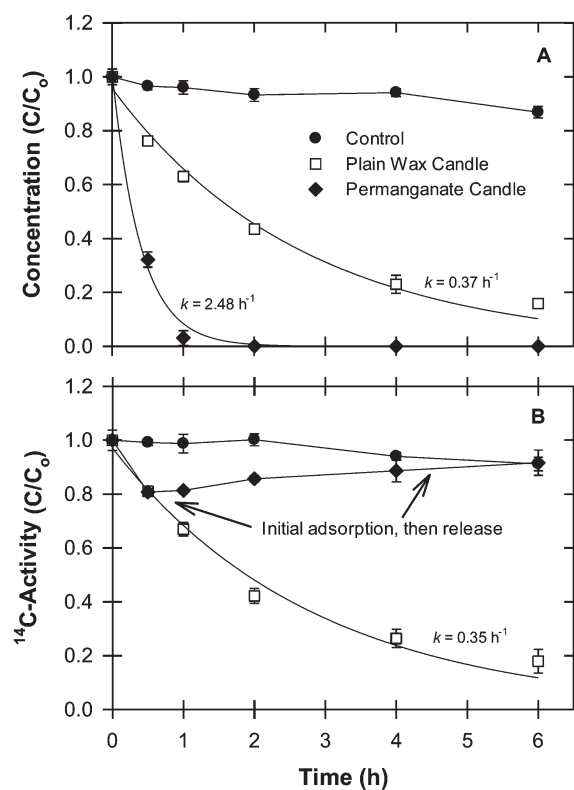


Figure 3. Changes in phenanthrene concentrations ($C_0 = 500 \mu\text{g L}^{-1}$) and ¹⁴C-activity following treatment with permanganate candles and wax candles (control candle).

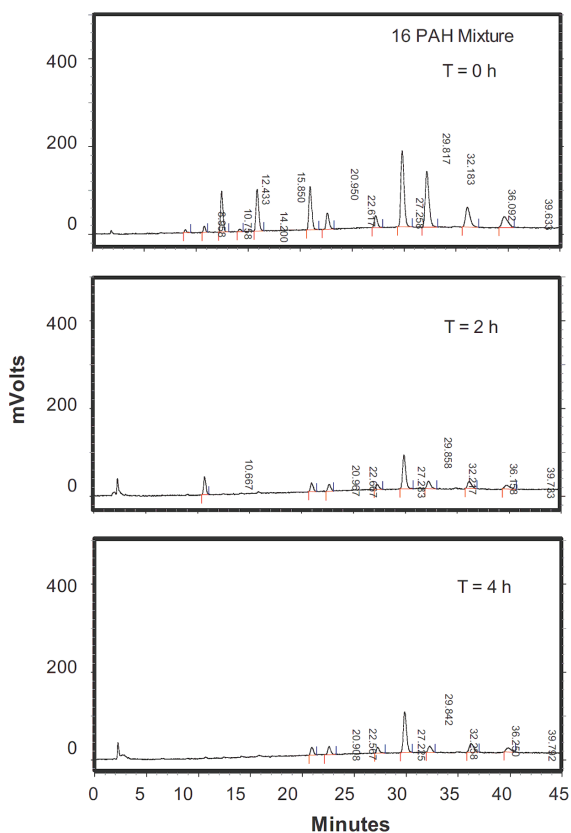


Figure 4. Chromatograph of 16 PAHs solutions treated with permanganate candles ($T = 0, 2, 4 \text{ h}$).

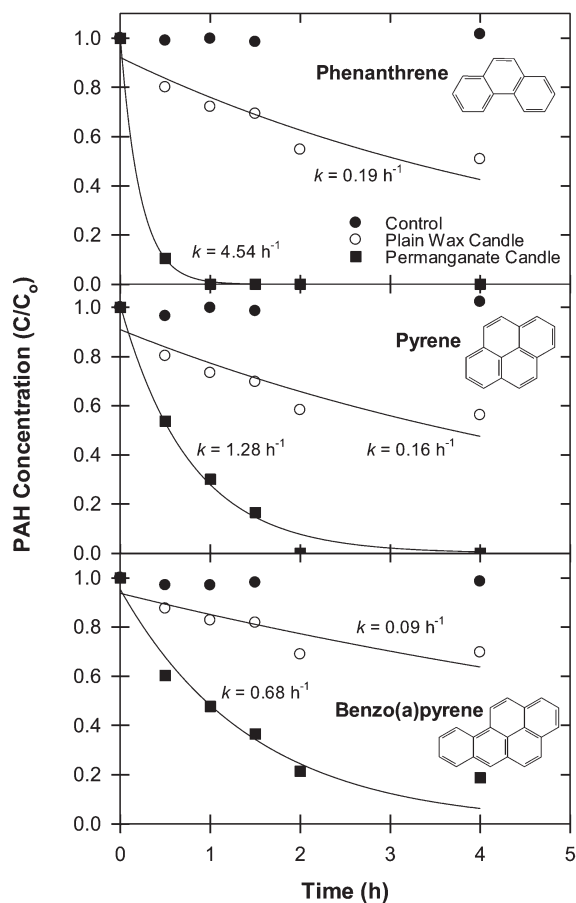


Figure 5. Changes in phenanthrene, pyrene and benzo(a)pyrene concentrations following treatment with permanganate candles and wax candles (control candle).

these decreases, we chose phenanthrene, pyrene and benzo(a)pyrene as test compounds for the mixture and repeated the experiment using permanganate candles, plain wax candles, and a control (PAH solution, no candle).

Temporal changes in PAH concentrations showed that phenanthrene, pyrene, and benzo(a)pyrene all decreased from solution when treated with slow-release permanganate candles. Phenanthrene was removed within 90 min; pyrene in 4 h; while benzo(a)pyrene was still detectable at 4 h (Figure 5), but no longer detectable after 24 h. Removal kinetics with permanganate candles showed phenanthrene was removed from solution the fastest ($k = 4.54 \text{ h}^{-1}$), followed by pyrene ($k = 1.28 \text{ h}^{-1}$), and benzo(a)pyrene ($k = 0.68 \text{ h}^{-1}$). Some of this initial removal from solution can be attributed to adsorption but removal kinetics by the plain wax candles were considerably slower than that achieved with the permanganate candle: phenanthrene, $k = 0.19 \text{ h}^{-1}$; pyrene, $k = 0.16 \text{ h}^{-1}$; benzo(a)pyrene, $k = 0.09 \text{ h}^{-1}$ (Figure 5).

The order of PAH removal of our three test compounds by the permanganate candles decreased with increased ring number (phenanthrene - 3 rings > pyrene - 4 rings > benzo(a)pyrene - 5 rings). Adsorption to the plain wax candles also followed this order but overall differences among adsorption rates were considerably less (i.e., k ranged from 0.19 to 0.09 h^{-1}). Brown et al. [19] found that the order of reactivity of soil-adsorbed PAHs toward permanganate was benzo(a)pyrene > pyrene > phenanthrene > anthracene > fluoranthene > chrysene. Reasons for this purported trend are that multiple rings allow for one ring to be attacked while still having one or more benzenoid rings intact [32].

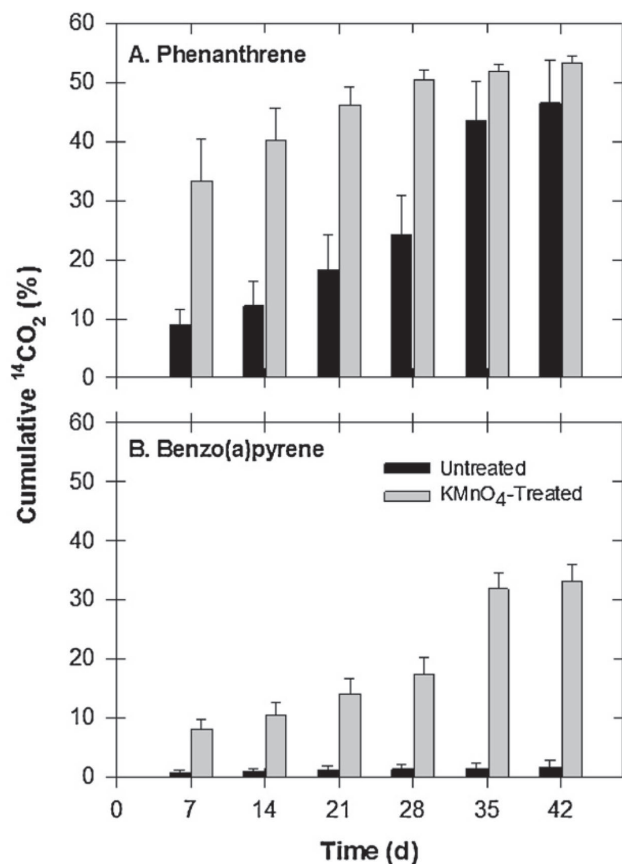


Figure 6. Cumulative ¹⁴CO₂ percent released from soil microcosms spiked with untreated and permanganate-treated ¹⁴C-phenanthrene and ¹⁴C-benzo(a)pyrene.

Forsey et al. [33] pointed out that predicting reaction rates based on ring number is a generalization because reaction rates can be affected by steric interactions, reaction conditions, and the connectivity of the aromatic rings. The Clar [34] model, which predicts chemical reactivity of PAHs based on the localization of aromatic sextets, indicates that the primary element toward reactivity is the number of true carbon-carbon double bonds [19]. Phenanthrene, pyrene and benzo(a)pyrene all contain one. Secondary factors include the number of stabilizing sextets and shared double bonds [19]. In this regard, both benzo(a)pyrene and pyrene contain the same number of sextets (2) and shared double bonds (1). This means other chemical factors than those identified in the Clar model may have been responsible for observed kinetics.

Possible reasons for why removal rates of our test PAHs differed from Brown et al. [19] include that both adsorption and degradation come into play when solutions are in contact with permanganate candles. Moreover, kinetic removal rates of our test compounds were performed using a mixture of 16 PAHs, not individual compounds, so competition among multiple PAHs likely occurred. Finally, benzo(a)pyrene was being treated at a concentration above its aqueous solubility. Trapido et al. [35] stated that the reaction rates differed in aqueous solutions versus suspended systems. Trapido et al. [35] also observed a dramatic decrease in benzo(a)pyrene's reaction rate when experiments were conducted at concentrations above benzo(a)pyrene aqueous solubility. Butkovic et al. [36], also working with benzo(a)pyrene above its aqueous solubility, found that benzo(a)pyrene had lower reactivity toward ozone than pyrene and phenanthrene.

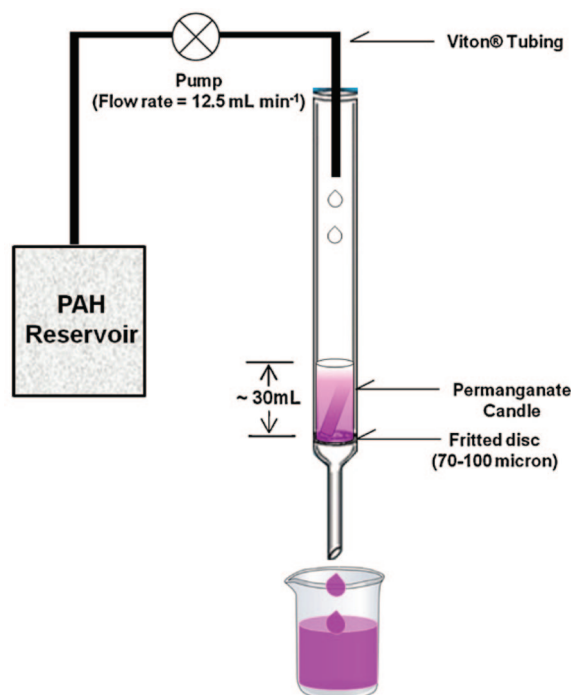


Figure 7. Diagram of the flow-through candle system.

3.3. Microcosm experiment

Initial experiments verified that permanganate could not mineralize phenanthrene or benzo(a)pyrene over the time course of our experiments. Consequently, we quantified how biodegradable the permanganate-transformed products were in soil microcosms. By comparing the cumulative ¹⁴CO₂ emitted by the parent compound versus the KMnO₄-transformed products, we observed the treated phenanthrene was significantly more biodegradable. After 14 d, the percent of added ¹⁴C converted to ¹⁴CO₂ was 40% for the KMnO₄-treated products versus only 12% for the parent phenanthrene. With time, the parent phenanthrene was eventually mineralized but in comparison to the permanganate-transformed phenanthrene, it is clear that the KMnO₄-transformed products were initially much more biodegradable (Figure 6A).

By comparison, the parent ¹⁴C-benzo(a)pyrene was not biodegradable but the KMnO₄-treated ¹⁴C-benzo(a)pyrene was, with >30% mineralization observed after 5 weeks. This stark difference is likely due to the low solubility and high adsorption potential of the parent benzo(a)pyrene versus the more polar functional groups found on the degradation products (Figure 6B). While individual degradation products were not identified for this study, past research indicates that oxidation products of PAHs treated with permanganate would likely include quinones, aromatic diols, and short chain alkanes [19,33]. These products would be more soluble and thus more available for natural biotic mineralization than the original parent structures, as evidenced by our mineralization results (Figure 6).

3.4. Flow-through experiments with urban runoff

The ability of a permanganate candle to treat PAH-spiked urban runoff in flow-through system (Figure 7) was investigated. Based on the initial concentration of the PAHs (1.5 µg L⁻¹) and the detection limit of the fluorescence detector (0.25 µg L⁻¹), we were able to quantify 5 of the 16 PAHs in the mixture. These included: anthracene, pyrene,

benzo(a)anthracene, benzo(k)fluoranthrene, and benzo(a)pyrene.

Temporal changes in PAHs concentrations showed that all PAHs decreased from solution when treated with a permanganate candle in the flow-through system (Table 2). The permanganate concentration in the runoff collection beaker after the first runoff cycle was 150 mg L⁻¹. Decreases in PAH concentrations immediately after passing through the flow-through system ($T = 20$ min) were evident with 4 of the 5 PAHs below detection limits. As expected, additional time allowed more degradation to occur and by $T = 24$ h, all five of the PAHs had been degraded. The control experiment, which was run without a permanganate candle showed that PAH losses after passing through the flow-through reactor ($T = 20$ min) were minimal (2–5.5%) but because the collection beaker was open to the atmosphere, greater losses due to volatilization and/or adsorption were observed at the later sampling times ($T = 2$ h, 9–51%; $T = 24$ h, 31–59%, see Supplementary material, Table SM 1). These losses were still significantly less than the losses observed with the permanganate candle (i.e., 100% removal).

Treating PAH-spiked urban runoff with the same permanganate candle for the next two cycles showed slower removal rates than the first cycle (Table 2). The permanganate candles generated an average permanganate concentration of 82 mg L⁻¹ in runoff collection beaker for the second cycle and 46 mg L⁻¹ for the third cycle. These lower permanganate concentrations resulted in less PAH degradation. However, after 24 h, we found that all PAHs were removed, except benzo(k)fluoranthrene. Given that benzo(k)fluoranthrene was removed during the first cycle, this PAH likely needs a higher permanganate concentration or longer reaction time. Moreover, given that PAH degradation rates will be dictated by the permanganate concentrations generated from dissolution of the candles, permanganate concentrations could be increased by changing the diameter, number, or formulation of permanganate candles (i.e., KMnO₄ mass) placed in a conduit to treat the incoming runoff.

Christenson et al. [28] estimated that material costs (US\$) for manufacturing field-scale sized (91.4 cm length) permanganate candles were ~\$18 (5.1-cm diameter) and \$40 (7.6-cm diameter). While some modifications to the size, dimensions or formulations of the candles used by Christenson et al. [28] may be needed to specifically treat urban runoff, the relatively low cost of manufacturing slow-release oxidant candles combined with their efficacy in removing PAHs, indicates that this technology offers a potentially low-cost, low maintenance approach to treating PAH-contaminated water.

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References

- [1] E. J. Hoffman, G. L. Mills, J. S. Latimer, J. G. Quinn, Urban runoff as a source of polycyclic aromatic hydrocarbons to coastal waters, *Environ. Sci. Technol.* 18 (1984) 580–587.
- [2] P. C. Van Metre, B. J. Mahler, E. T. Furlong, Urban sprawl leaves its PAH signature, *Environ. Sci. Technol.* 34 (2000) 4064–4070.
- [3] B. Ngabe, T. F. Bidleman, G. I. Scott, Polycyclic aromatic hydrocarbons in storm runoff from urban and coastal South Carolina, *Sci. Total Environ.* 255 (2000) 1–9.
- [4] A. Krein, M. Schorer, Road runoff pollution by polycyclic aromatic hydrocarbons and its contribution to river sediments, *Water Res.* 34 (2000) 4110–4115.
- [5] T. J. Slaga, J. DiGiovanni, Inhibition of carcinogenesis, in: C. E. Searle, ed., *Chemical Carcinogens*, 2nd edition. ACS Monograph 182, American Chemical Society, Washington, DC, 1984, pp. 1300–1302.
- [6] J. L. Durant, W. F. R. Busby, A. L. Lafleur, B. W. Penman, C. L. Crespi, Human cell mutagenicity of oxygenated, nitrated and unsubstituted aromatic hydrocarbons associated with urban aerosols, *Mutation Res.* 371 (1996) 123–127.
- [7] USEPA, Office of Solid Waste, Polycyclic Aromatic Hydrocarbons (PAHs), U. S. Environmental Protection Agency, 2008; <http://www.epa.gov/osw/hazard/wastemin/minimize/factshts/pahs.pdf>
- [8] R. G. Rice, C. M. Robson, G. W. Miller, A. G. Hill, Uses of ozone in drinking water treatment, *J. Am. Water Works Assoc.* 73 (1981) 44–57.
- [9] E. L. Stover, L. W. Wang, D. R. Medley, Ozone assisted biological treatment of industrial wastewaters containing biorefractory compounds, *Ozone Sci. Eng.* 4 (1982) 177–194.
- [10] G. R. Peyton, Destruction of pollutants in water with ozone in combination with ultraviolet radiation. 3. Photolysis of aqueous ozone, *Environ. Sci. Technol.* 22 (1988) 761–767.
- [11] M. M. Zein, P. X. Pinto, S. Garcia-Blanco, M. T. Suidan, A. D. Venosa, Treatment of groundwater contaminated with PAHs, gasoline hydrocarbons, and methyl tert-butyl ether in a laboratory biomass-retaining bioreactor, *Biodegradation* 17 (2006) 57–69.
- [12] E. Manoli, C. Samara, The removal of polycyclic aromatic hydrocarbons in the wastewater treatment process: experimental calculations and model predictions, *Environ. Pollut.* 151 (2008) 477–485.
- [13] S. Lundstedt, Y. Persson, L. Öberg, Transformation of PAHs during ethanolic-Fenton treatment of an aged gasworks' soil, *Chemosphere* 65 (2006) 1288–1294.
- [14] P. T. Souza e Silva, V. L. de da Silva, B. de Barros Neto, M. O. Simonnot, Phenanthrene and pyrene oxidation in contaminated soils using Fenton's reagent, *J. Hazard. Mater.* 161 (2009) 967–973.
- [15] E. Ferrarese, G. Andreottola, I. A. Oprea, Remediation of PAH-contaminated sediments by chemical oxidation, *J. Hazard. Mater.* 152 (2008) 128–139.
- [16] M. M. O'Mahony, A. D. W. Dobson, J. D. Barnes, I. Singleton, The use of ozone in the remediation of polycyclic aromatic hydrocarbon contaminated soil, *Chemosphere* 63 (2006) 307–314.
- [17] F. J. Rivas, Polycyclic aromatic hydrocarbons sorbed on soils: a short review of chemical oxidation based treatments, *J. Hazard. Mater.* 138 (2006) 234–251.
- [18] C. Cuyper, T. Grotenhuis, J. Joziassse, W. Rulkens, Rapid persulfate oxidation predicts PAH bioavailability in soils and sediments, *Environ. Sci. Technol.* 34 (2000) 2057–2063.
- [19] G. S. Brown, L. L. Barton, B. M. Thomson, Permanganate oxidation of sorbed polycyclic aromatic hydrocarbons, *Waste Manage.* 23 (1993) 737–740.
- [20] P. T. Souza e Silva, V. L. de da Silva, B. de Barros Neto, M. O. Simonnot, Potassium permanganate oxidation of phenanthrene and pyrene in contaminated soils, *J. Hazard. Mater.* 168 (2009) 1269–1273.
- [21] X. Guan, D. He, J. Ma, G. Chen, Application of permanganate in the oxidation of micropollutants: a mini review, *Front. Environ. Sci. Eng.* 4 (2010) 405–413.
- [22] R. Munter, Advanced oxidation processes – Current status and prospects, *Proc. Estonian Acad. Sci. Chem.* 50 (2001) 59–80.
- [23] R. Stewart, *Oxidation Mechanisms*, W. A. Benjamin Inc., New York, 1964.
- [24] N. Kang, I. Hua, P. S. Rao, Production and characterization of encapsulated potassium permanganate for sustained release as an in situ oxidant, *Ind. Eng. Chem. Res.* 43 (2004) 5187–5193.
- [25] C. Ross, L. C. Murdoch, D. L. Freedman, R. L. Siegrist, Characteristics of potassium permanganate encapsulated in polymer, *J. Environ. Eng.* 131 (2005) 1203–1211.

- [26] F. W. Schwartz, Semi-passive, Chemical Oxidation Schemes for the Long-Term Treatment of Contaminants, U. S. Department of Energy Final Report, Project 86642, 2005; <http://www.osti.gov/bridge/servlets/purl/861451-aSxkwo/861451.pdf>
- [27] A. Khambhu, S. Comfort, C. Chokeyaroenrat, C. Sakulthaew, Developing slow-release persulfate candles to treat BTEX contaminated groundwater, *Chemosphere*, pub. online July 7, 2012; <http://www.sciencedirect.com/science/article/pii/S0045653512007722>
- [28] M. D. Christenson, A. Kambhu, S. D. Comfort, Using slow-release permanganate candles to remove TCE from a low permeable aquifer at a former landfill, *Chemosphere*, pub. online July 10, 2012; <http://www.sciencedirect.com/science/article/pii/S0045653512007783>
- [29] USEPA, Methods for Organic Chemical Analysis of Municipal and Industrial, Method 610-Polynuclear Aromatic Hydrocarbons, 2007; http://water.epa.gov/scitech/methods/cwa/organics/upload/2007_07_10_methods_method_organics_610.pdf
- [30] C. Chokeyaroenrat, S. D. Comfort, C. Harris, D. D. Snow, D. Casada, C. Sakulthaew, T. Satapanajaru, Transformation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) by permanganate, *Environ. Sci. Technol.* 45 (2011) 3643–3649.
- [31] M. D. Christenson, Using slow-release permanganate to remove TCE from a low permeable aquifer at a former landfill, MS Thesis, University of Nebraska-Lincoln, 2011, <http://digitalcommons.unl.edu/natresdiss/29>
- [32] K. C. Huang, R. A. Couttenye, G. E. Hoag, Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE), *Chemosphere* 49 (2002) 413–420.
- [33] S. P. Forsey, N. R. Thomson, J. F. Barker, Oxidation kinetics of polycyclic aromatic hydrocarbons by permanganate, *Chemosphere* 79 (2010) 628–636.
- [34] E. Clar, *The Aromatic Sextet*, Wiley, London, 1972.
- [35] M. Trapido, J. Veressinina, R. Munter, Ozonation and advanced oxidation processes of polycyclic aromatic hydrocarbons in aqueous solutions – A kinetic study, *Environ. Technol.* 16 (1995) 729–740.
- [36] V. L. Butković, L. Klasinc, M. Orhanovic, J. Turk, Reactions rates of polycyclic aromatic hydrocarbons with ozone in water, *Environ. Sci. Technol.* 17 (1983) 546–548.
- [37] USEPA, Approved General-Purpose Methods, U. S. Environmental Protection Agency, 2011, http://water.epa.gov/scitech/methods/cwa/methods_index.cfm
- [38] APHA, AWWA, WEF, *Standard Methods for the Examination of Water and Wastewater*, 20th ed., American Public Health Association, American Water Works Association, Water Environment Federation, Washington, DC, 1998.
- [39] D. R. Hach, *2800 Spectrophotometer: Procedures Manual*, Hach Company, Germany, 2007.

Using slow-release permanganate candles to remediate PAH-contaminated water

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Supplementary Material

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1 Table

1 Figure

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Chemical analysis

Phenanthrene was analyzed by high performance liquid chromatography (HPLC) using a photo diode array detector (Shimadzu Scientific Instruments, Columbia, MD). Samples (20 μL) were injected into an isocratic mobile phase of 80:20 methanol-water. Using a flow rate of 1 mL min^{-1} , samples were separated by a 4.6- by 250-mm Shimadzu Premier C18 column (Kyoto, Japan) coupled with a guard column. Phenanthrene was quantified at 254 nm by an external calibration curve. Matrix blanks were analyzed with samples to ensure the absence of background peaks. Sample peaks were confirmed by comparing UV spectrum scans with spectrum scans of standards.

When multiple PAHs were used, a second HPLC method was used to account for differences in PAH solubility and detector sensitivity. This analytical method was a modification of EPA Method 610 [29], which is used for PAHs quantification in municipal and industrial wastewater. Using a flow rate of 1 mL min^{-1} , mobile phases of acetonitrile and H_2O were used with the following gradient: 70:30 ($\text{CH}_3\text{CN}:\text{H}_2\text{O}$) for 25 min followed by 100:0 for 20 min and then 70:30 for 5 min. Aqueous samples (20 μL) were injected into a Thermo Scientific Hypersil Green PAH column (Waltham, MA, USA) that was connected to a fluorescence and photodiode array detector. Fluorescence detection used an excitation wavelength of 220 nm and an emission wavelength of 400 nm. Peak areas from the fluorescence detector were compared to standard calibration curves generated for each PAH. The total run time was ~ 50 min per sample with the following elution times: phenanthrene, 10 min; pyrene, 15 min; and benzo(a)pyrene, 32 min.

^{14}C -activity was determined by removing 1 mL subsamples from either the batch or syringe reactors and mixing with 5 mL of Ultima Gold liquid scintillation cocktail. Samples were then mixed on a vortex mixer and allowed to settle for 24 h in the dark before analyzing on a Packard 1900TR liquid scintillation counter (LSC). A blank consisting of 5 mL Ultima Gold liquid scintillation cocktail was analyzed prior to running

the samples and used to correct for background matrix activity (dpms).

Permanganate concentrations were measured colormetrically at 525 nm with a Hach DR2800 spectrophotometer. When needed, samples were diluted with H₂O so that measured concentrations fell within the linear absorbance range (<150 mg L⁻¹).

Table SM 1

Temporal changes in PAH concentrations in urban runoff after running through the flow-through system without permanganate candle (Control)

PAH Concentrations and % Loss after running through flow-through system without permanganate candle †								
PAHs	0 h		20 min		2 h		24 h	
	Conc ($\mu\text{g L}^{-1}$)	% Loss	Conc ($\mu\text{g L}^{-1}$)	% Loss	Conc ($\mu\text{g L}^{-1}$)	% Loss	Conc ($\mu\text{g L}^{-1}$)	% Loss
Anthracene	1.45	0.00	1.37	5.51	0.81	44.13	0.60	58.62
Pyrene	1.78	0.00	1.74	2.24	0.87	51.12	0.86	51.68
Benzo(a)anthracene	1.49	0.00	1.46	2.01	1.27	14.76	0.94	36.91
Benzo(k)fluoranthrene	1.45	0.00	1.39	4.13	1.31	9.65	0.89	38.62
Benzo(a)pyrene	1.41	0.00	1.37	2.83	1.28	9.21	0.97	31.20

† Detection limits for the PAHs were $0.25 \mu\text{g L}^{-1}$.

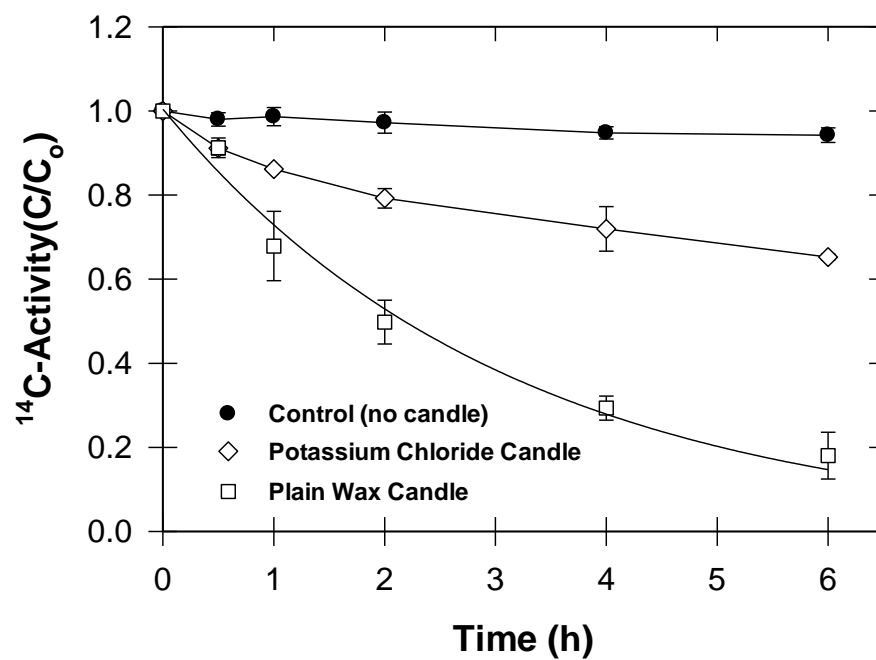


Figure SM-1. Comparison of ¹⁴C-phenanthrene adsorption by plain wax versus potassium chloride candles. Bars on symbols represent sample standard deviations.