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Removing PAHs from urban runoff water by combining ozonation and carbon nano-onions

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HIGHLIGHTS

- PAHs in runoff were transformed by ozone within minutes in a flow-through system.
- Ozone-treated PAHs were 100% adsorbed to carbon nano-onions or activated carbon.
- ^{14}C-labeled PAHs were used to track adsorption and mineralization.
- O_3-transformed PAHs adsorbed by CNOs were biodegradable.
- Without ozonation, PAHs adsorbed to CNOs are not biodegraded or released.

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ABSTRACT

Ozone (O_3) is a chemical oxidant capable of transforming polycyclic aromatic hydrocarbons (PAHs) in urban runoff within minutes but complete oxidation to CO_2 can take days to weeks. We developed and tested a flow-through system that used ozone to quickly transform PAHs in a runoff stream and then removed the ozone-transformed PAHs via adsorption to carbon nano-onions (CNOs). To quantify the efficacy of this approach, ^{14}C-labeled phenanthrene and benzo(a)pyrene, as well as a mixture of 16 unlabeled PAHs were used as test compounds. These PAHs were pumped from a reservoir into a flow-through reactor that continuously ozonated the solution. Outflow from the reactor then went to a chamber that contained CNOs to adsorb the ozone-transformed PAHs and allowed clean water to pass. By adding a microbial consortium to the CNOs following adsorption, we observed that bacteria were able to degrade the adsorbed products and release more soluble, biodegradable products back into solution. Control treatments confirmed that parent PAH structures (i.e., non-ozonated) were not biologically degraded following CNO adsorption and that O_3-transformed PAHs were not released from the CNOs in the absence of bacteria. These results support the combined use of ozone, carbon nano-onions with subsequent biological degradation as a means of removing PAHs from urban runoff or a commercial waste stream.

1. Introduction

Extensive sampling of aquatic sediments from around the world has revealed that polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in nature but found in most abundance in metropolitan centers (Miles and Delfino, 1999; García-Flores et al., 2013; Van Metre and Mahler, 2014; Yim et al., 2014). 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 mass of PAHs entering the environment. For this reason, similarities between the PAH patterns found in urban atmospheres and the PAHs concentrations in urban lake sediments have been identified.

Given that automobiles are a significant source of PAHs, it is perhaps not surprising that major metropolitan areas are observing a decline in water quality (Van Metre et al., 2000). Bangkok, Thailand is a mega-city with roughly 6 million inhabitants

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(Department of Provincial Administration, 2013). The number of gas- or diesel-powered vehicles is estimated at 8 million (Department of Land Transport of Thailand, 2013). This high vehicle density coupled with insufficient traffic lanes has resulted in serious traffic congestion and associated air pollution. Boonyatumanond et al. (2006) found that the canals and river waters in Bangkok are highly contaminated with PAHs and identified runoff of PAH-adsorbed street dust as a major contributor. Similar examples of PAH contamination in large cities can be found across the world in countries such as Laos, Jordan, and Japan (Supplementary material, Table SM-1). From the various research surveys conducted, PAH concentrations identified in water bodies have ranged from hundreds to thousands of ng L^{-1} (Table SM-1). Some of PAHs that have been observed in higher concentrations include: naphthalene, phenanthrene, fluoranthene, and pyrene (Table SM-1).

Because PAHs in urban runoff are significantly contributing to the deterioration of surface waters in urban centers, and some PAHs have been identified as carcinogenic, mutagenic and teratogenic, the need to curtail PAH inputs is paramount. Ozone has previously been reported to rapidly degrade a variety of PAHs (Trapido et al., 1994, 1995; Beltŕan et al., 1996). We recently reported that ozone was an effective oxidant for rapidly transforming PAHs in runoff water but complete mineralization to CO_2 required days to weeks to complete (Sakulthaew et al., 2014). Because these long ozonation times would be prohibitive for a realistic flow-through treatment system and the release of partially oxidized PAHs following short-term ozonation into the environmental may be prohibitive, a treatment scheme was undertaken that combined ozone, adsorption, and biological degradation. In this system, carbon nano-onions (CNOs) were compared to activated carbon as a medium for removing ozone-transformed PAHs from runoff water.

Carbon nano-onions (Fig. SM-1) are concentric multilayer giant fullerenes surrounded by onion-like nested spherical graphite layers (Butenko et al., 2005). While not commonly used in commercial water treatment, the unique properties of carbon nano-onions coupled with recent advances in manufacturing techniques have opened the door for a wide spectrum of applications, which includes water treatment. Originally obtained from electron beam irradiation of carbon soot (Ugarte, 1992), Gao et al. (2011) recently produced a highly efficient synthetic method of growing carbon nano-onions through laser resonant excitation of ethylene in a combustion process. This technique has been shown to produce larger quantities of CNOs with purities >99% and at a cost that is substantially less than other commercially available carbon-based nanomaterials. Because of these recent developments and the success other researchers have reported in adsorbing organic contaminants with carbon nanomaterials (Peng et al., 2003; Lu et al., 2005; Cheng et al., 2004, 2005; Yang et al., 2006; Pan and Xing, 2008; Kah et al., 2011; Wesołpwski et al., 2011; Li et al., 2013; Naghizadeh et al., 2013), our objective was to test a flow-through system that uses ozone to quickly transform PAHs in urban runoff and then removes the ozone-transformed PAHs via adsorption to CNOs. We then show that “ozone-transformed” PAHs removed from the runoff stream by the CNOs can be further biologically degraded.

2. Materials and methods

The chemicals and procedures used for chemical analysis are provided in supplementary material.

2.1. Batch adsorption experiments

Adsorption isotherms of the PAHs were obtained using a batch equilibration technique at 25 ± 1 °C. Experimental units were 45-mL Teflon centrifuge tubes that contained 1 mg of CNO or activated carbon. The activated carbon was untreated powder (Sigma–Aldrich), that has a particle size between 250 and 350 mesh. Initial attempts using greater masses of CNOs (i.e., >1 mg) showed that the CNOs removed all PAHs from solution and an equilibrium relationship between adsorbed and solution-phase PAHs could not be obtained. Hence, extra care was taken to specifically weigh out 1 mg of the CNO (Yang et al., 2006). To the CNO, we added 40 mL of test solution that varied in PAH concentration (H_2O matrix) to produce 6-point adsorption isotherms. The range in initial concentrations used were: phenanthrene ($1.1 \times 10^{-3} - 6.7 \times 10^{-3}$ mmol L^{-1}), diphenaldehyde ($9.5 \times 10^{-4} - 5.7 \times 10^{-3}$ mmol L^{-1}), ^{14}C-benzo(a) pyrene ($1.5 \times 10^{-6} - 8.1 \times 10^{-6}$ mmol L^{-1}), and ^{14}C-ozone treated benzo(a)pyrene ($1.5 \times 10^{-6} - 8.1 \times 10^{-6}$ mmol L^{-1}).

The experimental units were shaken for 24 h and centrifuged (3450×g) for 30 min. For phenanthrene and diphenaldehyde, 0.7 mL of supernatant was removed and added to 0.7 mL acetonitrile, then sealed in a HPLC vial for analysis. For ^{14}C-benzo(a) pyrene and ozone-treated ^{14}C-benzo(a)pyrene analysis, 1 mL of supernatant was removed and analyzed by liquid scintillation counting. The specific activity of ^{14}C-benzo(a)pyrene (25 mCi $mmol^{-1}$) was used to convert parent and ozonated benzo (a)pyrene activity to mmol L^{-1}.

Based on the initial concentrations added and the equilibrium concentrations (C_{eq}) following adsorption, the mass of PAHs adsorbed (C_{ads}) was calculated for each isotherm point and graphically displayed. Adsorption isotherm data were fitted to the Langmuir and Freundlich equations (Langmuir, 1918; Freundlich, 1926) using non-linear regression with the SigmaPlot scientific and graphing software (Systat Software, Inc., San Jose, CA).

2.2. Combining ozone and adsorption in flow-through experiments

To test a flow-through system that used ozone to quickly transform PAHs in a runoff stream and then remove the ozone-transformed PAHs via adsorption, a combined ozone and adsorption system was constructed and evaluated (Fig. 1). This system consisted of: (i) a runoff reservoir (350-mL); (ii) piston pump (FMI lab pump, model QSY-2, Syosset, NY); (iii) Viton® tubing (Masterflex, Coleparmer, Vernon Hills, IL); (iv) a 300-mL glass flow-through ozone reactor (Ace Glass, Vineland, NJ); (v) a 116-mL chromatographic glass column equipped with a fritted disc (Ace Glass, Vineland, NJ); (vi) ~30 mg CNOs or activated carbon; (vii) and a 250-mL beaker for collecting treated water; and (viii) ozone generator (Fig. 1).

Ozone was generated, measured, and destroyed (residual) via an OzoneLab generator (OL80W-R), analyzer (OLA/DLS), and catalytic destructor (Ozone Services, Burton, British Columbia, Canada). Gas flow was forced through the system with pressurized oxygen (Industrial Oxygen, Matheson, Lincoln, NE). A stainless-steel oxygen regulator (Smith Equipment, Watertown, SD), and Teflon volumetric flow meters with sapphire floats (Cole-Parmer Instrument Company, Vernon Hills, IL) were used to control gas flow through the system (Fig. 1). To quantify mineralization, the ozone/oxygen gas stream flowed from the glass reactor through FEP-lined flexible tubing (Tygon SE 200, 0.64 cm i.d.; 0.79 cm o.d.) into a series of two 25-mL glass midget bubblers (Ace Glass, Vineland, NJ) containing 15 mL of 0.5 M NaOH (Fig. 1, note – only one bubbler shown).

To run the flow-through system, PAHs were pumped from a reservoir into a flow-through reactor that continuously ozonated the solution. Outflow from the reactor then went to a chamber that contained either 30 mg of activated carbon or carbon nano-onion (CNO), which removed the O_3-treated PAHs and allowed clean water to pass into the collection beaker. The higher mass of CNOs used in this experiment versus the adsorption isotherm (30 vs. 1 mg) allowed for all PAHs (100%) to be adsorbed. Specific