

Technical Brief: PAH Interactions with Ozone

Polycyclic Aromatic Hydrocarbons, or PAHs, are a class of molecules that consist of numerous fused aromatic rings but do not contain heteroatoms or other substitutes. These compounds are often byproducts resulting from the incomplete burning of materials such as coal, oil, gas and garbage, and are often found in industrial sites involving coal tar production, fuel production, wood treatment, or gasworks.¹

PAHs also come in a variety of sizes, although five and six membered rings are most common. Larger PAHs are often lipophilic, non-water soluble and less volatile than smaller PAHs. As a result, these contaminants are notoriously persistent and have been found in numerous air, soil, and groundwater environments surrounding industrial plants.¹

Since PAHs have been identified as potential carcinogens, mutagens, and teratogens, it is necessary to limit human exposure and remove these contaminants of concern from the environment. Some well known examples of PAHs include benzo(a)anthracene, pyrene, phenanthrene, fluorine, creosote, benzo(a)pyrene, and naphthalene.¹

PAH degradation can occur in the environment through a variety of biological, chemical, or photochemical processes.² Of the three methods, biological decay is the first process responsible for natural removal of PAH in soil. Microorganisms such as bacteria and fungi have the ability to metabolize or break down PAH to a variety of non-toxic, organic products.² However, the ultimate result of PAH degradation is achieved when all organic compounds undergo complete mineralization to inorganics such as carbon dioxide and water.² This is most effective using oxidation chemistry.

In addition to biological processes, PAH break down occur faster through abiotic reactions involving chemical oxidants such as singlet oxygen, organic peroxides, hydrogen peroxide, ozone, and hydroxyl radicals. Photochemical process often go in hand with the aforementioned chemical oxidation processes because they regularly aid in the production of these oxidants in the soil

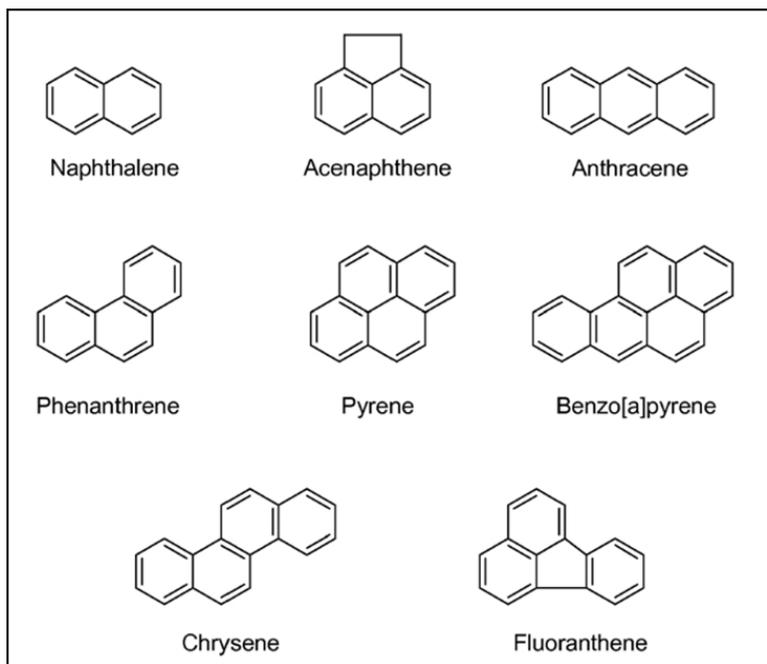


Figure 1

However, chemical reactions involving ozone and hydroxyl radicals have been the most widely studied due to their oxidation strength—2.1V and 2.7V for ozone and the hydroxyl radical, respectively—as well as their high degree of reactivity with PAHs. Molecular ozone is capable of PAH oxidation through two different pathways. Triatomic oxygen (ozone or O₃) can either directly attack the reactive, electron rich PAH double bonds or form reactive, highly unselective hydroxyl radicals through a slow decomposition reaction with water.²

Regardless of the pathway used, the ultimate result of contaminant degradation is to achieve total mineralization of PAH. However, the study of PAH ozone oxidation has revealed that these reactions produce a wide variety of intermediates and final products that can be resistant to complete mineralization.

Examples of PAH oxidation dead end products include carbonyl compounds such as ketones, quinones, dicarboxylic acids, anhydrides, and coumarins.² It is essential to monitor the progress of the ozonation reaction to ensure that if produced, these dead end products do not accumulate to unsafe concentrations. PAH oxidation also produces carboxylic acid and phenol compounds, which are easily degraded and transformed.²

Numerous studies have been conducted to study the effectiveness of ozone on PAH degradation. Masten and Davies investigated the efficacy of in-situ ozonation for the remediation of PAH contaminated soils and confirmed that ozone is extremely useful for PAH degradation.³ In-situ chemical oxidation with ozone has proven useful in enhancing

PAH biodegradation and increasing water solubility by producing reaction products that are more polar than the parent aromatic hydrocarbon.³ Since the polar products are hydrophilic, it is easier for hydroxyl radicals and direct ozonation to act upon the intermediates, facilitating rapid degradation to the final products.

Masten and Davies investigated the degradation of several PAHs including pyrene, naphthalene, chrysene, and phenanthrene with positive results. Greater than 95% removal of phenanthrene was achieved with an ozonation time of 2.3 hours at an ozone flux of 2.3 mg h⁻¹.³ Pyrene also achieved similar results, with 91% removal after four hours of treatment at an ozone flux of 600 mg h⁻¹.³ However, it was observed that more hydrophobic PAHs like chrysene reacted slower than expected with ozone. This was hypothesized to be due to partitioning of the contaminant into the soil organic matter, which would have likely reduced reactivity of the compound. Despite decreased reactivity, the concentration of chrysene was decreased from 100 to 50 mg/kg soil after four hours of exposure to ozone.³

Additional studies were conducted by Beltran, et al. investigating the oxidation of fluorene, phenanthrene, and acenaphthene in aqueous solution with ozone. The effects of pH on oxidation were also analyzed. The three PAH compounds evaluated in this study all demonstrated high oxidation rates with ozone, with effectiveness higher than 90% in most cases.⁴ Fluorene was determined to have the highest reactivity with ozone, followed by phenanthrene, and acenaphthene.

Application of hydroxyl radical inhibitors determined that of the three PAH analyzed, fluorene was the only one of the three compounds tested that underwent both direct ozone and hydroxyl radical reactions.⁴ Consistent with most studies, elevated pH levels demonstrated positive effects on the PAH oxidation of the compounds studied.⁴



Figure 2

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Ozone Injection Started October, 2009

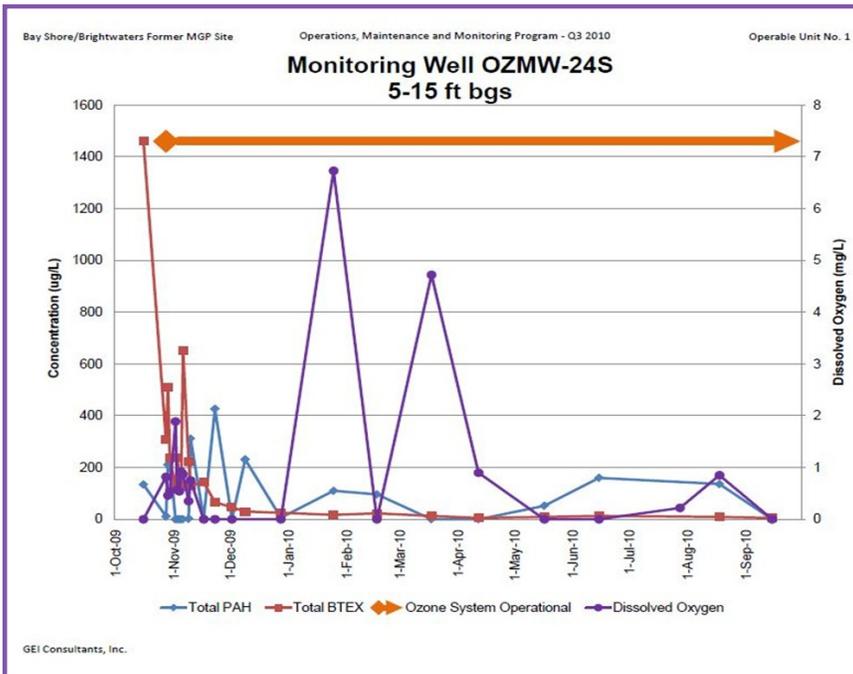


Figure 3 provides a detailed look at the degradation of BTEX and PAH throughout the first 11 months of ozone injection process. BTEX concentrations quickly drop to less than 5 ug/L within several months of ozone injections, while PAH slowly fluctuates in a downward trend and the system continues to operate to this day.

This illustration alone is a key to understanding that a pilot system with ozone should operate for a minimum of 3–4 months until an equilibrium is established.

Figure 3

Oxygen Injection Started February, 2008

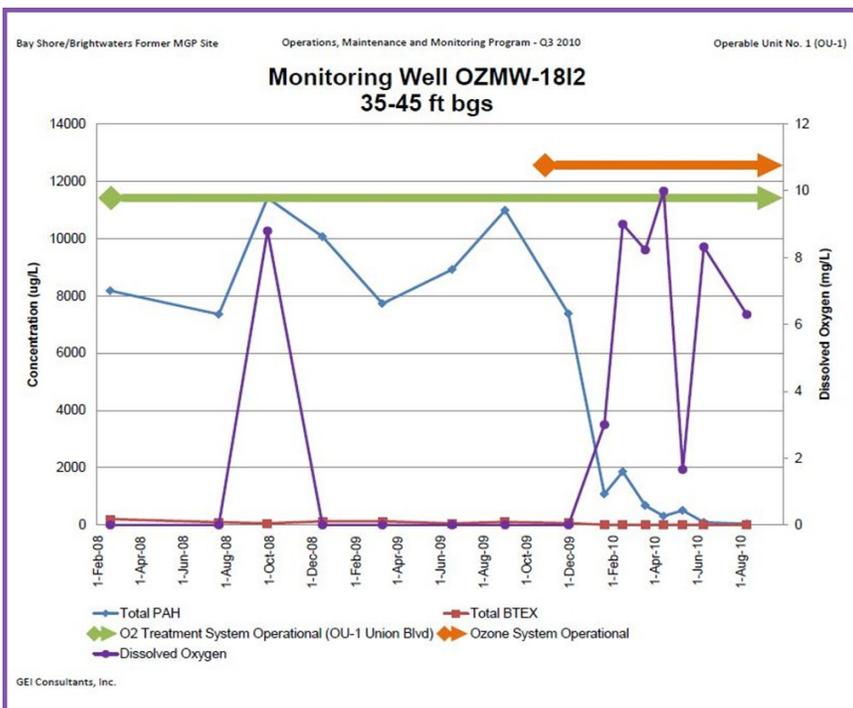


Figure 4 illustrates the fluctuations of PAH and BTEX throughout the duration of oxygen sparging, until the initiation of the ozone injections in October 2009. It is important to fully understand that fluctuations in contaminant concentration are common during the initial months of ozone injection.

The success of this case study along with extensive laboratory research provides strong support that ozone is highly effective in reducing PAH concentrations to optimal levels in soil and groundwater environments surrounding industrial sites.

Figure 4

Piper Environmental Group, Inc, has an extensive history designing ozone remediation systems to properly treat a variety of contaminants, including PAH. Thorough data analyses of our remediation projects provides evidence that targeted compounds have been properly degraded to safe and satisfactory concentrations as desired by our clients.

An in-situ remediation project illustrated on previous page was conducted in Bay Shore/Brightwaters, New York to remediate BTEX and PAH contaminants in and around a former manufactured gas plant site. Piper's OU-1 Ozone Injection System was applied to the site, and oxygen and ozone were introduced to the affected location through 63 unique injection points. Oxygen sparging was applied for the 2.5 year duration of the treatment to enhance aerobic bioremediation of organic compounds, specifically BTEX and naphthalene. Ozone injections were initiated in order to ensure complete degradation of the desired COCs. This is one of five examples of PAH destruction specific to former manufactured gas sites.

At Piper, we are able to effectively custom design and build a variety of ozone remediation systems—including Advanced Oxidation Processes—to best accommodate the remediation needs of the contaminant at hand.

References

¹ US Environmental Protection Agency Office of Solid Waste. (2008, January). *Polycyclic Aromatic Hydrocarbons (PAH)* (US EPA, Comp.).

² Lundstedt, S. (n.d.). *Analysis of PAHs and their transformation products in contaminated soil and remedial processes*. Soljfadern Offset AB.

³ Masten, S. J., & Davies, S. H.R. (1997). Efficacy of in-situ ozonation for the remediation of PAH contaminated soils. *Journal of Contaminant Hydrology*, (28), 327-335.

⁴ Beltran, F. J., Ovejero, G., Encinar, J. M., & Rivas, J. (1995). Oxidation of Polynuclear Aromatic Hydrocarbons in Water. 1.

Company Profile

Piper Environmental Group, Inc. offers ozone technology, equipment, and services for a wide-range of environmental applications. The company designs, manufactures, and integrates ozone systems and related equipment for short and long-term projects, offering equipment for rent or purchase. Services include project design assistance, oxidation pilot studies, contract service, equipment repair, consulting, and chemical treatment.