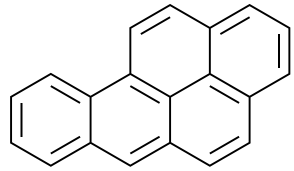
A Proposal for Optimal Removal of Benzo[a]pyrene from Houston Waterways



Benzo[*a*]pyrene

$C_{20}H_{12}$

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Writing 101: *H20 101*
Instructor: Jamie Browne

Specific Aim:

The goal of this research is to find the optimal removal method for one of the most dangerous polycyclic aromatic hydrocarbons—benzo[a]pyrene—from Houston waterways, as work to remove pollutants in these ecosystems is currently lacking. Houston is disproportionately affected by polycyclic aromatic hydrocarbon (PAH) pollution and has a population of nearly 2.5 million (Sansom et al. 2018). By working to find the best removal method, we will take a large step in the right direction to increase the quality of life for Houstonians while improving Houston's aquatic ecosystems. We believe that using a combination of iron oxide nanoparticles and biodegradable corn steep derived biosurfactants will provide the most cost-efficient, quantitatively effective, scalable, and nontoxic method to remove benzo[a]pyrene from Houston waterways.

Background and Significance:

Subsection 1: Introduction

Polycyclic aromatic hydrocarbons (PAHs) constitute a class of dangerous, highly toxic chemicals. Chemicals of this class are omnipresent, appearing in air, waterways, and often within the bodies of organisms. According to public health organizations such as the CDC and FDA, the carcinogenicity of these chemicals is well established (ATSDR 2013). The carcinogenic structural composition of PAHs is known to cause cancers of the skin, lung, bladder, liver, and stomach while also

Joseph Schwartz & Ben Platz, Ben Peng not shown

Joseph Schwartz

Over the course of the semester, my academic writing course H2O 101 introduced me to the struggles many face to ensure that the water in their environment is healthy from the perspectives of both personal use and ecological benefit. Our instructor, Jamie Browne, introduced us to carefully chosen case studies including Flint, Michigan, and the Keystone pipeline, which we collectively analyzed and discussed. This revealed the roles that factors like environmental justice, climate change, and ecological theory play in access to water that benefits people and their environment.

H2O 101 has also broadened my perspective of water beyond the Delmarva peninsula, the area where I was born and raised. The peninsula's intricate labyrinth of tributaries set between the Chesapeake Bay and Atlantic Ocean have always provided an abundance of opportunity in the area through ecotourism, trade, and other industries. I've benefited from such opportunities myself, working as a boat mechanic during high school. This class reaffirmed the idea that water is not always such a plentiful and useful resource. Even in places where it is abundant, access to water and the opportunities it can provide may be extremely limited. One great example of this is Houston, the location our research proposal aims to study. Despite its proximity to Galveston Bay, the Gulf of Mexico, and numerous tributaries, the water quality of the area varies greatly. Areas that are often near lower income communities tend to have worse water quality, and the onset of environmental changes like global warming only exacerbate the worsening water conditions. I feel fortunate to have learned about the societal nature of water through this class and to have had the chance to apply my knowledge in my group's research proposal.

I would like to thank my partners in my writing group, Ben Platz and Ben Peng, for their help constructing this proposal. I would also like to thank Jamie Browne for her continuous support and instruction that challenged us to better understand water's role in the world around us. Lastly, I would like to thank Dr. Sheryl Emch and the Deliberations Editorial Board for their constructive feedback that elevated our proposal.

Ben Platz

While taking Writing 101: H2O 101, I was exposed to many intricacies of water that I had never thought about before. From environmental justice to droughts to wetlands, the course focused on several case studies that provided constant new insights about water in the world. Specifically, as someone who has a special interest in healthcare, I found how pollutants interact with the body to pique my interest.

One place that comes to mind when I think of water pollution is somewhere I have visited countless times in my childhood – Houston in Harris County, Texas. With its numerous industrial districts, Houston is a hotspot of warehouses and factories that store and produce these chemicals as by-products and commercial goods. Even with several sources of clean water feeding into and around the area, the quality of water varies drastically throughout Houston proper and its suburbs, with some freshwater streams being perfectly safe and others putting you at risk of cancers and other debilitating medical conditions. As described in this paper, the goal of our proposal is to research and identify the most optimal method that would remove one of these toxic chemicals – benzo[a]pyrene – from Houston waterways.

Firstly, I would like to acknowledge and thank my research partners Joseph Schwartz and Benjamin Peng for their part in developing this proposal. I would also like to thank Jamie Browne, our H2O 101 professor, for giving us the opportunity to research and develop a project that means a great deal to me personally. Finally, I would like to thank Dr. Sheryl Welte Emch and the Deliberations Editorial Board for their suggestions and feedback throughout the editing process.

This group would like to thank Dr. Sheryl Welte Emch and the Deliberations editorial board for their many suggestions and the opportunity to share this culmination of research from this semester. We would also like to thank our professor, Jamie Browne, for pushing us at every turn to think as critically as possible and to see all aspects of pollution including activism, health, and conservation; this paper would not have been possible without her.

having detrimental impacts on the hematopoietic and immune systems (CDC 2022). Houston, Texas, a coastal city located along the Gulf of Mexico, is particularly vulnerable to the effects of this class of chemicals primarily due to the prevalence of industrial pollution, floods, and environmental justice concerns. Therefore, the best method of removing benzo[a]pyrene (a particularly dangerous PAH) from Houston waterways should be determined in order to benefit the corresponding aquatic ecosystems and to improve the health of those living there. Prior research has not considered Houston directly despite its susceptibility to such chemicals and their presence in urban waterways (Sansom et al. 2018, Bacosa et al. 2020).

Subsection 2: PAH Information

By definition, all PAHs contain multiple bonded rings of aromatic hydrocarbons, resulting in a very stable structure. Benzo[a]pyrene follows this definition with 5 conjoined aromatic rings totaling 20 carbons in structure. The inhalation and ingestion of this chemical are associated with hemolytic anemia, damage to the liver, and neurological damage (EPA 2000).

PAHs are primarily created through combustion. The most common sources of this combustion are fires, burning coal, and refineries. It should be noted that a large percentage of PAHs are formed when burning fossil fuels (ATSDR 2014). After their formation, PAHs enter the environment and bind tightly to particles in the air, water, and soil. Simply breathing, drinking, and eating can result in ingestion of PAHs into the body.

By themselves, PAHs pose little risk. However, the metabolism of PAHs causes a variety of dangerous deleterious effects. Once PAHs are in the body, they are oxidized and begin to react with DNA (Chakravarti et al. 2008). The products of these reactions can remove base pairs from DNA strands, and because of the stability of the new DNA structure, errors can occur in replication causing detrimental mutations. Soon after these mutations begin, they accumulate to such a high degree that cancers form.

Subsection 3: PAH relevance in Houston:

While PAHs can have concerning effects on ecosystems across the globe, Houston is particularly vulnerable to the negative effects of PAH contamination due to its environment and industrial capabilities. These factors can be clearly portrayed through an examination of Galveston Bay, which is encompassed by the Greater Houston area. Rowe et al. (2020) state that "The generally higher concentrations [of PAHs] in biota from Galveston Bay" are a result of "intermittent spills of gas and oil," the bay's proximity to the "urban industrial complex of [Houston]," and "periodic flood events" that redistribute PAHs from land surfaces to the bay. (Rowe et al. 2020). Houston's nearby bodies of water have been so aggressively polluted by PAHs through these means that certain species of fish like the Gulf killifish have changed genetically over time to adapt to the large PAH concentrations of its ecosystem (Franco et al. 2022). The adaptation of animals to this new environment demonstrates a fundamental shift in the state of Houston's aquatic ecosystem as a direct result of human pollution—a worrying trend that could amplify in magnitude over time if PAH levels are not reduced.

The negative effects of PAH pollution are not localized to certain species of fish and aquatic life. PAH pollution is also highly dangerous to humans. Consequently, environmental justice neighborhoods, or neighborhoods "disproportionately exposed" to carcinogens like PAHs "from both industry and transportation infrastructure" like "Manchester, located on Houston's East End" are a point of concern (Sansom et al. 2018). Thus, the removal or remediation of PAHs from Houston ecosystems will benefit both the local wildlife and many of the residents. While it may seem inappropriate to consider the primarily airborne pollution that environmental justice neighborhoods face when discussing the aquatic effects of PAH pollution, empirical research demonstrates that PAHs suspended in aquatic environments are able to circulate into the air in quantities that pose health risks to humans due to surface exchange (Tidwell et al. 2017). As Houston is a city with several large areas of open water, including the Galveston Bay, it stands to reason that lowering the concentration of PAHs in the water would lead to a lower concentration in the air, thus benefiting human health.

Houston's susceptibility to floods provides another dimension of importance for PAH removal, particularly when contextualized with the onset and growing impact of climate change. Floods caused by natural disasters like Hurricane Harvey redistribute PAHs from primarily industrial areas to the rest of Houston, including recreational and residential areas (Casillas et al. 2021). Moreover, in the years leading up to Harvey, the amount of pavement in the greater Houston area increased drastically, replacing the previously existing water-absorbing soil (Bogost 2017). This allows water to wash over the entire area, decreasing the ability to resist flooding. Additionally, floods can transport PAHs from land surfaces to the water, introducing them to aquatic ecosystems and locations farther inland. (Rowe et al. 2020). Quantitative evidence of this has been found through studies like that of Bacosa et al. (2020), which tested water samples in the Houston area shortly after Hurricane Harvey. They found that "four of ten [sampled] sites had benzo-a-pyrene concentrations exceeding the Texas Standard for Surface Water threshold" (Bacosa et al. 2020).

Subsection 4: Future Changes and Conservation:

These findings are particularly worrisome due to the threat of climate change. According to NASA's Earth Observatory, climate change is expected to increase the severity of natural disasters like hurricanes (NASA 2005). This will lead to more Harvey-level disasters, redistributing large quantities of PAHs from industrial areas into both aquatic ecosystems and residential areas more often than ever before. Additionally, climate change is expected to worsen the general water quality of Texas reservoirs (Gelca et al. 2016). By increasing pollutant 5 concentration and decreasing the overall quality of the water, climate change has a monumental capacity to damage or destroy Houston's aquatic ecosystems.

Consequently, finding optimal methods to eliminate toxic PAHs from Houston waterways can help to improve the conditions of Houston ecosystems. By doing so, they will not be sent into a worse stable state, which is a new equilibrium established by pushing an ecosystem from one basin of attraction to another through a stochastic event. This is especially applicable to Houston due to the continuous worsening of conditions and increases in stochastic events spurred on by climate change (Scheffer et al. 2001). By entering a worse stable state, the biological health of Houston ecosystems would be greatly diminished. Returning to the better stable state that the ecosystem currently exhibits would require conditions to be much better than they were at the time of the initial state-swap, which would be difficult to achieve (Scheffer et al. 2001). Avoiding such a state swap by improving the conditions through the removal of PAHs is the best way to ensure the future health of the Houston ecosystems.

Subsection 5: Benzo[a]pyrene Specifics:

Our proposal focuses on benzo[a]pyrene, a common PAH and carcinogen with the structure of a fused benzene and pyrene ring. Although all PAHs are dangerous, this chemical is particularly detrimental to the Houston area for multiple reasons. It is more water-soluble than most PAHs, posing a double threat to both the air and water systems of Houston. It is also identified by the USEPA as a priority contaminant due to its potent toxicity, demonstrating that it is more biologically detrimental than most PAHs (Mojiri et al. 2019). Lastly, benzo[a]pyrene is particularly prone to harmful environmental relocations through events like Hurricane Harvey (Bacosa et al. 2020). This leads to further environmental pollution, and it also means that global warming will greatly enhance this chemical's ability to cause damage. Therefore, in the context of PAH decontamination in the wider Houston area, the scope of this proposal is limited to the removal of benzo[a]pyrene.

Multiple different methodologies have been proposed and tested regarding the removal of PAHs in general and benzo[a]pyrene in particular, all with varying degrees of cost, efficacy, methodology, and support. Among them are the use of iron oxide nanoparticles (Hassan et al. 2018), activated carbon (Ilyas et al. 2021), and lipopeptide surfactants derived from corn (Vecino et al. 2015). This study, based on experimental findings in Houston, aims to evaluate their applicability and practicality to the Houston area's freshwater ecosystems and devise an optimal treatment plan for PAHs that primarily focuses on benzo[a]pyrene.

Overview:

To achieve our goal of determining which existing method of decontamination is most optimally suited to Houston's waterways, we must first consider what an "optimal" solution is. The first consideration is the efficacy of the method being examined—the percentage of PAHs in general and of benzo[a]pyrene in particular removed by the method. While a filtration technique may work in a laboratory setting, a wide variety of factors may make it unsuitable for use in large-scale aquatic ecosystems since they are many degrees of magnitude larger in volume than laboratories, and life within the ecosystem must be considered. Additionally, the optimal method must be environmentally safe; there is little reason to put our decontamination method into use if it also contaminates waterways in some other fashion. Taking all of these factors into account, the optimal decontamination method must be relatively cost-efficient, quantitatively effective at reducing PAH concentrations, scalable to Houston's waterways, and nontoxic.

Hypothesis:

Having reviewed the existing methods of benzo[a]pyrene decontamination present in the literature, we believe that a combination of green iron oxide nanoparticles (Hassan et al. 2018) and the use of corn steep derived biosurfactants (Vecino et al. 2015) is optimal for application to Houston's waterways. This is because these methods best target our outlined criteria. While iron oxide particles serve to catalyze the photodegradation of PAHs, meaning that they assist in the breakdown of PAHs after exposure to light, surfactants increase the solubility of PAHs by lowering the surface tension of water, making them more prone to biodegradation. Both are highly cost-efficient, as they can be derived from waste products from the agricultural industry, namely pomegranate peels and corn husks respectively. The cultivation of both products occurs in Texas. Unlike methods proposed by Gong et al. (2017) that require active human intervention and maintenance like the use of electrocoagulation (applying a surface charge to water that helps separate suspended matter), both iron oxide nanoparticles and biosurfactants work passively—no active attention is required to maintain their efficacy, making them practical for use in the wide array of Houston's aquatic systems. Even more importantly, they are both highly efficacious. Iron oxide nanoparticles remove benzo[a]pyrene experimentally at a rate of 99%, the highest out of all measured methods, and while corn steep derived biosurfactants were not as effective at removing pyrenes specifically, they proved highly effective at removing other carcinogenic PAHs. The two methods complement one another by optimizing the removal of benzo[a]pyrene as well as widespread PAH removal.

Additionally, and perhaps more critically, both iron

oxide nanoparticles and lipopeptide biosurfactants pose no threat to the environment due to their organic sourcing. Other methods, like the use of activated carbon, are deficient in this manner. For example, the activated carbon likely has no negative effects when used to process human wastewater (Ilyas et al. 2021). However, addition of carbon to aquatic ecosystems could unnaturally alter the carbon cycle of the ecosystem and negatively impact health, making it an unsuitable candidate. Due to these factors, we hypothesize that out of all studied methods, the combined use of biosurfactants and iron oxide are the most well suited for use in Houston's aquatic ecosystems. For these reasons, our study aims to provide an experimental evaluation of the efficacy and the efficiency of removing benzo[a]pyrene using this combination of decontaminants.

Proposed Methods:

As the majority of the literature referenced in the hypothesis was proposed and tested for its efficacy in decontaminating human wastewater, not naturally occurring aquatic ecosystems, further testing is needed to confirm our hypothesis. Firstly, although both decontaminants are hypothetically nontoxic, the environmental effects of our proposed decontaminants (iron oxides and biosurfactants) must still be determined. This will be done by comparing simulated aquatic environments in a lab environment treated with both decontaminants; natural aquatic environments will serve as controls. If this confirms that no environmental damage will result from the introduction of the proposed decontaminants, the main experiment will be conducted. Environmental impacts will also be evaluated in the field by comparing environmental metrics between our field data and our control environment. The same metrics checked in our simulated lab environment will be evaluated in the field to ensure that neither decontaminant is harming the environment. We plan to conduct our research in the Brays Bayou—the watershed of the aforementioned Manchester neighborhood that is a focal point of environmental justice (Sansom et al. 2018). In the bayou, 4 sections of comparable freshwater will each be subjected to different 9 treatments: biosurfactant and iron oxide, only biosurfactant, only iron oxide, and no treatment (a control). The effectiveness of all 4 trials will then be evaluated through PAH concentration measurements and other relevant empirical data using the quantitative measurements outlined in Li et al. (2016). The trials will take place over the course of one year to minimize the impact of seasonal variables on decontamination. Although more research must be done into the method's effects of saltwater decontamination, the best method of decontamination in freshwater will be established based on a comparison of these measurements and models.

Expected Results:

Based on thorough consideration of previous studies on biosurfactant and iron oxide particles, we expect that the experimental results will be in line with our hypothesis. While the concentrations of both agents are feasibly able to be reached in running water ecosystems, they may be lower than in controlled experiments. We still expect to see a significant drop in benzo[a]pyrene concentrations to a point where risks of negative effects on human and aquatic life will be significantly reduced—ideally at least to the EPA limit of 0.2 parts per billion (ATSDR 2013), but preferably as low as possible.

Conclusion:

PAHs in general, and benzo[a]pyrene in particular, are highly dangerous to both human and aquatic organism health. As an area presently contaminated with high levels of aquatic PAHs and uniquely poised to continue to be affected by PAH contamination events, Houston residents and wildlife are particularly vulnerable to the detrimental effects of PAH water contamination. We anticipate experimentation will reveal that the combined use of corn-derived biosurfactants and iron oxide nanoparticles will prove the most effective method for remedying aquatic PAH contamination similar in severity and salinity to the kind present in Houston. This research will not only provide pertinent findings on PAH decontamination in Houston, but also serve to improve other industrially polluted freshwater urban waterways across the globe.

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