An Overview of Volatile Organic Compound (VOC) Emissions from Wastewater Treatment and their Impacts

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I. Abstract

Volatile organic compounds (VOCs) are chemical compounds that can transform from an aqueous to a gaseous phase. This literature review explores the various emission mechanisms that VOCs are subjected through different wastewater treatment processes. Exploring the history of VOC emission regulations, the literature review builds up to the current state of VOC regulations on wastewater treatment plants (WWTPs). The main emissions stem from aeration type processes, as they increase the gas-to-air ratio of VOCs, allowing them to volatilize. The author uses their experience as a wastewater engineering intern at an oil refinery to explore the emissions calculation techniques used in industry and their effects on not only production but also the health of surrounding communities. VOCs have a range of health risks spanning from hazard risks to long-term health effects due to their toxic and carcinogenic nature. The literature review ends with a link between environmental justice and industrial pollution, noting the infamous "Cancer Alley." The review ends by claiming that the cost of industrial pollution, and its effects, are not internalized into the cost of manufacturing and that the burden must be built into the cost of these products so as to address the environmental justice issues of industry.

II. Introduction

The inspiration behind the topic of this honors thesis was an internship done by the author during the summer of 2020. At the ExxonMobil Baton Rouge Chemical Plant and Refinery, the author held the role of Environmental Intern for the complex, working on projects interfacing with each of the two wastewater treatment plants located within the complex. The author’s main project was the creation of a VOC emission model with the goal of estimating emissions from ancillary wastewater equipment to aid in Title V regulatory permit compliance.
This topic fascinated the author as it has a large impact on industry operations, the environment, and human health. Throughout the author’s experiences, he established an interest in industrial operations, as large industries, such as oil and gas, are often antagonized by the public; however, their functions are crucial to creating society’s modern lifestyle. The author is also interested in exploring the intersectionality between such industries and their impact on human health and the environment.

According to the Environmental Protection Agency (EPA), volatile organic compounds (VOCs) are chemical compounds that are characterized by a high vapor pressure and low water solubility [1]. These properties allow VOCs to easily leave solid and liquid phases as gases emitted into the atmosphere. “VOCs are often components of petroleum fuels, hydraulic fluids, paint thinners, and dry-cleaning agents” [1] making industries like petroleum refining, petrochemical and chemicals, and others subject to dealing with the regulatory implications of manufacturing such products. While there may be VOC emissions associated with the manufacturing process of these products, this research paper examines a once lesser known issue of emissions associated with the wastewater treatment of relevant industries.

VOCs have a slew of impacts on human health, the environment, and industry operations. Wastewater treatment plants run wastewater through a number of physical and chemical processes which allow for VOCs to transfer from an aqueous phase to a gaseous phase. The area surrounding these plants is often subject to volatile odors that can cause discomfort among plant employees and the surrounding community [4]. Depending on the composition of the wastewater, the VOCs emitted may be carcinogenic, damage to the liver, kidney, and/or central nervous system. “Moreover, some of these compounds can cause a number of psychosomatic symptoms such as anxiety, stress, headache and dizziness, nausea, [and] loss of consciousness”
Such emissions must be estimated by the plant and permitted with the appropriate environmental regulatory agency. Later in this paper, specific compounds and their impacts will be explored and elaborated upon as well as VOC estimation methods currently used.

III. History

In the past, more attention was given to managing emissions associated with highly visible area or point sources of VOC emissions, like boilers, incinerators, and wet gas scrubber smokestacks. Since wastewater treatment plants (WWTPs) did not intuitively fall under a potential source of air pollutants, regulatory attention on WWTP emissions did not start until the early 1990s with the onset of the 1990 Clean Air Act Amendments (CAAA) [2]. The reason for the amendments was a study done by the EPA that concluded certain industries which produce or create a byproduct of VOCs were subject to generating a high concentration of VOC emissions during wastewater treatment. To meet wastewater discharge permit limits (for parameters like dissolved organic compound concentrations, biological oxygen demand (BOD), and suspended solids), wastewater is passed through primary and secondary treatment processes which are very often open-air systems, allowing VOCs to make their way into the atmosphere with little to no control mechanisms [3].

Before the 1990 CAAA, WWTPs were regulated for the wastewater they produced and as such industries based their unit processes and treatment on NPDES (National Pollutant Discharge Elimination System) permit limitations. During this time period, the Air Force Institute of Technology recounted that despite upgrades to their own WWTPs to meet NPDES permit limits, they were already at risk of noncompliance with the added requirements of the Clean Air Act (CAA) [2]. Other industries like the organic chemicals and plastics, pesticides, pharmaceuticals, hazardous waste treatment and disposal, petroleum refining, and paper
industries were particularly subject to the new amendments as they were identified to be major contributors to the VOC emissions. For these specific industries, the EPA released a guideline series with recommendations for each industry to control their WWTP VOC emissions. The EPA realized the technological limitations in capturing and treating VOCs associated with wastewater treatment and as such recommended that industry “apply waste minimization techniques [upstream] to reduce the volatile organic loading of the wastewaters” [3].

A significant addition that came alongside the CAAA was the Benzene Waste National Emission Standards for Hazardous Air Pollutants (NESHAP) which “…[required] the control of benzene-containing wastewater streams generated by [chemical plants, refineries, and coke recovery plants]” [3]. A direct effect of this NESHAP was in the integration of benzene strippers that processes benzene containing wastewater and oil before treatment or recycling. There is no doubt that the discovery of Hazardous Air Pollutants (HAPs) emissions from wastewater treatment had a great impact on industry operations; thus, it is vital to consider how these changes began in order to understand why processes and regulations are the way they are now.

IV. VOC Emission Mechanisms for Wastewater Unit Processes

In this section, various wastewater unit processes will be explored as well as their associated emission mechanisms. The purpose of this section is to provide more background on wastewater treatment processes while also explaining how these processes can lead to VOC emissions. The list of unit processes is not comprehensive of all wastewater treatment plants.

Akin to the name, preliminary wastewater treatment happens before the water is run through the rest of the plant. There are different forms of preliminary treatment, one is to remove large solids by running the wastewater through bar racks or screens equipped with small
openings. The goal is to filter out various contaminants (like rags, gloves, ‘flushable’ wipes or sticks) that would otherwise damage or clog downstream equipment, pipes, or channels. These types of screens can typically be found at municipal wastewater treatment plants due to the wide variety of items people flush down the toilet or industrial wastewater treatment plants as debris can wash up in sewers making their way eventually to the WWTP. The main emissions associated with bar racks comes from the turbulence subjected to the wastewater when passing through the screens [5]. Turbulence causes the water to splash and form small droplets which increase the contact of wastewater to the atmosphere (creating a higher gas-to-liquid ratio). Gas-to-liquid ratio is a major contributor to VOC emissions having a directly proportional relationship to the amount of emissions [5].

Another form of preliminary treatment used in industrial applications are flow equalization tanks. These tanks are equipped with baffles that are meant to homogenize the wastewater prior to treatment. Wastewater is stored in these tanks prior to being fed to the downstream treatment processes in an effort to “…dampen flow rate variations and optimize downstream treatment process variations” [5].

A large contributor to WWTP VOC emissions is associated with aeration tanks. These tanks are typically open-top and run air bubbles through wastewater prior to further treatment. This should not be confused with the Dissolved Air Flotation (DAF) treatment process which will be discussed later on. The purpose of these aeration basins (in context with a refinery wastewater system) is to oxidize $\text{SO}_2$ (sulfur dioxide) into $\text{SO}_4^{2-}$ (sulfate) and to qualify for a specific hazardous waste exclusion. The purpose of converting sulfur dioxide into sulfate is to reduce chemical oxygen demand downstream of the treatment process to aid with biological treatment. The hazardous waste exclusion can be found within RCRA (Resource Conservation
and Recovery Act), which stipulates that (in the context of specific applications) if air is added to wastewater then the downstream effluent and solids are no longer considered hazardous waste. This allows wastewater treatment byproducts downstream to be recycled and converted into products or managed cheaper. Referencing the gas-to-liquid ratio concept mentioned above, by adding air to wastewater contaminated with VOCs, the ratio is increased thus causing more emissions. The air bubbles allow VOCs to volatilize and escape the wastewater [5]. Since the bubbles originate from the bottom of the tank and make their way toward the surface, there is a large amount of contact between the VOCs dissolved in the water and the air bubbles further contributing to emissions. Each VOC has a specific Henry’s law constant which is a measure of a compound’s volatility (ease of diffusion into the air), thus some compounds can more readily volatilize than others.

When wastewater reaches the DAF tanks, flocculant and coagulant have already been added and mixed. These chemicals are mixed typically in closed-top tanks with the purpose of allowing suspended solids to come together to form floc. According to the EPA, DAFs pressurize a portion of the wastewater stream to dissolve excess air and then depressurize to release the air. This process forms very small bubbles around suspended solids in the wastewater which start to rise to the surface. While the bubbles are rising, floc is drawn alongside them to the surface where a skimmer removes the floating solids. The magnitude of VOC emissions from DAF tanks varies depending on the saturation of bubbles and the presence of floating solids from the surface [5]; thus, optimal DAF function would ensure the float is skimmed in a timely manner. Since DAFs do not biologically process the VOCs, a way to estimate the VOC volatilization occurring during the process would be to sample both the inlet and outlet for targeted contaminants and perform a mass balance to analyze contaminant fate. A similar process
can also be done for other nonbiological process units, like the aeration tanks; however, this would be expensive as extensive sampling and monitoring would be required.

Biological treatment often relies on a process known as the activated sludge process. According to the EPA, this process “…removes about 85% of the organic matter in sewage by making use of the bacteria in it” [7]. The process works by utilizing the bacteria and microorganisms within the solids of the wastewater to digest and break down organic matter and compounds into less harmful byproducts. The suspended solids, also known as mixed liquor, are recycled to maintain a proper culture of bacteria that can readily process and breakdown organic compounds. Each wastewater treatment plant has a specific ‘culture’ of bacteria that is specialized to breakdown volatile organic compounds in the wastewater stream. It is the responsibility of the wastewater operators to ensure the bacteria are the appropriate age and readily digesting organic compounds. This is done by adding return activated sludge (RAS) to the biological treatment tank(s).

Biological treatment tanks are specialized with various types of aeration systems that contribute to VOC emissions differently. These systems include diffused air, mechanical aeration, and high purity oxygen (HPO) systems [5]. Diffused air systems infuse large volumes of ambient air into the activated sludge process to increase the dissolved oxygen (DO) concentration [5]. The purpose of increasing DO is to provide the aerobic biomass more oxygen than what is demanded to maximize the biodegradation efficiency of VOCs [5]. Similar to other aeration basins, the bubbles allow for the transfer of VOCs from the wastewater to the bubbles which are emitted at the surface. HPO systems are typically closed-top biological treatment tanks, where instead of atmospheric air, pure oxygen is injected into the wastewater. The use of pure oxygen rather than atmospheric air (which is only around 21% oxygen [8]), allows for a
much lower venting rate than in diffused air system [9,10] thus decreasing the amount of VOCs volatilized directly into the atmosphere. Venting rate is the amount of gas fed into the system over a period of time. Lastly, mechanical aeration systems allow for oxygen to be transferred from the atmosphere into the wastewater through mechanical agitation of the wastewater flow [5]. However, the aerators causing the agitation also create turbulence that create aerosol particles [10], leading to splashing which significantly increases VOC emissions.

Secondary clarification follows biological treatment. It is important to note that while it is typically penned ‘secondary’ clarification, for some industrial wastewater treatment plants, the ExxonMobil Refinery in Baton Rouge, this stage is the first occurrence of wastewater clarification. As the name, clarification, suggests, this stage of the wastewater treatment process allows suspended solids from upstream flow to settle in a tank shaped like a funnel. Wastewater enters through the center of the clarifier and is evenly distributed throughout the settling area towards the bottom [5]. The solids accumulate at the bottom of the funnel-shaped tank and are pumped out of the system in two flow streams. The first stream is return activated sludge (RAS) which is recycled back into the biological treatment tanks to maintain the bacteria at the appropriate age to digest organic compounds. The other flow is waste activated sludge (WAS) which is wasted sludge. Along the edges of the clarifier are weirs that allow clarified water at the surface to pass through. The weirs, which wastewater drops down into (typically a one-foot fall), contributes from 70 to 90% of the VOC emissions associated with clarifier function [10]. The other percentage is from volatilization at the clarifier surface as they are typically exposed to the atmosphere.
With a better understanding of the various unit processes integrated into wastewater treatment, the effects of VOC emissions can now be explored as well as the calculation techniques used by industries to report the emissions.

V. Emission Calculation Techniques and Industry Impacts

There is no exact and cost-effective method to quantify the amount of VOCs being emitted from wastewater unit processes. The wastewater suspected of emitting the VOCs on the other hand can be sampled directly, allowing the plant operators and engineers to know the exact concentration of dissolved VOCs in the water prior to discharge. Wastewater treatment plants use air emission models and factors to estimate the emissions associated with their specific operations. Air emission models rely on understanding the process flow and how it moves throughout the various unit processes. The most commonly used models are: WATER8/9, Toxic Chemical Modeling Program for Water Pollutant Control Plants (TOXCHEM), and the Bay Area Sewage Toxics Emissions (BASTE) Model [5]. WATER8 and WATER9 were created by the US EPA; however, they have not been updated since 2006 and while they are still recognized as an adequate modeling technique, some wastewater treatment plants have opted to use proprietary modeling software. The two proprietary modeling software products are TOXCHEM and BASTE, both created for use by municipal wastewater treatment plants. As such, they can run into some difficulties when modeling industrial wastewater flows. In the author’s experience using TOXCHEM to model wastewater flows, an issue that was experienced was that TOXCHEM cannot account for emissions associated with petrochemical-based oil layers. The program instead assumes oil layers are derived from mineral oil. This presents an issue because mineral oil blocks VOC emissions at the surface of wastewater tanks (underestimating possible emissions). In order to estimate the emissions associated with a petrochemical oil layer, the
Litchfield equation was developed for use by oil and gas refineries using percent volume loss. This workaround indicates the need for a model that is focused on estimating emissions from industrial wastewater applications. By using municipal VOC emission modeling softwares, emissions could be over- or under-estimated leading to inaccurate reporting and permit limits. This is ultimately the largest threat to the communities that house industrial wastewater treatment plants, as there is a possibility of a greater public health risk than what is believed to be true (or the opposite leading to vast restrictions on industrial operations).

It is important to consider the implications of VOC emissions and Title V air emissions reporting on industrial operations. The two are intrinsically interconnected: if pollutant discharge limits were tightened (allowing less to be emitted), then there is a strain on the amount of product able to be created. On the other hand, if pollutant limits were increased, then more product can be created without negative regulatory response. The issue stems from the inaccurate models used to estimate VOC emissions. If the VOCs are underestimated, then the WWTP operators, as well as the public, are at a greater risk of being subjected to high concentrations of atmospheric VOCs. Alternatively, if the emissions are overestimated then regulatory oversight could be too restrictive on industrial manufacturing causing economic strain.

**VI. Health Implications of Atmospheric VOCs**

Some VOCs can contribute to atmospheric photochemical reactions and have a detrimental effect on the environment as well as toxic health effects. A subsection of VOCs known as HAPs (Hazardous Air Pollutants) can cause various cancers and health effects like “eye and throat irritation, headaches, damage to liver, kidney, and central nervous system” [11]. Through inhalation exposure, wastewater treatment plant operators can be subjected to short- and long-term health effects. Subject to local air flows, gaseous VOCs disperse throughout the
atmosphere even further than a 4 km radius, potentially exposing people living in relatively far away areas to cancer risks as well [12]. While each wastewater treatment plant has different VOC speciations, it is important to know the non-cancer and cancer risks associated with site-specific VOCs.

Figure 1 below shows two percentile distributions quantifying the various non-cancer (a) and cancer (b) risks associated with different VOCs [13]. The box plots gauge risk by indicating the minimum (the line furthest left) and maximum (line furthest right) risk with a percentile distribution in the middle (the box). According to Zheng et. al. [13], values exceeding 1 should be paid more attention as they pose a greater risk. Figure 1a displays the hazard rations (HR) for 40 common VOC species. 1,3-butadiene (1.66), acrolein (22.8), and the 95th percentile of 1,2,3-trichloroethane (1.49) require additional attention and caution due to their >1 HR value. Compounds with an average HR between 0.1 and 1, like benzene (0.15), dichloroethane (0.37), and 1,2,3-trichloroethane (0.86) show potential risks. Any compound with an average HR less than 0.1 can be considered to have negligible risk [13].
Figure 1b shows the long-term cancer risk (LCR) of 18 possible cancer-causing VOCs. Anything with a risk $>10^{-4}$ is considered a definite risk, $10^{-5} – 10^{-4}$ a probable risk, $10^{-6} – 10^{-5}$ a
possible risk, and $< 10^6$ a negligible risk. 1,3 butadiene had the highest risk with an average LCR of $6.7 \times 10^{-3}$ [13].

While some of these compounds present less risk than others, it is still important for wastewater treatment plants to assess the speciation of their wastewater, and determine the risk wrought upon their employees and the surrounding community. In the author’s own experience, there were no apparent warnings when visiting a wastewater treatment plant, especially one of high risk associated with petrochemical wastewater. Given the inherent cancer risks involved, perhaps there should be a disclaimer to those living near and working at a WWTP.

Between Baton Rouge, Louisiana and New Orleans, Louisiana, there is a slew of petrochemical manufacturing sites, refineries, chemical plants, pesticide plants, and other industrial manufacturing complexes. These industries are historically known to volatilize VOCs through wastewater treatment and the surrounding communities have been affected as such. There is a nickname for the region located along the Mississippi River between Baton Rouge and New Orleans: Cancer Alley. The air pollution within the region’s communities is among the worst in the United States [14]. The burden is not equally distributed as the plants are built near racial minorities and low-income areas that often have little to no means of enacting change through their voices. While the industrial activity in this region predates a century, it is crucial for not only industry, but also the government to realize the harmful effects of VOCs on ordinary people and at least give disclaimers to those living in high-risk areas. These industries are crucial to supporting the lifestyle sought today; however, it is the responsibility of not only industry but the consumers who buy the products that are manufactured to pay for the externalities of industrial pollution. Including externalities into the cost of products will drive up the price and reduce the quantity of production; however, this is not entirely a negative consequence as
consumers must be aware of the side effects caused by industrial production. The cost is now being unjustly placed on poor communities who do not benefit from the revenues wrought by industry nor the products created by them. This additional cost must go to addressing the public health risks, as well as the environmental implications, of industrial manufacturing. Otherwise, environmental racism and injustice will continue to be an issue that disproportionately harms innocent people. There is a whole field of study that assesses the economics of pollution abatement; there is a solution to finding the intersection between the marginal environmental damage, health risks, and abatement costs to not only satisfy the needs of industry production and sales, but also to be conscious of the risks associated and take actions to mitigate them.

VII. Mitigation and Control Technologies

There are five potential control techniques available to wastewater treatment plants for controlling their respective emissions: traditional vapor phase control, nontraditional vapor phase controls, containment, process and practice modifications, and source control [5]. Each of these control techniques have their advantages and limitations which will be discussed in this section.

Traditional vapor phase control is a commonly used control technology utilized by other industries for VOC control [15]. Thermal oxidation and activated carbon adsorption fall under traditional vapor phase control; however, these are typically reserved for industrial processes that emit greater concentration of VOCs (like incinerators). While it can be applied to wastewater treatment processes, these options would be very expensive to implement and their effectiveness is not guaranteed as they have not been applied to many WWTPs. There is also concern that the water-vapor saturated gas streams associated with WWTPs will cause corrosion and performance issues [5].
Nontraditional vapor phase controls present a more realistic and cost-effective solution than traditional vapor phase controls as they can accommodate the large amount of VOC dilute air emissions associated with WWTPs. These technologies “…include containment by covers, biofilters, atomized mist scrubbers, packed tower scrubbers, IC engines, nonselective oxidizing agents such as ozone and hydrogen peroxide and ultraviolet radiation” [5, 15, 16, 17, 18]. While these control technologies were typically used for managing odor, there is possibility of VOC emission reduction capabilities that must be further researched and explored.

Another possible solution to controlling VOC emissions is containment. By covering treatment processes or simply performing them in tanks or vessels, VOCs are no longer openly emitted into the atmosphere. There are many types and configurations of covers that would need to be suited to the specific WWTP; however, they have been noted with great success. Floating roof covers are reported to have around 85 to 90% efficiency, air-supported structures have around 95% removal in air emissions, and floating spheres have been known to reduce emissions by around 90% and even “…reduce evaporative losses from crude oil plants in the range of 70 to 90%” [5, 19]. Expedited corrosion is a possible risk of this control technique; thus, any roofs or tank structures must be equipped with corrosion resistant coatings.

While the above control technologies can be implemented in new WWTPs, it may be costly to retrofit old WWTPs with new control technologies. In this case, it is worth considering process and practice modifications to limit the additional VOCs that are being emitted through poor process management. Weir drops are a significant source of VOC emissions, so by reducing their height there will be a decrease in emissions. Similarly, avoiding excessive turbulence (splashing) can also help to reduce VOC emissions. The use of high-purity oxygen can reduce
VOCs by 1 to 15%, and the installation of a trickling filter can provide further reductions of 70 to 80% of the influent VOCs.

Lastly, source control is a crucial step to limiting VOC emissions. By optimizing upstream processes to produce less byproducts, then the WWTP has to deal with less, ultimately resulting in a process optimization and less likelihood of wastewater permit breach downstream in the process. This step is crucial before any other step so that the baseline VOC concentrations in the wastewater can be reduced before other control technologies are implemented.

The ideal wastewater treatment plant should assess and utilize the VOC emission control technologies above and create a site-specific goal and plan to reduce emissions. While many WWTPs are already built and functioning, there are optimizations that can be made to address fugitive or additional emissions. New WWTPs should consider the available control technologies prior to building so that they can ensure permit compliance in the future as well as doing their due diligence with pollution abatement.

VIII. Conclusion

Wastewater treatment is not going anywhere anytime soon. While it may not be the most glamorous subject to talk about, without it the lifestyle society has known to come and love would not be the same. During the author’s experience at ExxonMobil, it was told to him that the wastewater contact engineer was often ‘ranked’ at the bottom of the social totem pole because there was no product or revenue associated with the wastewater plant. However, the wastewater contact engineer laughed and said that if the wastewater treatment plant was ever to cease operations, then the entire plant would also shut down. This interconnectedness between wastewater and the products that humans assign monetary and personal value to is crucial to understand and appreciate. Wastewater treatment comes with its own risks and while it is not
always regarded with the same fervor and passion as revenue creating streams, it must not be ignored. The risks associated with production continue to make themselves apparent through wastewater treatment emissions and the people who are disproportionately affected by the carcinogenic and chronic health effects associated with it. As a society, we must come to realize the externalities associated with manufactured products and internalize those costs. Plastic, a widely manufactured and used material in the 21st century is derived from crude oil. Imagine the burdens involved to extract the crude oil from the earth and transform it to create the water bottle near you. The plastic may have been cheap to buy, but its externalities have not been considered; the greenhouse gas emissions contributing to global warming, the cancer cases caused by VOCs emitted during production and wastewater treatment, and the microplastics embedded in animal tissue and human organs [20]. Who will pay the price?
References


[11] USEPA An introduction to indoor air quality (IAQ) , 5th December, 2011,


