Modeling Atmospheric Transport of Perfluorinated Alkyl Substances from Chemours Facilities Using CALPUFF View

Thesis

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Abstract

The Chemours Washington Works (Parkersburg, West Virginia) and Fayetteville Works (Fayetteville, North Carolina) facilities produce fluoropolymers using per- and poly-fluorinated alkyl substances (PFAS). Historically, these sites used perfluorooctanoic acid (PFOA) in the production of fluoropolymers, but due to health concerns and an effort to comply with U.S. EPA's Stewardship Program, PFOA was phased out and replaced by the hexafluoropropylene oxide dimer acid (HFPO-DA), or GenX, which is still in use today. Waste streams from this process includes both aqueous discharge from nearby rivers, and air emissions, which follow the prevailing winds. The Ohio River flows to the southwest away from the Washington Works site, while the Cape Fear River flows to the southeast away from the Fayetteville Works site. The prevailing wind direction is northeast for both Washington Works and Fayetteville Works.

At both sites, PFAS have been detected in downwind surface and ground waters, implying human health risk due to the air emission pathway. However, the extent and amount of contamination is uncertain. The purpose of this study is to model the atmospheric transport of both chemicals at both facilities using CALPUFF – a non-steady-state, long-range transport model. CALPUFF utilizes land use data and terrain data from the United States Geological Survey (USGS), as well as surface and upper air meteorological data. Here, prognostic meteorological data was used for the representative year of 2017. These data are used, along with the geographic inputs, characteristics of the chemicals, and emission information, to calculate dry, wet, and total deposition of each chemical. Modeled deposition rates are evaluated against soil samples and observed wet deposition near the sites, giving a better idea of how these substances behave and how the public is being affected. CALPUFF View (a Graphical Users Interface [GUI] for CALPUFF) is able to model at a larger spatial scale than the physical samples, giving us more insight into how these pollutants travel over time and space. Although it would be suspected to find higher concentrations downstream of the rivers, the model correlates with samples taken and indicates that higher readings are in the direction of the prevailing winds – proving that transportation by air is an important factor to consider in terms of emissions and deposition. The results of this study can be extended to predict atmospheric chemical transport and potential drinking water source contamination near any fluoropolymer manufacturing facility.

Dedication

To my parents, for all of their love and support throughout my academic journey.

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Chapter 1. Introduction/Literature Review

A. Background

Perfluorooctanoic acid (PFOA; sometimes referred to as C8) is a perfluoroalkyl substance that has been used in the production of fluoropolymers (Savitz et al. 2012; Gallo et al. 2012). Fluoropolymers are a popular surfactant for non-stick cookware. They can also be found in a number of other common products such as materials used in construction, automobiles, electronics, food packaging, and firefighting foam (Barry et al. 2013; Sajid and Ilyas 2017; Paustenbach et al. 2007). The use of PFOA has been phased out due to toxicity issues and its environmental persistence. In 2016, the United States Environmental Protection Agency (USEPA) established a health advisory level of 70 ng/L for the sum of both perfluorooctane sulfonic (PFOS) and PFOA (USEPA 2016; US EPA 2016). However, there is evidence that over 6 million US citizens are exposed to levels above this threshold (Hu et al. 2016). Although PFOA and PFOS have received much of the attention, there are still many similar compounds that are vastly underresearched (Lindstrom et al. 2011).

Due to the unique carbon-flourine bond of these compounds, PFOA and other per- and poly-fluorinated alkyl substances (PFAS) are resistant to degradation. Because of this, they have the tendency to persist in the evironment (Lindstrom et al. 2011). Today, there are many companies who use PFASs in their production of many different consumer products (Nakayama et al. 2007; Prevedouros et al. 2006). Many of the longer-chain

PFASs (e.g., PFOA, perfluorooctanesulfonic acid PFOS) have been phased out by the dominant fluorochemical companies due to health concerns (Gebbink et al. 2017; Ahrens et al. 2011); consequently, companies are now using shorter-chain PFAS as replacement compounds (Gebbink et al. 2017).

Even though use of these compounds has been reduced in most developed countries, it is difficult to say whether or not progress is being made in other parts of the world. As of now, there is nothing to replace these compounds in the industrial world. Because of this, it is quite likely that companies will continue to use substances like these for consumer products in the future.

In this work, the focus is primarily on PFAS use at DuPont/Chemours facilities (i.e., Teflon®-related processes). There are two sites of interest: one in Washington, West Virginia (Washington Works) and one in Fayetteville, North Carolina (Fayetteville Works). PFOA was phased out at Washington Works around 2013, but an emerging compound hexafluoropropylene oxide dimer acid (HFPO-DA), or GenX, was introduced shortly after to replace PFOA. GenX has been in use at the Fayetteville site for roughly the same time period (and is where GenX is actually produced), but at present, there are fewer references providing information about Fayetteville Works than about Washington Works.

B. Health Effects

Polyflourinated compounds (PFCs) have been in-use commerically for over 60 years, and have already proved to be toxic and bioaccumulative in food chains. In humans, PFOA is not easily biodegraded with a half-life of roughly 3-3.5 years (Winquist et al.

2013). Environmentally, PFOA is persistent, which is why it can be found globally, even in remote areas (e.g., the Arctic (Butt et al. 2010)). Drinking water is one of the major sources of human exposure. Other sources include ambient air, house dust, and eating contaminated produce (Herrick et al. 2017; Hoffman et al. 2011). Although it is estimated that 99% of humans have PFOA in their bloodstream with a mean serum concentration of approximately 4 ng/mL (Steenland and Woskie 2012; Post et al. 2012), the residents in Ohio and West Virginia exposed directly to contaminated drinking water have a median serum concentration of approximately 28.2 ng/mL. It is more common to see lower values distributed widespread, but there is evidence that even those who are exposed at low doses can experience an increase in their serum level (Post et al. 2012).

In terms of non-occupational exposure, the highest contributor of PFCs is likely to be contaminated food and drinking water. A study showed that a primary food pathway could be seafood that comes from polluted water (Fromme et al. 2009). Some bluegill that were sampled from the Mississippi River were shown to have between 50 – 100 ng/g of PFOS in them (Delinsky et al. 2009). Although fish is a prominent pathway, consumption of contaminated crops is also a concern seeing as agriculture is at risk to be treated with products with PFOS or PFOA in them. Plants absorb the chemicals from the soil, and then these plants are either directly eaten by humans or are eaten by animals who are then eaten by humans. Crops are also being treated with contaminated biosolids from industrial sources (Stahl et al. 2009; Yoo et al. 2011; Sepulvado et al. 2011).

PFAS can enter into the human body in a number of ways, including inhalation of outside air, dust, dietary consumption is a large portion, but the most important and largest exposure variable is drinking water (Hu et al. 2016; Rahman et al. 2014; Emmett et al. 2006; Hölzer et al. 2009). In the Little Hocking community drinking water distribution system, which is located next to DuPont in West Virginia, levels of PFOA were detected as high as 10,100 ng/L, with an average of 4800 ng/L (Rahman et al. 2014; Paustenbach et al. 2007). Due to the high water solubility of PFAS, contaminated drinking water is an especially dangerous source. (Hu et al. 2016; Emmett et al. 2006; Landsteiner et al. 2014). Even at low levels within the water, this can prove to be a hazard to the general population as this can lead to elevated levels in humans (Hu et al. 2016; Hurley et al. 2016). A study was done to find an immunotoxicity dose for children in terms of PFOA and PFOS. Another study with rats was done to measure sensitive points such as their mammary glands, and both of these studies yielded a result of approximately 1 ng/L (Hu et al. 2016; Post et al. 2012).

Health impacts from PFOA and other PFASs are widespread and all have a varying degree of uncertainty. Animal tests of mice, rats, and monkeys have found to cause liver, testical, and pancreas tumors, weight loss, impaired thyroid hormone homeostatis, decreases in some immune responses, negative reproudctive outcomes, liver enlargement, reduced birth weight, and neonatal death (Darrow et al. 2013; Gallo et al. 2012; Hoffman et al. 2011; Winquist et al. 2013; Steenland and Woskie 2012). These studies have proved, however, that the liver is the main target organ. (Frisbee et al. 2009; Griffith and Long 1980; Butenhoff et al. 2002; Paustenbach et al. 2007; Kennedy 1985, 1987, Kennedy et al. 1986, 2004) Causality cannot be referred back to correlation, but there is a strong consistency of certain endpoints (Post et al. 2012).

According to the USEPA Science Advisory Board, PFOA is classified as "likely to be carcinogenic in humans" (Post et al. 2012). A study of approximately 70,000 participants, deemed the "C8 Health Project," was conducted in 2001 due to a class action lawsuit against DuPont (Darrow et al. 2013; Frisbee et al. 2009; Gallo et al. 2012). In order to participate, the person had to have been exposed for a minimum of one year between 1950 and December 3rd, 2004 to one of the six contaminated water districts near Parkersburg. Generally, contaminated water was the major source of exposure to PFOA. Participants were asked to complete a health survey that asked for demographic information, family history, pregnancy history, water usage, and medical diagnoses including what medicine they were taking. Diagnoses that were reported and verified consisted of neurologic disorders, thyroid disease, autoimmune disorders, heart disease, pregnancy complications, and cancers. The C8 Science Panel, consisting of three epidemiologists, was assigned to determine as a goal whether the "probable link" between PFOA and human diseases that the court termed was valid or not. (Frisbee et al. 2009).

There were roughly 36,000 validated diagnoses in total. Some of the validated medical diagnoses that were reported were inflammatory and autoimmune disorders, cancers, thyroid disease, heart disease, and pregnancy complications. The self-reported diagnoses, confirmation or negation, and alternate diagnosis where it was applicable, were all reported for those diagnoses. The study later proved in their results that the unadjusted study population geometric mean (28.2 ng/L) was six to eight times higher than that of national values in a study done by the National Health and Nutrition Examination Survey (Frisbee et al. 2009).

Although the C8 Health Project is one of the most extensive and largest study of this type to date, there have been a variety of others that did similar work. There have been numerous studies that focus on the workers directly exposed to PFOA. One found a heart disease exposure-response trend that was positive (Sakr et al. 2007), while another found trends that were suggestively positive for prostate cancer and pancreatic cancer. However, these latter results had a small sample size (Lundin et al. 2009). There was a study done on DuPont workers that worked in the Parkersburg, West Virginia plant. The workers involved in this study were exposed to PFOA at two orders of magnitude greater than those in the general US population (median of ~403 ng/mL for workers, ~4 ng/mL for general population). The community surrounding the plant had a median level of 28 ng/mL in 2005 of PFOA (Steenland et al. 2009). The primary exposure paths of workers consist of ingestion, inhalation, and skin contact. Twelve deaths were reported in this study due to renal disease. They reported a positive exposure-response trend for renal disease in malignant and nonmalignant. Another study showed similar results in this area, finding the same amount of deaths and an elevated amount of kidney cancer (Leonard et al. 2008).

C. Water and Wastewater Treatment

Due to the concern of PFOA in the drinking water of those surrounding the area, the question arose of what treatment would be best in terms of the drinking water and wastewater. Because these chemicals are not as well studied by scientists as others might be, it makes it more difficult to find a treatment such as this for them. These PFASs come from the use and then the degradation of the products that contain them. At a later time these chemicals make their way into wastewater treatment plants. Because of this, wastewater treatment plants have been identified as a major source of PFASs to surface waters (Rahman et al. 2014; Boulanger et al. 2005; Sinclair and Kannan 2006; Möller et al. 2010; Xiao et al. 2012). Aside from this, any discharge from an industry (waste or biosolids) have also been reported to cause contamination of surface and groundwater (Rahman et al. 2014; Hölzer et al. 2009; Minnesota Department of Health; U.S. Department of Health and Human Services Agency for Toxic Substsances and Disease Registry 2008). It has also been discovered that it is possible that the biodegradation of the precursor compounds can increase the overall concentration of the perfluoroalkyl substances, thus increasing air emissions of PFASs from WWTPs (Ahrens et al. 2011; Schultz et al. 2006; Huset et al. 2008; Hu et al. 2016; Post et al. 2012).

In terms of water treatment in itself, there have been different studies done concerning which treatments are most effective to rid of PFASs in drinking water systems; the rest of this paragraph describes these findings. With the emergence of different kind of PFASs throughout the years, the limited amount of knowledge with these is that any kind of wastewater treatment with short-chain PFASs will ultimately be ineffective (Appleman et al. 2014; Rahman et al. 2014; Hopkins et al. 2018). It has also been shown that treatments such as oxidation, granular/micro-/ultra-filtration, conventional coagulation, sedimentation, ferric or alum coagulation, UV irradiation at commonly utilized disinfection doses and at higher doses typically used for contamination removal, and aeration were all that proved mostly ineffective at removing PFASs from drinking water (Appleman et al. 2014). On the other hand, granular activated carbon treatment proved to be one of the more effective treatments in removing these chemicals, at least in the form of the longer-chains

(Rahman et al. 2014; Hopkins et al. 2018). Reverse osmosis is another method that did a significantly better job at removal, even the smaller compounds (Appleman et al. 2014; Hopkins et al. 2018).

D. Motivation

Washington Works near Parkersburg, West Virginia and Fayetteville Works in North Carolina were the two facilities chosen in this study because of their history of perfluorochemical use and previous research conducted at these sites. Drinking water around the facility in Parkersburg had presumably been contaminated since 1951 (Shin et al. 2011). Considering Washington Works, emissions from the plant were released through the air from stacks and through wastewater discharge into the Ohio River, which resulted in contaminated drinking water sources for local residents of the area (Vieira et al. 2013).

An undergraduate researcher at The Ohio State University performed water and soil sampling around the Washington Works. At first he went downstream of the facility, expecting that the Ohio River would carry any pollutants in this direction. After completing this, he went upstream to take some samples because he figured this water would be pollutant-free, and he wanted some clean samples as a comparison. However, he found that these samples were much higher than those of his downstream trip. The direction of the prevailing winds at Washington Works are from the southwest, indicating that it could be possible that the pollutant was carried upstream by these winds.

The purpose of this thesis is twofold – to discover if these chemicals are indeed being transported atmospherically, and also to find the extent of the pollutant to determine the possible hazards of any communities. This goes for both the facilities in West Virginia as well as North Carolina. Our hypothesis is that these contaminants are indeed being carried via air and then deposited downwind in rivers, streams, and also soil where it then percolates to groundwater.

E. Prior Modeling Efforts

There have been multiple modeling efforts done prior to ours – all with varying approaches and results. With the advancement of air modeling came new studies. The majority of modeling done previously was done at a smaller scale than ours (< 50 km). Also, our focus was mainly downwind of the facility, whereas many of these are focused on the downstream impacts of the chemicals in the Ohio River. Past studies also focused on the effect of the river itself. Although we acknowledge the river as a form of transportation, our primary focus is the transportation of the chemicals in the atmosphere, how it deposits into the soil and then leaches into drinking water.

A study was previously completed at the Washington Works in the early 2000s site using The Industrial Source Complex Short Term Model (ISCST3) (Barton et al. 2006). Along with modeling, actual air sampling of PFOA was done using Occupational Safety and Health Administration Versatile Sampling (OVS) tubes. The highest PFOA samples were detected directly downwind of the facility.

Another study, this time using the American Meteorological/Environmental Protection Agency Regulatory Model (AERMOD) was performed by the same authors (Barton et al. 2010). In this study, their focus was to determine how useful AERMOD is when predicting air concentrations and deposition of PFAS. Deposition is an important factor when considering the transport of PFOA and GenX. The particles in the air of these contaminants can be deposited into surface water or soils via dry or wet deposition. After this, it can then leech further into possible ground water. In order to measure something like this with an atmospheric dispersion model, samples were taken of soil/grass concentrations and then compared to the model's deposition results. There were 42 of these samples available at 16 locations within 3.2 km collected in September and October of 2005. In the end they found that AERMOD was fairly accurate in their case and can be trusted in similar situations. More often than not, however, AERMOD overpredicted the value. To overpredict is more favorable than underpredict, seeing as it would be the more conservative estimate.

The ISCST3 model was used in a different study (Paustenbach et al. 2007), this time to approximate not only the concentrations in the air, but also that in the drinking water, soil, and garden vegetables. It was determined that the most likely case of exposure would be through deposition of particulates from the air to the soil, then from the soil to the groundwater after that. Air samples in local communities show that PFOA is not detected in the vapor phase, and when the model is ran in the vapor phase alone, it underpredicts the values.

Another study took a different approach, using both ISCST3 and AERMOD and comparing them to each other, while also using the EPA vadose zone model PRZM-3 (Shin et al. 2012). The predicted deposition values that came from the air dispersion models were used as inputs for the vadose model and thus used to predict soil concentrations of PFOA. This study chose to primarily focus on soil samples because they believed that they would be less effected by meteorological conditions and changes in emission rates when compared to air concentrations. Measured soil concentrations were compared to the predicted ones produced by the model. Concentrations within the first 30 cm were underpredicted, whereas concentrations beyond 30 cm were overpredicted.

CALPUFF was chosen for this study because it has the advantage of performing better in complex terrain. This is something that AERMOD does an adequate job of, but because CALPUFF is not constant in space and time, it is able to pick up on these finer details. Because Washington Works is in an area with many hills and valleys, we thought it would be best to use this approach instead. Although CALPUFF has never been used for these facilities that we are aware of, we found it appropriate to do research on the work of this model in other places. A hexafluoride tracer experiment was conducted (cui et al. 2011) and CALPUFF was used to model the tracer. The results of this experiment were compared to observational data to compare the quality of the model in a near-field complex terrain setting. With a near-field setting, they tried to simulate an episode of high-pollution, which means conditions of light/calm winds, little to no precipitation, and shallow mixing heights. When winds are very light or calm, they are also highly variable, and the turbulent motions of the atmosphere may be of the same magnitude of the wind speed. Because of these weak dynamics, it is harder for the CALPUFF model to accurately process the tracer.

This experiment was conducted on the bank of the GanJiang River, China, in early May, 2010. Sulfur hexafluoride is released at a steady emission of 5.5 g/s and most of the sampling sites are downwind of the emission site. In order to build a wind field, the five meteorological stations were used as surface data, and upper air data was retrieved twice a day from the GANJIANG station. The wind field was developed using a combination of observation data and data from MM5, a prognostic meteorological model. Based on the wind fields developed by the post-processor, the wind fields looked much more complicated towards the surface. Besides the sharp terrain differences, there was also the river which was changing the winds. The grid for MM5 was not fine enough to improve the wind field, so there were some uncertainties that were taken into consideration. Most of these were seen at the one-hour level, so it was concluded that this was not a sufficient time period to take into serious consideration for results.

The results of this tracer study proved that CALPUFF is able to accurately model the shape and direction of the tracer cloud. However, the one-hour time period is not recommended, as the model cannot accurately represent all of the features in the short-range setting. CALPUFF repeatedly underestimated emissions at peak concentration time. The model generally performs pretty well in long-term settings, but not short-term. Lastly, when it comes to the short-range setting, the dispersion methods are critical. Sharp wind changes can affect the cloud as well as the mixing height, which can affect other components (cui et al. 2011).

CALPUFF consists of 3 components – CALMET (the meteorological preprocessor), CALPUFF itself, and CALPOST (the postprocessor). There are different parameters that go into CALPUFF, but the core parameters are meteorological data (either prognostic or measured), land use and terrain data, and also source parameters. Figure 2 shows this visually.

Chapter 2. Methods

A. Site Description

There were two different sites that were focused on in this case study – Washington Works located near Parkersburg, West Virginia and Fayetteville Works near Fayetteville, North Carolina. Both of these companies were previously owned by DuPont before they transitioned into a spinoff company called Chemours. Our main focus is on Washington Works, as PFAS has been in use here since the 1940s and we have some previous field sampling near this location. However, we do repeat the analysis for Fayetteville Works, but on a smaller scale. The domain at each site was 50 km x 50 km, with the facility located at the center of the domain.

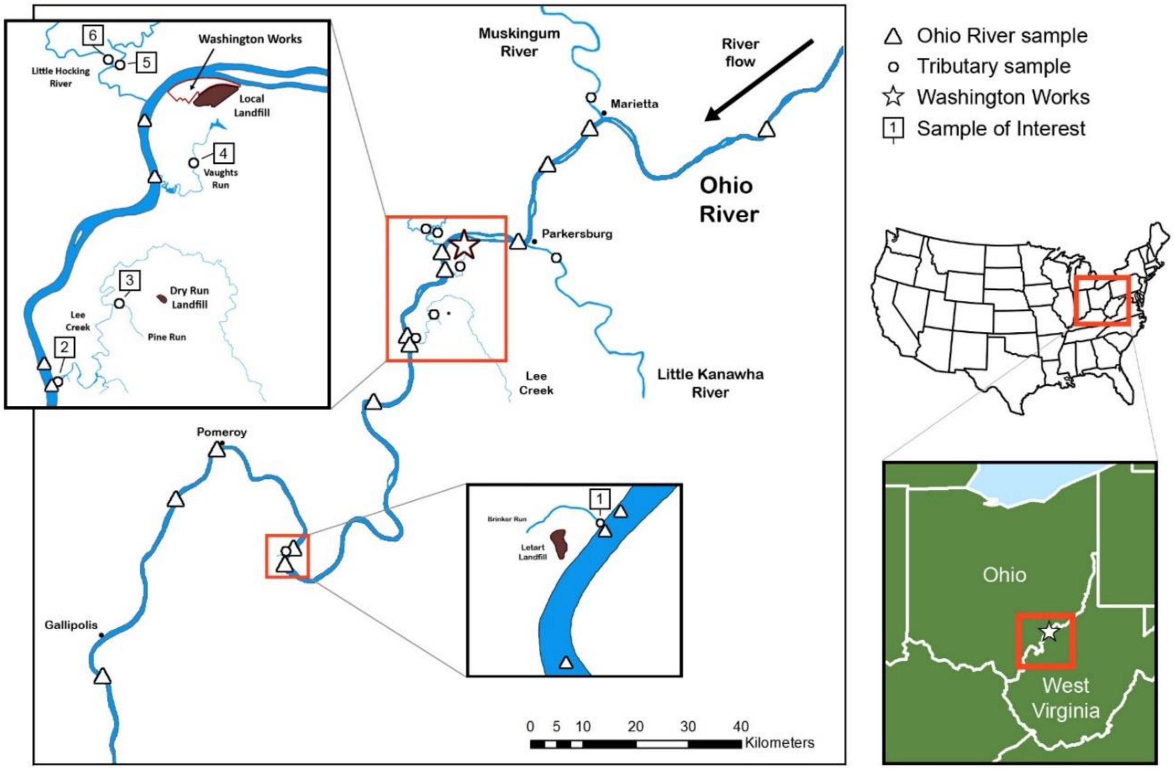


Figure 1. Location of Washington Works (Galloway et al. (in prep))

Washington Works began the use of perfluorooctanoic acid (PFOA) in 1941 and did not begin to phase it out until the early 2010's, in which they introduced a new chemical, GenX, which is still in use today. The Ohio River flows from Northeast to Southwest, but our main concern was Northeast of the facility, because the direction of the prevailing winds are from the Southwest.

B. CALPUFF Model

CALPUFF is a non-steady state puff model developed by Exponent. Although it is described as a long-range model, it can be used for near-field in the cases of complex terrain, atmospheric inversions, coastal locations, and calm/light wind conditions. In this study, we deal with complex terrain since Washington Works is located in the hills of the Ohio River Valley. Specifically, we used CALPUFF View, a GUI (Graphical User Interface) version of the software provided by Lakes Environmental (Waterloo, Canada). This GUI version has the advantage of provided direct graphical outputs compared to the FORTRAN version.

Considering Washington Works is in the Ohio River Valley, it is also very likely to be prone to temperature inversions. Normally, temperature decreases with height, so it is difficult for a model to understand an inversion taking place and temperature increasing with height. A past study used CALPUFF to model a facility that was located in a mountainous region where nighttime winds would often decrease to very calm, thus causing valley flow and non-uniform winds (MacIntosh et al. 2010). This is where the most errors with a model will take place. Dramatically changing winds are difficult for a model to predict, and inversions are often where the most ozone exceedances take place. Pollutants often become trapped in the valley or in between mountains, thus making it nearly impossible for it to disperse how it normally would. This is why models have trouble accurately representing an area of complex terrain such as the Ohio River Valley. According to the same study, CALPUFF is able to provide "reasonably accurate predictions of the patterns of long-term air pollutant deposition in the near-field associated with emissions from a discrete source in complex terrain" (MacIntosh et al. 2010).

The domain is 20 km x 20 km, with grid spacing of 200 m. CALPUFF was run in "regulatory default" mode, found in the User's Guide. Puff and slug methods were both used and then compared at the end. The slug method is where it is a long strand of continuous puffs with very short distances in between them. This is not the recommended setting, as it takes longer than a regular puff run would take. However, in the near-field setting, it can be useful when considering an abrupt change in the tracer and also taking into consideration lower wind speeds. The results proved that the slug method was more efficient in showing short distance movements, but in the longer distances both methods behaved relatively similar. The slug method also proved to perform better in unstable conditions when there is more convection. Overall, slug and puff perform similarly except in near-field settings.

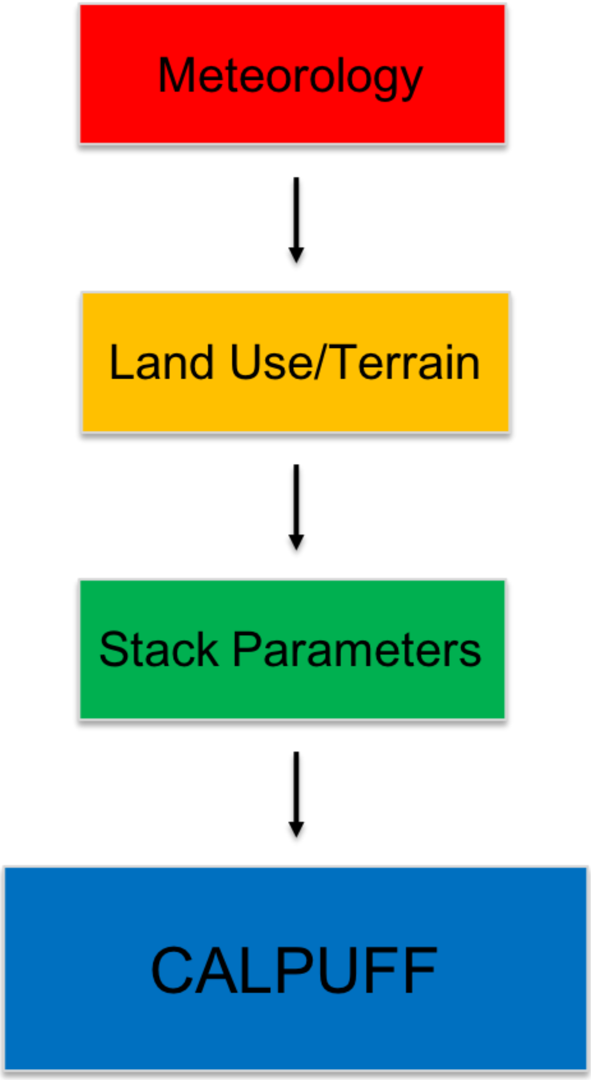


Figure 2. CALPUFF Flow Chart

B.1. CALMET

As previously mentioned, CALMET is the meteorological preprocessor that compiles the information from the meteorological data into a form that is useful for CALPUFF. The types of data that go into this preprocessor are surface data that can be acquired from a weather station, and upper air data that come from airports. CALMET has a three-dimensional (U, V, W) gridded field of air temperature and wind components. It also has two-dimensional fields of mixing height, surface friction velocity, convective velocity scale, precipitation rate, and PGT stability class. The model can use an ISCMET.DAT file and the meteorological type is of ISC3. The minimum data requirement for the file includes hourly wind speed, temperature, mixing height, vector flow direction, and stability class, which can be found in the ISC3 format. Since this research will also model deposition (dry and wet), more variables are also required on an hourly basis: Monin-Obukhov length, surface friction velocity, precipitation rate, and a time-varying surface roughness length. Potential temperature lapse rate and power law profile exponent for wind speed are optional variables, and if they are being used, do not have to be entered every hour – the model will just use its default.

Other data linked with the meteorological data can be found in the CALPUFF.INP control file. Some of these are elevation, land use type, anemometer height, surface roughness length, and leaf area index of the modeling region. The elevation is used to determine the height of the receptor grids that is generated by the model. The land use category is used to determine ground surface parameters such as albedo, Bowen ration, surface roughness, leaf area index, and whether rural or urban dispersion coefficients are needed. Anemometer height is required by the vertical power law extrapolation of wind speed. If dry deposition velocities are being calculated, then leaf area index is used.

SURFACE.DAT and PROFILE.DAT can be used in the model without any additional changes. However, in some optional settings, there are variables that have to be added to the SURFACE.DAT data file. Examples of these are relative humidity, solar radiation, and precipitation data. Included in this file are surface roughness, Monin-Obukhov length, surface friction velocity, and hourly mixing height. PROFILE.DAT is useful in the sense that it takes measurements at multiple heights above the ground rather than just one, creating an accurate vertical profile and representation of upper-air flow. The user of the model generates this file. Included in this file are wind speed and direction, temperature, and turbulence. A potentially useful feature of the “extended” version of PROFILE.DAT is that it can calculate the temperature jump of an inversion above the mixed layer. When judging the potential of a plume to break through the top of a mixed layer, this temperature jump is used as a measure of the strength of the plume (Scire et al. 2000).

B.1.1. WRF

An aspect of CALPUFF that is beneficial is that it can use both observational and prognostic meteorological data. Some examples of prognostic data are MM5 (Pennsylvania State University / National Center for Atmosphere Research Mesoscale Model Version 5) and WRF (Weather Research and Forecasting Model). With prognostic data, the user can input any desirable coordinate, thus allowing to pinpoint the exact location of the facility or the area that is being reviewed. This is especially important in rural areas, where the next meteorological station could be 50 – 100 km away from the actual area that needs to be measured. In the cases of complex terrain, this feature can be especially helpful because the weather station could be located in a valley, whereas the actual facility might not be, or vice versa. Prognostic meteorological models, such as WRF, reduces many of the limitations in CALMET, such as the proper spatial and temporal definition of atmospheric properties, including vertical temperature inversions, distribution of wind field, among others. In this case, a one-year representative dataset (2017) was used. Running WRF for any longer in CALMET would have been too computationally expensive in our scenario.

B.2. CALPUFF

As previously mentioned, CALPUFF is generally ran with a wind and temperature field of three dimensions, and other variables with two-dimensional fields. In the case of a near-field, uniform terrain setting, a single-station data file could be used. When this happens, one value for each variable is assigned to every grid point by the model, which creates a uniform grid. Even with this uniform grid, however, CALPUFF does not make the assumption that meteorological conditions are in a steady-state. Therefore, even with just one station, all the important effects are still taken into account. Transport is still modeled well with curved trajectories and other time sensitive variables. However, since the terrain is not uniform in the Ohio River Valley, we will not be applying this option (Scire et al. 2000).

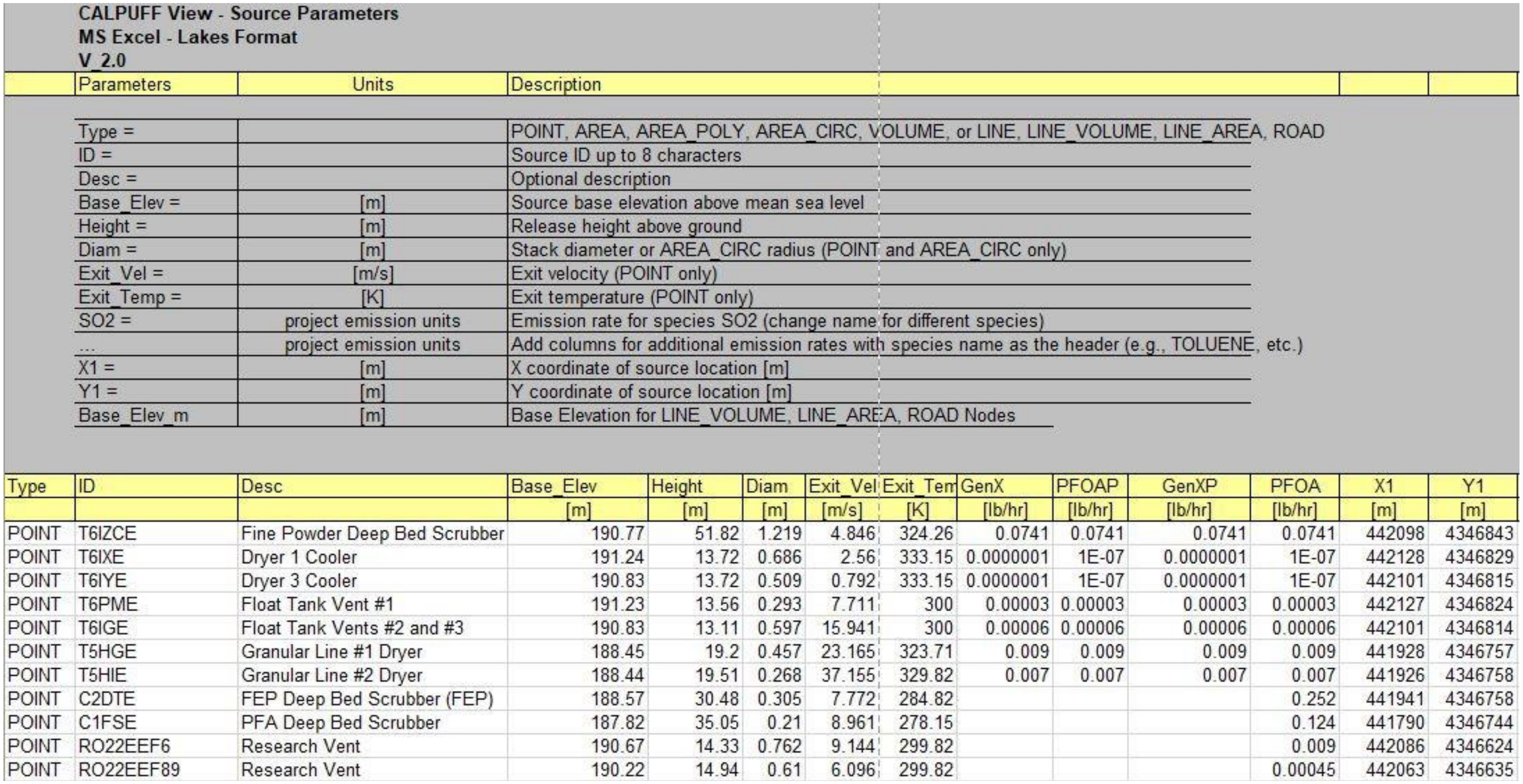
One important factor that affects plume dispersion and transport is vertical wind shear. If pollutants are dispersed at different heights, the different wind speeds and directions could cause different advections of these pollutants. Even if the plume is all emitted at the same height, it may be split because of the shear. There are times when the plume may be brought to the ground because of vertical mixing. In this instance, the horizontal dispersion could be enhanced because of the differential transport. Each puff is modeled independently with its own average wind speed and direction, therefore allowing wind shear effects and mixing to be shown on each one. By taking the profiles from the top and bottom of the puff of wind speed and direction, the average wind for any puff can be found.

Most puff models use a “snapshot” approach in order to determine the concentration at a certain receptor. A sampling step is when a puff is frozen at a certain time interval. At this sampling step, the concentration of the puff is calculated. After this is completed, the puff then moves along and changes until the next sampling step takes place. In order to calculate the concentration at a receptor, the sum of all the nearby puffs are averaged of all the samplings steps inside of a basic time step. A common setback of a puff model is the fact that it may not release as many puffs as may be required to accurately represent a plume. If the distance between the puffs is wider than $2\sigma_y$, then results are not as accurate. Distance between puffs should be no more than σ_y. If the puffs are too far apart and do not overlap like they should, then a receptor could get caught in between them and underestimate a reading, or overestimate if it is directly in the middle of one.

As briefly mentioned before, the slug method is when the puffs are much closer together and overlapping more. Technically, it is supposed to represent a continuous emission of puffs, thus a better representation of a plume. This way, it helps to reduce overlap problems that could be found in the snapshot method described above. Although this feature could be more computationally expensive, it might be worth it in the near-field setting (Scire et al. 2000).

Source parameters for both Washington Works and Fayetteville Works can be found in Tables 1 and 2 below. Necessary stack information is included here. Emission rates are given in lb/hr for both PFOA and GenX – particle phases of these chemicals are indicated by a "P" at the end of the name. The other ones are purely gas phase. These chemicals exist in both gas and particle phase, but this is difficult to model. Although it is believed that PFOA likely exists primarily in the gas phase (and thus, we suspect, GenX), we performed the study in both phases as a way to be more certain of our results. Parameters that we are lacking for both sites, however, are building dimensions. This is an aspect of our study where uncertainty lies, because we were unable to accurately incorporate downwash due to our lack of information in terms of building inputs, we were not able to include this aspect of modeling.

Table 1. Sources for Washington Works (Paustenbach 2007)

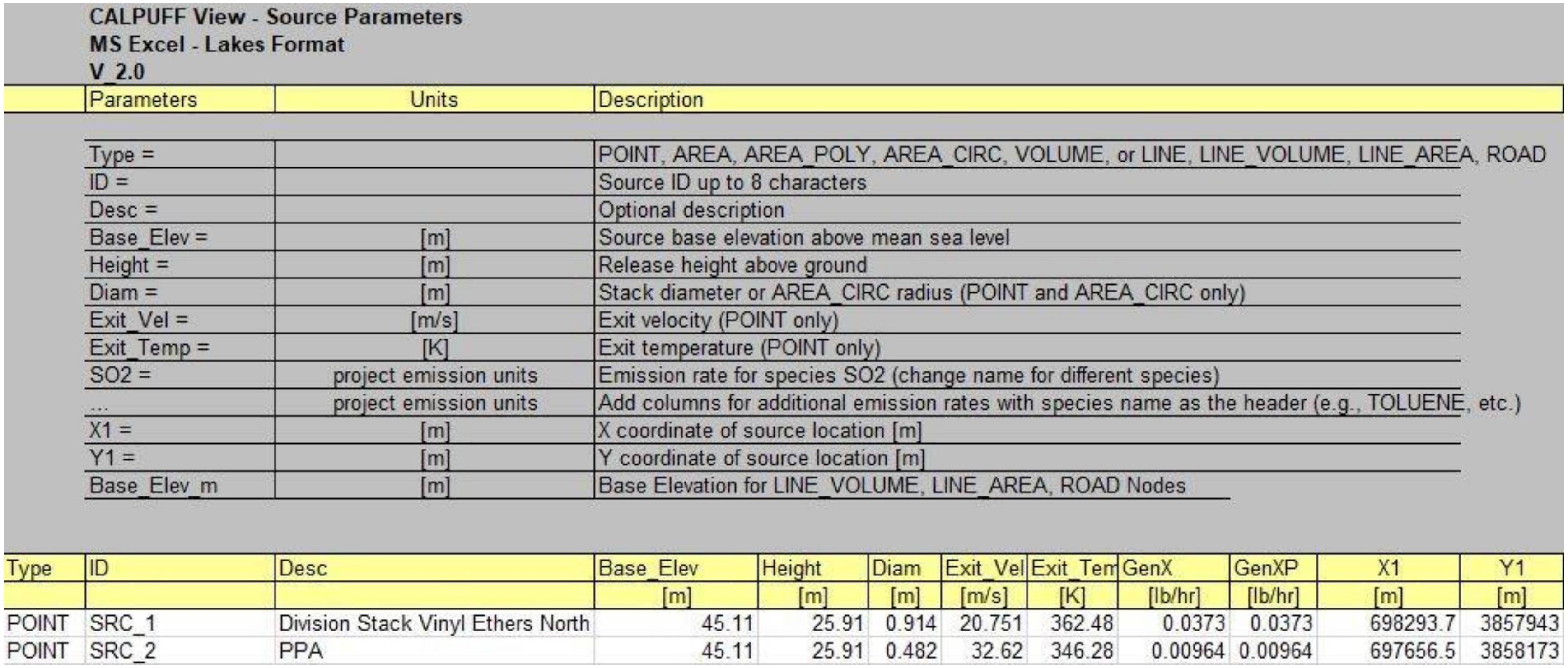


CALPUFF View - Source Parameters
MS Excel - Lakes Format
V_2.0

Parameters	Units	Description
Type =		POINT, AREA, AREA_POLY, AREA_CIRC, VOLUME, or LINE, LINE_VOLUME, LINE_AREA, ROAD
ID =		Source ID up to 8 characters
Desc =		Optional description
Base_Elev =	[m]	Source base elevation above mean sea level
Height =	[m]	Release height above ground
Diam =	[m]	Stack diameter or AREA_CIRC radius (POINT and AREA_CIRC only)
Exit_Vel =	[m/s]	Exit velocity (POINT only)
Exit_Temp =	[K]	Exit temperature (POINT only)
SO2 =	project emission units	Emission rate for species SO2 (change name for different species)
...	project emission units	Add columns for additional emission rates with species name as the header (e.g., TOLUENE, etc.)
X1 =	[m]	X coordinate of source location [m]
Y1 =	[m]	Y coordinate of source location [m]
Base_Elev_m	[m]	Base Elevation for LINE_VOLUME, LINE_AREA, ROAD Nodes

Type	ID	Desc	Base_Elev	Height	Diam	Exit_Vel	Exit_Tem	GenX	PFOAP	GenXP	PFOA	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]	[lb/hr]	[lb/hr]	[lb/hr]	[lb/hr]	[m]	[m]
POINT	T6IZCE	Fine Powder Deep Bed Scrubber	190.77	51.82	1.219	4.846	324.26	0.0741	0.0741	0.0741	0.0741	442098	4346843
POINT	T6IXE	Dryer 1 Cooler	191.24	13.72	0.686	2.56	333.15	0.0000001	1E-07	0.0000001	1E-07	442128	4346829
POINT	T6IYE	Dryer 3 Cooler	190.83	13.72	0.509	0.792	333.15	0.0000001	1E-07	0.0000001	1E-07	442101	4346815
POINT	T6PME	Float Tank Vent #1	191.23	13.56	0.293	7.711	300	0.00003	0.00003	0.00003	0.00003	442127	4346824
POINT	T6IGE	Float Tank Vents #2 and #3	190.83	13.11	0.597	15.941	300	0.00006	0.00006	0.00006	0.00006	442101	4346814
POINT	T5HGE	Granular Line #1 Dryer	188.45	19.2	0.457	23.165	323.71	0.009	0.009	0.009	0.009	441928	4346757
POINT	T5HIE	Granular Line #2 Dryer	188.44	19.51	0.268	37.155	329.82	0.007	0.007	0.007	0.007	441926	4346758
POINT	C2DTE	FEP Deep Bed Scrubber (FEP)	188.57	30.48	0.305	7.772	284.82				0.252	441941	4346758
POINT	C1FSE	PFA Deep Bed Scrubber	187.82	35.05	0.21	8.961	278.15				0.124	441790	4346744
POINT	RO22EEF6	Research Vent	190.67	14.33	0.762	9.144	299.82				0.009	442086	4346624
POINT	RO22EEF89	Research Vent	190.22	14.94	0.61	6.096	299.82				0.00045	442063	4346635

Table 2. Sources for Fayetteville Works (North Carolina Department of Environmental Quality 2019)



CALPUFF View - Source Parameters
MS Excel - Lakes Format
V_2.0

Parameters	Units	Description
Type =		POINT, AREA, AREA_POLY, AREA_CIRC, VOLUME, or LINE, LINE_VOLUME, LINE_AREA, ROAD
ID =		Source ID up to 8 characters
Desc =		Optional description
Base_Elev =	[m]	Source base elevation above mean sea level
Height =	[m]	Release height above ground
Diam =	[m]	Stack diameter or AREA_CIRC radius (POINT and AREA_CIRC only)
Exit_Vel =	[m/s]	Exit velocity (POINT only)
Exit_Temp =	[K]	Exit temperature (POINT only)
SO2 =	project emission units	Emission rate for species SO2 (change name for different species)
...	project emission units	Add columns for additional emission rates with species name as the header (e.g., TOLUENE, etc.)
X1 =	[m]	X coordinate of source location [m]
Y1 =	[m]	Y coordinate of source location [m]
Base_Elev_m	[m]	Base Elevation for LINE_VOLUME, LINE_AREA, ROAD Nodes

Type	ID	Desc	Base_Elev	Height	Diam	Exit_Vel	Exit_Tem	GenX	GenXP	X1	Y1
			[m]	[m]	[m]	[m/s]	[K]	[lb/hr]	[lb/hr]	[m]	[m]
POINT	SRC_1	Division Stack Vinyl Ethers North	45.11	25.91	0.914	20.751	362.48	0.0373	0.0373	698293.7	3857943
POINT	SRC_2	PPA	45.11	25.91	0.482	32.62	346.28	0.00964	0.00964	697656.5	3858173

Table 3. Species Parameters

	Henry's Law Coefficient (unitless)	Alpha Star	Diffusivity cm**2/s	Mesophyll Resistance	Reactivity	Scavenging Coefficient (1/s) Liquid Precip	Scavenging Coefficient (1/s) Frozen Precip	Geometric Mass Mean Diameter (microns)	Geometric Standard Deviation (microns)
PFOA	0.001	1	0.0422	0	0.001	0.001	3E-5	-	-
PFOAP	-	-	-	-	-	0.001	3E-5	0.48	2
GENX	2.37E-10	1	0.0422	0	1	0.001	3E-5	-	-
GENXP	-	-	-	-	-	0.001	3E-5	0.48	2

B.3. CALPOST

CALPOST is the post-processor of the program. It is this that generates the output files that can then be read and plotted by the user. The default control file in which the user can specify certain inputs is CALPOST.INP. CALPUFF produces a file containing data on concentration and deposition fluxes, MODEL.DAT, which is then read by CALPOST. There are also visibility and background concentration files that can also be read by CALPOST, VISB.DAT & BACK.DAT. Timeseries files are also able to be developed by this post-processor, in the time averages of 1-hour, 3-hour, 24-hour and N-hour. Up to four can be produced, and it is up to the user which ones they choose to select (Scire et al. 2000).

With the CALPUFF GUI, these post files are able to be read and turned into a visual representation of the concentration and deposition fluxes. An animated plume is developed, and the user can fast forward or rewind through the time period they have chosen for their run. They can also look at the time averages visually, with the extent of the concentration or deposition flux portrayed. The user can export these results into Google Earth, where it is easier to compare the special context of the results. An example of this is below (Figure 3). Another possible option, if no GUI is available, is to write a code that can produce these visual images. An example of this in Matlab is also below (Figure 4).

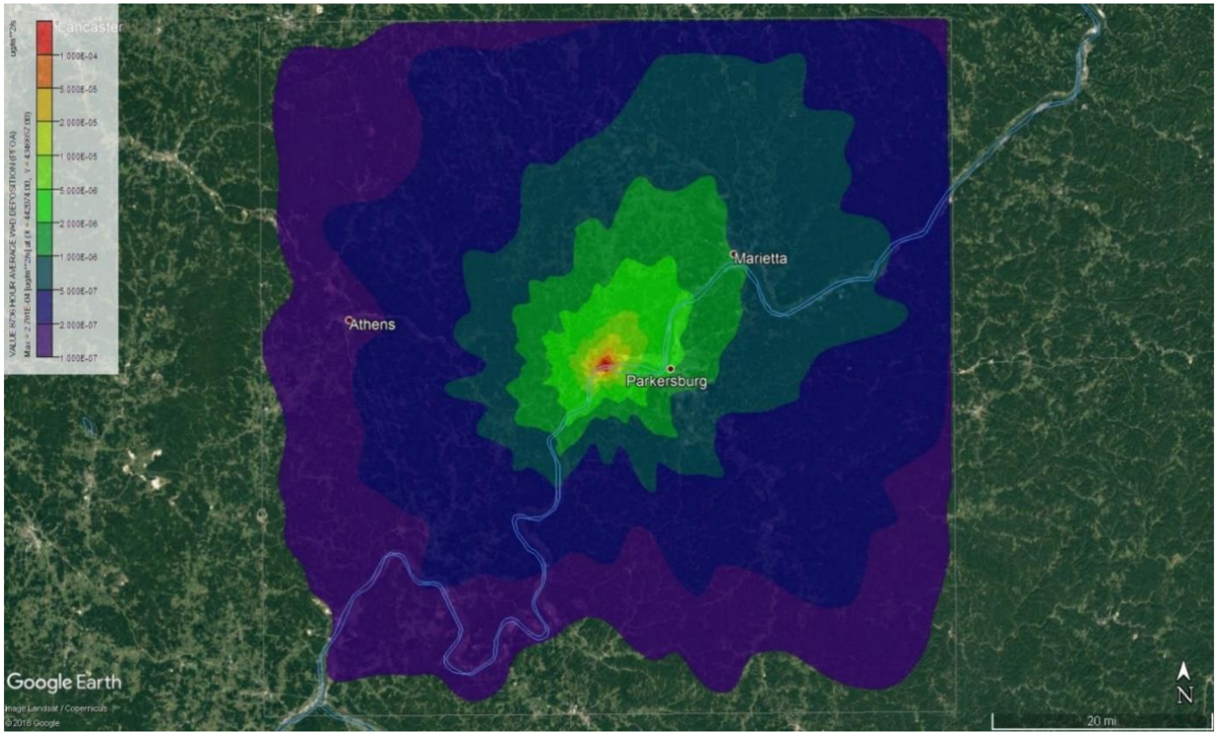


Figure 3. Google Earth Results from CALPUFF View

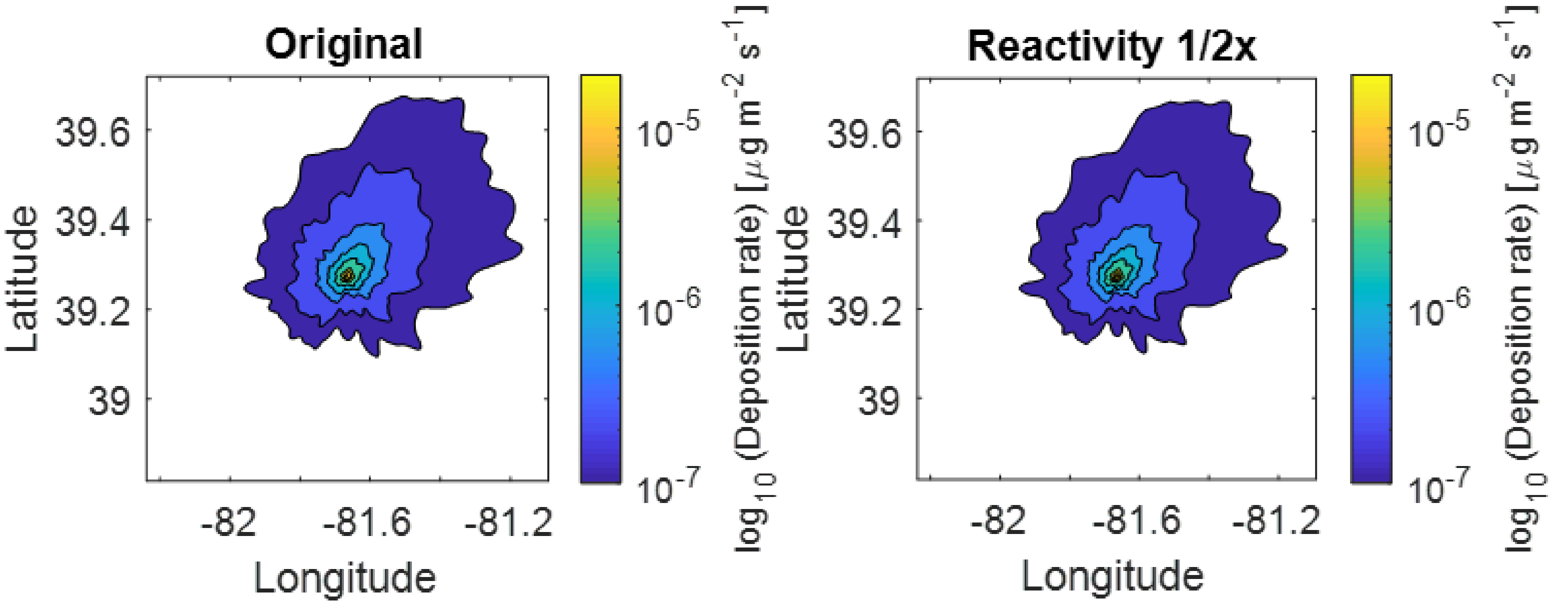


Figure 4. MATLAB Results from CALPUFF View

C. Sensitivity Analyses

Even though some PFAS have existed for decades, there are still many physicochemical parameters that remain unknown. Due to this, there were a number of parameters in our study that had to be estimated. We performed a sensitivity analyses with some of the parameters that we found to be most important and that we found to have the greatest difference in values. We performed these analyses on the Henry's Law coefficient, reactivity, and the scavenging coefficient.

Our original dimensionless Henry's Law values were taken from EPI Suite. PFOA was calculated to have a value of 0.001, and 2.37E-10 for GenX. The second set of values we found on EPA's CompTox. These were 8.26E-09 for PFOA and 9.69E-09 for GenX. The relative percent difference for PFOA simulated in the gas phase can be seen in Figure 6. The differences can dominantly be seen along the Ohio River, although even with a large change in value, there is a relatively small change in the results. For reactivity, we estimated PFOA to be 0.001 because we knew that it was not very reactive with the atmosphere. We expect GenX to be slightly more reactive than PFOA, so we gave it a value of 1. For these analyses, these values were both doubled and halved. Results are shown with GenX in the gas phase in Figure 7. The largest differences here can be found upwind. Because the values here are so small, if a small difference were to be divided by a small number, it would make sense that a larger number would be yielded as the result. The scavenging coefficients are how the chemical behaves during wet deposition. For liquid precipitation, we set both chemicals to 0.0001. For frozen precipitation, we set both chemicals to 3E-05. Liquid precipitation was changed to 3E-05 and frozen precipitation was changed to 0.

Again, we looked at PFOA in the gas phase. Although the difference was slightly higher for this variable, relatively the trend is the same. A conclusion we can reach from this is that regardless of changes in the magnitude of parameters, results are generally similar. The pattern is the same throughout all of the cases, regardless of change in parameter or by how much.

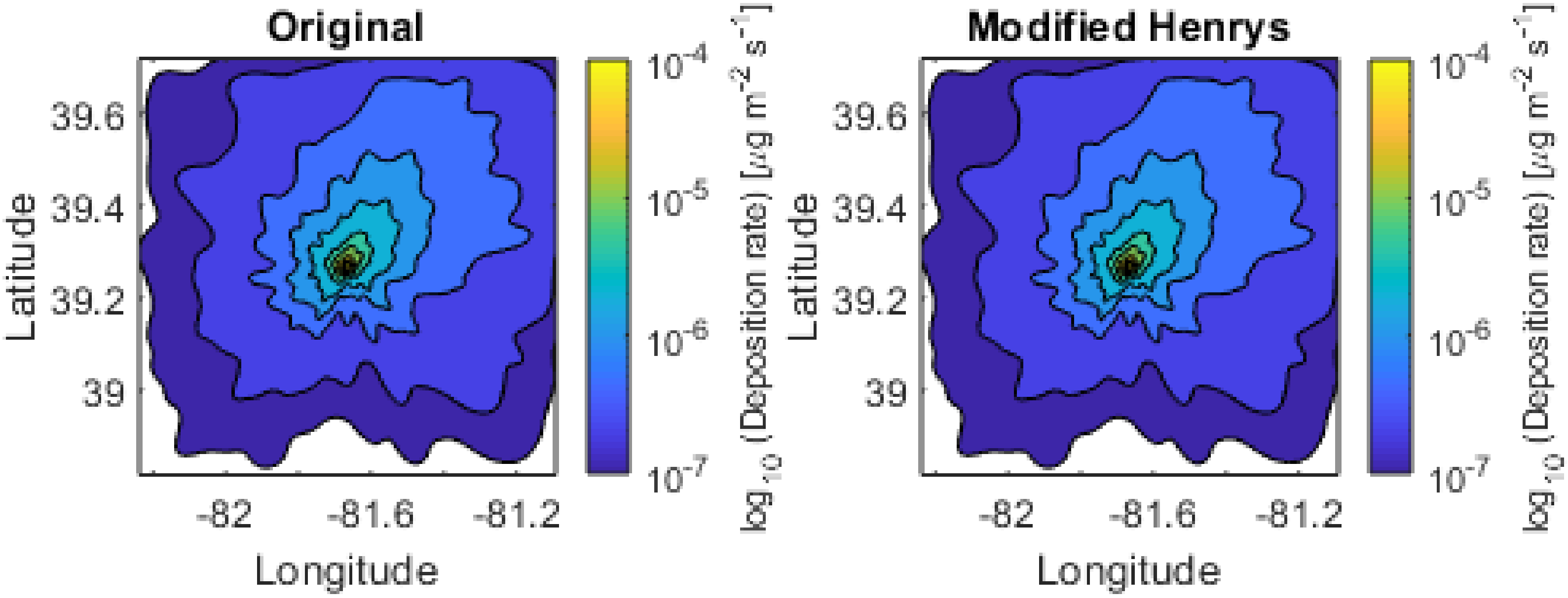


Figure 5. Original PFOA Gas vs. Reduced Henry’s Law of PFOA Gas

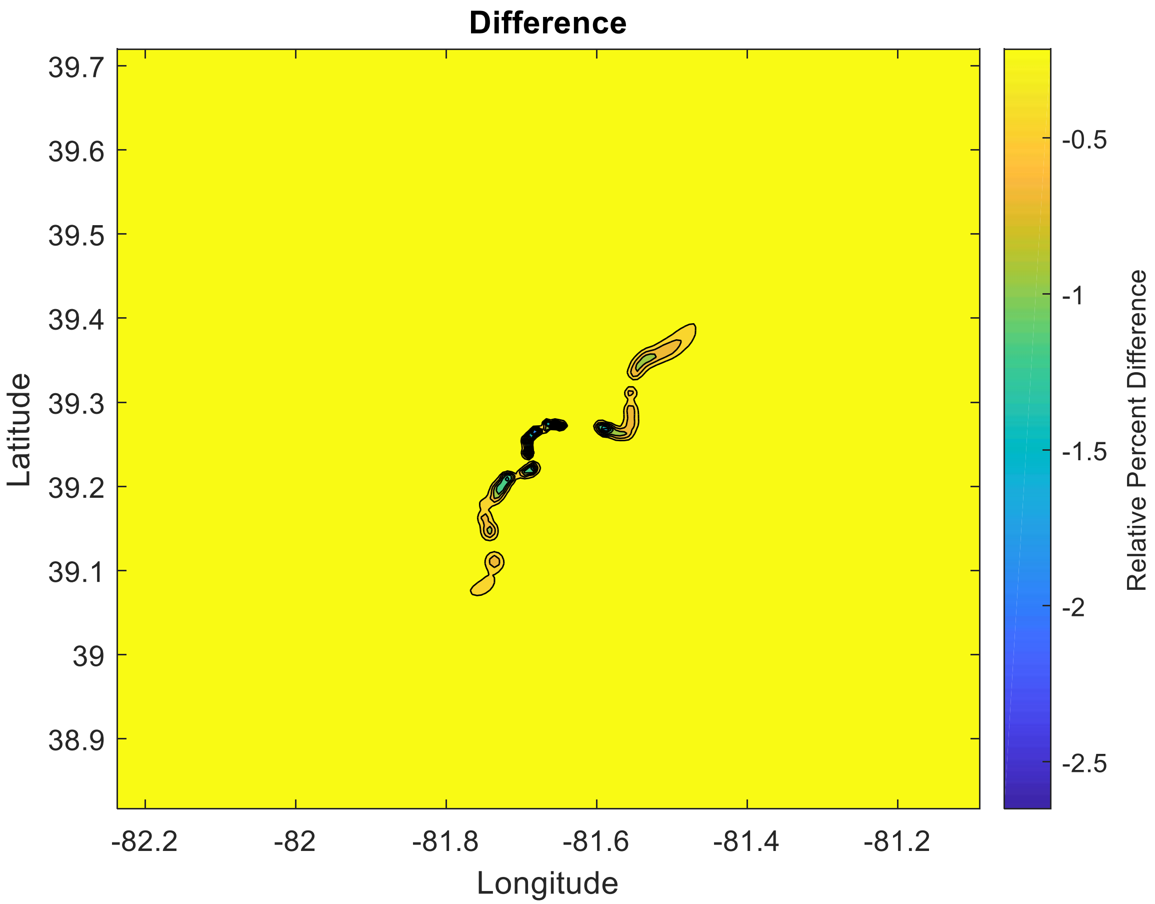


Figure 6. Relative Percent Difference of PFOA Gas Henry's Law

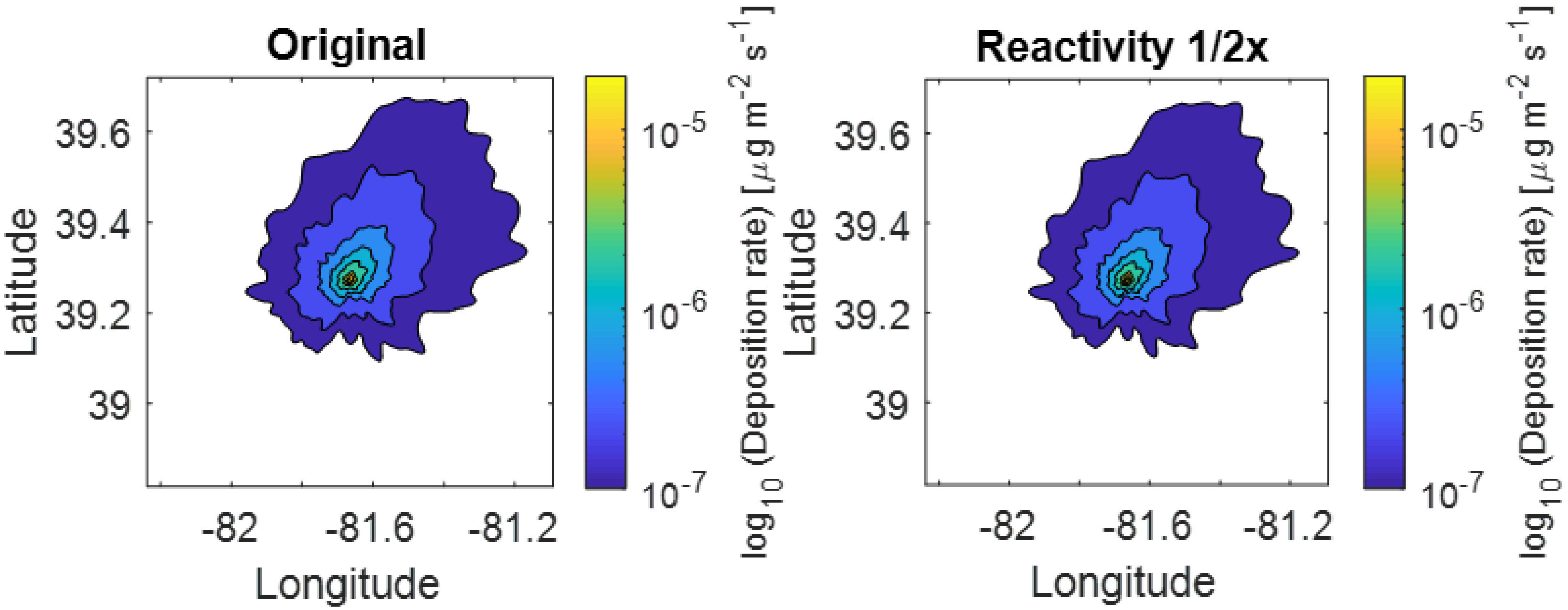


Figure 7. Original GenX vs. Halved GenX Value

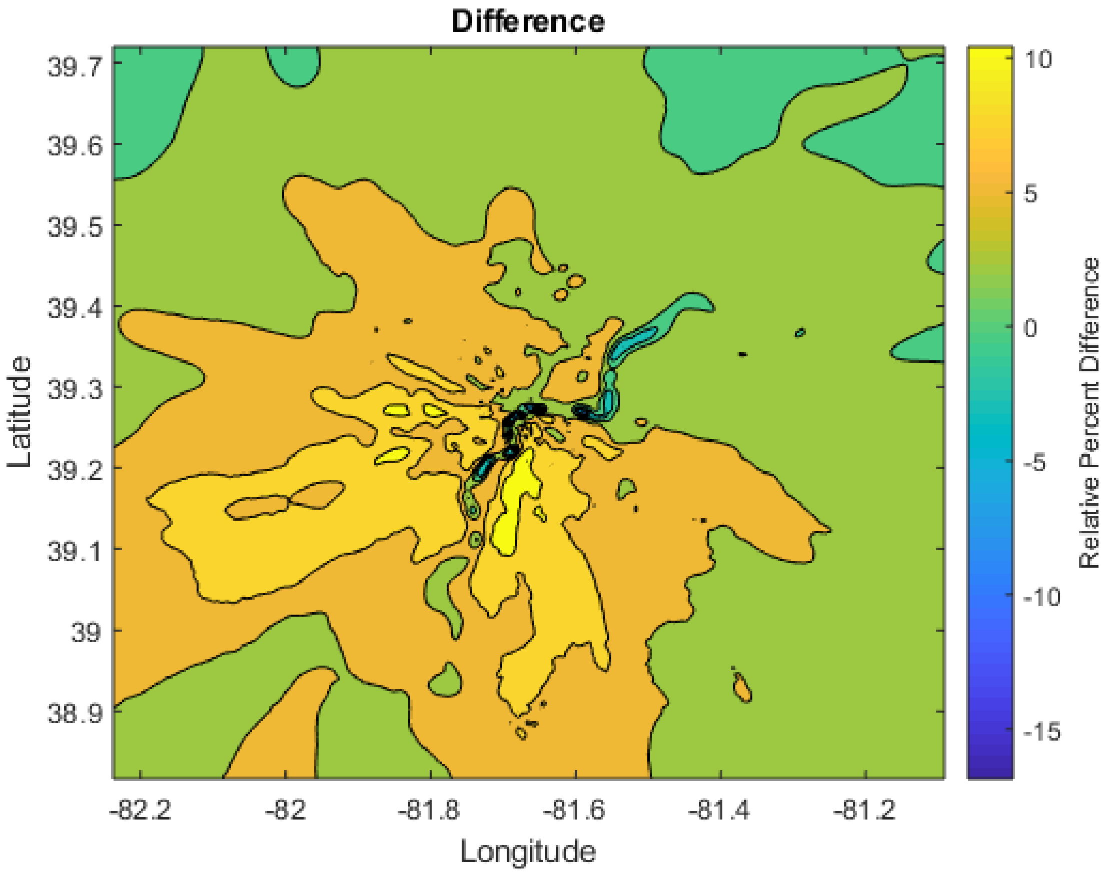


Figure 8. Relative Percent Difference of Halved GenX

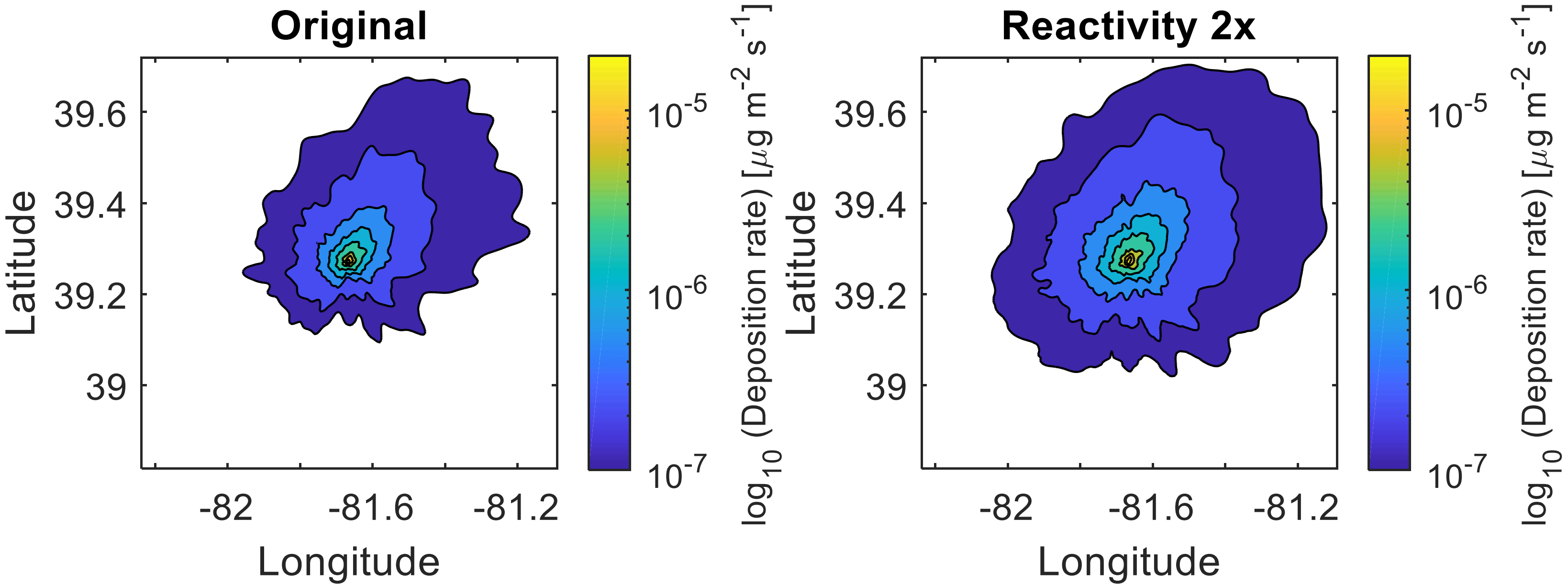


Figure 9. Original GenX vs. Doubled Reactivity

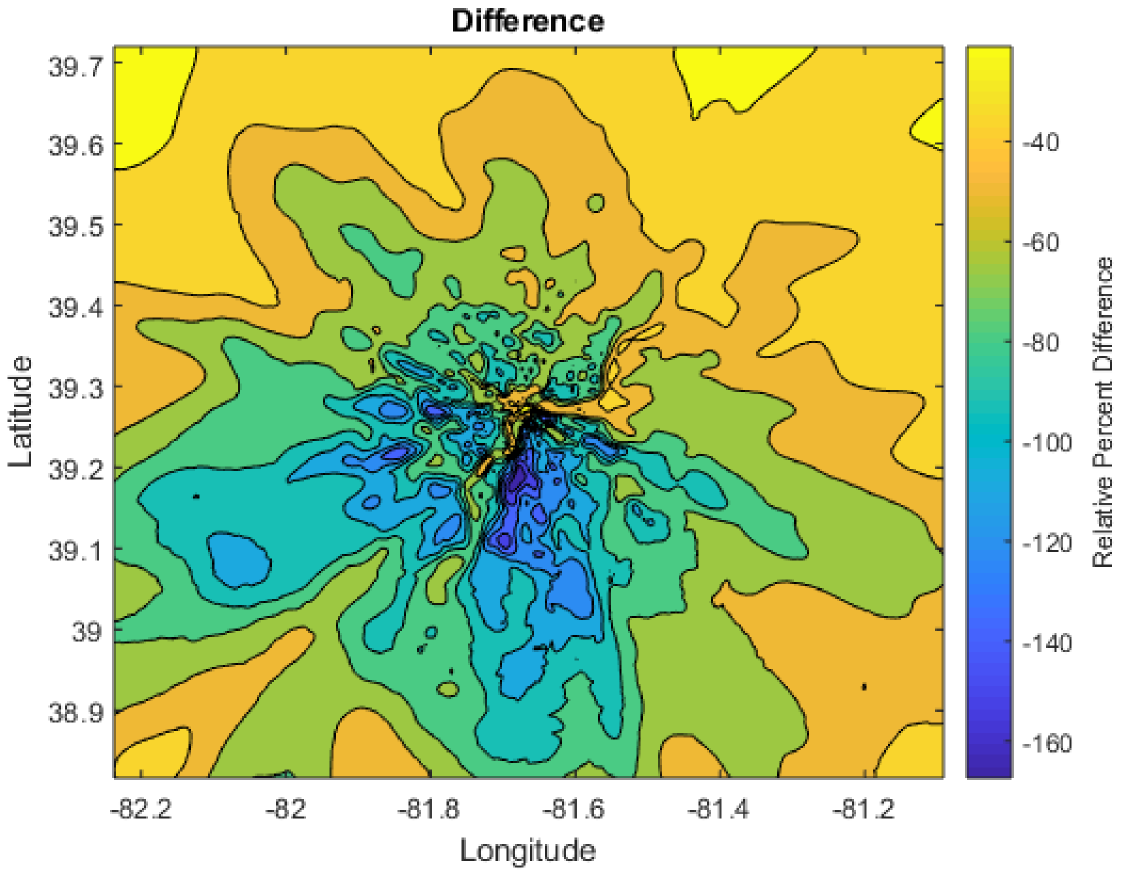


Figure 10. Relative Percent Difference in Original GenX and Doubled Reactivity

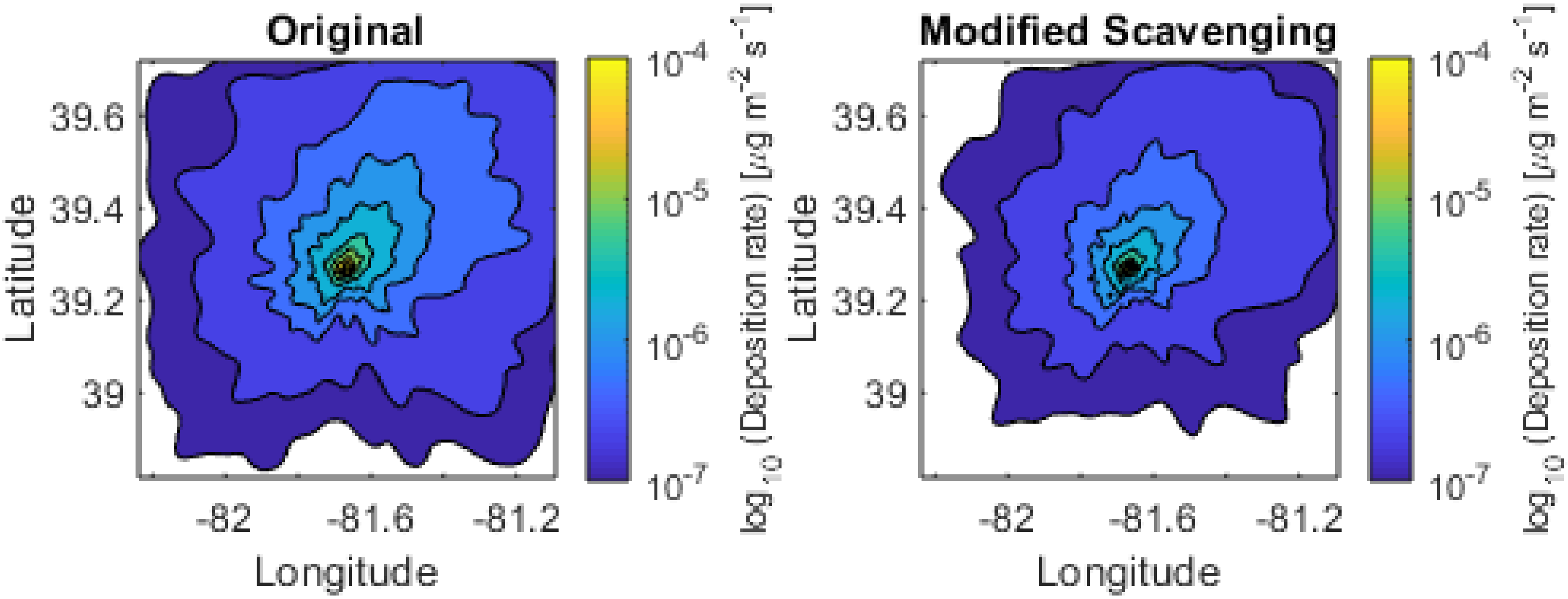


Figure 11. Original PFOA in Gas Phase vs. Reduced Scavenging Coefficient

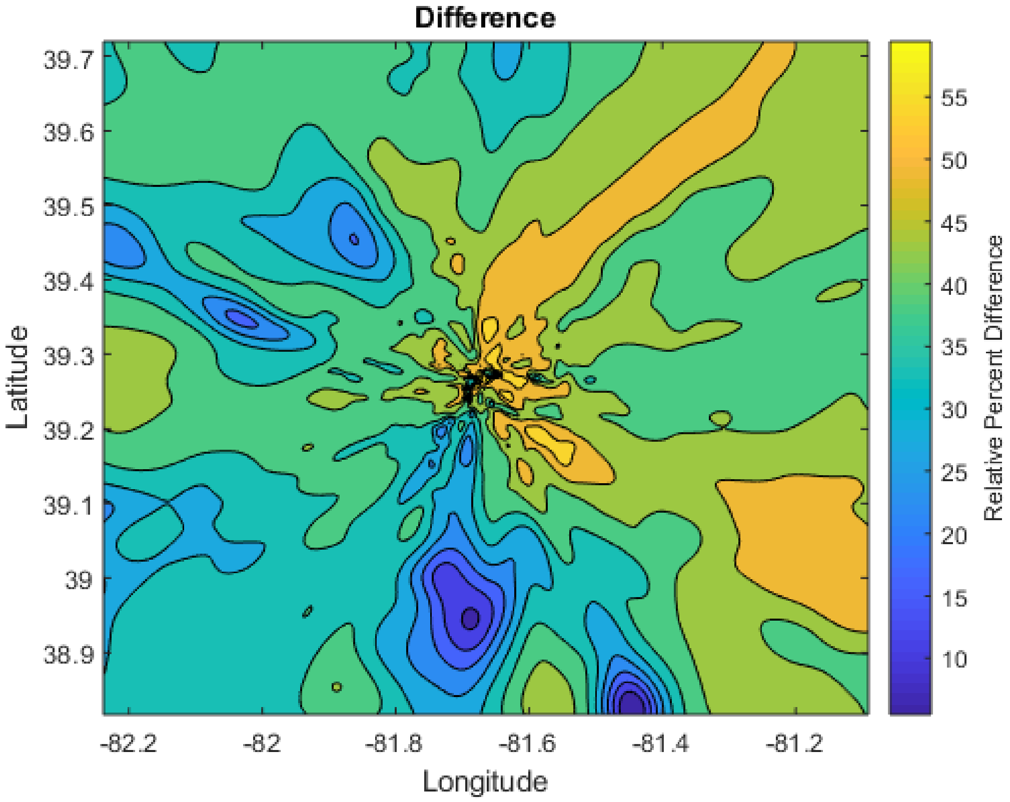


Figure 12. Relative Percent Difference in Original PFOA and Modified Scavenging Coefficient

Chapter 3. Washington Works

A. Background

DuPont Washington Works facility is located near Parkersburg, West Virginia. This is a fluoropolymer production plant that was the place of employment for over 20,000 residents of Parkersburg. They became most well known for their invention of Teflon and the non-stick pan, which includes PFOA as a primary ingredient for use as a surfactant. PFOA was used at this facility from 1946 to 2013. In the year 1961, DuPont scientists discovered that PFOA was toxic. 3M, which is the company that produced PFOA, did a study and found that the workers at their facility were accumulating PFOA in their blood. DuPont moved women out of the Teflon division and followed up on the women who were pregnant before the move. Two out of the eight babies that were born from these women had eye defects when they were born (Lerner 2015).

A family in Parkersburg sold part of their land to DuPont in 1984 for a landfill that included waste from PFC manufacturing. This family then claimed that 300 of their cattle as well as other animals died because of the chemicals that were getting released into the landfill, as well as illnesses in the family. DuPont and the family then settled in 2001 for an undisclosed amount of money. After this, public awareness was increased to the issue. A class action lawsuit was filed against DuPont, which resulted in $70 million being awarded to the members of the lawsuit, and $20 million going to research on the pollutant itself – two key components being water treatments for the six predominately affected communities, and whether there was a "probable link" between PFOA and illnesses (Frisbee et al. 2009).

B. Previous Work

After the news began to spread about what was happening at this plant in West Virginia, it received a lot of attention of not only the public, but scientists as well who wanted to know more about this issue. This is why a student at The Ohio State University in Columbus, OH, chose to do samplings of these chemicals in the waters by the DuPont plant. He chose to do sampling downstream of the Ohio River, hypothesizing that the contaminants deposited in the river would be carried to that area. The concentrations he found were not very high – but he still decided to sample upstream to find out what "clean water" would look like. After going upstream, he discovered that the readings here were actually higher than his downstream samples.

He sampled for both PFOA and hexafluoropropylene oxide dimer acid (GenX) during three separate trips in 2016 and once in 2018. In total, there were 13 soil samples and 102 water samples taken. Equipment used to take these samples were received from the EPA laboratory in Research Triangle Park, North Carolina, and then returned after collection for analysis. The first sampling trip focused downstream of the facility. In terms of samples in the Ohio River for PFOA, the highest reading downstream was 15 ng/L. There were two other readings slightly lower than that, but the rest of the samples were below the level of quantitation (LOQ) of 10 ng/L. However, the samples that were taken from the tributaries downstream of the Ohio River had much higher limits ranging from 51 ng/L to 1250 ng/L. The highest reading was taken at Vaughts Run, which ends up draining from Local Landfill. This was also the only place that had a reading above the LOQ for GenX, with 71.2 ng/L.

The second trip was focused more on upstream samples. Most of these were taken northeast of the facility, following the prevailing winds. Samples were taken as far out as 16 km with the intent to explore atmospheric transport and deposition. The range of PFOA here was from 319 ng/L to 2570 ng/L. Approximately 85% of these samples had GenX concentrations above the LOQ, with the highest being 227 ng/L. The farthest point, the one 16 km out, had a PFOA reading of 781 ng/L and GenX reading of 30.4 ng/L.

The focus of the third sampling trip was to continue to probe the extent of the contamination due to atmospheric transport. That being said, Galloway sampled farther out this time than what was previously done. In terms of the highest concentrations, a similar result was produced to the second trip. The highest concentration of PFOA was recorded at 1310 ng/L and GenX was 137 ng/L, both north/northeast of the facility. The farthest sample was taken 48 km northeast of the facility in the Little Muskingum River watershed and it showed no measurable PFOA or GenX that was above the LOQ. A different sample, taken 41 km away in the same direction as the previous one, had a level of PFOA of 33.7 ng/L, but the level of GenX was still not above the LOQ. Overall, the concentrations in the third sampling trip were lower than that of the second. There are multiple possible contributions to this. One of these is changes in runoff flow based on the amount of precipitation that had occurred recently. Another being that the temperature effect on the K_{ow} value and thus the movement of PFOA into the surface water itself.

Soil samples were also taken in 2016 and 2018 at multiple locations near DuPont. Archers Fork was the sample taken farthest out at 48 km, and recorded PFOA at a level of 4.96 ng/g but no level of GenX. Similar to the surface water samples, the highest recorded samples were detected north/northeast of the facility in 2016. Veto Lake is approximately 8.5 km out and had PFOA at a level of 18.4 ng/g and GenX at 8.14 ng/g. Drag Strip Road is approximately 4 km out and had PFOA at a level of 26.9 ng/g and GenX at 3.20 ng/g. Samples that were taken at Little Hocking Water Association (LHWA) in 2004 showed levels of PFOA between 59.1 – 66.2 ng/g but no indication of GenX, but another sample done in 2018 at the same place had levels of PFOA at 6.68 ng/g with GenX at 3.09 ng/g (Galloway et al., in prep)

Based on his results, Galloway speculated that a portion of this contamination was due to atmospheric transport from the facility itself. Seeing as Vaughts Run and the Little Hocking both had traces of these contaminants, it is possible that the Local Landfill was a contributor. However, GenX was not put into production until three decades after the landfill was shut down. Taking this into consideration, it is likely that these areas close the landfill and even the landfill itself are receiving deposition from DuPont via air emissions (Galloway et al., in prep)

Taking this into consideration, we found it important to model the air emissions coming from Washington Works to determine whether this hypothesis had scientific reasoning to support it. To do this, CALPUFF View was used, an atmospheric transport model created by Lakes Environmental. Using this model along with samples from water and soil, we can make a conclusion as to whether the facilities in this study are the source of harmful contamination.

C. Results/Discussion

The modeling domain in this study was 100 km x 100 km, which was a greater distance than what was previously done by most studies that used a type of dispersion model. (Barton et al. 2010; Shin et al. 2012; Paustenbach et al. 2007) The results that we saw were consistent with our hypothesis in that there was a clear downwind pattern in the visual results of the model.

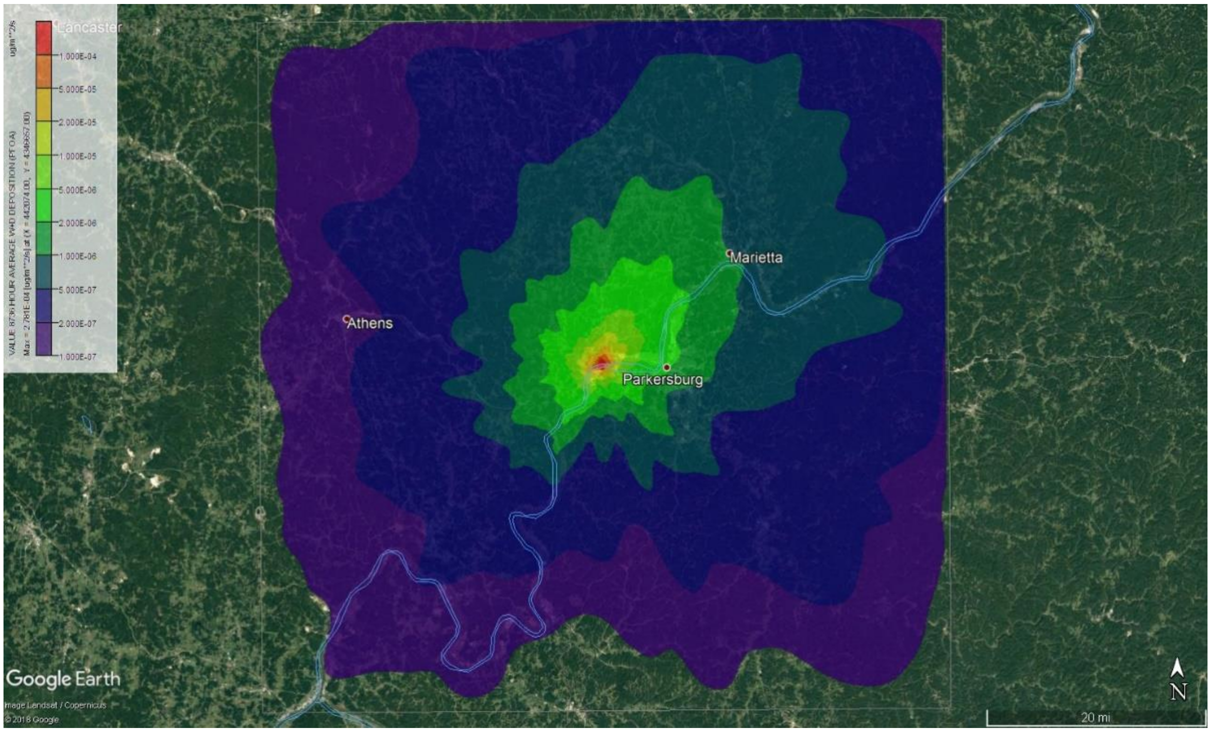


Figure 13. Total Deposition Results from Washington Works

Based on Figure 14 of total (wet and dry) deposition rates, it can be inferred that PFOA is transported upstream by the prevailing winds and then deposited along the Ohio River and nearby surface waters. This is similar to what we would expect to see, considering the results are prominently in the northeast direction. It is deposited onto soil, where it can undergo transport into the groundwater. As can be seen in the figure, there are at least two moderately sized communities being directly affected by the downwind influence from Washington Works, not including all of the smaller communities that are not pictured. As discussed before, Galloway et al. (in prep) did surface water sampling upstream once he discovered this was where the majority of the contamination was taking place. Besides this, he also did some soil sampling around the area.

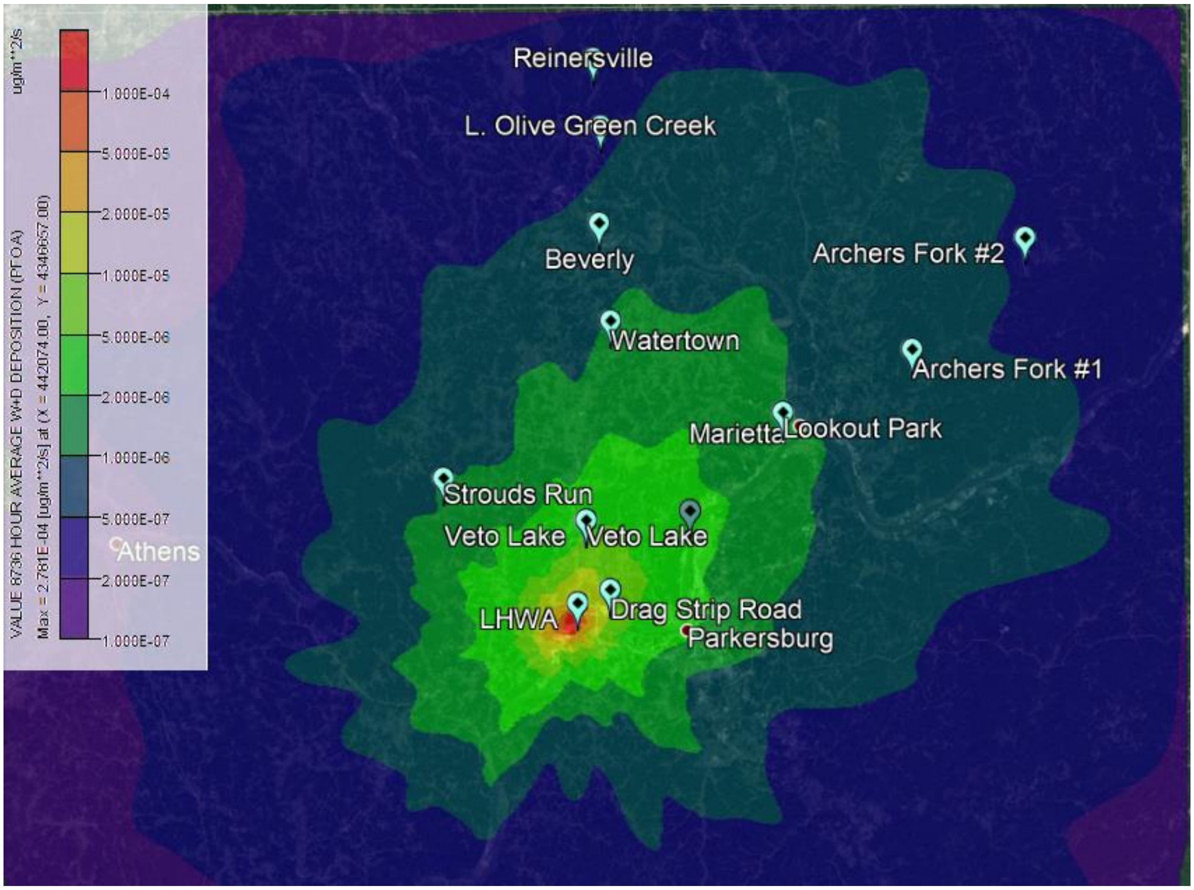


Figure 14. Deposition Results in Comparison to Soil Samples

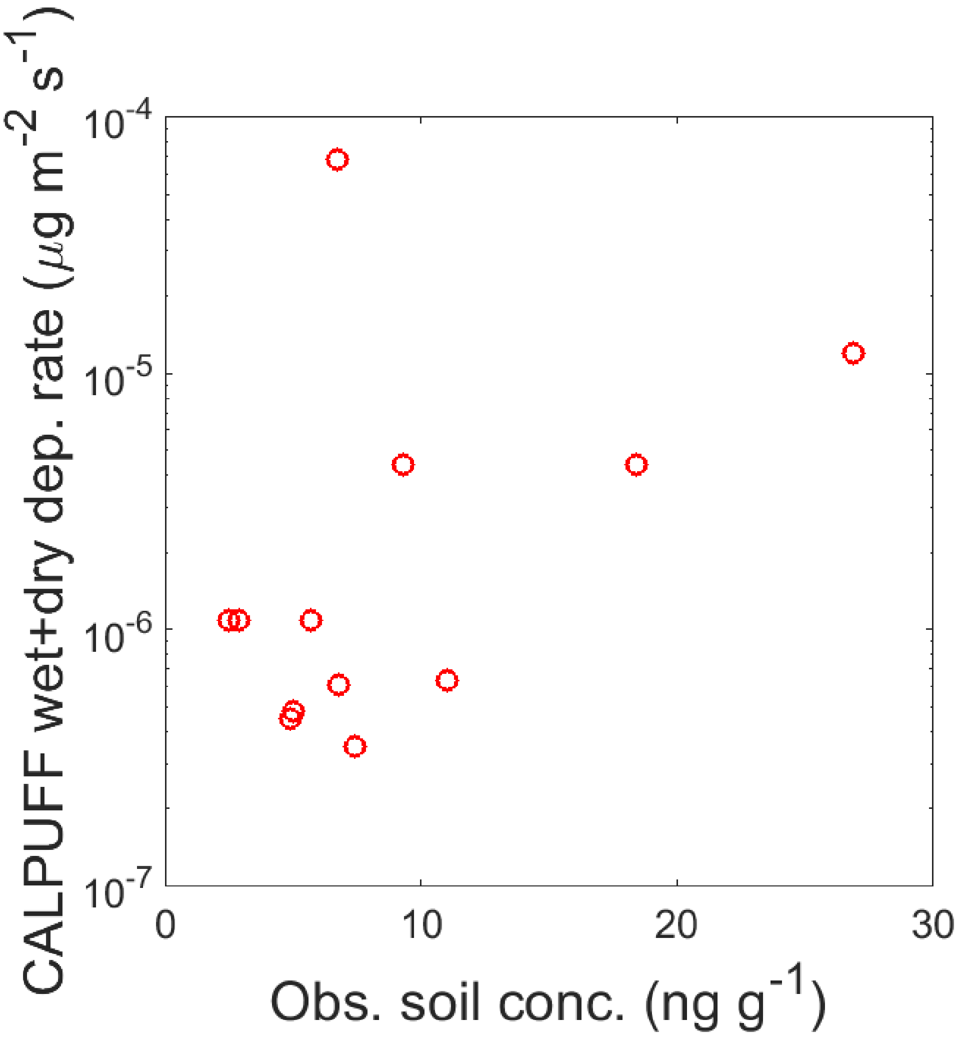
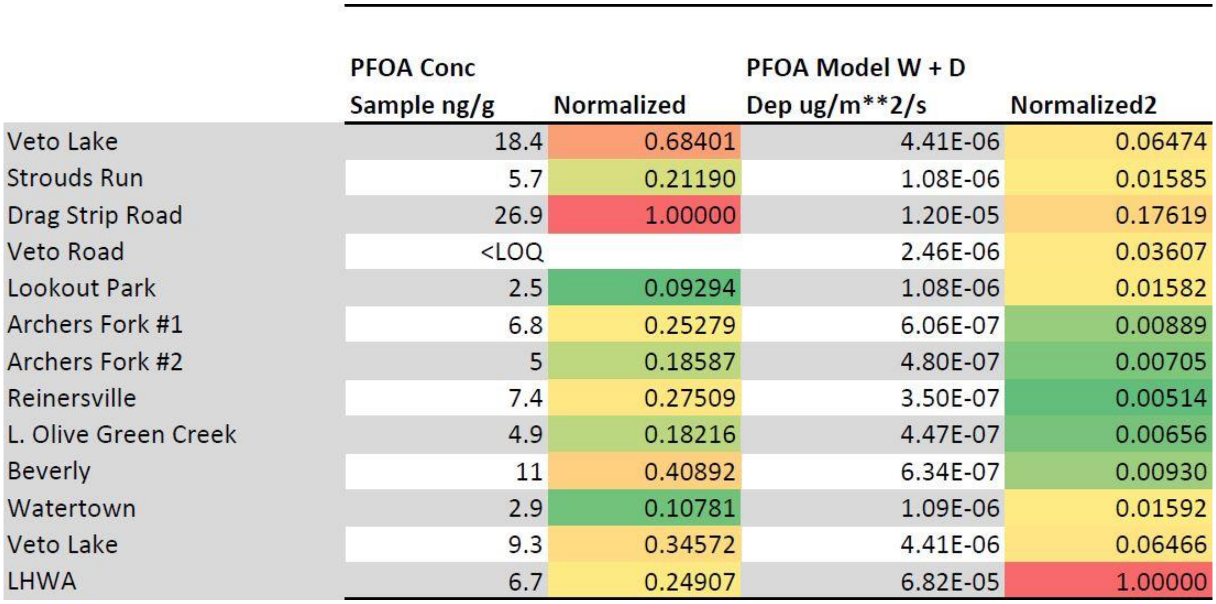


Figure 15. Observed Soil Concentrations vs. Modeled Deposition Rates

Figure 13 is a visual representation of the sample sites in respect to the deposition results. He sampled in a northeast pattern due to the direction of the prevailing winds here, so the samples are generally in line with the direction of the deposition as well. Looking at Figure 14, There is a noticeable outlier point at the top of this plot, we calculated our statistical values with and without it. My model is showing this point (Little Hocking Water Association – LHWA) as the highest reading to its proximity to the plant. This is not the highest reading in the actual samples and this could be due to a number of reasons – different soil type, elevation change, terrain (the sample was taken on a slope), model over-prediction, or measurement uncertainty. It is also possible that this land could have been affected by remediation efforts in this area. With this point, the R^2 value is 0.003 and the p value is 0.8641. Without this point, the R^2 value of these points is 0.8 and the p value is 0.0002.

Table 4. PFOA Soil Sample Results vs. Modeled Deposition Results



	PFOA Conc Sample ng/g	Normalized	PFOA Model W + D Dep ug/m**2/s	Normalized2
Veto Lake	18.4	0.68401	4.41E-06	0.06474
Strouds Run	5.7	0.21190	1.08E-06	0.01585
Drag Strip Road	26.9	1.00000	1.20E-05	0.17619
Veto Road	<LOQ		2.46E-06	0.03607
Lookout Park	2.5	0.09294	1.08E-06	0.01582
Archers Fork #1	6.8	0.25279	6.06E-07	0.00889
Archers Fork #2	5	0.18587	4.80E-07	0.00705
Reinersville	7.4	0.27509	3.50E-07	0.00514
L. Olive Green Creek	4.9	0.18216	4.47E-07	0.00656
Beverly	11	0.40892	6.34E-07	0.00930
Watertown	2.9	0.10781	1.09E-06	0.01592
Veto Lake	9.3	0.34572	4.41E-06	0.06466
LHWA	6.7	0.24907	6.82E-05	1.00000

The table above (Table 4) shows the exact comparison of the soil samples taken to the modeled results. Because of the difference in units, both were normalized for a better comparison to each other. For a better visualization, normalized values are color coded according to their ranking (red being the highest value and green being on the lower end). The results of the model decrease linearly with distance away from the facility, while the soil samples are a little more sporadic but still have a similar pattern. As mentioned previously, my model shows LHWA to have the highest concentration due to its proximity to the facility, while the sampled results show that Drag Strip Road has the highest concentration. Referring to Figure 14, Drag Strip Road is the second closest point in this sample group.

Although community members may be affected by direct inhalation, more importantly their drinking water is being contaminated by this upstream deposition. Because these communities that are located upstream were less of a concern previously, it is possible that they are unaware of just how seriously they were being effected during the time period of PFOA/are currently being effected by GenX. It is also possible that these smaller communities do not have the correct form of drinking water mediation to combat the contamination that they are facing.

Based on Galloway's previous surface water sampling, accumulation is evident of these perfluoralkyl substances. PFOA was in use for approximately 60 years and has been phased out for approximately 5-10 years now, however there are still highly elevated concentrations that were detected in 2017 when Galloway took these samples. Because the chemical makeup of GenX is so similar, it is expected that a similar result will be seen with this chemical as well if there is no intervention in terms of emission control.

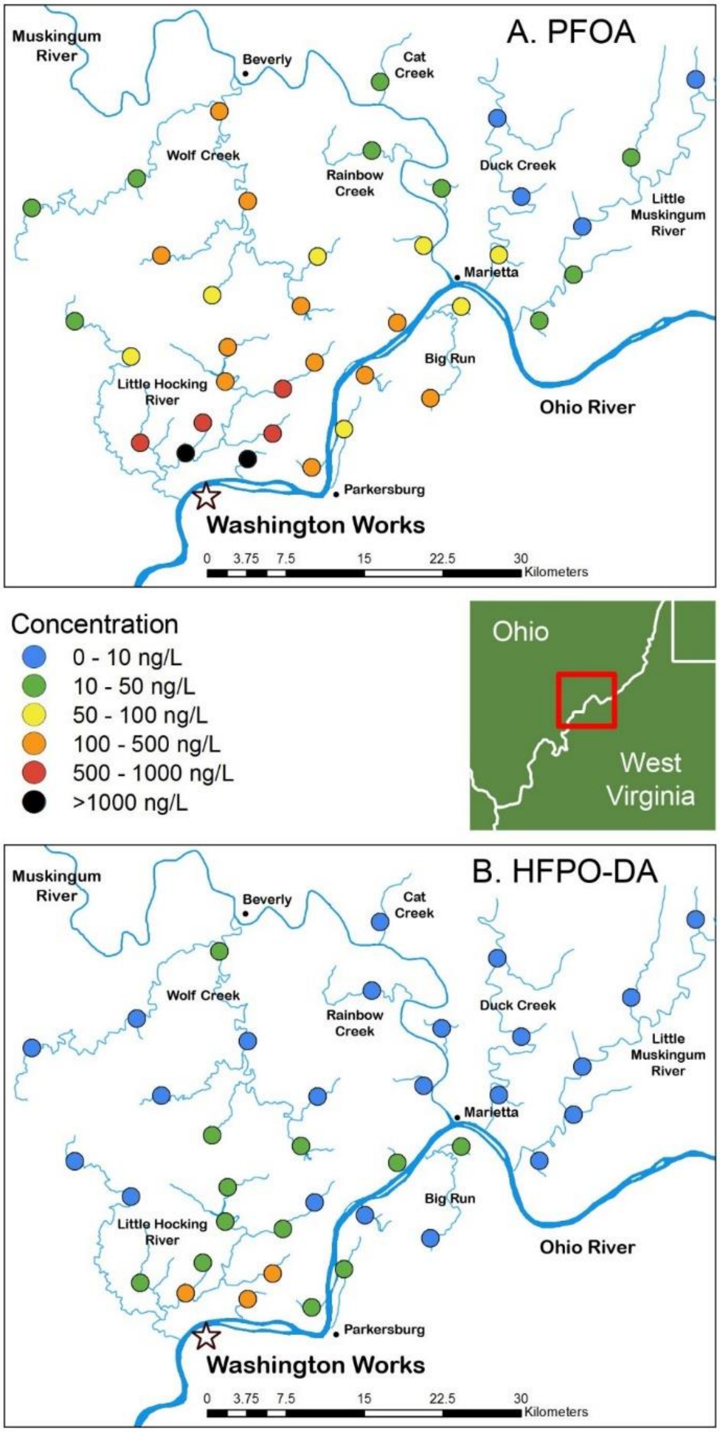


Figure 16. Ohio River and Tributaries Surface Water Sampling (Galloway et al. (in prep))

Concentrations can be found exceeding 1000 ng/L by the plant in surface water. The issue extends past the direct vicinity of the plant, however. Due north concentrations can be detected between 100-500 ng/L. There are several possibilities as to why concentrations are higher directly north in surface water as opposed to northeast, which is the direction of the prevailing winds and where the higher modeled concentrations are located. The first is that we know of a notable hill that is located northeast of the facility. On days of stagnant winds where the mixing height is low and the plume is unable to rise very high, it is quite possible that the pollution is unable to get over the hill to keep heading northeast, but rather heads due north instead, keeping close to the ground with elevated concentrations due to low amounts of mixing. The second possibility is that because the Ohio River runs along the direction of the prevailing winds and thus receiving direct deposition, and there are tributaries that come from the river itself, it's possible the tributaries are receiving some of that deposition.

Galloway's perimeter is approximately 40 km, so these readings can be found approximately 35 km out. Even with GenX (HFPO-DA), directly north/northwest of the facility concentrations can be detected between 100-500 ng/L. This is only after roughly 5 years of production, so if the same pattern continues it is likely that concentrations will meet or exceed those produced by PFOA. This is one of the main concerns – seeing as the purpose for creating GenX was to make a chemical that was less impactful and environmentally resistant than PFOA.

We believe it is possible that concentrations are higher due north rather than northeast (in the direction of the prevailing winds) due to the terrain. There is a larger hill that is directly northeast of the facility, so it is likely that the plume dispersed from the facility is getting trapped on the north side of this hill, especially on days when winds are calmer and the plume does not have the upward vertical motion to make it over the hill. These are also the days that will result in higher concentrations at the surface due to stagnant air and decreased amount of turbulence. Figure 6 indicates the wind patterns in the center of my domain where the facility is located. Analyzing this, it can be determined that the majority of the winds occur below 11mph. Understanding this, it is likely that there would be a quantifiable number of days where there is calmer winds coming from the southwest blowing towards the northeast, causing these higher concentrations north of the facility. Additionally, there are tributaries flowing from the river in the north/northwest direction. It is quite possible that these tributaries are carrying contaminated surface water in this direction, making the northern vector appear to have the highest concentrations in samplings.

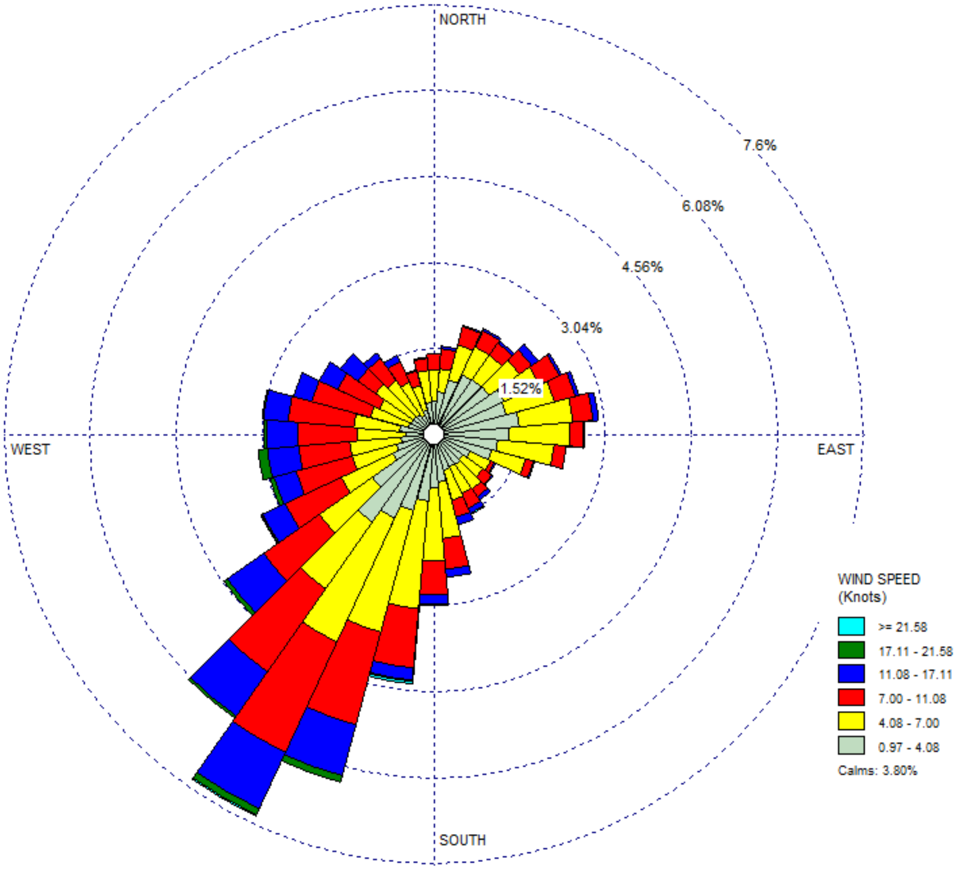


Figure 17. Windrose Generated by CALPUFF View at Washington Works Location

D. Human Health Risk Assessment

We also performed a multi-pathway Risk Assessment, like the one in the USEPA's Human Health Risk Assessment Protocol for Air Toxics (HHRAP) and implemented into IRAP View. This takes into consideration the concentrations of the area, as well as other parameters such as the soil type, terrain, and the possible lifestyle of the person at risk (e.g., resident or farmer). The purpose of our study was to understand the atmospheric influence of these perfluoroalkyl substances. Although we believe this to be important, as well as water contamination, it is also important to understand how the residents are being/going to be affected.

This assessment calculated both the cancer risk, which is the probability of an individual developing cancer because of exposure to the concentration of a pollutant, in this case PFOA. It also calculated the hazard quotient, which is the possibility of someone developing non-cancer health effects (Lakes Evironmental). Unlike cancer risk, the hazard quotient is not a probability. It is calculated as a ratio of a person's exposure to the standard exposure level. These values are then compared to the thresholds that the U.S. EPA Region 6 has set – 1.00E-05 for the cancer risk and 0.25 for the hazard quotient (US EPA 1998). The table below (Table 5) indicates the values found for residents in the Parkersburg area.

Table 5. Human Health Risk Assessment Results

Total Cancer Risk	Value
Resident Adult	2.04E-05
Resident Child	9.11E-06
Total Hazard Quotient	**Value**
Resident Adult	5.76E+01

Values in red indicate an exceedance of the threshold. This does not indicate that the people within this region are going to for certain experience harmful health effects. An exceedance would mean that it is more likely, and also lead to more consideration in terms of the scientific understanding of the scenario, as well as any uncertainties involved in the risk calculation. Cancer risk can be calculated by the amount of indirect exposure to the pollutant along with the amount of direct exposure (such as inhalation), multiplied by the toxicity of the pollutant itself. Hazard quotient can be found by dividing an average daily dose of the pollutant to the receptor (e.g., resident adult) by the reference dose (Lakes Evironmental).

Chapter 4. Fayetteville Works

A. Background

Fayetteville Works, located in North Carolina, is where GenX is primarily produced before being shipped to other places such as Washington Works. The river that runs through this town, the Cape Fear River, has been shown to have up to 10 different PFASs, as well as 7 newer perfluoroalkyl ether carboxylic acids (PFECAs) (Sun et al. 2016). Similar to Washington Works, community members were generally unaware of any type of contamination at first.

According to Chemours' own National Pollutant Discharge Elimination System (NPDES) permit renewal application (consistent with USEPA's 2009 consent order), any and all wastewater from the facility is to be shipped offsite for proper disposal (The Chemours Company 2016). However, there has been evidence of GenX downstream of this facility with concentrations as high as 4,500 ng/L as far as 90 mi. downstream (Hopkins et al. 2018; Strynar et al. 2015; Sun et al. 2016). On June 15, 2017, Chemours admits that GenX had been released into the river since 1980 by the wastewater treatment plant (Hopkins et al. 2018). GenX is being produced as a byproduct of fluoropolymer products, and according to the USEPA consent order, the rules do not apply when it is being produced as a byproduct without intent on using it separately (USEPA 2009; Hopkins et al. 2018).

Back in 2007, a study was done in the Cape Fear Drainage Basin to discover if there were any PFCs that were detectable. 100 samples from 80 locations were taken, and PFCs were detected in every single sample. The highest concentrations were found in the middle of the Drainage Basin, while the lowest were found in smaller sized tributaries of the river. The highest level for PFOA was recorded at 287 ng/L, and PFOS was at 132 ng/L (Nakayama et al. 2007).

Levels of up to 4,000 ng/L of GenX were detected upstream of the NC facility in local drinking water wells. Because these levels were so high and it was upstream, it is likely that the wind is carrying GenX and its precursors in this direction, it then deposits in water and reacts. Modeling done by North Carolina Department of Environmental Quality (NCDEQ) show that the facility could have emitted upwards of 500-670 lb of C3 dimer acid fluoride (a precursor of GenX) into the air every year in between 2012 and 2016. When this precursor comes in contact with water, it forms GenX. However, it is possible that these emissions could be even higher than these. (Oppenheimer, J. 2007; NC DEQ 2017, 2018a,b).

B. Results/Discussion

Our hypothesis for Fayetteville Works was the same as Washington Works – that the dominant wind pattern was a transport mechanism for PFASs from the Chemours facility. Once upstream, the chemical is then deposited and leaches into the soil and enters into drinking water pathways. After completing modeling runs with CALPUFF as we did with the West Virginia site, it can be seen that the pollutant is carried upstream due to the prevailing winds in the area. The Cape Fear River runs from northwest to southeast, whereas the predominant winds blow from the southwest to the northeast.

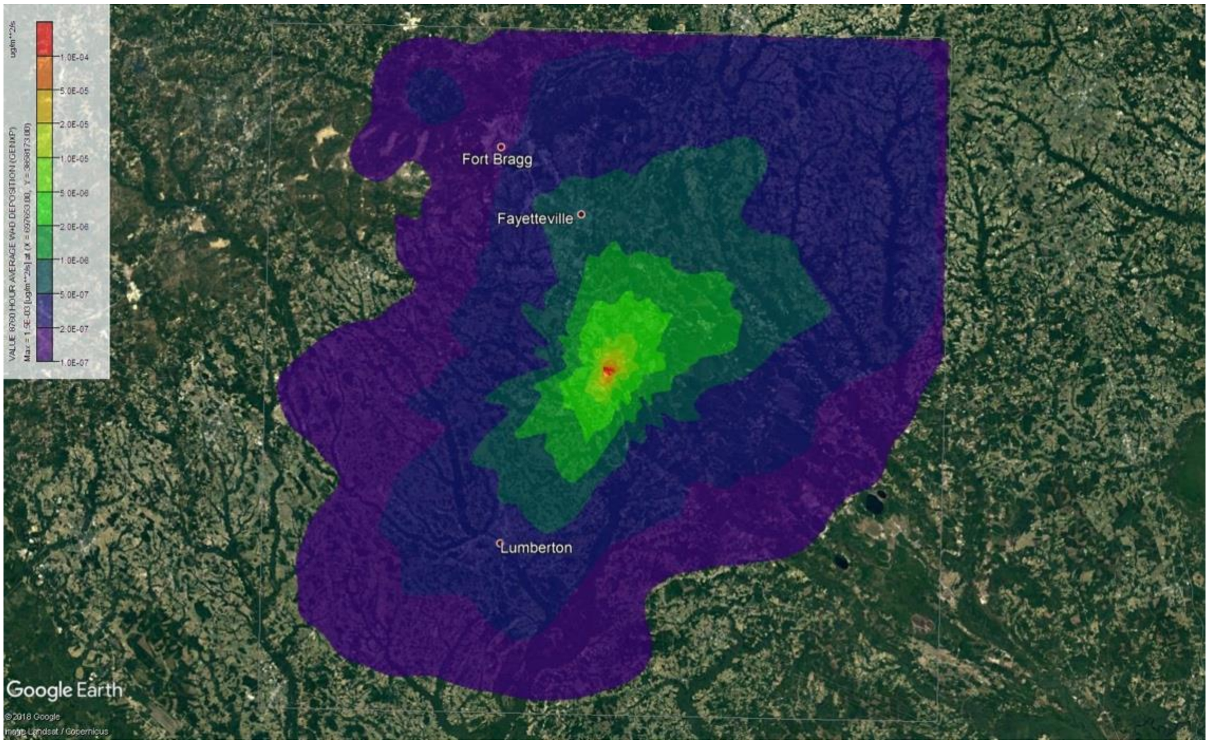


Figure 18. Deposition Results from Fayetteville Works

Although it is less likely that the chemicals are being deposited into the river due to the wind, there is already clear evidence of them being discarded directly into the river in large quantities. Because the communites northeast of the site are not directly affected by the river, it is possible that they are less aware of the possible contamination. However, these communities are facing a larger amount of contamination than they would likely have thought of. The contaminants are not being deposited directly into the river in this area, but there are still private drinking water wells to take into consideration. That being said, the extent of contaminated drinking water is possibly quite larger than originally expected, and further research should be done to look further into this.

It is quite evident that PFOA and GenX behave quite similarly, especially when comparing results from Fayeteville to Washington. CALPUFF was chosen as the model for this study because of puff models' better performance in areas of complex terrain. Although the terrain of Fayetteville is not as complicated as that in the Ohio River Valley, the performance is comparable to what was seen in Parkersburg, and performed in greater detail than that of studies done previously with different models. These results can have utility by researchers in North Carolina who wish to explore the impact of atmospheric transport near that facility.

Chapter 5. Summary and Future Work

Perfluoralkyl substances (PFASs) have emerged quite rapidly in the industrial scene within the past 60 years (Hu et al. 2016). These compounds have a unique carbon-fluorine bond that makes them resistant to biodegradation in the environment and in the body. Perfluorooctanoic acid (PFOA) is on the most commonly detected PFASs, along with perfluorooctanesulfonate (PFOS). Due to health concerns, different PFASs, PFOA included, have been phased out or are in the process of being phased out. In the United States, the U.S. EPA along with 8 fluorochemical companies voluntarily entered into a stewardship agreement to phase out long chain PFASs by 2015 (Strynar et al. 2015; United States Environmental Protection Agency 2006). DuPont was one of these companies.

DuPont used PFOA for approximately 60 years before phasing it out and then replacing it with another chemical called Hexafluoropropylene Oxide (HFPO) Dimer Acid (GenX) at their Washington Works location. A wind rose at this location showed that the winds are predominately blowing from the southwest to the northeast. Previous sampling was done at this location by a colleague, Jason Galloway. He took surface water samples downstream and upstream of the facility, as well as soil samples north/northeast of the facility as well. Our hypothesis was that the pollutants were being carried by the wind and deposited upstream of the facility, then leeching into soil, groundwater, and the Ohio River and contaminating residents' drinking water. We ran CALPUFF View, an atmospheric transport model that uses land use, meteorology, and stack parameters as inputs for this site for one representative year. We modeled both PFOA and GenX with CALPUFF. It showed both of these chemicals being carried in the northeast direction, following these winds.

We performed the same procedure for Fayetteville Works, the location where GenX is actually produced and then shipped out. The prevailing winds at this location are also from southwest to northeast, however the Cape Fear River flows from northwest to southeast here. CALPUFF runs showed similar results to those of Washington Works, with both PFOA and GenX being carried in the northeast direction. Although there were not any quantitative sampling to compare modeling results to, it is important to see where these pollutants are being carried and what communities could possibly be affected.

The results of this study are relevant due to the fact that there are many people who have to drink this contaminated water and suffer from the health effects that come with it. The U.S. EPA issued a health advisory of 70 ng/L for both PFOA (USEPA 2016b) and PFOS (USEPA 2016a) together, or one standing alone. However, it has been proven that there are over 6,000,000 people in the US that are drinking water with levels above this (Hu et al. 2016; Hopkins et al. 2018). Citizens of Parkersburg, West Virginia, and surrounding areas were unaware of the PFASs issue for decades. Even then, many people did not take it seriously. DuPont was the biggest industry in the area, thus the biggest supplier of jobs. Nobody wanted to go against a company that loomed this large. In North Carolina, most people were not aware that there was GenX in the Cape Fear River until an article came out in the *Washington Star News* (Hopkins et al. 2018, Hagerty 2017). There were over 200,000 people that were being affected contaminated drinking water in North

Carolina alone (Sun et al. 2016; Hopkins et al. 2018), and that number is expected to be staggeringly larger in West Virginia.

This study differs than those that have come before it due to the fact that a puff model was used for the first time to our knowledge, and we then compared these results (at least in the case of Washington Works) to recent sampled surface water results. This modeling domain was greater than that of previous studies, which gave us a bigger picture look at the spreading of these chemicals. Even towards the outer perimeter of our domain, there were still trace amounts of these chemicals in the atmosphere. Although the levels are not necessarily harmful at these distances, constant exposure even at small doses is suspected. This study also used prognostic meteorology data, which is less common due to the computing power and resources to obtain this data. Especially in an area of complex terrain, prognostic data is favored over measured data.

Because the time scale for this study was limited, there were many aspects of this case that went unexplored for us. However, we believe that there should be continued research done in this area. The downwind/upstream influence of this contaminant was larger than what was originally expected to find. It is possible that the people in this area do not have the proper remediation tools to combat their contaminated water, if they are even aware of the extent of their water contamination. Further studies should be done that are more focused on drinking water and groundwater contamination in both the Parkersburg and Fayetteville areas. Since drinking water is such a large influence in terms of human exposure, it is imperative that this area is well researched.

Although the topic of perfluoroalkyl substances is still relatively newer in the science and research world, it is one of the more pressing issues. There are many aspects of these compounds that are still unknown to researchers, and due to this knowledge gap, we believe that there should be more research on these substances and how they are influencing the environment, as well as the public. Until there is a substance that is able to replace PFASs, they will continue to be used by fluorochemical companies across the world. With our knowledge of their environmental persistence and resistance to biodegradation, as well as their rate of accumulation in the environment, we believe that these substances will continue to be an issue for years to come.

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