Review of GenX Pollution: GenX Pollution of the Cape Fear River in North Carolina, U.S.A.

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Abstract: - This review paper explores GenX pollution of Cape Fear River in North Carolina. This review will focus on the history of GenX, its manufacturing and uses, its associated toxicity and what is being done about its environmental pollution. The study will be supported by statistical data to ensure reliability. Current data suggest that in addition to its oral and respiratory toxicity, GenX can cause dermal irritation and corrosion. In a study conducted to review the current technology that Chemours uses to manufacture GenX, it was noted that the chemicals used had negative impact on reproduction in mice. It was also associated with kidney and liver damage as well as significant weight loss and changes in cholesterol levels. As a result of such health hazards, the authorities in North Carolina have imposed several penalties on Chemours, the manufacturer of GenX and other related toxins. Similarly, the citizens of North Carolina are questioning the dumping of Chemours' chemical effluents into the Cape Fear River. This paper will examine these issues in detail.

Keywords: - DuPont, Chemours, GenX, Pollution, North Carolina, Cape Fear River, Toxicity, Health hazards

1 Introduction

The industrial production of per-and poly-fluorinated alky substances (PFAS) and their industrial production of various products dated back to over 70 years ago. Since then, PFAS have been used extensively in the production of plastics, food-packaging coatings, water and stain repellents, fire-fighting foams and many other products (Kissa 2001 [18], Buck 2011 [4], Buck et al. 2015 [3]). Their widespread use has led to their release into the environment and their environmental presence has been detected and documented by various studies (Heydebreck et al., 2015 [14], Sun et al., 2016 [26], Gebbink et al., 2017 [11]). The two most notable and widely used PFAAs are the long-chain perflourooctane sulfate (PFOS) (Fig. 1) and perfluorooctanoic acid (PFOA) (Fig. 2). The major US producer of PFOA and PFOS compounds is DuPont Chemicals. These chemicals have been found to be toxic and carcinogenic, hence the search by DuPont for

safer replacement chemicals for the manufacture of fluoropolymers (Lau et al, 2007 [19]). As early as 1963, DuPont had evidence that PFOA might be hazardous to human health and its environment. Health and environmental concerns over the toxicity of these compounds led to search for alternative compounds that may have less negative impacts hence the discovery of the shorter-chain per- and poly-fluorinated ether carboxylic acids (PFECAs) that have higher water solubility, less persistent in the environment and generally less toxic to aquatic and terrestrial animals (Ritter, 2010 [25]], Buck et al., 2011[4], Gannon et al., 2016 [10], Hoke et al. 2016 [15]). Following a class-action lawsuit in which DuPont was barred from producing PFOA, it embarked on the production of an alternative replacement for PFOA. A compound that came into wide use as an alternative to PFOA is ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropxy)-propanoate (FRD-902) with the trade name GenX (Fig. 3) which is the conjugate base ammonium salt of 2,3,3, -tetrafluoro-2-(heptafluoropropxy)-propanoic acid (FRD-903). GenX consists of shorter chains compared to PFOA and the chemical structure of the dimeric acid form is abbreviated as PFPrOPrA (Sun et al. 2016 [27]) (Fig. 3). The acid form of GenX is a liquid while the ammonium salt is a white/colorless sold at ambient temperature of 20 ^{o}C. The chemical structures of PFOA, PFOS, and GenX are shown in Figures 1-3.

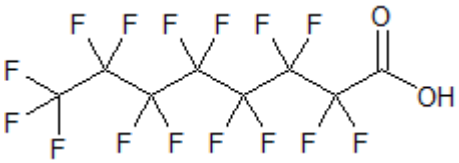

Fig. 1. PFOA: Perfluorooctanoic acid

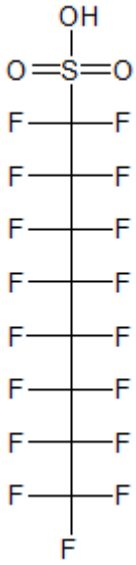

Fig. 2. PFOS: Perfluorooctanesulfonic acid

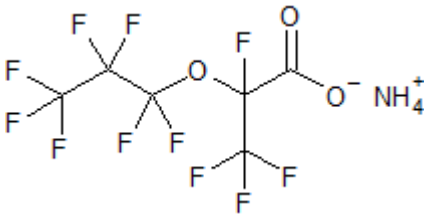

Fig. 3. GenX: Ammonium 2,3,3,3-tetrafluoro-2-(heptafluoropropoxy)propanoate
Or Ammonium perfluoro(2-methyl-3-oxahexanoate)

In 2009, DuPont introduced GenX to replace PFOA which is known to possess health and environmental hazards. PFOA is used in the manufacture of coatings for waterproof clothing as well as stain-resistant carpets. The compound is also useful in the production of Teflon. The GenX chemicals are manufactured by Chemours, a subsidiary company of DuPont. The chemicals are used in a number of consumer products such as paints, cleaning products, non-stick coatings, food packaging, outdoor fabrics, and fire-fighting foams (Shea, 2018 [26]). GenX chemicals replaced Perfluorooctanoic acid (PFOA) (C8) in the manufacturing of fluoropolymers such as Teflon by DuPont-Chemours (Beekman et al., 2016 [2]). The abbreviations PFOA and C8 are used interchangeably to refer to the same compound. Chemours located in Fayetteville, North Carolina (NC), is a spinoff company of DuPont that manufactures GenX. The

manufacturing of GenX by the Chemours plant led to the spilling of GenX compounds into the Cape Fear River which is a source of drinking water for several NC communities including Wilmington which is about 100 miles downstream of the Chemours plant (Fig. 4).

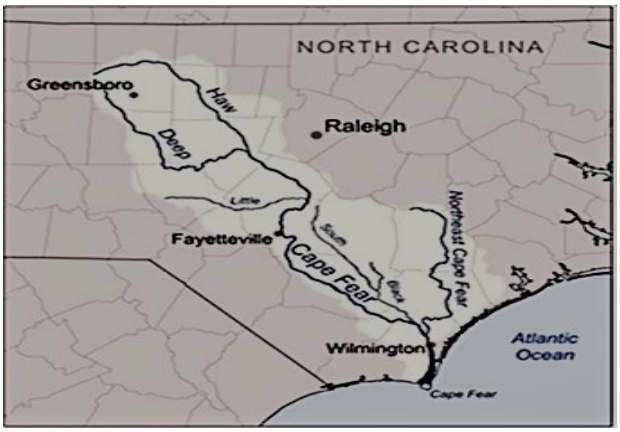

Fig. 4. North Carolina's Cape Fear River Basin. Source river for drinking water for several communities in the state (Open source map).

The Cape Fear River may have been contaminated with GenX for several years before the observation of its potential health effects for populations downstream of the Cape Fear River and beyond the Chemours plant. Unfortunately, there is very little research on GenX and its health effects. There are no federal standards that regulate its use as the USEPA classifies it as an "emerging contaminant" that needs to be studied. There is very little information about the health effects of GenX. The NC Department of Health has set a health goal of 140 parts per trillion (ppt) as a safety but non-legally enforceable limit of ingestion. The chemical has been detected in Wilmington's drinking water. It has been found in more than 80 drinking water wells near the Chemours plant, and at levels almost 15X the health limits set by NC state officials in honey collected by a farmer living two miles from the Chemours plant. Research is emerging, albeit limited showing that GenX has similar health effects as PFOA (Lerner, 2017). These effects include reproductive problems as well as cancer. This review will focus on the available research on GenX. The literature review section below will discuss the known health effects in detail.

2 Literature Review

2.1 Statistical Figures

In a recent and continuing study of the health goal in the State of North Carolina in regards to GenX, Shea (2018) analyzed currently available GenX toxicity data with the goal of obtaining a drinking water health advisory limits for GenX [26]. The State of North Carolina issued a provisional lifetime health goal that was initially set at 71,000 ng/L and later revised to 140 ng/L. The Scientific Advisory Board (SAB) of the NC Department of Environmental Quality and the NC Department of Health and Human Services monitor and may further revise the limits downward based on further research. In view of the highly water soluble nature of GenX, available data suggest that contaminated water is the primary source of exposure to the chemical with negligent exposure via inhalation and food. The levels of GenX present in the Cape Fear River drinking water is 631 parts per trillion (ppt or ng/L with one sample measuring as high as 4,500 ppt, a value that is much higher than the recommended levels for PFOA in water. Recently, the USEPA set the recommended a health advisory level (HAL) for PFOS and PFOA found in water at 70 ppt (Sun et al. 2016). Other agencies such as the New Jersey Drinking Water Quality Institute have set the level to as low as 14 ppt (Post, et al. 2009) [22]. Therefore, water contamination by GenX in the Cape Fear River is extremely high. Sun et al. (2016) [27] noted that GenX was the primary pollutant in the Cape Fear River. They measured and mapped out levels of GenX along the Cape Fear River and found significant levels of the compound at sites downstream of the Chemours Plant (the source points) with insignificant levels at points upstream of the Plant (non-source points). The amounts of PFOA, PFOS and PFPrOPrA detected downstream were higher than 600 ng/L. These findings clearly support the Chemours Plant as the source of the GenX contamination and that

GenX remains a dominant pollutant in the Cape Fear River (Fig. 5).

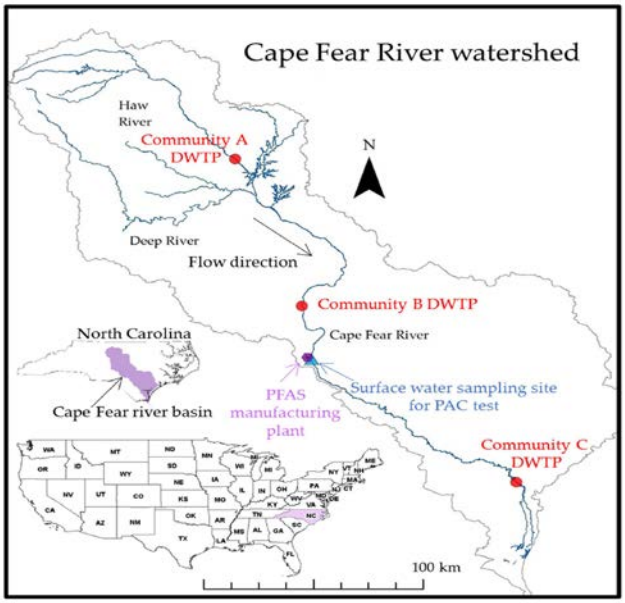

Fig. 5: From Sun et al. 2016 – Mapping and determining concentrations of legacy PFAS and GenX at different points A, B, (nonpoint sources) and C (point source) along Cape Fear River in North Carolina. Evidence of the Chemours Plant as source of GenX in the River [27].

In their study, Sun et al. (2016) [27] examined three communities A, B and C, located at the different points along Cape Fear River in regards to the levels of various PFAS including PFOA, PFOS and GenX in their drinking water. Whereas Communities A and B are located at nonpoint sources Community C, on the other hand, resided downstream of Chemours Plant, the source of GenX. The population of people in Community C is more than 250,000. Sun et al. (2016) [27] sampled drinking water in the three communities for 127 days between June and December 2013. Individual samples with concentrations below quantitation limits (QLs) were considered as zero while average concentrations below QLs were not included in the mean values. They found only legacy PFAS (PFOA and PFOS) in communities A and B with community A with a mean level of 355 ng/L and B with a mean value of 62 ng/L. In community A, the mean levels of PFOS and PFOA during the sampling period exceeded the USEPA health advisory level of 70 ng/L on 57 of the 127 days. In community B, located at a point of convergent tributaries, the mean PFOS and PFOA levels were lower than in community A at 59 ng/L. Community C had relatively low levels of the legacy PFAS but high levels of GenX at a mean concentration of 631 ng/L, 9X the recommended USEPA HAL (Sun et al., 2016) [27]. Therefore, statistical information suggests that the release of GenX from Chemours poses a danger to both human beings and their surroundings. In response to the increasing insight into the effects of GenX on humans, Cape Fear River, wells and the environment, a group from Chemours was sent to carry out research and write a report on the findings. The section below will examine the conclusions of the report.

2.2 Netherlands National Institute for Public Health and the Environment (RIVM) Report

Beekman et al. (2016) [2] conducted research on the possible health effects of GenX on human and wrote the RIVM Report. According to the report, Chemours had developed a new technology in the manufacture of Teflon that eliminates PFOA in the process. This course of action followed the class-action lawsuit that penalized the company billions of dollars. The new technology now makes GenX using three primary compounds namely E1, FRD-903, and FRD-902 (Beekman et al. 2016) [2]. The aim of the report was to evaluate the extent to which the three compounds, primarily FRD-902, would affect people living near the manufacturing plant. In brief, the report demonstrated that the new compounds were associated with negative health effects that were similar to those of the legacy PFOA. However, the extent to which they affect human health was very low (Beekman et al. 2016) [2]. They noted that the compounds are poorly biodegradable and do not bio-accumulate in human bodies. To add weight to their hypothesis, they carried out several experiments on female and male rats in a controlled environment. They obtained and reported their findings with FRD-902 as the representative GenX species in regards to its oral toxicity,

inhalation toxicity, dermal toxicity, mutagenicity, carcinogenicity, reproductive effectives, and organ toxicity.

2.3 Oral Toxicity

Beekman et al. (2016) [2] analyzed two studies that utilized rats and mice in a controlled environment. In both studies, the sample population was given different amounts of FRD-902 through gavage. The researchers administered 5000 mg/kg, 1750, 550 and 175 to diverse categories of female and male mice and rats. The entire study lasted 14 days after which they necropsied the mice and rats. These mg/kg (ppm) concentrations are 1000-fold higher than the ng/L (ppt) values in the Cape Fear water basin.

The majority of female rats given 5000 mg/kg of FRD-902 died on day 1. Two of them died within one to two days after administration. Close and post-mortem examinations of these animals showed discoloration of the liver, mandibular nymph, and the lungs (Butenhoff et al. 2004). The animals also showed signs of hair loss, prostate damage, clear ocular discharge, stained skin and fur, high position, salivation and partially closed eyes. The male rats within the group given 5000 mg/kg died after five days. These rats showed wet fur, lethargy, increased lung size, discolored eyes, and stomach as well as stained skin. However, the symptoms reversed on the second day. In the rest of the dosage groups, symptoms such as lethargy, wet fur, and stained skin were observed (Gannon et al. 2016).

Among the panel of mice, the entire samples dosed at 5000 and 1750 mg/kg died by the end of the seventh day of the study. They showed symptoms of low posture and lethargy. In all the other doses, there were signs of discolored lungs and cyst in the ovaries was observed in one mouse. Other symptoms included non-specific lesions in some rats (Hoke et al. 2016) [15].

From the results, it can be concluded that FRD-902 has harmful effects on rats and one may infer similar threat to human health. As the compound is able to induce cells to grow uncontrollably, it may lead to the onset of negative outcomes such as cancer. Thus, it is important to monitor levels of GenX in Cape Fear River and surrounding wells. The Organization for Economic Cooperation and Development (OECD) classifies values greater than 1750 ppm (mg/kg) to be highly toxic based on these findings (IARC, 2016) [16].

2.4 Inhalation Toxicity

The inhalation study was performed using OECD guidance number 403 (IARC 2016) [16]. The investigators separated the rats into three groups and exposed them to varying aerosol concentrations. The different groups of mice were subjected to aerosol at levels of 5200, 100 and 13 mg/m^3 for four hours. The study period ranged from 2 to 14 days after the exposure to the aerosol. After the appropriate study period, microscopic analysis of the respiratory system tissues as well as necropsy of the exposed animals were done. The results showed stained faces, red discharge around the nose, mouth, and eyes among the rats in the 5200 mg/m^3 concentration group. Similar results of red nasal discharge were reported in rats subjected to 100 mg/m^3 of the aerosol with no death of the rats. The observable signs and symptoms reversed after two days. However, inhalation was associated with 2.5-6.8% decrease in body weight among rats in the highly concentrated group (Lau et al. 2007) [19]. Minor losses in weight were also observed in the 100 and 13 mg/m^3 dosage groups.

2.5 Dermal Toxicity

Two rabbits were used for the dermal experiment. The rabbits were subjected to occlusive patches at the dose level of 5000 mg/kg for 24 days after which the concentrated compounds were washed off. Exposure via the occlusive patch did not result in the death of the rabbits. However, cases of moderate to mild erythema were observed at the site of application. These observations reversed after ten days. Sloughing and epidermal scaling were also observed.

The study demonstrated that FRD-902 is corrosive to the skin when applied at relatively high concentrations. However, the effect of the chemical on the skin can be reversed by

washing with a lot of running water. In other studies, the compound is known to cause eye damage (Rae et al. 2015). According to OECD classification, the compound is classified under category 1 of eye-damaging agents (Hoke et al. 2016) [15]. The release of GenX byproducts into the air may present a medical threat to humans. However, the extent remains unknown since no available data focuses on the effects of FRD-902 on humans.

2.6 Mutagenicity

Beekman and his colleagues confirmed from results of the study that FRD-902 caused insignificant effects on the genetic composition of the rats under study. However, at extremely high amounts of gavage administered to the rats, there was an alteration in their bone marrow but an insignificant change in chromosomal aberration of the animals under study. Others died as a result of high concentrations of FRD-902 (Beekman et al. 2016) [2]. Once again, mutagenicity in human beings remains unknown.

2.7 Carcinogenicity

The OECD guideline 453 was utilized to perform the carcinogenicity experiment involving a total of eighty rats. From the study, it was noted that with time, the number of tumors increased variably in males and females exposed to FRD-902 (Beekman et al. 2016 on RIVM report 2016-0174 [2]). Hepatocellular adenoma in females increased from the historical 5% to 15.71% in rats in the highly concentrated group. Similarly, hepatocellular carcinoma increased from 1.7% to 5.71%. In males, pancreatic acinar cell adenoma decreased slightly from 5% to 4.29%. However, despite the outcome, Beekman and his colleagues reported that the carcinogenic properties observed are standard in rodents but not in human beings [2].

2.8 Reproduction Effect

In the to determine the reproductive effects of FRD-902, it was noted that administration of the compound caused early deliveries in rats. Similarly, there was decreased fetal mass at delivery ranging from 8.8% - 28%. There was a decline in gravid uterine weight, hypertrophy as well as increased weight of the liver. In some cases, the parental animals increased their consumption habits, which led to a significant increase in their body weight. Other observable effects on males included delayed sexual maturation. However, the researchers related this delay to the decrease in body weight and poor eating habits. There were no observable traits in the development of the offspring.

2.9 Organ Toxicity

Presence of GenX in drinking water presents a potential danger to human health. Scholars suggest that it may lead to accelerated puberty, the growth of cancerous cells, abnormal changes in cholesterol levels as well as liver and kidney damages in humans (Rae et al. 2015) [24]. As a result of such adverse effects of GenX on the rats tested, authorities have intervened to address the issue. The section below examines the steps that different authorities have taken to ensure water safety as well as the elimination of GenX in Cape Fear River.

3 What is being done?

3.1 Imposing Penalties to Production Plants

The USEPA has penalized DuPont and Chemours financially to the tune of $680 million for environmental pollution and discharge of toxins into the Cape Fear River. This course of action is meant to discourage the companies from discharging GenX into the river. Similarly, other companies planning to participate in the production of Teflon chemicals will have to reconsider dumping their untreated waste into the river. In the long run, the amount of GenX in the Cape Fear River will be drastically reduced to acceptable levels. Similarly, the action of imposing penalties on polluting firms will force the companies to become more responsible for their actions. The production facilities will participate in preservation activities other than polluting. As a recommendation, the USEPA and Cape Fear River Watch should set higher penalties for polluting firms.

3.2 Cleaning the Contaminated Water

The Chemours plant has chosen to clean the contaminated water as well as end the dumping of GenX into the river. They have setup a clean-up facility in Fayetteville that will capture, screen and treat he contaminated water before releasing it into the river. They also promised to pump out contaminated water that has a higher concentration than the recommended level HAL of 70 ppt.

3.3 Cape Fear River Watch

The Cape Fear River Watch will monitor, watch and ensure the safety of drinking water collected from Cape Fear River. The agency has been educating the public on the toxicity caused by GenX and other toxins as well as possible treatment options. The Watch has decided to:

(a) Push for a binding agreement with the manufacturing company that they will end the dumping of their waste into Cape Fear River.

(b) Force the NC Department of Environmental Quality (NCDEQ) to review the permits of local plants to tighten and remove the loopholes that allow companies to discharge chemicals into the river. Currently, the Chemours permit is under consideration.

(c) Advocate for transparency in the Cape Fear Public Utility Authority (CFPUA) so that the citizens will be notified in a timely way of toxins to which they may be exposed. Citizens should not be kept in the dark especially on matters that affect their health and wellbeing.

(d) Push the state to install facilities at the treatment plants that will capture and eliminate particles of PFOS reported in Cape Fear River water. Similarly, the state will focus on carrying out intensive research that seeks to reveal how much of the toxins are available at each water treatment plant.

3.4 Education on Removing PFOS and PFOA in Drinking Water

The USEPA has recommended that system operators at water treatment plants should assess water samples to determine the levels of PFOA and PFOS present in the water (Chagawa, 2016) [6]. Any amount above 70 ppt. should be treated before it reaches the public. The report recommended several treatment alternatives which include:

(a) River bank floatation
(b) Anion exchange
(c) Granular activated carbon (GAC)
(d) Microfiltration and
(e) Reverse osmosis
(f) Nano filtration

According to the report, anion exchange was highly effective in removing PFOS from the water. However, it was moderately effective in the removal of PFOA. The method was unable to filter some shorter chain PFOS and PFOA. GAC proved to be an effective treatment alternative for removal of many PFOA and PFOS. It is a less costly and fairly reliable procedure. On the other hand, reverse osmosis and nano filtration proved to be unsuitable in treating even the short chain PFOA and PFOS from the drinking water.

With the current regulation and combined efforts from relevant authorities, the citizens whose drinking water source is from the Cape Fear River can be assured of safe drinking water.

4 Conclusion

GenX is a close associate of C8 and other PFOA produced by DuPont and Chemours. This compound consists of shorter chains compared to the PFOA. Its chemical structure is abbreviated as PFPrOPrA. In the past year, various studies have shown that GenX has similar health effects as the previous legacy PFOA and PFOS. These effects include accelerated puberty, growth of cancerous cells, abnormal changes in cholesterol levels as well as liver and kidney damages. It is also closely associated with skin irritation and corrosion as well as carcinogenicity. Because of such potential health hazards, authorities have intervened to address the problem. Example of interventions includes educating the public, providing bottled water to homes whose wells were contaminated with Gen X, imposing penalties on polluting firms, encouraging corporate social responsibility and identifying technologies for treating water. Examples of

these technologies to remove GenX compounds include granular activated carbon, nano filtration, river bank floatation, anion exchange, microfiltration and reverse osmosis.

In a bid to ensure safe drinking water in North Carolina and other states (Vermont, Massachusetts, New York, Delaware, Virginia, and Michigan), the amount of GenX and similar compounds should not exceed 70 ppt. Therefore, each treatment plant should test water samples and screen for any traces of GenX, PFOS and PFOA and related compounds. In the case where the pollutants exceed 70 ppt, the treatment facility should consider using any of the measures discussed above to remove the pollutant.

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