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**RETROSPECTIVE MODELING OF POTENTIAL RESIDENTIAL EXPOSURE TO PERFLUOROOCTANOIC
ACID (PFOA) RELEASES FROM A MANUFACTURING FACILITY**

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ABSTRACT

A retrospective exposure analysis using various environmental models was conducted to estimate potential intake of perfluorooctanoic acid (PFOA) over the past 53 years by persons residing in parts of Ohio and West Virginia. A processing aid, ammonium perfluorooctanoate (APFO), was used in the manufacture of the fluoropolymers and released to the environment in air, water and solid waste emissions. In the environment, APFO disassociates to its anion form which is referred to as PFOA. Following considerable analyses, particulate deposition from facility air emissions to soil and the subsequent transfer of the chemical through the soil was determined to be the most likely source of the PFOA detected in the groundwater near the facility. A mass balance analysis of APFO used and released by the facility for each year of operation from 1951-2003 was the foundation of this analysis. Air emissions and deposition rates were modeled using U.S.EPA's ISCST3 model. Air deposition rates were then used as continuous input into the PRZM-3 model to estimate the PFOA concentrations in surface soil and the movement of the chemical to the groundwater. Estimates of the intake of PFOA by residents were model estimated for each water district for all relevant routes of exposure. Exposures were modeled for a 185 square mile area surrounding the facility. The highest off-site environmental concentrations were predicted to occur about 1 mile away. For this 1 square mile area, during the time period 1951 -2003, the model estimated air concentration was 0.2 $\mu\text{g}/\text{m}^3$, the estimated surface soil concentration was 11 $\mu\text{g}/\text{kg}$, and the estimated drinking water concentration was 3 $\mu\text{g}/\text{L}$. Similar data were generated for each of the other 18 areas around the facility. Comparison of measured PFOA concentrations in groundwater in the various water districts indicated that the models over predicted recent groundwater concentrations by factor of 3 to 5. The predicted historical lifetime and average daily estimates of PFOA intake by persons who lived within 5 miles of the plant over the past fifty years were about 10,000 fold less than the doses that were considered acceptable. To our knowledge, this is the first case study where air deposition of an organic chemical from an industrial facility impacted groundwater which served as a source of public drinking water. The methodology for exposure assessment used here may well be applicable to other water soluble, persistent chemicals emitted to the air.

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INTRODUCTION

A synthetic surfactant with the chemical name of ammonium perfluorooctanoate (APFO) is used as an essential processing aid in the production of fluoropolymers, but is typically not present in finished consumer articles (e.g., it is removed or destroyed during their manufacture). APFO is non-volatile and highly water soluble. It has low to moderate soil binding capabilities and is persistent in the environment due to its resistance to environmental and biological degradation. The anionic form of APFO is found in the environment and is commonly referred to as perfluorooctanoic acid (PFOA).

Over the past 50 years, APFO has been used in the manufacture of fluoropolymers at the DuPont facility in Washington, WV (DuPont Washington Works). In the mid-1980s, PFOA was intermittently detected in some of the public drinking water sources in communities near the plant. The processes by which APFO was transported to the groundwater have been investigated by experts at DuPont, U.S.EPA Region III and West Virginia DEP. There is agreement among these groups that APFO air emissions and subsequent deposition onto soil, as well as releases to surface water, were the most likely sources of the PFOA in the groundwater for residents living within about ten miles of the facility (WVDEP, 2003). (Figure 1)

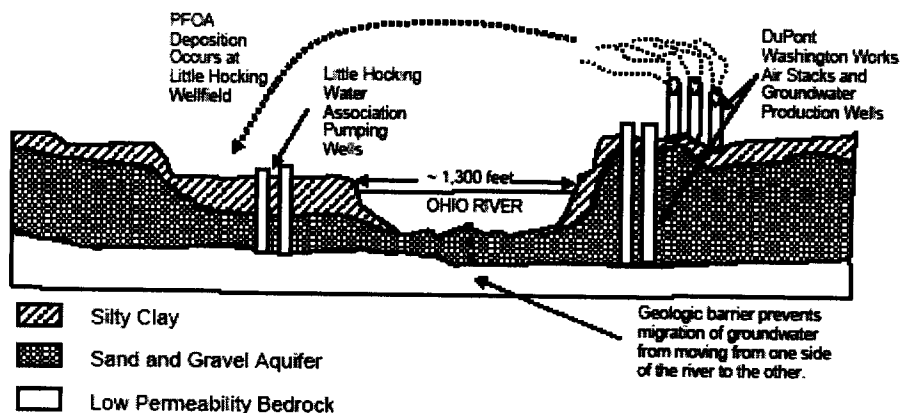


Figure 1. Cross Section of Ohio River near Little Hocking Water Association Public Water Supply Wells (adapted from DuPont, 2003a).

In this analysis, we developed mass balance and environmental migration models that predicted PFOA concentrations in air, soils, groundwater, surface water and other environmental media each year throughout the operational history of the facility (1951-2003). We also evaluated the likely routes of human exposure to PFOA in these media and developed plausible estimates of PFOA exposure as a function of duration of

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residential occupancy in the nearby communities. These exposures were characterized using a margin of exposure (MOE) analysis.

METHODS

Materials Balance

APFO was used in seven different fluoropolymer processes at the plant during various times from 1951 to 2003. For each process and year, the amount of PFOA used, released, or destroyed was quantified. Specifically, the mass of PFOA recovered in the process, destroyed through treatment or released to the environment via air, water or land was calculated for each year from 1951-2003.

The amount of APFO used by process and year was obtained by reviewing cost sheet records from the facility. Cost sheets were available for every year from 1951 to 1980, 1983, 1987 – 1991, and 1993 – 2003. For the years and processes for which data were missing, APFO use was estimated using linear interpolation between the years where data did exist. The amounts of APFO in each process partitioning to air, wastewater, aborted batches, solid waste, and supernate were estimated based on information from APFO mass balances constructed by process engineers at the plant.

Environmental Modeling

Because measurements of PFOA in various environmental media were only available for recent years in a limited number of locations, environmental fate and transport models were used in conjunction with mass balance information to estimate historical PFOA concentrations that may have been present in air, soil and groundwater in the communities surrounding the fluoropolymer plant. Concentrations were estimated for each year from 1951-2003. The predicted concentrations were then compared to the limited measured data to determine the degree to which concentrations were over or underestimated by the model.

Air Modeling

Airborne PFOA resulting from particulate emissions at the facility were evaluated using U.S.EPA's Industrial Source Complex Short Term version 3 (ISCST3) model (U.S.EPA, 1995a,b). The ISCST3 model was used to estimate annual average air concentrations of PFOA ($\mu\text{g}/\text{m}^3$), and dry and wet deposition of PFOA to the soil ($\text{g}/\text{m}^2\text{-yr}$), for more than 4,700 receptor points within 19 zones in the modeling domain (Figure 2). Of the seven processes which used APFO, only four had the potential for air emissions. Prior to 1990, APFO was emitted from the fluoropolymer plant stacks of the Fine Powder, FEP, and Granular dryers. Two water districts were not included in the air modeling domain (not shown in Figure 2).

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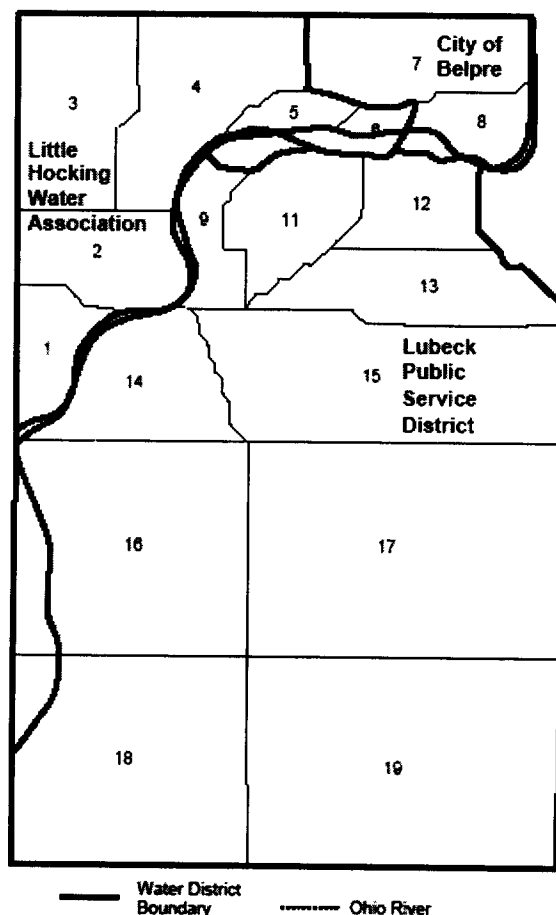


Figure 2. Schematic Illustrating 19 Exposure Zones with Air Dispersion Modeling Results and Their Respective Water Districts. The predominant wind direction at the facility is from the southwest.

Unsaturated Zone Soil Modeling

Historical soil concentrations of PFOA were estimated using U.S.EPA's Pesticide Root Zone Model Version 3.12 (PRZM-3) (U.S.EPA, 2001). The model consists of two linked modules which calculate fate and transport in the surface root zone (PRZM module) and subsurface soil (VADOFT module). The same exposure zones as those used in the air dispersion modeling were used in modeling historical soil concentrations. Input parameters for the soil modeling were selected based on the soil characteristics for the zones modeled. Soil types for the public water supply well locations were obtained from a recent regional groundwater assessment (DuPont, 2003b). For the soil types in areas having both public water supplies and private wells, soil information was obtained from the United States Department of Agriculture (USDA) National Resource Conservation Service (NRCS). Specifically, NRCS's State Soil Geographic (STATSGO)

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database was the primary source of information. General and zone-specific input parameters for calculating the water balance in PRZM were selected from model defaults based on surface and subsurface soil type and depth, selection of vegetative cover, chemical transport parameters and local meteorology.

Groundwater Modeling

The public water districts' production wells for drinking water are completed in the sand and gravel layer due to the high well yields that are achievable (Figure 1). To account for the contribution of surface water and recharge (i.e., filtration) to the well capture zones from PFOA deposition to soil, a lumped parameter model was used to calculate groundwater concentrations. Historical annual average surface water concentrations of PFOA were calculated using estimates of flow rate in the Ohio River and the ass release rate of PFOA in the river.

Calculation of PFOA in Garden Vegetables

Because air releases could result in deposition onto locally grown produce, concentrations of PFOA in garden vegetables were calculated. PFOA concentrations for typical home garden vegetables including corn, beans, and potatoes, known to have been grown in the area near the facility, were estimated using U.S.EPA's Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, Volumes 1 & 2 (U.S.EPA, 1998a,b).

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RESULTS

Materials Balance

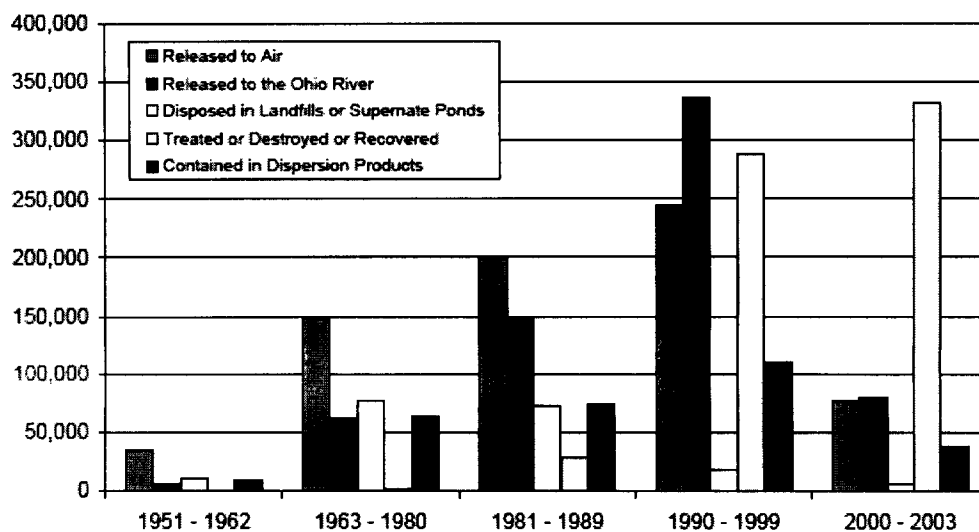


Figure 3. Estimated Historical C-8 Material Balance for the Washington Works Facility from 1951 to 2003 for All Processes Combined.

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Model Predictions

Table 1: The Highest Predicted Air Concentrations And Soil Deposition Occurred In Zone 5; The Lowest Occurred In Zone 19.

Zone	Annual Average Airborne PFOA Concentration by Exposure Scenario and Zone ($\mu\text{g}/\text{m}^3$)		
	Scenario 1 1995 - 2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003
1	0.02	0.02	0.01
2	0.05	0.04	0.03
3	0.04	0.03	0.02
4	0.11	0.09	0.06
5	0.3	0.2	0.2
6	0.07	0.06	0.04
7	0.08	0.07	0.05
8	0.03	0.02	0.01
9	0.08	0.06	0.05
10	0.5	0.5	0.3
11	0.07	0.05	0.04
12	0.02	0.02	0.01
13	0.01	0.01	0.01
14	0.02	0.01	0.01
15	0.01	0.01	0.01
16	0.01	0.01	0.004
17	0.004	0.003	0.002
18	0.004	0.003	0.002
19	0.002	0.002	0.001

Table 2: The Highest Predicted Drinking Water Concentrations Were For The Little Hocking Water Association Followed By The Lubeck Public Service District.

Water District	Average PFOA Drinking Water Concentration by Exposure Scenario ($\mu\text{g}/\text{L}$)		
	Scenario 1 1995 - 2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003
Little Hocking Water Association	8	5	3
City of Belpre	1	0.7	0.4
Lubeck Public Service District	1	1	0.7
Tuppers Plains/Chester Water District	0.3	0.2	0.1
Village of Pomeroy	0.3	0.2	0.1

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Little Hocking (Zone 5) Modeled and Measured Public Well Data

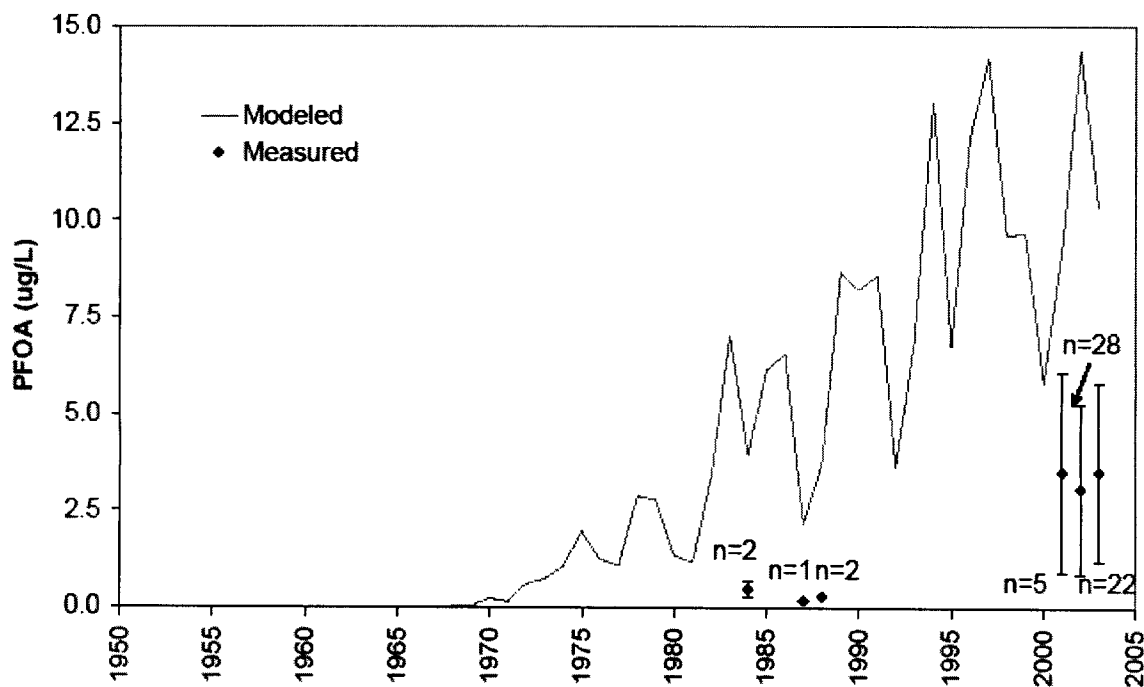


Figure 4. Comparison Of Little Hocking (Zone 5) Modeled And Measured Public Well Data Which Shows That Modeled Drinking Water Concentrations Were 5-fold Higher Than Measured Concentrations.

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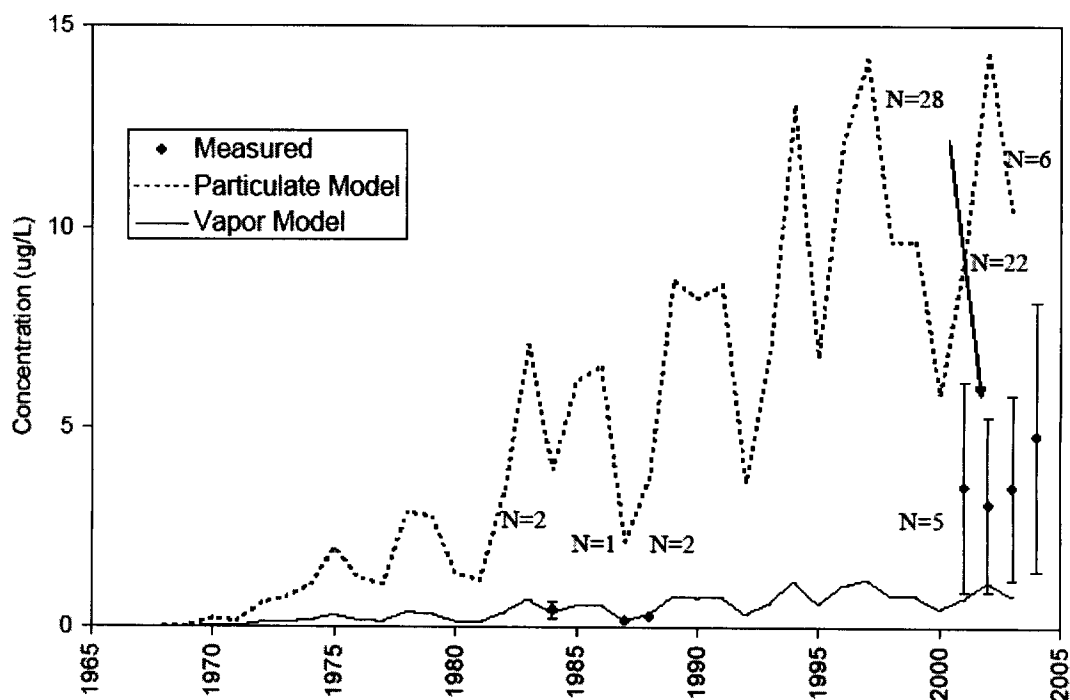


Figure 5. Uncertainty In Particle Size Data Was Evaluated Using An “All Vapor” Scenario And Found That The All Vapor Scenario Would Have Under Predicted Groundwater Concentrations.

Estimates of PFOA exposure are presented in Table 3. The exposures presented are annual average daily doses which were calculated using typical exposure parameters and various residency time periods.

- Predominant pathway of exposure was via drinking water;
- Highest exposures are predicted for residents in the zones served by Little Hocking Water Association.

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Table 3: Modeled Average Exposures to PFOA in Various Media from 1951 to 2003.

Water District	Scenario 1 1995 - 2003	Scenario 2 1974 - 2003	Scenario 3 1951 - 2003
Little Hocking Water Association			
Air Concentration ($\mu\text{g}/\text{m}^3$)	0.10	0.08	0.06
Surface Soil ($\mu\text{g}/\text{kg}$)	8	5	3
Drinking Water ($\mu\text{g}/\text{L}$)	8	5	3
Average Daily Dose (mg/kg-day)	1.8E-04	1.3E-04	7.8E-05
City of Belpre			
Air Concentration ($\mu\text{g}/\text{m}^3$)	0.05	0.04	0.03
Surface Soil ($\mu\text{g}/\text{kg}$)	2	2	1
Drinking Water ($\mu\text{g}/\text{L}$)	1	1	0.4
Average Daily Dose (mg/kg-day)	3.5E-05	2.5E-05	1.6E-05
Lubeck Public Service District			
Air Concentration ($\mu\text{g}/\text{m}^3$)	0.02	0.02	0.01
Surface Soil ($\mu\text{g}/\text{kg}$)	1	1	1
Drinking Water ($\mu\text{g}/\text{L}$)	1	1	1
Average Daily Dose (mg/kg-day)	2.6E-05	2.2E-05	1.4E-05
Tuppers Plains/Chester Water District			
Air Concentration ($\mu\text{g}/\text{m}^3$)	—	—	—
Surface Soil ($\mu\text{g}/\text{kg}$)	—	—	—
Drinking Water ($\mu\text{g}/\text{L}$)	0.3	0.2	0.1
Average Daily Dose (mg/kg-day)	6.0E-06	4.0E-06	2.0E-06
Village of Pomeroy			
Air Concentration ($\mu\text{g}/\text{m}^3$)	—	—	—
Surface Soil ($\mu\text{g}/\text{kg}$)	—	—	—
Drinking Water ($\mu\text{g}/\text{L}$)	0.3	0.2	0.1
Average Daily Dose (mg/kg-day)	6.0E-06	4.0E-06	2.0E-06

DISCUSSION

A large toxicological database exists for PFOA and includes developmental, reproductive, immunotoxicity, genotoxicity, carcinogenicity, pharmacokinetics and various mode of action studies. A recent toxicological review of PFOA by Kennedy et al. (2004) summarized the current animal and human toxicity data. Acute toxicity animal studies indicate that PFOA exhibits moderate acute oral and inhalation toxicity and slight acute dermal toxicity. The sub-chronic and chronic studies in animals (rats, mice, monkeys, rabbits) indicate that the liver is the primary target organ (Griffith and Long, 1980; DuPont, 1981; Kennedy, 1985, 1986, 1987; Perkins; 1992; Butenhoff et al., 2002). PFOA is not mutagenic and has not shown teratogenic or fetotoxic effects at doses below those which caused maternal toxicity (Staples et al., 1984; Staples, 1985). The carcinogenicity of PFOA has been investigated in rodents (Biegel et al., 2001). Increased incidences of benign tumors of the liver, pancreas (acinar cells) and testes (Leydig cell) were found following a 2-year rat bioassay at dietary exposures of 300 ppm. One rat study also found increased incidences of mammary gland tumors in female rats exposed to PFOA, although the increase was not reflective of an effect of PFOA (Sibinski, 1987; Riker et al., 1987). U.S.EPA's Science Advisory Board recently reviewed the cancer data for PFOA and recommended a designation of "likely human carcinogen." This designation has been questioned by others due to the lack of

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relevance of the PPAR- α mode of action to humans (Rickard, 2006; Zobel, 2006). In contrast to animal studies, epidemiology investigations of APFO production workers have not shown increased cancer mortality of other adverse chronic systemic effects (Ubel et al., 1980; Gilliland and Mandel, 1986; Alexander, 2001; Alexander et al., 2003; Olsen et al., 1998, 2000, 2003).

In the absence of a standard health benchmark for PFOA, a MOE analysis was conducted as a means of understanding potential health risks due to releases of PFOA from Washington Works. The MOEs were calculated using the administered benchmark dose of 3.9 mg/kg-day developed by Butenhoff et al. (2004). For non-cancer end-points, the MOEs were calculated using averaged daily doses for residents potentially exposed for 9 years, 30 years and 53 years. The highest potential doses and consequently the lowest MOEs were calculated for residents living closest to the plant during the time period 1995 – 2003. The MOEs for these years ranged from approximately 9,000 to 13,000. These values are similar to or higher than MOEs calculated by Butenhoff, et al. (2004) and U.S.EPA (2002) for the general population. However, the MOEs for the residents were calculated using the administered dose, whereas Butenhoff et al. (2004) and U.S.EPA (2002) calculated MOEs based on a comparison of background blood levels of PFOA to the animal blood levels that corresponded to the administered dose.

In summary, the primary exposure pathway by which persons living near this production facility received exposure to PFOA was through ingestion of drinking water. A comparison of the expected intake of PFOA by citizens living near this facility with a non-cancer benchmark dose indicates that adverse health effects would not have been expected to occur. The methods used to estimate historical PFOA concentrations in the environment near the plant have been shown to be reasonable, although they likely overestimated the actual exposure of residents.

ACKNOWLEDGEMENTS

The research underlying this work was funded by DuPont. They have been involved in litigation regarding the presence of PFOA in groundwater at the facility described here.

REFERENCES

Available upon request.