Taylor & Francis
Taylor & Francis Group

A Methodology for Estimating Human Exposure to Perfluorooctanoic Acid (PFOA): A Retrospective Exposure Assessment of a Community (1951–2003)

Dennis J. Paustenbach
ChemRisk, Inc., San Francisco, California

Julie M. Panko, Paul K. Scott, and Kenneth M. Unice
ChemRisk, Inc., Pittsburgh, Pennsylvania, USA

Perfluorooctanoic acid (PFOA) is a persistent chemical that was recently shown to be widely distributed in the ambient environment. Because of concerns about the possible adverse health effects on persons exposed to PFOA, a retrospective exposure assessment was conducted for a population of about 50,000 persons who reside near one of the facilities where this chemical was used. No similar study of any chemical with the properties of PFOA had ever been performed; thus, several novel methods were developed and applied in this analysis. Historical records of the emissions from the facility were the basis for the estimates of the potential intake of (PFOA) by residents over the past 53 yr. Various well-accepted environmental models were dynamically combined in order to estimate the concentrations in all relevant environmental media including ambient air, surface soil, drinking water, and homegrown vegetables. 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 PFOA that was detected in groundwater. The highest off-site environmental concentrations were predicted to occur about 1 mile away. For this approximately $1\frac{1}{2}$ square mile area, during the time period 1951–2003, the model-estimated average air concentration was 0.2 $\mu g/m^3$, the estimated surface soil concentration was 11 $\mu g/kg$, and the estimated drinking water concentration was 4 $\mu g/L$. Similar data were generated for 20 additional geographical areas around the facility. Comparison of measured PFOA concentrations in groundwater in the various water districts indicated that the models appeared to overpredict recent groundwater concentrations by a 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 50 yr were about 10,000-fold less than the intake of the chemical not considered as a health risk by an independent panel of scientists who recently studied PFOA.

Ammonium perfluorooctanoate (APFO), also known as "C-8" by some in the fluoropolymer industry, is used as a surfactant in the production of fluoropolymers. Fluoropolymers are high-performance materials used in electronics, aerospace, automotive, chemical processing, pollution control, and consumer houseware applications (Gangal, 2004). APFO is typically not present in finished consumer articles derived from fluoropolymer products (e.g., it is removed or destroyed during their manufacture) at concentrations that are readily detectable (Washburn et al., 2005).

APFO is nonvolatile yet highly water-soluble, with a vapor pressure of 0.00812 Pa and a water solubility greater than 500 g/L (Shinoda et al., 1972). APFO has captured the attention of the scientific and regulatory communities over the past 5 yr due to its persistence in the environment and questions concerning its chronic toxicity (APME, 2003; Cousins et al., 2005; Mabury, 2005).

APFO dissociates into ammonia and the anion form in environmental media [e.g., $CF_3(CF_2)_6COOH\text{-}NH_3 = CF_3(CF_2)_6 COO^- + H^+ + NH_3$]. Although perfluorooctanoic acid (PFOA) is more frequently used to describe the APFO anion, it should be noted that the anion converts to the acid form only under highly acidic environmental conditions. To maintain consistency with other literature, the term PFOA is used in this article when referring to the anion form of APFO. While both APFO and PFOA are nonvolatile and highly soluble, PFOA has a higher vapor pressure and lower solubility than APFO (Table 1).

APFO has been used for more than 50 yr by the fluoropolymers industry and attracted little attention, due to (1) apparent

TABLE 1
Physicochemical Properties for APFO and PFOA

Property	APFO	PFOA	Reference
CAS number	3825–26–1	335–67–1	U.S. EPA, 2005a
Molecular weight	431	414	U.S. EPA, 2005a
Solubility in water at 25°C (g/L)	>500	4.4	Shinoda et al., 1972
Vapor pressure (Pa)	0.00812 at 20°C	2.253 at 20°C	DuPont internal data
K_{oc} organic carbon distribution coefficient (dimensionless)	NA	108.2	The values for silty clay loam, sandy clay loam and sandy loam were similar and thus averaged (DuPont, 2003c).
Henry's Law constant (unitless)	NA	8.5×10^{-5}	Calculated using U.S. EPA Soil Screening Guidance (U.S. EPA, 1996): PFOA does not readily partition from water to air.

Note. NA, not available.

low to moderate acute toxicity and (2) lack of evidence of adverse human health effects observed in APFO manufacturing workers. 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 from studies of acute, subchronic, and chronic exposures via various routes of exposure and in a variety of animal species. The acute toxicity animal studies indicate that PFOA exhibits moderate acute oral and inhalation toxicity based on lethality, where oral doses ranged from 178 to 1800 mg/kg and air concentrations were 0.98 mg/L and 18.6 mg/L. Additionally, acute dermal toxicity based on lethality was considered slight (e.g., >2000 mg/kg). Most toxicology studies have involved the ammonium salt as the test compound. The subchronic and chronic studies in animals (rats, mice, monkeys, rabbits) indicate that the liver is the primary target organ (Griffith & Long, 1980; Kennedy, 1985, 1987; Kennedy et al., 1986, 2004; Perkins, 1992; Butenhoff et al., 2002). PFOA is not mutagenic and has not produced teratogenic or fetotoxic effects at doses below those that induced maternal toxicity (Staples et al., 1984; Staples, 1985). Lau et al. (2004) summarized the developmental toxicity of PFOA. Recent postnatal studies on developmental and reproductive effects using doses of 1, 3, 10, or 30 mg/kg-day indicate that effects in the F1 generation were unremarkable during the lactational period with the exception of a significant lag in weight gain in the offspring of the 30-mg/kg treated group during the first postnatal week and a significant decrease in the lactation index. However, postweaning mortality and delays in pubertal onset in the F1 generation at 30 mg/kg by gavage were noted (Butenhoff et al., 2004a). The carcinogenicity of PFOA has been investigated in rodents (Biegel et al., 2001). Increased incidences of benign tumors of the liver, pancreas (acinar cell), and testes (Leydig cell) were found following a 2-yr rat bioassay at dietary exposures of 300 ppm. One rat study

also found increased incidence of mammary-gland tumors in female rats exposed to PFOA, although the increase was not reflective of an effect of PFOA (Riker et al., 1987). The U.S. Environmental Protection Agency (EPA) Science Advisory Board reviewed the cancer data for PFOA and concluded that because there are inadequate data in human studies and uncertainty regarding the relevance of the rodent tumors, PFOA may be suggestive of carcinogenicity, although the U.S. EPA also considered a cancer descriptor of "likely" (U.S. EPA, 2005a, 2005b). In contrast to animal studies, epidemiology investigations of APFO production workers have not shown increased cancer mortality or other adverse chronic systemic effects (Ubel et al., 1980; Gilliland & Mandel, 1996; Alexander, 2001; Alexander et al., 2003; Olsen et al., 1998, 2000, 2003).

Beginning in about 2000, there were indications that PFOA was present in measurable concentrations in wildlife in a number of locations worldwide (Kannan et al., 2002a, 2002b; Moody et al., 2002; 3M, 2003; Tomy et al., 2004). Additionally, detectable levels of PFOA were found in the blood of children, adults, and the elderly in the United States and numerous other countries (Olsen et al., 2003, 2005; Kannan et al., 2004). While PFOA is a biopersistent chemical, bioconcentration factors ranging from 3 to 9 indicate that PFOA is not bioaccumulative (Morikawa et al., 2006; U.S. EPA, 2002). As a result of these observations, both state and federal regulatory agencies developed an interest in understanding the fate and transport of these chemicals in an effort to understand why PFOA was being detected. The interest in this family of chemicals has become sufficiently great that the first International Symposium on Fluorinated Alkyl Organics in the Environment was recently convened in Toronto, Canada, with nearly 600 scientists and with about 100 papers presented.

To understand the possible exposure of approximately 50,000 persons in the community surrounding a fluoropolymer manufacturing facility, mass balance and environmental migration models that predict PFOA concentrations in air, soils, groundwater, surface water, tap water, and other

environmental media each year throughout the operational history of the facility (1951–2003) were developed. The likely routes of human exposure to PFOA in these media were also evaluated and plausible estimates of PFOA intake as a function of duration of residential occupancy in the nearby communities were developed. The resulting intake of PFOA was characterized by comparing the estimates of intake to health-based exposure criteria that were developed for PFOA (Butenhoff et al., 2004b). It is acknowledged that there is some level of background exposure to PFOA to the general U.S. population. This assessment, however, focused only on the release of PFOA from one facility and on its presence in air, soil, drinking water and vegetables surrounding the facility. A comparison of the estimated exposures of the local population to that of the general population was made.

This exposure assessment is the first attempt to develop a generally applicable model for estimating the concentration of PFOA in environmental media due to emissions in air and water from an industrial facility, as well as the resulting intake of PFOA by persons exposed to them. Because the fluorinated chemicals possess unique chemical and physical properties, a novel application for estimating concentrations in the environment due to airborne emissions using a combination of generally accepted models needed to be developed, and this approach should be applicable to other highly water-soluble chemicals released to the ambient environment as a vapor or fume.

DESCRIPTION OF THE MANUFACTURING FACILITY

Over the past 50 yr, APFO was used in the manufacture of fluoropolymers at the DuPont facility in Washington, WV (DuPont Washington Works). The plant is located approximately 10 miles southwest of Parkersburg, WV, along state Route 61. This facility was established in the 1940s and began using APFO in some of its manufacturing processes in 1951. APFO serves as a surfactant in the fluoropolymer production process and is neither consumed nor destroyed in the process.

Seven fluoropolymer processes at the plant came on line at various times over the years of operation and each used APFO at some point from 1951 to 2003. These processes are: fine powder, polytetrafluoroethylene (PTFE) dispersion, fluoroethylene propylene (FEP), FEP dispersion, granular, PFA process K, and PFA dispersion. Each process is briefly described next.

Fine Powder Process

This line began in 1951 and the product (fine powder) is used in a wide range of goods, including membranes for apparel, wire and cable, and filled products. APFO is added at the start of this process and was released via airborne emissions, as well as in liquid and solid wastes. The primary source of air emissions were from the dryer exhausts. After 1990,

a scrubber was installed to reduce air emissions and recover PFOA from this waste stream. In addition, wastewater was treated using an Oberlin filter to remove large solids prior to treatment in carbon beds, which started in 2001.

PTFE Dispersion Process

Polytetrafluoroethylene (PTFE) is similar to the fine powder product; however, it is not dried but instead was sold as a liquid for coating applications. This product line began in 1951 at the same time as the fine powder line. Since the product is not dried, there are no aerial emissions from this process. Some residual APFO remains in the product until it is further processed by the industrial customer.

FEP Process

The fluoroethylene propylene (FEP) product line began in 1963 and is sold in cube or flake form. It is used to make extrudable resins which are often used to coat wire and cable. APFO is added at the start of the process and was released via air emissions and in liquid and solid wastes. The dryer exhausts are the primary source of air emissions for this process. Starting in 1968, scrubbers were installed on the dryer exhausts and the recovered PFOA was released to the Ohio River until 1997. In 1997, the recovered PFOA from this process was recycled. In addition, beginning in 2001, wastewater was treated using an Oberlin filter to remove large solids prior to carbon treatment.

FEP Dispersion Process

This product line is similar to FEP; however, it is not dried but sold as a liquid dispersion. This product line also began in 1963. There are no air emissions from this process because the product is not dried. Some residual APFO remains in the product until it is further processed by the industrial customer.

Granular Process

The granular process began operation in 1951, but APFO was not used until 1965. This product is sold in solid granular form and is used for making molded products and skived sheets. APFO is added at the start of the process and is released via air emissions and in liquid wastes. The dryer exhausts are primary sources of air emissions for this process. No scrubbers were installed for this process because of the low amount of APFO used relative to the other processes. In addition, the wastewater from this process was not carbon treated for the same reason.

PFA Process K

The PFA process K product line began in 1998 and the solid material is sold for wire, cable, and semiconductor applications. APFO is added at the start of the process and was released

via air emissions and in liquid and solid wastes. From the start of this process, a scrubber has been in place to reduce air emissions and the wastewater is treated with carbon treatment prior to discharge.

PFA Dispersion Process

The PFA dispersion product is similar to PFA Process K, although it is sold as a liquid dispersion. This process began in 1973 and the material was manufactured at the FEP plant. APFO is added at the start of the process and released in liquid and solid wastes.

Environmental Monitoring at the Site

In the mid-1980s, PFOA was intermittently detected in some of the tap-water sources in communities near the plant. In recent years (approximately 2000 to present), more than 200 samples of raw or finished drinking water were collected from public water districts or private wells near the Washington Works facility (hereafter referred to as the plant).* Concentrations of PFOA greater than 0.05 μg/L (contemporary quantification level of PFOA in water) were found in the drinking water of 5 local water districts: Little Hocking Water Association, Lubeck Public Service District, City of Belpre, Tuppers Plains/Chester Water District, and the Village of Pomeroy, over the past 5 yr (2000–2005). Figure 1 shows the locations of these water districts' service areas in relation to the plant. A summary of the historical drinking-water sampling data for PFOA in the relevant water districts is presented in Table 2.

Each of these water service providers obtains their water from groundwater in the Dunkard Group bedrock and Ohio River alluvial terrace deposits. The saturated portion of the Ohio River alluvial terrace deposits comprise the principal regional aquifer used for public and industrial water supply purposes. The Ohio River Alluvial Aquifer occurs at depths ranging from 15 to 70 ft below ground surface at the various water-district well fields. Groundwater investigations at the plant demonstrated that, due to the pumping rates of the facility and another industrial facility (operated by General Electric) adjacent to the plant, the public water supplies are hydrogeologically isolated from the portion of the aquifer from which the plant draws its water (DuPont, 2003a).

Over the years, the water districts extended their service areas to include increasing numbers of customers in the geographical area. Additionally, prior to 1992, the wells which supplied water to the town of Lubeck were located on what

*Water samples were collected at Little Hocking Water Association, Lubeck Public Service District, City of Belpre, Parkersburg Water Department, Tuppers Plains/Chester Water District, Village of Pomeroy, Ravenswood Municipal, Mason County Public Service District, Village of Racine, New Haven Water Department, and Village of Syracuse.
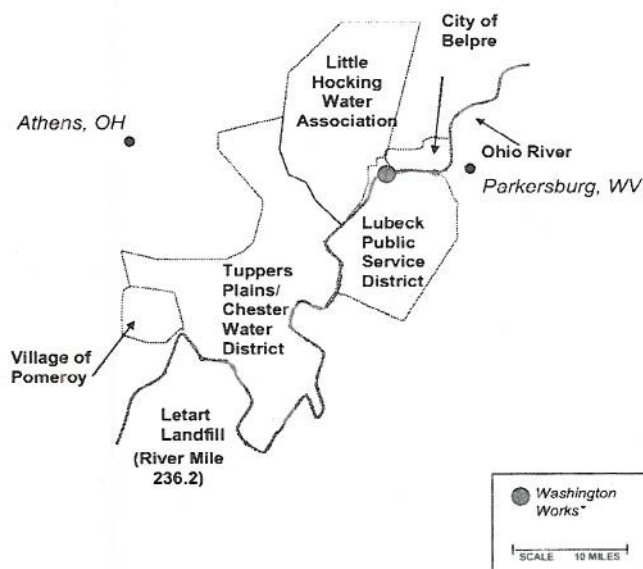

FIG. 1. Approximate location of public water supply current service boundaries in relation to the DuPont Washington Works Facility.

now is plant property. In 1992, this water district drilled new wells located approximately three miles south of the old wells.

The wet and dry deposition of APFO vapors and fumes onto soil, which is later transported to the groundwater due to rain, was investigated by DuPont, U.S. EPA Region III, and West Virginia Department of Environmental Protection (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 10 miles of the facility (WVDEP, 2003).

METHODS

A material mass balance for APFO (the quantity used and released) from the facility for the years of interest (1951–2003) was developed. These data were then used as input to various environmental fate and transport models to quantify the amount of PFOA in various environmental media over time. Based on the results of the modeling, the pathways for human exposure to PFOA were identified and the magnitude of total PFOA intake by residents was estimated.

Materials Mass Balance

A material balance of APFO for the plant was based on information obtained via annual purchasing records, which dated back to 1951. In addition, other plant documents were reviewed and numerous interviews with facility engineers were conducted to understand the seven different processes in which APFO was used. Given the general agreement regarding

TABLE 2
Historical Drinking-Water Measurements of PFOA

Public water district	Groundwater modeling zone	Year	Average PFOA concentration (μg/L) and (range)	Detection frequency (LOD) (μg/L)
Little Hocking	5	1984	0.45 (<0.6–0.6) $n=2$	1/2 (0.6)
		1987	<0.4 $n=1$	0/1 (0.4)
		1988	<0.6 $n=2$	0/2 (0.6)
		2001	3.5 (0.844–7.66) $n=5$	5/5
		2002	3.1 (0.42–8.58) $n=28$	28/28
		2003	3.5 (0.733–8.97) $n=22$	22/22
		2004	4.8 (0.487–10.1) $n=6$	6/6
Belpre	8	2002	0.095 (<0.05–0.141) $n=14$	11/14 (0.05)
Lubeck (old well field)	9B	1984	1.1 (<0.6–1.5) $n=5$	4/5 (0.6)
		1987	1.6 (1.3–1.9) $n=4$	4/4
		1988	1.7 (1.4–2.2) $n=3$	3/3
		1989	0.7 $n=1$	1/1
		1991	3.5 (0.9–8.8) $n=10$	10/10
Lubeck (new well field)	9A	1991	0.43 (<0.1–1) $n=8$	3/8 (0.1–1)
		1992	0.3 (0.2–0.4) $n=2$	2/2
		2000	0.45 (0.073–0.81) $n=15$	15/15

(*Continued*)

TABLE 2
(Continued)

Public water district	Groundwater modeling zone	Year	Average PFOA concentration (μg/L) and (range)	Detection frequency (LOD) (μg/L)
		2001	0.38 (0.055–0.694) $n = 11$	11/11
		2002	0.62 (0.283–1.21) $n = 37$	37/37
		2003	0.49 (0.19–1.09) $n = 23$	23/23
		2004	0.46 (0.27–0.637) $n = 6$	6/6
Tuppers plains	20	1984	<0.6 $n = 1$	0/1 (0.6)
		2002	0.33 (<0.05–0.726) $n = 27$	24/27 (0.05)
		2003	0.28 (<0.05–0.726) $n = 19$	15/19 (0.05)
Pomeroy	21	2002	0.058 (<0.05–0.085) $n = 7$	5/7 (0.05)
Private wells	Various	2001–2002	0.83 (<0.05–8.59) $n = 104$	67/99 (0.05)

the role of air emissions as a primary source of PFOA in the drinking water (WVDEP, 2003), particular emphasis was placed on understanding the aerial releases of APFO for each process. Air emissions of PFOA potentially occurred during the manufacture of fluoropolymers when "dry" products were manufactured, and for each of the dry manufacturing processes there were one or more emission sources, typically dryers. Based on interviews with facility engineers and plant documents, fluoropolymer products that were manufactured and sold in a liquid form produced no significant air emissions of PFOA.

For each process and year, the following equation was used to describe the disposition of APFO used in that process:

$$[Used] = [Recovered] + [Destroyed] + [Air]$$
$$+ [Land - on\text{-}site] + [Ohio\ River]$$
$$+ [Ponds] + [Product] + [Land - off\text{-}site]$$
$$+ [Water - off\text{-}site]$$

where |Used| is the total amount of APFO used in each process (lb), [Recovered] is the amount of APFO recovered (lb), [Destroyed] is the amount of APFO destroyed in-situ or through treatment (lb), [Air] is the amount of APFO emitted to air from the plant (lb), [Land – on-site] is the amount of APFO sent to landfills near the plant (lb), [Ohio River] is the amount of APFO released from the plant to the Ohio River (lb), [Ponds] is the amount of APFO sent to on-site anaerobic digestion ponds (lb), |Product| is the amount of APFO in the liquid dispersion products that is sent to industrial end users (lb), [Land – Off-site] is the amount of APFO in solid waste and treatment residuals from supernate sent to a landfill (lb), and [Water – off-site] is the amount of APFO in wastewater from supernate sent for off-site treatment at an out-of-state facility.

The amount of APFO used by process and year was obtained by reviewing cost sheet records from the plant. These records were available for every year from 1951 to 1980, 1983, 1987 to 1991, and 1993 to 2002. For 1981, only data for FEP were available. For the years and processes in which data were missing, except for 2003, APFO use by the plant was estimated

by linear interpolation between the years with existing data. For 2003, the estimates of APFO were provided by the plant engineering staff.

The amount of APFO in each process released to air, wastewater, aborted batches, solid waste, and supernate were estimated based on information from APFO mass balances for the seven processes as described in various internal documents prepared by DuPont for the years 1978, 1983, 1993, and 1995 through 2000, as well as, discussions with DuPont engineers at the plant. The documentation of the magnitude of APFO released was based on first principles or actual intermittent sampling of the process streams.

Process-specific air emission source information from the air dispersion modeling, which was performed for years 2000 and 2002 as part of the plant's air permitting process with WVDEP (DuPont, 2002, 2003b), was used in our analysis. The historical APFO mass balances were generated using available data and professional judgment, where necessary, to estimate the amount of APFO released to the environment by the plant from 1951 to 2003.

Because the amounts of APFO used in these processes for the majority of years are from the accounting records for each process, there is little uncertainty in the estimate of the amount of APFO used per year in the each process. In addition, based on plant documents, the percent of total APFO used for each process that was released to air, in wastewater, as supernate, or as solid waste varied at most by ±30%. Records of APFO removal, destruction, and recovery from the various pollution control devices were available starting in 1992. Any uncertainty associated with the amount removed, destroyed, or recovered is due to the measurement and estimation uncertainty associated with the engineering records and temporal uncertainty due to not having records from 1990 to 1992. When professional judgment was used, estimates of air emissions and wastewater emissions were maximized versus the estimates of APFO removed, destroyed, recovered, or disposed of as solid waste or offsite.

Environmental Modeling
Estimation of Airborne PFOA Concentrations and Total Deposition of PFOA Onto Soil

The deposition of airborne PFOA emissions at locations outside the facility was evaluated using the U.S. EPA Industrial Source Complex Short Term version 3 (ISCST3) model (U.S. EPA, 1995a, 1995b). This model is a Gaussian plume model that may be used to characterize pollutant concentrations from a wide variety of sources that are often present at manufacturing sites. This model accounts for wet and dry deposition of particles; downwash; point, area, line, and volume sources; plume rise as a function of downwind distance; separation of point sources; and limited terrain adjustment (U.S. EPA, 1995a, 1995b). Additionally, the ISCST3 model takes into account site-specific meteorological data. This model was

used to estimate annual average air concentrations of PFOA ($\mu g/m^3$), dry deposition of PFOA to the soil (g/m^2-yr), and wet deposition of PFOA to the soil (g/m^2-yr) for the areas in vicinity of the plant. The average air concentrations, dry deposition, and wet deposition were calculated considering both dry and wet depletion.

Regulatory default settings were used in the model (U.S. EPA, 1995a, 1995b; *Federal Register*, 2003). Based on the land use analysis previously performed by DuPont in their year 2002 Air Dispersion Modeling Analysis of APFO Emissions for the Washington Works Facility (DuPont, 2003b), the rural land use option was selected in the ISCST3 model. Further, because the facility is located within the Ohio River valley and there are significant terrain features on both sides of the river valley near the plant, terrain elevations were incorporated into the analysis (DuPont, 2003b).

Emission sources. Aerial APFO emissions were modeled for the years 1951 through 2003. A listing of stack parameters by source and year is provided in Table 3. Only point sources for PFOA emissions from the fluoropolymer manufacturing processes were included in the model. Because the fluoropolymer manufacturing was conducted in enclosed facilities, fugitive emissions were not included, as their contributions to off-site PFOA concentrations would have been trivial relative to the stack emissions.

In order to account for the effects of building downwash in estimating onsite airborne PFOA concentrations, the configuration of buildings at the facility was considered. The geographical location of the buildings for the facility was taken from previous air dispersion modeling performed by DuPont (2003b). Based on this building configuration, the U.S. EPA Building Profile Input Program (BPIP) program (U.S. EPA, 1995c) was used to estimate the downwind and crosswind dimensions of the buildings for use in ISCST3.

Particle size distribution of PFOA emissions. Based on interviews with facility engineers, in this analysis the hot PFOA in the dryer atmosphere was assumed to be present as a vapor. When the hot PFOA vapors exit the dryer to a stack and/or to the ambient air, the hot vapor changes physical form as it cools and condenses to form a fume. Fumes are comprised of ultrafine particulates (Seidel et al., 1991; Oberdorster et al., 2000; Mendez et al., 2000), and after several minutes in the ambient air, ultrafine particulates tend to coagulate and nucleate to form submicron sized particles in the range of 0.1 to 1 μm (U.S. EPA, 1990; Seidel et al., 1991; Flagan, 1994; Oberdorster et al., 2000). This is consistent with recent studies demonstrating that airborne PFOA at the plant fenceline was only detectable as a particle and not as a vapor (Barton et al., 2006).

In 1996, DuPont characterized the particle size distribution of PFOA from the fine powder scrubber exhaust to evaluate the effect of particle size on scrubber efficiency, and those data were subsequently used for the air dispersion modeling of year 2000 (DuPont, 2002). Although there were no particle size data available for the airborne emissions of PFOA prior to 1996,

TABLE 3

Historical Stack Information Used in Air Dispersion Modeling of the Washington Works Facility

Description	Process	Stack height (ft)	Stack diameter (ft)	Stack exit velocity (ft/s)	Stack temp. (deg F)	Years of operation
Research device in B-62	Fine powder	48	2	6.50	183	1951 to 1958
No. 1 tray drier	Fine powder	48	2	20.80	183	1958 to 1963
No. 2 tray drier	Fine powder	48	2	20.80	183	1959 to 1963
No. 1 belt drier	Fine powder	48	1.67	37.28	183	1961 to 1969
No. 2 belt drier	Fine powder	48	1.67	37.28	183	1965 to 1981
No. 2 belt drier	Fine powder	78	1.67	37.28	183	1982 to 1989
No. 3 belt drier	Fine powder	48	1.67	37.28	183	1965 to 1981
No. 3 belt drier	Fine powder	78	1.67	37.28	183	1982 to 1989
Scrubber	Fine powder	59	1.5	170	111	1990–2002
DB scrubber	Fine powder	170	4	15.9	124	2002–2003
D1 cooler	Fine powder	45	2.25	8.4	176	2002–2003
D3 cooler	Fine powder	45	1.67	2.6	112	2002–2003
D1 bypass	Fine powder	69	1.67	57	230	2002
D3 bypass	Fine powder	69	1.67	57	230	2002
No. 1 oven	FEP	61	1	33.32	82	1963 to 1986
No. 2 oven	FEP	61	1	33.51	82	1963 to 1986
No. 1 wet finishing	FEP	53.6	1	70.03	82	1963 to 1978
No. 1 wet finishing	FEP	71	1	70.03	82	1979 to 1996
No. 1 wet finishing	FEP	92	0.67	24.39	148	1997 to 2003
No. 2 wet finishing	FEP	80	2.5	40.74	82	1982 to 1996
No. 2 wet finishing	FEP	99	0.67	33.89	128	1996 to 2003
Line 3 wet finishing	FEP	114.5	0.5	89.04	117	1998 to 2003
HF scrubber	FEP	80	1.3	34.53	82	1986 to 2003
Granular line 2	Granular	64	0.88	111.7	139	1965–2003
Granular line 1	Granular	63	1.5	61.1	142	1965–2003
PFA dryer	PFA process K	110	0.65	52.7	171	2003
PFA filter/receiver	PFA process K	72.5	0.27	28.7	110	2003

the installation of the scrubbers may have reduced the particle size of the fume. Thus, use of the post-1996 particle size data may result in the underprediction of PFOA deposition near the source of release and over prediction of PFOA distant from the source. As such, the airborne APFO emissions were modeled as particulates since the available information indicates that APFO vapors quickly condense to fumes after they exit the stack. The particle size distribution used in the air modeling is presented in Table 4. Air sampling of PFOA's at the fenceline (Barton et al., 2006) included a particle size distribution analysis, and those results were consistent with that presented in Table 4.

Meteorological data. Five years of on-site meteorological data from 1996, 1999, 2000, 2001, and 2002 were available to characterize the variability in meteorological conditions at the plant. The on-site data from 1999 to 2002 were compiled from the hourly readings of wind direction, wind speed, ambient air temperature, cloud cover, cloud ceiling

TABLE 4

Particle Size Distribution for PFOA Emissions (Based on Particle Size Data Collected from the Fine Powder Packed Bed Scrubber Exhaust in 1996)

Minimum particle size for category (μm)	Maximum particle size for category (μm)	Mean particle size (μm)	Mass fraction
3.0	5.0	4.0	3.3%
1.0	3.0	2.0	12.7%
0.5	1.0	0.75	3.5%
0.3	0.5	0.4	26.7%
0.1	0.3	0.2	53.8%

height, surface pressure, and solar radiation from the SAFER on-site meteorological system. These data were then combined with mixing height data from Wilmington, OH, and hourly

precipitation data for Liverpool, WV, to assemble meteorological data sets suitable for ISCST3 (U.S. EPA, 1995a, 1995b).

Because of the high percentage of calm hours in the on-site data for 2001 (51.7%, or 4530 of 8760 h), this data set was not used in the subsequent air dispersion modeling. Calm hours occur when the hourly wind speed is less than 1 m/s for a given hr of data. For these hours, ISCST3 does not calculate air concentration or total deposition to soil.

Figure 2 presents the combined wind rose for the four years of data used for this air dispersion modeling. For all four years, the predominant wind direction was from the southwest to the northeast for the majority of hourly meteorological data. For hours when this was not the predominant wind direction, the predominant wind direction was northeast to the west by southwest. Based on the windrose map and distance from
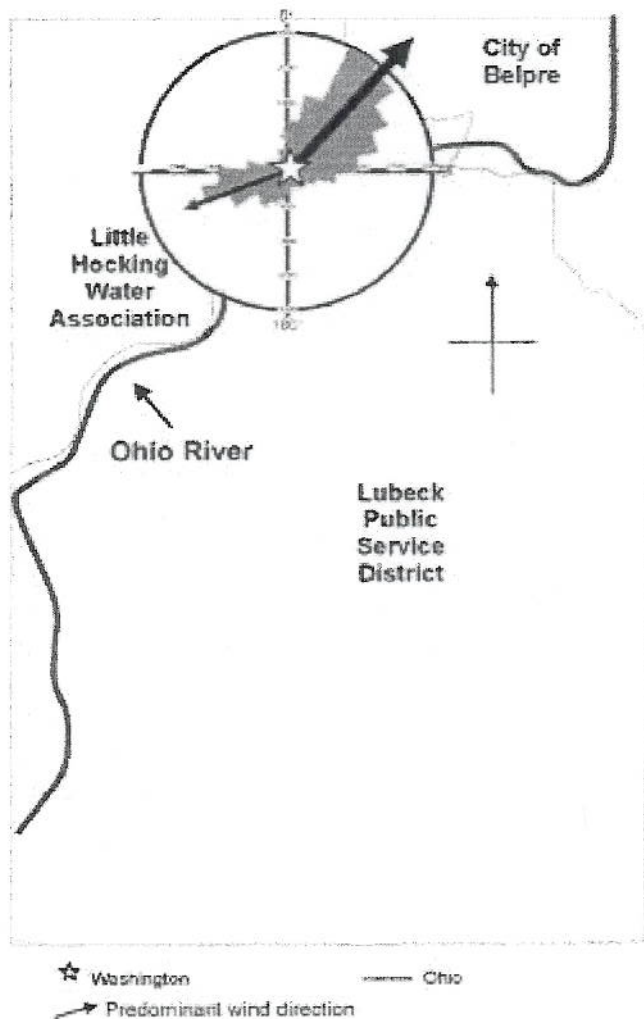
the plant, two of the affected water districts, Tuppers Plains and Pomeroy, were not likely to have been impacted by air emissions and therefore were not included in the air dispersion/deposition modeling domain.

Because the year-to-year variability associated with wind speed and direction is lower than the year-to-year variability of annual precipitation, the annual amount of precipitation for each year was used to determine which of the four on-site data sets would be more representative for each year from 1951 to 2003. For years with less than 95 cm of precipitation, either the 1999 or 2000 data set was used. For years with precipitation amounts between 95 cm and 120 cm, the 2002 data set was used. For years with greater than 120 cm of precipitation, the 1996 data set was used.

Geographical locations of residents. The ISCST3 air dispersion model defines geographical locations as nodes (sometimes called receptors) located at the center of a square cell with each cell located on a grid. In this analysis, for locations close to the plant, a fine grid was established with cell sizes of 250 m by 250 m (i.e., about 15 acres). For more distant locations (situated more than $5\frac{1}{2}$ miles south of the facility), a coarse grid of cells 500 m by 500 m (i.e., about 62 acres) was used. Receptor coordinates are defined in Universal Transverse Mercator (UTM) coordinates. The facility and entire model domain are located in UTM Zone 17.

The fine and coarse receptor grids were defined for all historical areas serviced by the Little Hocking Water Association (LHWA), the City of Belpre Water Department, and the Lubeck Public Service District (LPSD). The fine grid spans 17.5 km from east to west and 14.25 km from north to south and includes the plant. The coarse grid spans 17.5 km from east to west and 14 km from north to south and is located 10 km south of the plant. The total modeling domain encompassed a 191 square mile area.

Exposure zones. For ease of communicating the results of the assessment, the communities served by the water districts were divided into zones. Beginning with the 191 square mile grid, a 185 square mile (479,150,000 m²) portion of the grid was divided into a total of 19 zones (areas) based on production well capture zones and service districts of LHWA, the City of Belpre, and LPSD. The remaining 6 square mile area (15,500,000 m²) was outside of the area of interest for this exposure assessment. These areas within the water districts are shown in Figure 3.

The selection of the boundaries of the 19 zones were identified using the following criteria:

- Public water supply and plant water pumping zones of influence (zones 5, 6, 8, 9, and 10);
- Historical boundaries of the water supply district;
- Distance from the plant.
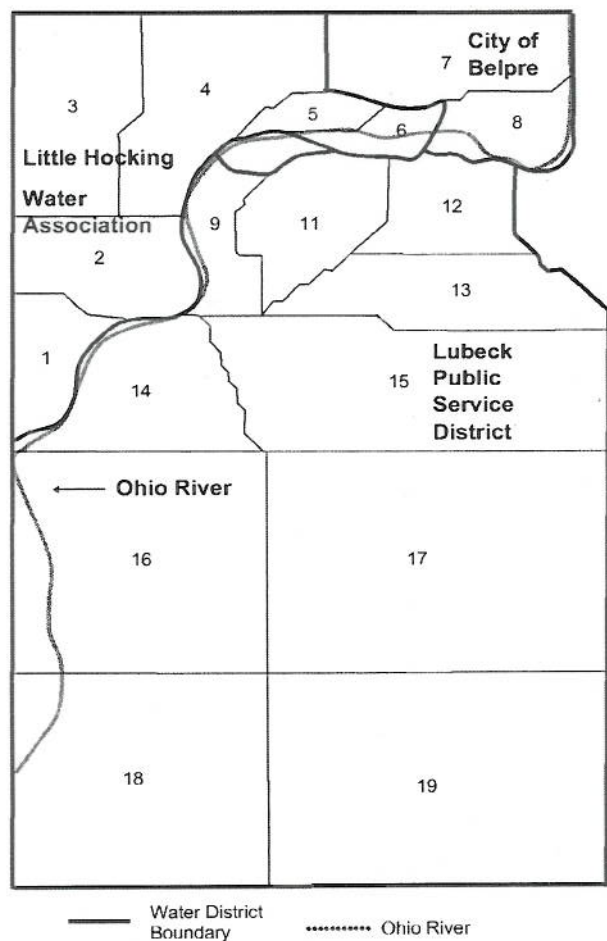- Boundaries of residential developments within each water supply district.

FIG. 2. Wind rose map for meteorological data used in the air dispersion modeling including years 1996, 1999, 2000, and 2002.

FIG. 3. Schematic illustrating how the 185 square miles of residential and rural areas were divided. The areas or zones correspond to specific water districts or subdistricts.

For each of these zones, the annual average airborne PFOA concentrations and total PFOA deposition onto soil at the receptor locations within these zones were averaged together to generate air concentrations and deposition rates averaged by zone.

For each of the 19 zones, area-weighted average airborne PFOA concentrations and total PFOA deposition rates were calculated and used to estimate surface soil concentrations, groundwater concentrations, vegetable concentrations, and average daily doses (ADDs).

Unsaturated Zone Soil and Groundwater Modeling

Historical soil concentrations of APFO 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.

Several resources were used to characterize the unsaturated zone soils that cover the underlying Ohio River Valley sand and gravel aquifers serving the public water supply wells. The following soil parameters were needed to perform the unsaturated zone modeling:

- Dominant surface soil texture/hydrologic soil group:
- Dominant subsurface soil texture:
- Rate of groundwater recharge:
- Typical depth to groundwater table.

Table 5 presents a summary of these soil parameters for 3 of 5 water districts where air deposition to soil was a relevant transport mechanism. Based on the parameters just described, U.S. EPA PRZM-recommended soil-texture-specific guidelines or other technical guidance was used to determine physical soil properties such as bulk density, hydraulic conductivity, and porosity and the annual average rate of recharge. The

TABLE 5
Summary Soil Properties for Unsaturated Zone in Public Supply Well Capture Zone

System	Dominant surface soil type	Soil Conservation Service (SCS) hydrologic soil group	Dominant unsaturated zone subsurface soil type	Depth to groundwater near well field	Average annual recharge
Little Hocking Water Association (zone 5)	Silty clay	D	Silty clay	20 ft	6 inches
City of Belpre (zone 8)	Silt loam	B	Silt loam	22.5 ft	8 inches
Lubeck Public Service District—new wells (zone 9A)	Sandy clay	C	Sandy clay	12 ft	8 inches
Lubeck Public Service District—old wells (zone 9B)	Silt loam	B	Sandy loam	55 ft	8 inches

unsaturated zone soil properties for the public water supply wells located in air dispersion modeling zones were known and accounted for in the modeling.

Data collected by the U.S. Department of Agriculture (USDA) National Resource Conservation Service (NRCS) were used to estimate PFOA soil concentrations in private well zones. Specifically, the NRCS State Soil Geographic (STATSGO) database was the primary source of information. The STATSGO database subdivides a geographical region into map units of similar soil type and assigns each area a map unit identification number (MUID). Each map unit consists of up to 21 component soils, which are further divided into layers. Because individual components are not depicted graphically on a map unit, results for each area are typically presented statistically (e.g., percentage of soils classified as clay). Table 6 presents a summary of the soil parameters from STATSGO for each of the modeling zones. The STATSGO database is available from the U.S. EPA grouped by watershed hydrologic unit map (HUC) number as part of the Better Assessment Science Integrating Point and Nonpoint Sources (BASINS) model.[†]

One of the limitations of the STATSGO dataset is that soil data are generally only available to a depth of 5 to 7 ft. As such, two conditions required judgments regarding the depth to groundwater. First, where the depth to water was indicated in the STATSGO database as greater than or equal to 5 ft, the effective depth to groundwater was determined to be the depth to bedrock. The concentration of PFOA in the shale and sandstone bedrock was then considered to be equal to the concentration of PFOA at the interface of bedrock and overburden. As such, any fate and any transport process in the bedrock that would tend to restrict the movement of PFOA downward to the private well capture zone were neglected. Second, for map units where both the depth to bedrock and depth to water are defined as greater than 5 or 6 ft, the depth to groundwater was based on the depth to groundwater for the nearest public water supply zone.

The amount of recharge that occurred in each private well zone was set equal to the amount of recharge that was specified for the public water supply well zones based on Hydrologic Soil Group. This approach likely overestimated recharge for the upland areas because recharge to the bedrock is likely to have been as low as 0.1 inches/yr in bedrock aquifer areas (DuPont, 2003a). The assigned annual average recharge rates of 6 to 8 inches/yr were similar to the annual average recharge rate provided by the Ohio State University Extension (2004) of 6 inches/yr for Washington County.

Water balance. The water balance in the PRZM model consists of the addition of water in the form of rainfall or snow, storage in the canopy and surface soil, runoff losses to surface water, evapotranspiration losses to the atmosphere, and finally,

leaching of water to the subsurface soil column. Precipitation data were input on a daily basis, with precipitation occurring at temperatures below 0 °C determined to occur as snow. Runoff loss was estimated using the USDA Soil Conservation Service curve number approach, which is a function of soil classification (hydrologic soil group) and type and condition of groundcover. In the absence of site evaporation data, the total evapotranspiration demand was calculated using tabulated pan evaporation data available from the U.S. EPA (2004) for the nearest regional meteorological station.

After the total evapotranspiration demand was determined, PRZM sequentially extracted water from the canopy, ponded surface water, and finally by crop transpiration. Water was extracted from each surface soil layer until the soil water content reached the wilting point, the minimum moisture content to sustain plant growth. Finally, water was determined to leach from the surface soil to subsurface soil until the surface soil water content was equal to the field capacity, which was assumed to occur within a 24-h period in the absence of additional precipitation.

The flux rate of water leaching below the root zone was used as input to VADOFT. This module simulates transient vertical groundwater under variably saturated groundwater conditions and is based on the Richard's equation for infiltration of water in the vadose zone (Jury et al., 1991; U.S. EPA, 2001). Groundwater flow in the unsaturated zone is a function of two key relationships: relative permeability versus water saturation and pressure head versus water saturation. These relationships depend on soil properties such as pore size distribution. The functional relationships of van Genuchten (Jury et al., 1991; U.S. EPA, 2001) were used in VADOFT along with the associated tabulated empirical constants, which are available for various soil classifications.

Groundcover (crop). Because PRZM was originally designed to aid in crop pesticide management, the land cover was specified as a crop. For the purpose of modeling soil concentrations in the water district well fields and residential areas, the groundcover was selected to be Kentucky Blue Grass, with the growing season determined by average data for Washington County, OH. The maximum depth of the root zone for this grass was determined to be 30 cm and the grass was considered to be trimmed regularly to maintain an average height of 5.1 cm. Grass canopy coverage was set equal to 50 to 75% of the surface, with the remaining 25 to 50% consisting of bare soil. The setting of canopy coverage was based on a calibration of the water balance discussed previously. The growing season was based on dates of first and last frost for Washington County, OH. The USDA TR-55 cover type that was selected was "Pasture, grassland, or range-continuous forage for grazing."

Chemical deposition. Atmospheric deposition to soil was assumed to be mixed within the top 1 cm of soil, with concentration linearly decreasing with depth (NCEA, 1998). Daily deposition was entered in units of kilograms per hectare per day

[†] Soil data available at http://www.epa.gov/waterscience/ftp/basins/gis_data/huc

TABLE 6

National Resource Conservation Services State Soil Geographic Database Soil Survey Map Units for Each Exposure Zone With Air Dispersion Modeling Results

Zone	Primary map unit	Most frequent surface texture	Most frequent hydrologic soil group	Typical depth to water table[a]	Typical depth to bedrock	Subsurface soil texture profile for the most frequently occurring component in map unit	
1	OH095	Silt loam	C	>5 ft[b]	2.5–5 ft	Silt loam[c]	0–0.7 ft
						Channery loam[d]	0.7–2.5 ft
						Unweathered bedrock	2.5 ft
2	OH155	Silt loam	B	>5 ft[b]	>7 ft	Silt loam	0–1 ft
						Sandy clay loam[c]	1–6.9 ft
						Loamy sand	6.9–8.3 ft
3	OH095	Silt loam	C	>5 ft[>b]	2.5–5 ft	Silt loam[c]	0–0.7 ft
						Channery loam[d]	0.7–2.5 ft
						Unweathered bedrock	2.5 ft
4	OH155	Silt loam	B	>5 ft[b]	>7 ft	Silt loam	0–1 ft
						Sandy clay loam[c]	1–6.9 ft
						Loamy sand	6.9–8.3 ft
6	OH142	Silt loam	B	>5 ft	>5 ft	Silt loam	0–1 ft
						Silty clay loam[c]	1–3.7 ft
						Stratified (silty clay loam/silt loam)	3.7–5 ft
7	OH139	Silty clay loam	C	>5 ft[b]	3.5 to 5 ft	Silty clay loam[c]	0–4.5 ft
						Unweathered Bedrock	>4.5 ft
10	WV060	Silt loam	B	>5 ft[b]	>6 ft	Silt loam	0–0.7 ft
						Silty clay loam	0.7–3.7 ft
						Stratified (silty clay loam/gravel with sandy loam)[c]	3.7–6 ft
11–12	WV056	Silty clay loam	D	>5 ft[b]	3.5 to 6 ft	Silt loam[c]	0–6 ft
13–19	WV036	Silty clay	D	>5 ft	3.5 to 6 ft	Silty clay	0–3.5 ft
						Silty clay loam[c]	3.5–6 ft
						Weathered bedrock	>6 ft

[a] Depth to water table is for seasonal high water table.
[b] Perched water observed in some components of this map unit.
[c] The subsurface soil texture used in the subsurface unsaturated zone groundwater modeling.
[d] The adjective channery describes flat rock fragments 2–150 mm long.

39

(kg/ha-day). The conversion from the air dispersion modeling deposition results in grams per square meter per year (g/m²-year) to units of kilograms per hectare per day is given here for non-leap years:

$$C \,(\text{kg/ha-day}) = C \,\left(\text{g/m}^2\text{-yr}\right) \times \left(10,000 \,\text{m}^2/\text{ha}\right)$$
$$\times \,(0.001 \,\text{kg/g})/(365 \,\text{days/yr})$$

Chemical transport. The chemical fate and transport processes for the surface root zone and subsurface soil for PFOA include chemical advection, dispersion, and reversible linear adsorption. A portion of the dissolved phase chemical located in the top 2 cm of surface soil is considered available for extraction due to mixing with surface water runoff. The fraction of chemical available for extraction decreases exponentially with depth. Chemical loss due to soil erosion and volatilization was considered to be negligible due to the high solubility, low Henry's law constant, and moderate K_{oc} of PFOA (Table 1). Additionally, because PFOA is not transformed or degraded in the environment, chemical loss due to biological or photochemical degradation was considered negligible.

Estimation of Drinking Water Concentrations

General hydrogeologic conceptual model for Washington and Wood counties. The Ohio River Valley, which passes through Washington County, OH, and Wood County, WV, is characterized by coarse-grained Ohio River Alluvium overlain by fine-grained overbank deposits. The geology and hydrogeology of the region were summarized in the DuPont Revised Groundwater Model for the Washington Works Facility (DuPont, 2003a). As shown in Figure 4, production wells for drinking water were completed in the Pleistocene sand and gravel layer due to the high well yields that are achievable. Due to the proximity of this soil unit to the Ohio River and high hydraulic conductivity, high pumping rates tend to result in river leakage flowing from the Ohio River to the capture zone of the well when the amount of water pumped exceeds the amount replaced from recharge due to infiltration from precipitation.
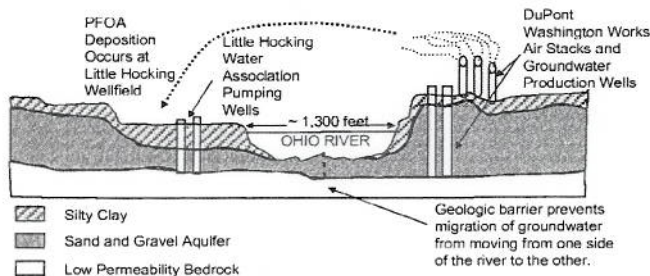
Groundwater modeling for public water supply wells. A detailed groundwater modeling assessment was previously performed by DuPont for the region near the plant (DuPont, 2003a). This assessment was prepared with input from the U.S. EPA, U.S. Army Corps of Engineers, and U.S. Geological Survey. Because the groundwater domain is bounded by bedrock, a complete "mass balance" for water flow was determined. As illustrated in Figure 5, there are two sources of water to the alluvial aquifer. The primary source is river leakage from the Ohio River to the alluvial aquifer. The secondary source is recharge from precipitation. It is important to note that the water balance presented is a global mass balance. The mass balance for each individual well zone is based on the area of the capture zone over which recharge is occurring and the pumping rate. For example, an intermittently used well with a low pumping rate of 50 gal/min (gpm) might obtain all of its water from rainfall recharge.

The Little Hocking well capture zone was calculated in the DuPont groundwater modeling report (DuPont, 2003a). These results demonstrate that the Little Hocking well field ultimately receives water from the Ohio River (shorter flow lines) and recharge (longer flow lines). To verify this conclusion, the well capture zone was estimated using the U.S. EPA Wellhead Analytical Element Model (WhAEM). The WhAEM also indicated that Ohio River leakage and recharge from the surface soil contribute to the water pumped from the well field and is consistent with that predicted by DuPont.

It should be noted that for the combination of the subsurface vadose zone soil modeling and groundwater modeling, the major resistance to PFOA transport from surface deposition to the public supply groundwater wells is the soil absorption and restricted flow that occurs though the silt and clay-rich, variably saturated overburden. Water achieves much slower velocities in silt and clay dominated unsaturated soils than in sand and gravel rich saturated soils. PFOA was also shown to adsorb to soil surfaces (DuPont, 2003c). Therefore, it is
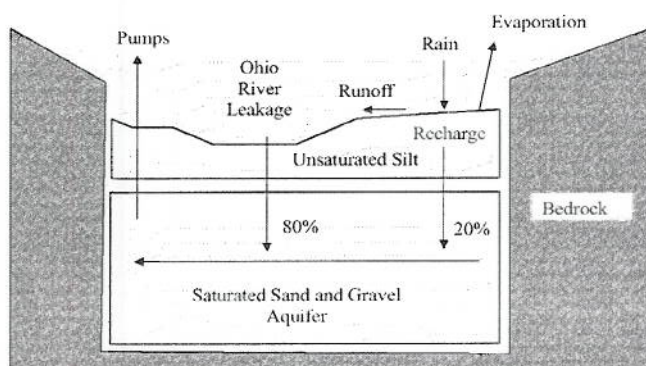
FIG. 4. Cross section of Ohio River near Little Hocking Water Association public water supply wells (adapted from DuPont, 2003a).

FIG. 5. Global net mass balance of water in Ohio River alluvial aquifer indicating percentage of pumped water from aquifer obtained from Ohio River leakage and recharge based on DuPont groundwater flow model (2003a).

reasonable to consider the low-permeability silty clay over-burden as the primary barrier to PFOA transport to the public water supply wells.

Surface water concentrations. As indicated in the conceptual exposure model, facility releases to surface water were a source of PFOA in the Lubeck PSD, Tuppers Plains/Chester WD, and Village of Pomeroy public water supplies via the surface water to groundwater pathway. Historical annual average concentrations of PFOA in the Ohio River downstream of the facility were calculated using the methodology for the case of plug flow with incremental dilution by downstream watershed runoff (Thomann & Mueller, 1987).

It was assumed that the concentration of PFOA in the surface runoff water and groundwater draining to the Ohio River downstream of the facility was negligible. The PRZM soil modeling indicated that for the plant, the cumulative mass of PFOA lost to surface runoff from 1951 to 2003 would be 43 lb, or less than 1 lb/yr. This amount of PFOA is negligible compared to the 53-yr average mass of PFOA determined in the mass balance to be discharged at Outfall No. 005 of 12,000 lb/yr. Because annual average estimates of exposure are being considered, the equation used does not account for lateral dispersion, which may be of interest for much shorter time scales.

Annual average flow rates were obtained from the U.S. Geological Survey (USGS) for the Ohio River at selected gauging stations for specific time periods. Locations where historical flow rates were calculated include:

- DuPont Washington Works Facility, WV (River Mile 190.7);
- Lubeck, WV (River Mile 191.2 from 1/1960 to 11/1991 and River Mile 193.7 from 12/1991 to present);
- Tuppers Plains PSD, OH (River Mile 209);
- Letart Landfill–Mason County, WV (River Mile 236.2);
- Village of Pomeroy, OH (River Mile 250).

Because flow rate data were not collected at these locations, estimates of flow rates were made by using flow rates collected at nearby gauging stations along the Ohio River. Flow rates were extrapolated from gauged to ungauged locations using one of the approaches published and used by the Texas Resource Conservation Commission (TNRCC) (Wurbs, 2001). The methodology considered flow rate changes in the river to be proportional to differences in drainage area, annual precipitation, runoff potential and channel losses.

The mass of APFO released to the Ohio River is a function of the surface water concentrations in the outfall water and the effluent flow rate from the outfall to the Ohio River. Typically these flow rates would be available from the plant NPDES Permit. However, the flow rates would have considerable variability over time and may perhaps exhibit considerable deviation from the calculated values. In addition,

historical flow rates were not available, and the mass released was affected by the addition of process water from carbon treatment beginning in 1996. Therefore, the materials mass balance for APFO processed at the plant was used to estimate the combined mass of APFO released in process water and discharged to the Ohio River. This is believed to represent a more accurate estimate of the amount discharged. It was assumed that the majority of APFO was released at the plant's Outfall 005.

Estimated Concentrations of PFOA in Locally Grown Produce

PFOA concentrations were calculated for the edible portions of corn, beans, and potatoes using the U.S. EPA Human Health Risk Assessment Protocol for Hazardous Waste Combustion Facilities, volumes 1 and 2 (U.S. EPA, 1998a, 1998b). These calculations incorporated uptake of PFOA from soil (corn, beans, and potatoes) and direct deposition (corn and beans). The concentration of PFOA in corn and beans equals the sum of the contributions from direct deposition and root uptake, and the concentration of PFOA in potatoes equals the contribution from root uptake. Although the PFOA concentrations in this produce are theoretically estimated, no samples of locally grown produce were analyzed for PFOA.

Soil concentrations, as well as dry and wet deposition onto soil, were calculated from the air dispersion and unsaturated zone soil modeling results; however, for all other parameters, U.S. EPA default values were used in the calculations in accordance with U.S. EPA guidance when site-specific information was not available.

Quantification of Possible PFOA Exposure for Residents

Human exposures to PFOA were estimated for 21 exposure zones surrounding the plant. These zones included the 19 zones located within the air modeling domain and shown in Figure 3, as well as a zone for the Tuppers Plains/Chester Water District (zone 20) and the Village of Pomeroy Water District (zone 21).

Using the results of the environmental fate and transport modeling, the following pathways of human exposure were quantitatively evaluated:

- Inhalation of PFOA from ambient air (zones 1–19);
- Consumption of drinking water containing PFOA (all zones);
- Dermal contact with PFOA in water during showering (all zones);
- Incidental ingestion of soil containing PFOA (zones 1–19);
- Dermal contact with soil containing PFOA (zones 1–19);
- Consumption of locally grown produce containing PFOA (zones 1–19).

Average Daily Doses (ADDs) were estimated for residents in each of the 21 zones for the following scenarios:

- Scenario 1: An adult resident lives in one of the 21 exposure zones for 9 yr, from 1995 to 2003. This represents the mean number of years a person lives in a single residence (U.S. EPA, 1997):
- Scenario 2: An adult resident lives in one of the 21 exposure zones for 30 yr, from 1974 to 2003. This represents the upper bound (95th percentile) number of years a person lives in a single residence (U.S. EPA, 1997).
- Scenario 3: An adult resident lives in one of the 21 exposure zones for the entire 53 yr that fluoropolymers have been manufactured at the plant (1951 to 2003). This represents an estimate of the dose that might have been received since operations began at the plant until 2003.
- Scenario 4: A child, ages 0 through 6 yr, lives in one of the 21 exposure zones for 6 yr, from 1998 to 2003.

The ADDs for these pathways and scenarios were calculated using standard equations (U.S. EPA, 1989, 1997) and the exposure parameters used in those equations are presented in Table 7.

RESULTS

Materials Mass Balance

The historical use of APFO at the plant over time is shown in Figure 6. It is evident that the use increased steadily over the years from 29 lb when operations started to a peak amount of approximately 174,000 lb in 2000. The results of the APFO mass balance for all of the processes combined from 1951 to 2003 are shown in Figure 7.

The highest air emissions of approximately 34,000 lb are estimated to have occurred in 1999 with other local peaks in emissions occurring in 1966, 1989, 1996, and 2000. Before 1978, air emissions were less than 10,000 lb/yr, and emissions
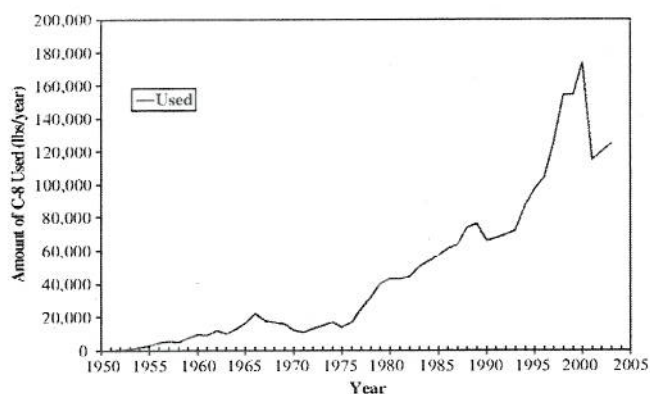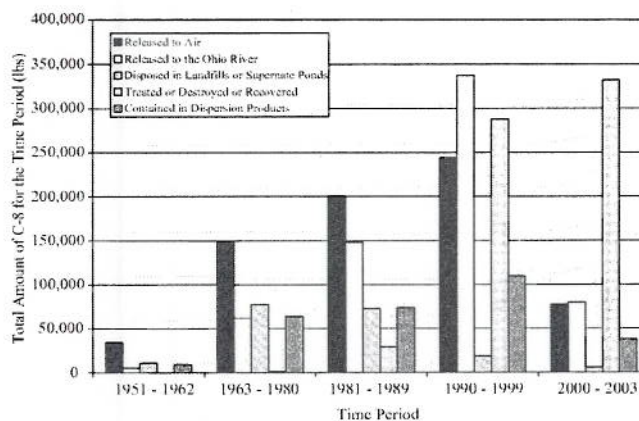
FIG. 7. Estimated historical C-8 material balance for the Washington Works Facility from 1951 to 2003 for all processes combined.

started to increase after 1977. Even though the amount of APFO used at the plant has consistently increased over time, air emissions decreased following the installation of scrubbers and improvements to existing scrubbers for each process.

Releases of APFO to the Ohio River rose with increased APFO use through the late 1990s until the installation of the Oberlin filter and the start of carbon treatment for wastewater. Since 2000, releases of APFO to the Ohio River have markedly decreased due to these improvements in wastewater treatment.

Conceptual Exposure Models

Two of the water districts (i.e., Little Hocking and the City of Belpre) are located upstream from the plant and three are located downstream. Figure 1 shows the locations of the various districts in relation to the plant. Water samples collected from the Ohio River upstream of the facility do not contain detectable concentrations of PFOA and therefore the Ohio River is not likely to be a contributing source of PFOA in groundwater for water districts located upstream of the facility. However, PFOA was detected in samples collected downstream of the facility and therefore it is reasonable to expect that the Ohio River is a possible contributor to groundwater PFOA concentrations for water districts located downstream of the facility.

Air Emissions of PFOA and Air Dispersion Modeling Results

The mass balance calculations indicated that since operations using APFO began at the plant in 1951, over 700,000 lb PFOA were released to the air. The highest three years of APFO emissions, in order from highest to lowest, are 1999, 1989, and 2000. Table 8 summarizes the air emissions of PFOA from the facility over time. From these estimated historical air emissions, the annual average airborne PFOA concentrations

FIG. 6. Total amount of C-8 used in fluoropolymer production at the plant from 1951 to 2003 based on purchasing records.

TABLE 7
Exposure Parameters Used in the ADD Calculations

Parameter	Adult	Child	Units	Reference
Inhalation rate	0.63	0.32	m^3/h	Long-term inhalation rates (Table 5–23; U.S. EPA, 1997)
Drinking-water ingestion rate—mean	1.4	0.35	L/d	Mean drinking-water ingestion rates (Table 3–30, U.S. EPA, 1997, 2002)
Drinking-water ingestion rate—lower bound	0.61	Not evaluated	L/d	10th percentile drinking-water rate for adults (Table 3–8; U.S. EPA, 1997)
Drinking-water ingestion rate—upper bound	2.3	Not evaluated	L/d	90th percentile drinking-water ingestion rate for adults (Table 3–8; U.S. EPA, 1997)
Soil ingestion rate	50	100	mg/d	Recommended mean soil ingestion rates (Table 4–23; U.S. EPA, 1997)
Corn ingestion rate	10,220	7215	mg/d	Average ingestion rate converted from mg/kg-d using the adult body weight of 70 kg and child body weight of 15 kg (Table 9–5; U.S. EPA, 1997)
Beans ingestion rate	7700	4736	mg/d	Average ingestion rate converted from mg/kg-d using the adult body weight of 70 kg and the child body weight of 15 kg (Table 9–5; U.S. EPA, 1997)
Potatoes ingestion rate	62,265	27,238	mg/d	Average ingestion rate converted from mg/kg-d using the adult body weight of 70 kg and the child body weight of 15 kg (Table 9–5; U.S. EPA, 1997)
Fraction from contaminated source—vegetables	0.25	0.25	Unitless	Soil Screening Guidance, Appendix G (U.S. EPA, 1996)
Fraction from contaminated source—all other media	1	1	Unitless	Default = 1 (100%)
Dermal absorption fraction	1	1	Unitless	Default = 1 (100%)
Permeability constant	0.0043	0.0043	cm/h	E-mail correspondence with Dr. Hinderliter at DuPont
Total skin surface area for contact with drinking water	18,000	6600	cm^2	Total body surface area (Exhibit 3–2; U.S. EPA, 2001)
Exposed skin surface area for soil contact	5700	2800	cm^2	Exposed skin—central tendency and upper bound (Exhibit 3–5; U.S. EPA, 2001)
Adherence factor	0.01	0.04	mg/cm^2	Central tendency (Exhibit 3–5; U.S. EPA, 2001)
Exposure frequency for all pathways	365	365	d/y	Assumed exposure occurred every day of the year
Exposure time	24	24	h/d	Residential exposure—assumed exposure occurred 24 h/day
Showering time	0.25	0.25	h/d	Recommended central tendency showering time (Exhibit 3–2; U.S. EPA, 2001)
Exposure duration—scenario 1	9	Not applicable	yr	1995 through 2003
Exposure duration—scenario 2	30	Not applicable	yr	1974 through 2003
Exposure duration—scenario 3	53	Not applicable	yr	1951 through 2003
Exposure duration—scenario 4	Not applicable	6	yr	1998 through 2003
Body weight	70	15	kg	U.S. EPA, 1989

TABLE 8
Summary of Estimated PFOA Air Emissions from APFO Mass Balance Estimates for 1951 to 2003

Year	Air emissions of PFOA (lb)	Year	Air emissions of PFOA (lb)	Year	Air emissions of PFOA (lb)
1951	10	1970	4900	1990	18,000
1952	100	1971	4200	1991	18,000
1953	300	1972	5100	1992	19,000
1954	700	1973	6400	1993	21,000
1955	1400	1974	6900	1994	25,000
1956	2700	1975	5400	1995	27,000
1957	3000	1976	7100	1996	29,000
1958	2800	1977	9500	1997	26,000
1959	4400	1978	12,000	1998	26,000
1960	6200	1979	14,000	1999	34,000
1961	5500	1980	14,000	2000	32,000
1962	7700	1981	16,000	2001	23,000
1963	5800	1982	16,000	2002	15,000
1964	6500	1983	17,000	2003	7400
1965	7900	1984	19,000		
1966	12,000	1985	21,000		
1967	10,000	1986	23,000		
1968	8400	1987	25,000		
1969	6900	1988	31,000		
		1989	32,000		

and PFOA deposition rates onto soil were estimated for each of the 19 exposure zones in the vicinity of the plant. The estimated annual average historical air concentrations and total deposition onto soil by exposure scenario are presented in Table 9. The exposure zone with the highest predicted air concentrations (excluding the plant—zone 10) was zone 5. The differences in average air concentration by zone and scenario are low because scenarios 1, 2, and 3 all contain years with the highest air emissions (1994 to 2003). For individual years (not shown), the annual average air concentrations in zone 5 ranged from 0.00008 to 0.39 μg/m^3.

Similar to the estimated airborne concentrations, the zones with the highest estimated deposition rates of PFOA, in order from highest to lowest, are zone 10, zone 5, and zone 9. For all of the zones, 1989 was the year with the highest deposition rate followed by 1996. The three zones with the lowest rates are zone 17, zone 18, and zone 19. Averaged over all years and all zones, the percent of the total deposition due to wet deposition was 69% and dry deposition accounted for the remaining 31%.

Surface Water Modeling Results
The annual average concentrations of PFOA in the Ohio River downstream of the plant near the water supply wells of interest are presented in Table 10. The highest concentrations for the river were found near the Lubeck well fields. For individual years (not shown), the calculated PFOA concentrations

in the Ohio River near the Lubeck well field ranged from 0.00001 μg/L in 1951 to 0.69 μg/L in 1999.

Predicted Soil Concentrations Over Time
The model estimated historical air deposition rates per exposure zone (see Table 9) were used to predict soil concentrations by zone and year. The average predicted surface soil concentrations by time period are presented in Table 11. The exposure zone with the highest predicted soil concentrations (excluding the plant—zone 10) was zone 5. For individual years (not shown), the predicted annual average soil concentrations in zone 5 ranged from 0.0014 to 30 μg/kg.

The results of the soil modeling were used to model the mass flux rates of PFOA from soil to groundwater at the Little Hocking, City of Belpre, and Lubeck well fields. The average predicted flux rates by time period are presented in Table 12. Consistent with the highest soil concentrations, the highest flux rates are also predicted to have occurred at the Little Hocking well fields. For individual years (not shown), the annual average soil flux rates for Little Hocking ranged from zero to 0.004 g/m^2-yr.

Predicted Drinking-Water Concentrations Over Time
Historical groundwater concentrations of PFOA were derived in accordance with the conceptual models for each water district whereby the contribution from infiltration from

TABLE 9

Summary of Annual Average Estimated Airborne PFOA Concentrations and Total Deposition onto Soil by Exposure Scenario and Zone From 1951 to 2003

| Zone | Annual average airborne PFOA concentration and total deposition by exposure scenario and zone | | | |
	Scenario 1 1995–2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003	Scenario 4 1998 to 2003
Airborne Concentration $\mu g/m^3$				
1	0.02	0.02	0.01	0.02
2	0.05	0.04	0.03	0.05
3	0.04	0.03	0.02	0.03
4	0.1	0.09	0.06	0.09
5	0.3	0.2	0.2	0.25
6	0.07	0.06	0.04	0.06
7	0.08	0.07	0.05	0.08
8	0.03	0.02	0.01	0.02
9	0.08	0.06	0.05	0.07
10	0.5	0.5	0.3	0.4
11	0.07	0.05	0.04	0.07
12	0.02	0.02	0.01	0.02
13	0.01	0.01	0.01	0.01
14	0.02	0.01	0.01	0.02
15	0.01	0.01	0.01	0.01
16	0.01	0.01	0.004	0.007
17	0.004	0.003	0.002	0.004
18	0.004	0.003	0.002	0.003
19	0.002	0.002	0.001	0.002
Total Deposition mg/m^3-yr				
1	0.3	0.3	0.2	0.3
2	0.9	0.7	0.5	0.7
3	0.6	0.5	0.3	0.5
4	2	2	1	2
5	7	6	4	6
6	2	1	1	1
7	1	1	0.7	1
8	0.5	0.4	0.3	0.4
9	2	2	1	2
10	20	20	10	14
11	1	1	0.8	1
12	0.5	0.4	0.3	0.4
13	0.2	0.2	0.1	0.2
14	0.3	0.2	0.2	0.2
15	0.2	0.1	0.1	0.1
16	0.1	0.1	0.1	0.1
17	0.1	0.04	0.03	0.05
18	0.04	0.03	0.02	0.03
19	0.02	0.02	0.01	0.02

the soil column and the contribution from surface water were included as appropriate. The average predicted groundwater concentrations by time period for each public water district are shown in Table 13. The highest groundwater concentrations are predicted to have occurred at the Little Hocking water district. For individual years (not shown), the groundwater concentrations of PFOA at Little Hocking are predicted to have ranged from 0 to 14 $\mu g/L$.

TABLE 10
Summary of Estimated Annual Average Concentrations of PFOA in Ohio River Near Affected Water
Districts by Exposure Scenario

Water district[a]	Surface water concentrations (μg/L)			
	Scenario 1 1995–2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003	Scenario 4 1998 to 2003
Lubeck	0.4	0.2	0.1	0.4
Tuppers Plains	0.3	0.2	0.1	0.3
Pomeroy	0.3	0.2	0.1	0.3

[a]These are the water districts that draw water from the Ohio River.

TABLE 11
Summary of Annual Average Modeled PFOA Concentrations for 6-Inch Thick Layer of Surface Soil
by Exposure Scenario and Zone From 1951 to 2003

Zone	Average PFOA surface soil concentration by exposure scenario (μg/kg)			
	Scenario 1 1995–2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003	Scenario 4 1998 to 2003
1	0.8	0.6	0.4	0.8
2	2	2	1	2
3	1	1	0.7	1
4	5	4	2.6	5
5	22	17	11	20
6	4	3	2	4
7	3	2	2	3
8	1	0.9	0.6	1
9	5	4	3	4
10	40	34	23	37
11	4	3	2	4
12	1	1	0.7	1.3
13	0.7	0.5	0.3	0.7
14	0.8	0.6	0.4	0.8
15	0.5	0.4	0.2	0.5
16	0.3	0.2	0.2	0.3
17	0.2	0.1	0.1	0.2
18	0.1	0.09	0.06	0.1
19	0.08	0.06	0.04	0.08

For the purposes of exposure assessment, PFOA concentrations in the groundwater were used as surrogates for tap-water concentrations. In doing so, it is likely that historical drinking-water concentrations were overestimated because the mixing model used to estimate groundwater concentrations did not take into account the transit times of PFOA in the saturated zones (i.e., transit time in the saturated zone was set at zero). This approach was used because the groundwater transit time through the sandy clay unsaturated zone was estimated to be much greater than the transit time through the saturated

sand and gravel aquifer. As such, the entire mass of PFOA entering the saturated aquifer was considered to be immediately extracted by the production wells: clearly an implausible assumption, but this ensures that water concentrations were not underpredicted. Additionally, for the Tuppers Plains and Pomeroy water districts, the groundwater concentrations were set equal to the predicted surface-water concentrations, and therefore the contribution of infiltration water that was determined not to contain PFOA was neglected. Thus, the historical groundwater concentrations are overestimated by not

TABLE 12

Summary of Annual Average Estimates of PFOA Flux to Groundwater by Exposure Scenario and Water District From 1951 to 2003

| Water district[a] | Average PFOA flux to groundwater by exposure scenario (g/m^2-yr) | | | |
	Scenario 1 1995–2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003	Scenario 4 1998 to 2003
Little Hocking Water Association	0.003	0.002	0.001	0.003
City of Belpre	0.0003	0.0002	0.0001	0.0003
Lubeck Public Service District	0.0005	0.0005	0.0003	0.0005

[a]These are the water districts that are impacted by the deposition of PFOA and its subsequent transport through soil to groundwater.

TABLE 13

Summary of Annual Average Estimated PFOA Drinking Water Concentrations by Exposure Scenario and Water District From 1951 to 2003

| Water district[a] | Average PFOA drinking water concentration by exposure scenario (μg/L) | | | |
	Scenario 1 1995–2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003	Scenario 4 1998 to 2003
Little Hocking Water Association	10	6	4	10
City of Belpre	1	1	0.4	1
Lubeck Public Service District	2	2	0.9	1
Tuppers Plains/Chester Water District	0.3	0.2	0.1	0.3
Village of Pomeroy	0.3	0.2	0.1	0.3

[a]These are the water districts that have had quantifiable concentrations of PFOA in their drinking water.

accounting for the mixing of the surface water with the infiltration water through the unsaturated zone. Further, because the Little Hocking and Lubeck water districts did not come on line until 1968 and 1970, respectively, groundwater concentrations in hypothetical private wells were calculated and served as the estimated drinking-water concentrations for the years prior to the water districts beginning operations.

Predicted Local Produce Concentrations

The average predicted total vegetable concentrations (including corn, beans and potatoes) by time period are presented in Table 14. The exposure zone with the highest predicted vegetable concentrations (excluding the plant—zone 10) was zone 5.

Quantification of Total PFOA Intake by Residents

Estimates of the total intake of PFOA over time were made by considering all relevant routes of potential exposure. These exposures were quantified in terms of the dose to an adult and child for various combinations of years from 1951 through 2003. Dose estimates (and relative contributions to total dose)

were developed for three pathways of exposure: inhalation, ingestion, and dermal contact. A summary of PFOA intake by route of exposure, zone, and scenario is presented in Table 15.

Inhalation Dose Estimates

The estimated intakes of PFOA due to inhalation of ambient air were developed for each exposure zone within the air modeling domain and for the four exposure scenarios. Excluding the plant (zone 10) PFOA intake from inhalation was predicted to be highest in zone 5. For the adult during the time period from 1995 to 2003 the inhalation annual average daily dose was estimated to be 0.06 μg/kg-day. For the child during the time period from 1998 to 2003, the inhalation annual average daily dose (ADD) was estimated to be 0.05 μg/kg-day.

Ingestion of Drinking-Water Dose Estimates

The estimated intake of PFOA from ingestion of drinking water were calculated for each exposure zone and for each exposure scenario. Excluding the plant drinking water, PFOA intake from drinking water was predicted to be the highest in the Little Hocking Water District (zones 1–6) across all time periods evaluated. For both the adult, the highest annual ADD

TABLE 14
Summary of Modeled Concentrations for All Vegetables

	Average PFOA concentration in vegetables[a] (μg/kg)			
Zone	Scenario 1 1995–2003	Scenario 2 1974 to 2003	Scenario 3 1951 to 2003	Scenario 4 1998 to 2003
1	11	9	6	10.1
2	29	23	16	27
3	20	16	11	17
4	69	56	37	61
5	280	223	148	247
6	57	48	32	50
7	46	37	24	42
8	17	14	9	15
9	68	56	38	60
10	567	492	338	488
11	53	41	27	50
12	18	14	9	16.6
13	9	7	5	8.6
14	11	8	6	9.4
15	6.3	5	3	6.1
16	3.9	3	2	3.6
17	2	2	1	2.1
18	2	1	0.8	1.5
19	1	0.8	0.5	1.03

[a]These vegetable concentrations are the sum of concentrations for corn, beans, and potatoes.

due to ingestion of drinking water was 0.2 μg/kg-day during the time period 1995–2003.

Estimated Doses from All Other Sources of Exposure

The estimated intakes of PFOA from all other sources (media and routes) including dermal contact with water during showering, incidental ingestion of surface soil, dermal contact with surface soil, and ingestion of locally grown produce were calculated for each exposure zone and for the three exposure scenarios. As with the inhalation and drinking-water ingestion pathways, the highest intake of PFOA for all other pathways (excluding zone 10) was predicted for zone 5. For the adult, the highest annual average daily dose from all other sources of exposure was estimated to be 0.03 μg/kg-day during the time period 1995–2003. For the child, the highest annual average daily dose was estimated to be 0.06 μg/kg-day.

Total Aggregate Dose

The highest predicted total doses (excluding zone 10) are for zones 1–6, with total aggregate doses ranging from 0.2 to 0.3 μg/kg-day adults during the time period 1995–2003 and from 0.2 to 0.3 μg/kg-day for the child during the time period 1998–2003. The percent contribution of each exposure pathway differs by year and zone, but overall, either inhalation of ambient air or drinking-water ingestion predominates.

Although it is believed that use of average or central tendency exposure parameters was appropriate for estimating long-term exposures such as those described by scenarios 1–4, uncertainty around the exposure estimates can be evaluated by using different exposure parameter values. Because ingestion of drinking water was the primary route of exposure for each of the scenarios, uncertainty around the central tendency estimate was assessed by using a lower bound and upper bound drinking-water ingestion rate (see Table 7). For zone 5, where for all scenarios, the drinking water doses were highest, the lower bound dose ranges from 0.08 μg/kg-day for scenario 3 to 0.2 μg/kg-day for scenario 1. The upper bound doses range from 0.2 μg/kg-day for scenario 3 to 0.4 μg/kg-day for scenario 1. Thus, the upper bound dose might be perhaps 1.5 times higher than that estimated using the central tendency values.

Risk Characterization

Historically, PFOA was not considered to be a chemical that produces significant toxicity nor has it been one to which persons have been appreciably exposed. As a result, no risk criteria or health benchmarks were developed for PFOA by the U.S. EPA, ATSDR, or OSHA. In 2002, the West Virginia DEP (WVDEP, 2002) convened a panel of experts known as the C8

TABLE 15

Summary of the Annual Average Daily Doses (ADDs)[a] for Exposure to PFOA by Exposure Scenario and Zone From 1951 to 2003

Exposure zone	Scenario 1, adult, 1995–2003				Scenario 2, adult, 1974–2003				Scenario 3, adult, 1951–2003				Scenario 4, child, 1998–2003			
	Ambient air inhalation	Drinking-water ingestion[b]	All others	Total dose	Ambient air inhalation	Drinking-water ingestion[b]	All others	Total dose	Ambient air inhalation	Drinking-water ingestion[b]	All others	Total dose	Ambient air inhalation	Drinking-water ingestion[b]	All others	Total dose
1	4.7E-06	2.0E-04	3.7E-06	2.1E-04	3.7E-06	1.2E-04	2.4E-06	1.3E-04	2.6E-06	7.3E-05	1.5E-06	7.7E-05	4.5E-06	2.0E-04	3.6E-06	2.0E-04
2	1.1E-05	2.0E-04	5.1E-06	2.2E-04	8.7E-06	1.2E-04	3.5E-06	1.4E-04	6.0E-06	7.2E-05	2.2E-06	8.0E-05	1.0E-05	2.0E-04	4.9E-06	2.1E-04
3	7.6E-06	2.0E-04	4.4E-06	2.2E-04	6.5E-06	1.2E-04	3.0E-06	1.3E-04	4.3E-06	7.3E-05	1.8E-06	7.9E-05	6.8E-06	2.0E-04	4.1E-06	2.1E-04
4	2.3E-05	2.0E-04	8.3E-06	2.4E-04	2.0E-05	1.2E-04	6.1E-06	1.5E-04	1.3E-05	7.2E-05	3.9E-06	8.9E-05	2.0E-05	2.0E-04	7.7E-06	2.2E-04
5	6.2E-05	2.0E-04	2.7E-05	2.9E-04	5.3E-05	1.2E-04	2.0E-05	2.0E-04	3.6E-05	7.2E-05	1.3E-05	1.2E-04	5.4E-05	2.0E-04	2.4E-05	2.8E-04
6	1.6E-05	2.0E-04	7.2E-06	2.3E-04	1.3E-05	1.2E-04	5.3E-06	1.4E-04	8.9E-06	7.2E-05	3.4E-06	8.4E-05	1.4E-05	2.0E-04	6.7E-06	2.2E-04
7	1.8E-05	2.4E-05	3.9E-06	4.5E-05	1.4E-05	1.4E-05	3.0E-06	3.2E-05	9.8E-06	8.2E-06	2.0E-06	2.0E-05	1.6E-05	2.3E-05	3.7E-06	4.3E-05
8	5.7E-06	2.4E-05	1.6E-06	3.1E-05	4.6E-06	1.4E-05	1.2E-06	2.0E-05	3.2E-06	8.2E-06	8.2E-07	1.2E-05	5.1E-06	2.3E-05	1.5E-06	3.0E-05
9	1.6E-05	3.1E-05	5.8E-06	5.3E-05	1.4E-05	3.0E-05	4.7E-06	4.9E-05	9.9E-06	1.7E-05	3.2E-06	3.1E-05	1.6E-05	2.9E-05	5.3E-06	5.0E-05
10	1.0E-04	6.4E-04	5.4E-05	7.9E-04	1.0E-04	3.4E-04	4.3E-05	4.8E-04	7.4E-05	1.9E-04	2.9E-05	3.0E-04	9.0E-05	6.9E-04	5.0E-05	8.3E-04
11	1.4E-05	3.1E-05	4.8E-06	5.0E-05	1.2E-05	3.0E-05	3.7E-06	4.6E-05	8.1E-06	1.7E-05	2.5E-06	2.8E-05	1.4E-05	2.9E-05	4.7E-06	4.8E-05
12	5.1E-06	3.1E-05	1.9E-06	3.8E-05	4.1E-06	3.0E-05	1.5E-06	3.6E-05	2.8E-06	1.7E-05	9.7E-07	2.1E-05	4.9E-06	2.9E-05	1.8E-06	3.6E-05
13	2.9E-06	3.1E-05	1.2E-06	3.5E-05	2.3E-06	2.5E-05	9.1E-07	2.8E-05	1.6E-06	1.5E-05	5.9E-07	1.7E-05	2.8E-06	2.9E-05	1.2E-06	3.3E-05
14	3.6E-06	3.0E-05	1.3E-06	3.5E-05	2.9E-06	2.2E-05	9.7E-07	2.6E-05	2.0E-06	1.5E-05	6.6E-07	1.7E-05	3.4E-06	2.9E-05	1.2E-06	3.4E-05
15	2.1E-06	3.1E-05	9.6E-07	3.4E-05	1.6E-06	2.3E-05	7.2E-07	2.5E-05	1.1E-06	1.4E-05	4.6E-07	1.6E-05	2.1E-06	2.9E-05	9.3E-07	3.2E-05
16	1.6E-06	2.6E-05	6.9E-07	2.8E-05	1.2E-06	1.2E-05	4.2E-07	1.4E-05	8.6E-07	7.7E-06	2.8E-07	8.9E-06	1.5E-06	2.9E-05	7.1E-07	3.1E-05
17	8.8E-07	2.5E-05	5.3E-07	2.6E-05	7.0E-07	9.9E-06	2.7E-07	1.1E-05	4.8E-07	5.9E-06	1.7E-07	6.6E-06	8.8E-07	2.9E-05	5.8E-07	3.1E-05
18	7.6E-07	2.5E-05	4.8E-07	2.6E-05	5.9E-07	9.3E-06	2.3E-07	1.0E-05	4.1E-07	5.5E-06	1.4E-07	6.1E-06	7.4E-07	2.9E-05	5.3E-07	3.0E-05
19	5.0E-07	2.4E-05	4.2E-07	2.5E-05	3.9E-07	8.4E-06	1.8E-07	9.0E-06	2.7E-07	4.9E-06	1.1E-07	5.3E-06	5.2E-07	2.9E-05	4.9E-07	3.0E-05
20	0.0E+00	6.0E-06	8.3E-08	6.1E-06	0.0E+00	3.6E-06	5.0E-08	3.7E-06	0.0E+00	2.1E-06	2.9E-08	2.1E-06	0.0E+00	6.1E-06	8.4E-08	6.2E-06
21	0.0E+00	5.9E-06	8.2E-08	6.0E-06	0.0E+00	3.6E-06	5.0E-08	3.6E-06	0.0E+00	2.1E-06	2.9E-08	2.1E-06	0.0E+00	6.0E-06	8.2E-08	6.1E-06

Note. The inhalation average daily dose was not calculated for zones 20 and 21 because the inhalation of PFOA was not a complete exposure pathway for these zones.

[a] ADDs in mg/kg-day.

[b] Drinking water for zones 1–6 comes from the Little Hocking Water Association, for zones 7–8 from the City of Belpre, for zones 9 and 11–19 from the Lubeck Public Service District, for zone 10 from the Washington Works facility, for zone 20 from Tuppers Plains/Chester Water District, and for zone 21 from the Village of Pomeroy.

49

Assessment of Toxicity Team (CATT) to (1) determine risk-based human health screening levels (SL) for PFOA in air, water, and soil; (2) provide health risk information to the public; and (3) determine an ecological health protective SL for C8 in surface water. The CATT determined an oral health benchmark for C8 of 0.004 mg/kg-day. This benchmark was used to derive a safe drinking-water level of 150 μg/L and a soil screening level of 240 mg/kg. Also, the CATT determined an ambient air health benchmark for the inhalation route of exposure of 1 μg/m³.

There has been sufficient interest in understanding the possible risks to the general population due to background intake of PFOA that a risk characterization was published (Butenhoff et al., 2004b). In this analysis, potential health risks were characterized using a margin of exposure (MOE) analysis. The MOE is traditionally calculated at a dose related to a health effect divided by a dose related to human exposures. An MOE equal to 1 suggests that the human exposure dose of interest is at the dose where there is concern for a health impact. This health-related dose could be perhaps an administered dose from an animal toxicity study or a dose from an epidemiological study, and the human exposure dose could be a background dose, an occupational dose, or a different human exposure dose. A benchmark dose of 3.9 mg/kg-day was developed by Butenhoff et al. (2004b). This was based on the lower 95% CI of the benchmark dose (LBMD$_{10}$) based on the multistage model and a 10% response for increased liver-weight-to-brain-weight ratio in cynomolgus monkeys. Increased liver weight effect was determined to be the most sensitive endpoint from various rat and monkey studies. Because a background dose level for the general population was not available, the blood level in the monkey that corresponded to the benchmark dose was compared to the average PFOA blood level in the general U.S. population, and the MOEs ranged from 1600 to 8900.

The U.S. EPA has issued a draft hazard assessment (U.S. EPA, 2002) and a draft risk assessment (U.S. EPA, 2005a). In the draft risk assessment, U.S. EPA used a margin of exposure (MOE) analysis to describe the potential for adverse health effects associated with exposure to PFOA. The MOEs were based on lowest observed adverse effect levels (LOAEL) of 3 mg/kg-day in the cynomolgus monkey during a 6-mo study, where increased liver weight was the observed effect, 1 mg/kg-day in the male rat during a 2-generation reproductive study where F1 body weights were the critical effect, and a no-observed-adverse-effect level (NOAEL) of 10 mg/kg-day in a female rat during a 2-yr repeat dose study. Additionally, the U.S.EPA evaluated developmental endpoints where NOAELs ranged from 3 to 10 mg/kg-day in F1 male and female rat pups. Again, because background dose levels of PFOA were not available for the general human population, the MOEs were calculated by comparing the animal blood levels that corresponded to the various NOAELs and LOAELs to the average U.S. general population blood level. The draft MOEs ranged from 398 to 16,789 for the adult endpoints and from 10,484 to 78,546 for the developmental endpoints. The U.S. EPA noted that the developmental endpoints do not include all relevant juvenile exposure periods (e.g., lactation period). It should be noted that although the U.S. EPA evaluated the carcinogenicity data in the draft risk assessment, a quantitative risk assessment was not conducted and there is some disagreement over whether the data support a "likely" cancer descriptor (U.S. EPA, 2005b).

In the absence of a standard health benchmark for PFOA, an 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. (2004b). The MOEs were calculated using averaged daily doses for residents potentially exposed for 9, 30, or 53 yr and are presented in Table 16. 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 9000 to 13000. These values are similar to or higher than those calculated by Butenhoff et al. (2004b) and the U.S. EPA (2002) for the general population. However, the MOEs for the residents were calculated using the administered dose, whereas Butenhoff et al. (2004b) and the 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. The MOEs for the population near the Washington Works are much greater than the minimally acceptable MOE values of 100–1000 (European Commission, 2000) and indicate that the likelihood of adverse health effects due to exposure to PFOA, based on currently available information, is extremely low.

DISCUSSION

In this analysis, the temporal modeled estimates of PFOA concentrations in various environmental media were based on numerous assumptions involving mass balance, emissions, fate and transport characteristics, and other factors. The degree of uncertainty in the PFOA dose estimates is directly influenced by the relative accuracy of the exposure point concentrations, and it is therefore important to assess the degree to which the actual measured concentrations are consistent with the model estimated values.

Measurements of airborne PFOA concentrations in the community were not available at the time of our analysis. However, DuPont recently performed a comparison of modeled to measured air concentrations at the facility fenceline (Barton et al., 2006). Results showed the ISCST3 model overpredicted 32% of the time, and was in agreement 68% of the time (i.e., both modeled and measured values were below the method detection limit) and never under predicted the field data. However, the model estimates were about sixfold higher than measured values (well within that considered acceptable

TABLE 16
Margin of Exposure (MOE) Summary for Total Dose

Public water service provider	Exposure zone	Scenario 1, adult, 1995–2003	Scenario 2, adult, 1974–2003	Scenario 3, adult, 1951–2003	Scenario 4, child 1998–2003
Little Hocking Water Association	1	18,000	30,000	51,000	20,000
	2	18,000	28,000	48,000	19,000
	3	18,000	29,000	49,000	19,000
	4	17,000	26,000	44,000	18,000
	5	13,000	20,000	32,000	14,000
	6	17,000	27,000	46,000	18,000
City of Belpre	7	86,000	120,000	200,000	91,000
	8	130,000	200,000	320,000	130,000
Lubeck Public Service District Plant	9	73,000	80,000	130,000	78,000
	10	4900	8000	13,000	4700
Lubeck Public Service District	11	77,000	85,000	140,000	81,000
	12	100,000	109,000	180,000	110,000
	13	110,000	140,000	220,000	120,000
	14	110,000	150,000	220,000	110,000
	15	110,000	150,000	250,000	120,000
	16	140,000	280,000	440,000	130,000
	17	150,000	360,000	590,000	130,000
	18	150,000	390,000	640,000	130,000
	19	150,000	430,000	740,000	130,000
Tuppers Plains	20	640,000	1,100,000	1,800,000	630,000
Village of Pomeroy	21	650,000	1,100,000	1,800,000	640,000

Note. The MOE is the ratio of the health benchmark (3.9 mg/kg-day) to the calculated dose (mg/kg-day).

for this kind of modeling). Thus, although measured community air concentrations were not available, these results support historical evaluations of the ISCST3 model that indicated that it is an approach that yields reasonable estimates and is more likely to overpredict, rather than underpredict, actual airborne concentrations (NCEA, 1998).

At the time of this analysis, only two soil borings from beyond the plant fenceline were available for comparison purposes were tested for the presence of PFOA. However, in the future additional soil samples are likely to be collected and these can be used to verify the model. To compare the modeled soil concentration, which is an annual average value, to the transient values represented by soil borings, a weighted average soil concentration should be calculated for the vertical soil profile for both the measured and modeled data. Such a comparison is reasonable because the weighted average represents the total mass of PFOA in the soil column (which reflects long-term average deposition) rather than the vertical concentration profile during 1 day. This comparison was conducted for the two soil borings collected at the Little Hocking Water Authority property and the modeled estimates for zone 5. The results indicate that the modeled concentrations under predicted the measured concentrations (i.e., 14 μg/kg modeled versus 18 μg/kg measured). Although this data set is very limited, the

analysis shows that the model reasonably predicted the soil concentrations.

In addition to the soil borings, measurements of PFOA concentrations in cistern water were collected in zones 4 (2002) and 11 (2001, 2002). A cistern is a reservoir or container used to store rainwater for uses such as irrigation. Because the source of PFOA to these cisterns could only have been the result of air deposition, the cistern measurements were useful in evaluating the reasonableness of the air deposition modeling estimates and hence surface soil concentration estimates. The modeled cistern annual average concentrations were calculated by dividing the deposition rate of PFOA by the water volume. To estimate the cistern water volumes, the lower bound volume was set equal to the recharge rate (total rainfall minus evapotranspiration) in the soil for each zone, and the upper bound volume was set equal to the total rainfall amount for zones 4 and 11. For zone 4, the modeled concentrations ranged from 1.4 to 6.8 μg/L and the average measured concentration was 3 μg/L ($n = 12$). For zone 11, the modeled concentrations ranged from 0.6 to 12 μg/L and the average measured concentration was 2.5 μg/L ($n = 5$). This comparison indicates that the air deposition modeling was reasonably accurate in predicting surface soil concentrations.

Model estimated surface water concentrations of PFOA were compared to measured values obtained from samples collected in the Ohio River at locations near the public water supply wells considered in this assessment. For each of these locations, there was only one year (2002) of data available for comparison. Sampling data representative of a single day at each location indicates that PFOA average concentrations in surface water ranged from 0.11 to 0.35 μg/L. The modeled concentrations that represent predicted annual average concentrations ranged from 0.12 to 0.16 μg/L. Although the measured data set is admittedly limited, this comparison suggests that the modeled surface water concentrations are reasonable and useful for estimating the contribution of surface water PFOA to the groundwater.

The results of the model estimated groundwater concentrations were compared to the public well data. For each of the water districts, there were between one and seven years of sampling data available for comparison (see Table 2). Figure 8 shows a comparison of modeled and measured groundwater concentrations of PFOA. These indicate that modeled concentrations exceeded measured concentrations for all water districts except Tuppers Plains. Specifically, the average ratio of modeled to measured groundwater concentrations was 4.1 for the water districts.

The generally high bias of the estimated groundwater concentrations is not unexpected because most of the air, soil, and water model parameters were selected based on site conditions and were not adjusted via a calibration process. The only parameter that was adjusted was the condition of the land cover
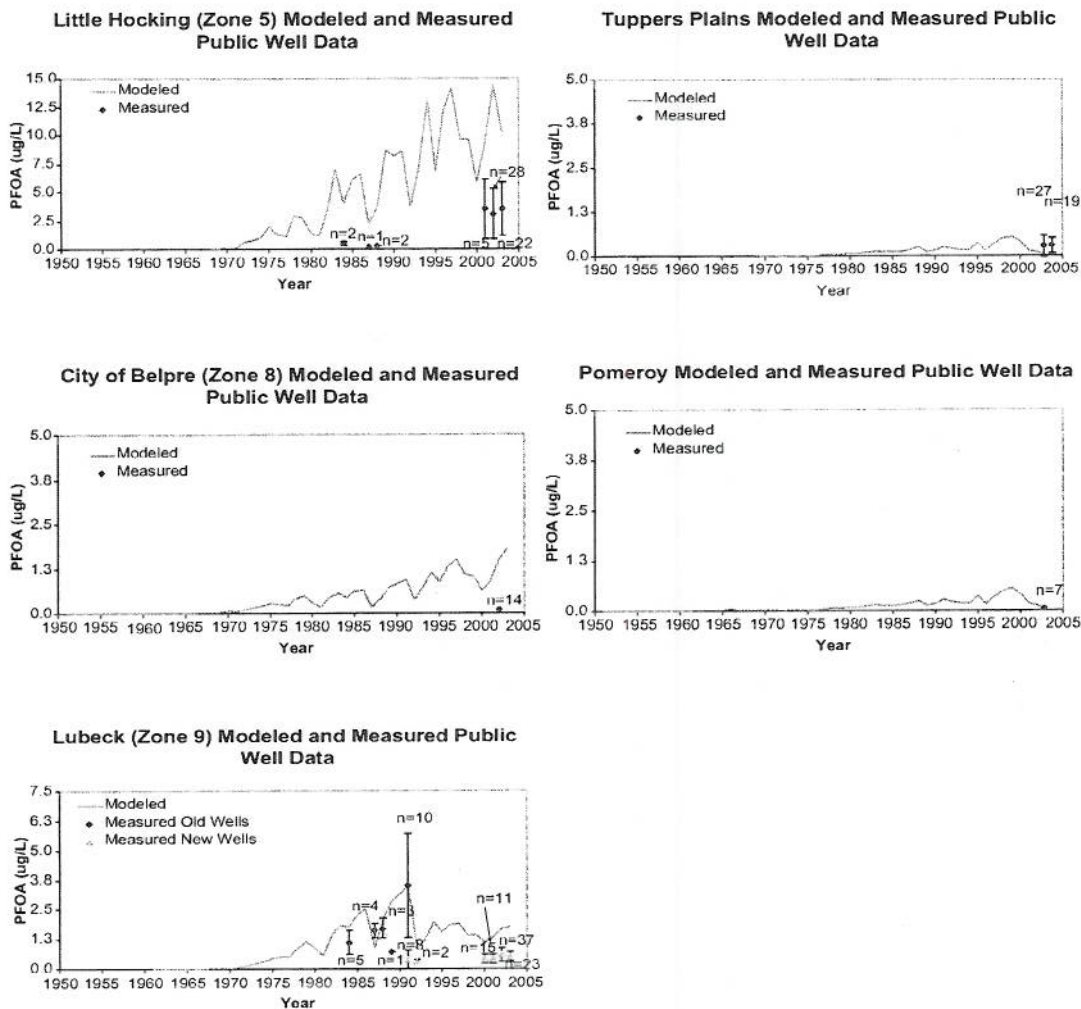

FIG. 8. Model estimated vs. measured public well groundwater concentrations.

(percent covered by vegetation) to ensure that the amount of water recharge from rainfall that was predicted by the model was consistent with values from the literature. Furthermore, modeling was performed using fairly conservative U.S. EPA models (ISCST3 and PRZM).

A limited sensitivity analysis of the air dispersion and mass balance components of the exposure model was also conducted. For the air dispersion modeling, it was assumed that all PFOA emissions were in the particulate phase. To evaluate the sensitivity of this parameter, the model was also run to determine the historical groundwater concentrations if it was assumed that 100% of the emissions were as a vapor. Since vapors do not deposit readily, it was anticipated that soil and ultimately groundwater concentrations would be inconsistent with data collected near the plant over the years. As shown in Figure 9, the 100% particulate and 100% vapor emission profiles for Little Hocking result in groundwater concentrations that represent the upper and lower bounds of measured data, respectively. This figure shows that the "all vapor scenario" under predicts groundwater concentrations for the years where seasonally representative data were available ($n \geq 5$), by factors of three- to fourfold, which suggests that the assumption that PFOA was emitted as a particulate was reasonable.

A simple source mass balance calculation verified that all of the APFO used at the plant was accounted for in the various environmental media by the model (that is, the amount released over time equaled the amount contained in the various environmental media and nonenvironmental compartments) (Table 17). The calculations show that the sum of the total mass of PFOA in each of the compartments equals the total amount of APFO used at the plant for each year. In short, the 2,464,200 lb APFO used by the facility over the 50 yr equals the sum of PFOA predicted to be present in each of the environmental media and non-environmental compartments.

The accuracy of the predicted groundwater concentrations can be assessed (within an order of magnitude) using the ISCST3 modeled deposition rates, and an estimation of the delay time or lag between deposition of the PFOA and completion of transit through soil to the top of the water table. This
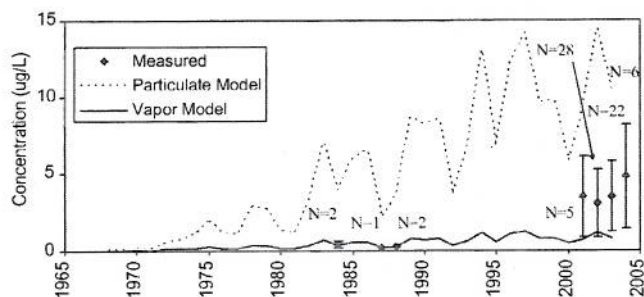
was done by dividing the ISCT3 modeled deposition rate for the last 10, 20, or 30 yr by the rainfall recharge rate and the fraction of total recharge from rainfall. The results of this approach, using lag times of 10, 20, and 30 yr, are presented in Figure 10.

As shown in Figure 10, the 30-yr lag time appears to best predict the measured data for the Little Hocking Water Association. This is consistent with the modeled data, which suggest that the lag time for the transport of PFOA deposited on the soil surface to the water table (for the Little Hocking water district) was approximately 23 yr. As discussed previously, in the groundwater modeling analysis, the travel time of PFOA from the bottom of the unsaturated zone through the saturated aquifer to the water supply wells was not incorporated in the calculations. This is due to the assumption that the transport of PFOA was limited primarily by the silty clay in the unsaturated zone. The reasonable agreement between the modeled and measured groundwater concentrations confirms that the lag time is due to the unsaturated zone transport. It is acknowledged that our fourfold over estimate of the concentrations may be a result of uncertainty and/or variability in the true size distribution of particulate emissions (Figure 9) or neglecting the transit time through the saturated zone (Figure 10); however, the available data are far too sparse for concluding that our estimates are significantly different than the concentrations which will be measured in the future.

High confidence exists in our predictions of the distribution of the airborne emissions in the environment. Field studies indicate that the ISCST3 model generally predicts annual average air concentrations within one order of magnitude and, in some cases within a factor of three- or fourfold of field measurements (NCEA, 1998). Further, the U.S. EPA validation of the model showed reasonable accuracy of the gravitational dry and wet deposition functions, although they typically overpredict deposition rates at locations near the source of release, and underpredict deposition at a distance greater than 3.2 km (i.e., 2 miles). It should be noted, however, that for the PFOA analysis, all of the areas included in the air modeling were within 3.2 km (i.e., 2 miles) except for the new Lubeck wells. Uncertainty associated with the air dispersion modeling conducted in this assessment is primarily associated with our less-than-perfect knowledge of the particulate size distribution, meteorological data, and the impact of wind speed and wind direction.

In our analysis, recent information was incorporated which indicated that the APFO at this facility was released as a particle with a specific size distribution (Barton et al., 2006). This information is consistent with the physical/chemical properties of APFO, since the vapors leaving the stack would be expected to condense to a fume (i.e., particulate form). Recent community air samples indicate that PFOA was not detected in the vapor phase.

The uncertainty in the meteorological dataset is primarily associated with the use of site specific data for the four most recent years and extrapolation of these data to previous years.

FIG. 9. Comparison of modeled and measured groundwater concentrations when 100% vapor versus 100% particulate air emission profiles were considered.

TABLE 17

Complete Environmental Material Balance by Decade (Based on Model)

Mass of PFOA (lb)

Year	Total C-8 used	Non environmental compartment (recovered, destroyed, end product)	PFOA disposed of on land	PFOA discharged to the Ohio River[a]	PFOA dispersed within plant fence line or beyond modeling Area	PFOA dispersed with air modeling domain[a]		PFOA sum of all compartments
						PFOA flux to groundwater	Net addition of PFOA in soil	
1951–1959	28,965	5014	5993	2672	14,941	8	337	28,965
1960–1969	143,645	21,903	26,669	17,855	75,405	282	1529	143,643
1970–1979	196,882	38,665	45,563	37,181	73,391	1206	880	196,886
1980–1989	565,573	87,140	105,670	157,902	209,413	2033	3422	565,580
1990–1999	996,977	257,049	159,091	337,158	237,244	4185	2253	996,980
2000–2003	532,194	323,530	51,500	79,700	75,830	1534	101	532,195
Total	**2,464,200**	**733,302**	**394,486**	**632,468**	**686,223**	**9249**	**8521**	**2,464,200**

[a]Includes small contribution from surface water runoff.

54

Simple Groundwater Model for Little Hocking:
Groundwater Concentration Equals Deposition Rate (10, 20 or 30 years
previous) divided by Rainfall Recharge Rate multiplied by Fraction of
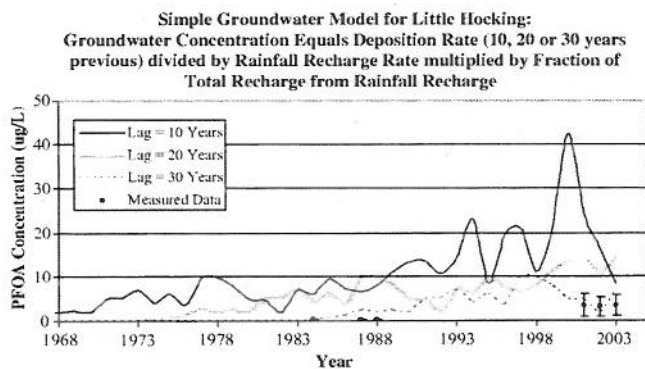Total Recharge from Rainfall Recharge

FIG. 10. Simple groundwater model using Little Hocking air deposition rates and rainfall recharge in conjunction with various lag times.

To conduct the extrapolation, annual rainfall amounts for the local area were used to select which of the site specific data sets should be considered representative for the year. Because wind speed/wind direction was not highly variable, only hourly rainfall amounts may have affected aerial deposition rates. However, because each of the four years of site specific data included high, low and medium rainfall rates, hourly rainfall rates would likely have been equally overestimated and underestimated throughout the year and would not likely have an impact on aerial deposition rates as an annual average.

In summary, the primary exposure pathway by which persons living near this production facility received exposure to airborne emissions of PFOA was through ingestion of drinking water. A comparison of the expected intake of PFOA by citizens living near this facility with several risk criteria 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 were shown to be reasonable, although they likely overestimated the actual exposure of residents. Over time, it is almost certain that additional data will be collected in groundwater, surface water, and the soil that will characterize the precision of our estimates.

REFERENCES

3M Company. 2003. Final Report. Descriptive analyses of serum fluorochemical concentrations form Cottage Grove employee participants of the 2002 Medical Surveillance Program. 3M Medical Department, June 17, 2003. U.S. EPA Public Docket No. AR-226–1352. Washington, DC.

Alexander, B. H. 2001. Mortality Study of Workers Employed at the 3M Cottage Grove facility. St. Paul, MN: 3M Company. U.S.EPA Public Docket AR-226–1030a018, Washington. D.C.

Alexander, B. H., Olsen, G. W., Burris, J. M., Mandel, J. H., and Mandel, J. S. 2003. Mortality of employees of a perfluorooctanesulphonlyl fluoride manufacturing facility. Occup. Environ. Med. 60:722–729.

Association of Plastics Manufacturers in Europe. 2003. Adsorption/desorption of ammonium perfluorooctanoate to soil (OECD 106). EMSE Study/Project EMSER TO111/14107. Report EMSER 17–03.

Barton, C. A., Butler, L. E., Zarzecki, C. J., Flaherty, J. M., and Kaiser, M. A. 2006. Characterizing perfluorooctanoate in ambient air near the fence line of a manufacturing facility: Comparing modeled and monitored values. J. Air Waste Manage. Assoc. 56:48–55.

Biegel, L. B., Liu, R. C. M., Hurtt, M. E., and Cook, J. C. 2001. Mechanisms of extrahepatic tumor induction by peroxisome proliferators in male CD rats. Toxicol. Sci. 60:44–55.

Butenhoff, J., Costa, G., Elcombe, C., Farrar, D., Hansen, K., Iwai, H., Jung, R., Kennedy, G., Jr., Lieder, P., Olsen, G., and Thomford, P. 2002. Toxicity of ammonium perfluorooctanoate in male cynomolgus monkeys after oral dosing for 6 months. Toxicol. Sci. 69:244–257.

Butenhoff, J. L., Kennedy, G. L., Jr., Frame, S. R., O'Connor J. C., and York, R. G. 2004a. The reproductive toxicology of ammonium perfluorooctanoate (APFO) in the rat. Toxicology 196:95–116.

Butenhoff, J. L., Gaylor, D. W., Moore, J. A., Olsen, G. W., Rodricks, J., Mandel, J. H., and Zobel, L. R. 2004b. Characterization of risk for general population exposure to perfluorooctanoate. Regul. Toxicol. Pharmacol. 39:363–380.

Cousins, I. T., Prevedouros, K., Buck, R. C., and Korzeniowski, S. H. 2005. Mass balance investigation of perfluorooctanoic acid (PFOA) environmental levels, emissions, and sinks in the Northern Hemisphere. Organohalogen Compounds 67:741–744.

DuPont. 2002. Memo from M. Ann Bradley to Armando Benincasa and Dr. Dee Ann Staats of the West Virginia Department of Environmental Protection. Air dispersion modeling for Year 2000. June 13, 2002.

DuPont. 2003a. Revised groundwater flow model. DuPont Washington Works, Washington, WV. January 2003. DuPont Corporate Remediation Group and URS Diamond. EPA Docket OPPT-2003–0012, Document ID 0868.

DuPont. 2003b. Follow-up to September 15, 2003 submission of DuPont progress report on environmental assessments pursuant to the APFO users LOI dated March 14, 2003: Air dispersion modeling results. Letter to the Office of Pollution Prevention and Toxics from David M. Rurak of DuPont, dated October, 20, 2003. Containing the following attachments authored by DuPont: (1) Year 2002 Air Dispersion Modeling Analysis of APFO Emissions (October 17, 2003), and (2) September 2002 through August 2003 air dispersion modeling analysis of APFO emissions (October 17, 2003). EPA Docket OPPT-2003–0012, Document ID 0206, 0224, 0225.

DuPont. 2003c. Adsorption/desorption of ammonium perfluorooctanoate to soil (OECD 106). April 2003. E. I. du Pont de Nemours and Company Central Research and Development sponsored by Association of Plastic Manufacturers in Europe. EPA Docket OPPT-2003–0012, Document ID 0401.

European Commission. 2000. First report on the harmonization of risk assessment procedures. Part 1: The report of the Scientific Steering Committee's Working Group on harmonization of risk assessment procedures in the Scientific Committees advising European Commission in the area of human and environmental health, pp. 26, 27. October. Accessed at http://ec.europa.eu/food/fs/sc/ssc/out83_en.pdf on 9/22/05.

Federal Register. 2003. Revision to the guidance on air quality models: Adoption of a preferred long range transport model and other revisions: Final rule. Vol. 68, pp. 18440–18482.

Flagan, R. C. 1994. Combustion fume structure and dynamics. Prepared for the Department of Energy under contract DE-FG22 90PC90286. Accessed at http://www.osti.gov/bridge/servlets/purl/10174893-wRPGTs/10174893.PDF on 4/22/04.

Gangal, S. B. 2004. Perfluorinated polymers. In Kirk-Othmer encyclopedia of chemical technology. John Wiley & Sons. DOI: 10.1002/0471238961.2005201807011407.a02.pub2; accessed October 12, 2005.

Gilliland, F. D., and Mandel, J. S. 1996. Serum perfluorooctanoic acid and hepatic enzymes, lipoproteins, and cholesterol: A study of occupationally exposed men. Am. J. Ind. Med. 29:560–568.

Griffith, F. D., and Long, J. E. 1980. Animal toxicity studies with ammonium perfluorooctanoate. Am. Ind. Hyg. Assoc. J. 41:576–583.

Jury, W., Gardner, W. R., and Gardner, W. H. 1991. Water movement in soil. In Soil physics. 5th ed., pp. 73–121. New York: John Wiley & Sons.

Kannan, K., Choi, J. W., Iseki, N., Senthilkumar, K., Kim, D. H., and Giesy, J. P. 2002a. Concentrations of perfluorinated acids in livers of birds from Japan and Korea. Chemosphere 49:225–231.

Kannan, K., Corsolini, S., Falandysz, J., Oehme, G., Focardi, S., and Giesy, J. P. 2002b. Perfluorooctanesulfonate and related fluorinated hydrocarbons in marine mammals, fishes, and birds from coasts of

the Baltic and the Mediterranean Seas. *Environ. Sci. Technol.* 36: 3210–3216.

Kannan, K., Corsolini, S., Falandysz, J., Fillmann, G., Kumar, K. S., Loganathan, B. G., Mohd, M. A., Olivero, J., Van Wouwe, N., Yang, J. H., and Aldoust, K. M. 2004. Perfluorooctanesulfonate and related fluorochemicals in human blood from several countries. *Environ. Sci. Technol.* 38:4489–4495.

Kennedy, G. L., Jr. 1985. Dermal toxicity of ammonium perfluorooctanoate. *Toxicol. Appl. Pharmacol.* 81:348–355.

Kennedy, G. L., Jr. 1987. Increase in mouse liver weight following feeding of ammonium perfluorooctanoate and related fluorochemicals. *Toxicol. Lett.* 39:295–300.

Kennedy, G. L., Jr., Hall, G. T., Brittelli, M. R., Barnes, J. R., and Chen, H. C. 1986. Inhalation toxicity of ammonium perfluorooctanoate. *Food Chem. Toxicol.* 24:1325–1329.

Kennedy, G. L., Jr., Butenhoff, J. L., Olsen, G. W., O'Connor, J. C., Seacat, A. M., Perkins, R. G., Biegel, L. B., Murphy, S. R., and Farrar, D. G. 2004. The toxicology of perfluorooctanoate. *Crit. Rev. Toxicol.* 34: 351–384.

Lau, C., Butenhoff, J. L., and Rogers, J. M. 2004. The developmental toxicity of perfluoroalkyl acids and their derivatives. *Toxicol. Appl. Pharmacol.* 198:231–241.

Mabury, S. 2005. Environmental fate of polyfluorinated chemicals. *Organohalogen Compounds* 67:4–7.

Mendez, P. F., Jenkins, N. T., and Eagar, T. W. 2000. Effect of electrode droplet size on evaporation and fume generation in GMAW. Proc Gas Metal Arc Welding for the 21st Century Conference, Orlando, FL, December 6–8.

Moody, C. A., Martin, J. W., Kwan, W. C., Muir, D. C., and Mabury, S. A. 2002. Monitoring perfluorinated surfactants in biota and surface water samples following an accidental release of fire-fighting foam into Etobicoke Creek. *Environ. Sci. Technol.* 36:545–551.

Morikawa, A., Kamei, N., Harada, K., Inoue, K., Yoshinaga, T., Saito, N., and Koizumi, A. 2006. The bioconcentration factor of perfluorooctane sulfonate is significantly larger than that of perfluorooctanoate in wild turtles (*Trachemys scripta elegans* and *Chinemys reevesii*): An Ai river ecological study in Japan. *Ecotoxicol. Environ. Safety.* 65: 14–21.

NCEA. 1998. Methodology for assessing health risks associated with multiple pathways of exposure to combustor emissions. EPA 600/R-98/137. December. Washington, DC: U.S. EPA National Center for Environmental Assessment.

Oberdorster, G., Finkelstein, J. N., Johnston, C., Gelein, R., Cox, C., Baggs, R., and Elder, A. C. 2000. Acute pulmonary effects of ultrafine particles in rats and mice. *Res. Rep. Health Effects Inst.* 96:5–74; disc. 75–86.

Ohio State University Extension. 2004. Fact sheet: Washington County ground-water resources. AEX-490.84. Accessed at http://ohioline.osu.edu/aex-fact/0490_84.html on 2/20/04.

Olsen, G. W., Gilliland, F. D., Burlew, M. M., Burris, J. M., Mandel, J. S., and Mandel, J. H. 1998. An epidemiologic investigation of reproductive hormones in men with occupational exposure to perfluorooctanoic acid. *J. Occup. Environ. Med.* 40:614–622.

Olsen, G. W., Burris, J. M., Burlew, M. M., and Mandel, J. H. 2000. Plasma cholecystokinin and hepatic enzymes, cholesterol and lipoproteins in ammonium perfluorooctanoate production workers. *Drug Chem. Toxicol.* 23:603–620.

Olsen, G. W., Logan, P. W., Hansen, K. J., Simpson, C. A., Burris, J. M., Burlew, M. M., Vorarath, P. P., Venkateswarlu, P., Schumpert, J. C., and Mandel, J. H. 2003. An occupational exposure assessment of a perfluorooctanesulfonyl fluoride production site: Biomonitoring. *Am. Ind. Hyg. Assoc.* 64:651–659.

Olsen, G. W., Huang, H. Y., Helzlsouer, K. J., Hansen, K. J., Butenhoff, J. L., and Mandel, J. H. 2005. Historical comparison of perfluorooctanesulfonate, perfluorooctanoate, and other fluorochemicals in human blood. *Environ. Health Perspect.* 113:539–545.

Perkins, R. G. 1992. Investigation of ammonium perfluorooctanoate effect on hormone levels and peroxisomal proliferation in the rat. *Toxicologist* 12:52.

Riker, C. D., Wright, R. K., Matusiak, W., and de Tuscan, B. E. 1987. Massive metoprolol ingestion associated with a fatality–a case report. *J. Foren. Sci.* 32:1447–1452.

Seidel, W. C., Scherer, K. V., Jr., Cline, D., Jr., Olson, A. H., Bonesteel, J. K., Church, D. F., Nuggchalli, S., and Pryor, W. A. 1991. Chemical, physical, and toxicological characterization of fumes produced by heating tetrafluoroethene homopolymer and its copolymers with hexafluoropropene and perfluoro (propyl vinyl ether). *Chem. Res. Toxicol.* 4: 229–236.

Shinoda, K., Hato, M., and Hayashi, T. 1972. The physiochemical properties of aqueous solutions of fluorinated surfactants. *J. Phys. Chem.* 76: 909–914.

Staples, R. E. 1985. Improper interpretation of data concerning teratogenicity: a case report. In *Prevention of physical and mental congenital defects. Part C: Basic and medical science, education, and future strategies*, ed. M. Marois, pp. 161–163. New York: Alan R. Liss.

Staples R. E., Burgess, B. A., and Kerns, W. D. 1984. The embryo-fetal toxicity and teratogenic potential of ammonium perfluorooctanoate (APFO) in the rat. *Fundam. Appl. Toxicol.* 4:429–440.

Thomann R. V., and Mueller, J. A. 1987. *Principles of surface water quality modeling and control.* New York: Harpin Collins.

Tomy, G. T., Budakowski, W., Halldorson, T., Helm, P. A., Stern, G. A., Friesen, K., Pepper, K., Tittlemier, S. A., and Fisk, A. T. 2004. Fluorinated organic compounds in an eastern Arctic marine food web. *Environ. Sci. Technol.* 38:6475–6481.

Ubel, F. A., Sorenson, S. D., and Roach, D. E. 1980. Health status of plant workers exposed to fluorochemicals—A preliminary report. *Am. Ind. Hyg. Assoc. J.* 41:585–589.

U.S. Environmental Protection Agency. 1989. *Risk assessment guidance for Superfund*, vol. I, *Human health evaluation manual (Part A)—Interim final.* EPA/540/1–89/002. December. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1990. *Compilation of air pollutant factors*, vol. 1, *Stationary point and area sources (AP-42)*, 4th ed., U. S. Environmental Protection Agency. Appendix B.2. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1995a. *User's guide for the industrial source complex (ISC3) dispersion models*, vol. 1: *User instructions*. Office of Air Quality Planning and Standards. Emissions. EPA/454/B-95/003a. September. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1995b. *User's guide for the industrial source complex (ISC3) dispersion models*, vol. II: *Description of model algorithms*. Office of Air Quality Planning and Standards. EPA/454/B-95/003b. September. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1995c. *User's guide to the Building Profile Input Program*. Office of Air Quality Planning and Standards. EPA/454/R-93/038. October 1993, rev. February 1995. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1997. *Exposure factors handbook*, vols. I, II, and III. Office of Research and Development. EPA/600/P-95/002F. August. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1998a. *Human health risk assessment protocol for hazardous waste combustion facilities, Peer review draft*, vol. 1. EPA530-D-98–001A. July. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 1998b. *Human health risk assessment protocol for hazardous waste combustion facilities, Peer review draft*, vol. 2. EPA530-D-98–001B. July Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 2001. Pesticide Root Zone Model—Release 3 (PRZM) Version 3.12.1. Center for Exposure Assessment Modeling (CEAM). August. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 2002. Revised draft hazard assessment of perfluorooctanoic acid and its salts. Office of Pollution Prevention and Toxics. Risk Assessment Division. November. EPA Docket OPPT-2003-0012, Document ID number 0011. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 2004. Meteorological data (1961–1990) for Charleston, WV. EPA Center for Exposure Assessment Modeling (CEAM). Accessed at http://www.epa.gov/ceampubl/tools/metdata/index.htm on 2/2/04. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 2005a. Draft risk assessment of the potential human health effects associated with exposure to perfluorooctanoic acid and its salts. Office of Pollution Prevention and Toxics, Risk Assessment Division. January. Washington, DC: U.S. EPA.

U.S. Environmental Protection Agency. 2005b. Draft minutes from the EPA Science Advisory Board Perfluorooctanoic Acid (PFOA) Draft Risk Assessment Review Panel Telephone Conference Meeting, July 6. Washington, DC: U.S. EPA.

Washburn, S. T., Bingman, T. S., Braithwaite, S. K., Buck, R. C., Buxton, L. W., Clewell, H. J., Haroun, L. A., Kester, J. E., Rickard, R. W., and Shipp, A. M. 2005. Exposure assessment and risk characterization for perfluorooctanoate in selected consumer articles. *Environ. Sci. Technol.* 39:3904–3910.

West Virginia Department of Environmental Protection. 2002. Ammonium Perfluorooctanoate (C8) Assessment of Toxicity Team (CATT) Report—Final. August. EPA Docket OPPT-2003–0012. Document ID 0015.

West Virginia Department of Environmental Protection. 2003. Ammonium Perfluorooctanoate (C-8) Groundwater Investigation Steering Team Report. Final C-8 GIST Report. Division of Water and Waste Management. Charleston WV. August. EPA Docket OPPT-2003-0012. Document ID number 0204

Wurbs R. A. 2001. *Reference and users manual for the Water Rights Analysis Package (WRAP)*, 3rd, ed. July. Prepared for Texas National Resources Conservation Commission. Texas Water Resources Institute Technical Report 180. Accessed at http://www.tceq.state.tx.us /assets/public/permitting/watersupply/water_rights/maps/wrap_manual.pdf on 5/28/04.