

# Health Consultation

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3M CHEMOLITE

PERFLUOROCHEMICAL RELEASES AT THE  
3M – COTTAGE GROVE FACILITY

CITY OF COTTAGE GROVE, WASHINGTON COUNTY, MINNESOTA

EPA FACILITY ID: MND006172969

FEBRUARY 18, 2005

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES  
Public Health Service  
Agency for Toxic Substances and Disease Registry  
Division of Health Assessment and Consultation  
Atlanta, Georgia 30333

## **Health Consultation: A Note of Explanation**

An ATSDR health consultation is a verbal or written response from ATSDR to a specific request for information about health risks related to a specific site, a chemical release, or the presence of hazardous material. In order to prevent or mitigate exposures, a consultation may lead to specific actions, such as restricting use of or replacing water supplies; intensifying environmental sampling; restricting site access; or removing the contaminated material.

In addition, consultations may recommend additional public health actions, such as conducting health surveillance activities to evaluate exposure or trends in adverse health outcomes; conducting biological indicators of exposure studies to assess exposure; and providing health education for health care providers and community members. This concludes the health consultation process for this site, unless additional information is obtained by ATSDR which, in the Agency's opinion, indicates a need to revise or append the conclusions previously issued.

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Prepared by:

Minnesota Department of Health  
Under Cooperative Agreement with the  
U.S. Department of Health and Human Services  
Agency for Toxic Substances and Disease Registry

## U.S. Department of Health and Human Services

### FOREWORD

This document summarizes public health concerns at a hazardous waste site in Minnesota. It is based on a formal site evaluation prepared by the Minnesota Department of Health (MDH). For a formal site evaluation, a number of steps are necessary:

- *Evaluating exposure:* MDH scientists begin by reviewing available information about environmental conditions at the site. The first task is to find out how much contamination is present, where it is found on the site, and how people might be exposed to it. Usually, MDH does not collect its own environmental sampling data. Rather, MDH relies on information provided by the Minnesota Pollution Control Agency (MPCA), the U.S. Environmental Protection Agency (EPA), and other government agencies, private businesses, and the general public.
- *Evaluating health effects:* If there is evidence that people are being exposed—or could be exposed—to hazardous substances, MDH scientists will take steps to determine whether that exposure could be harmful to human health. MDH’s report focuses on public health—that is, the health impact on the community as a whole. The report is based on existing scientific information.
- *Developing recommendations:* In the evaluation report, MDH outlines its conclusions regarding any potential health threat posed by a site and offers recommendations for reducing or eliminating human exposure to contaminants. The role of MDH in dealing with hazardous waste sites is primarily advisory. For that reason, the evaluation report will typically recommend actions to be taken by other agencies—including EPA and MPCA. If, however, an immediate health threat exists, MDH will issue a public health advisory to warn people of the danger and will work to resolve the problem.
- *Soliciting community input:* The evaluation process is interactive. MDH starts by soliciting and evaluating information from various government agencies, the individuals or organizations responsible for cleaning up the site, and community members living near the site. Any conclusions about the site are shared with the individuals, groups, and organizations that provided the information. Once an evaluation report has been prepared, MDH seeks feedback from the public. *If you have questions or comments about this report, we encourage you to contact us.*

*Please write to:*           Community Relations Coordinator  
                                  Site Assessment and Consultation Unit  
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## Summary

3M produced perfluorochemicals (PFCs) at their Cottage Grove facility from the late 1940s until 2002 (on a pilot scale or in full production), using an electrofluorochemical process. PFC products were produced, handled, used or packaged at several locations at the site. During production, air emissions of PFCs occurred, and may have extended off the site property. Wastes from the PFC production process were disposed in an on-site pit, and possibly in off-site locations as well. Wastewater treatment plant effluent containing PFCs was discharged to the adjacent Mississippi River for decades, and sludge from the wastewater treatment plant and ponds that contained PFCs were also disposed on site. Fire-fighting foams containing PFCs were also used at a fire-training area on the west side of the site.

The results of limited environmental monitoring to date indicate that groundwater beneath the site is contaminated with perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), in some locations at levels significantly in excess of the MDH Health-Based Values (HBVs) for groundwater. The full extent of the groundwater contamination has not been identified. Much of the contaminated groundwater is contained and collected by an extensive system of production wells, and is processed through the site wastewater treatment plant. The plant has not historically been able to remove the PFCs from the effluent. However, the recent (year) addition of a large granular activated carbon treatment system has effectively eliminated PFC discharges to the Mississippi River. An area of shallow groundwater contamination (in the D1 Area) is not captured by the production wells, and likely discharges to the Mississippi River. The effects of past discharges to the Mississippi River on surface water, sediments, or biota have not been determined. Low levels of PFCs may also be discharged to the river by the adjacent Eagles Point wastewater treatment plant.

Soil data for PFCs were not available for the site. Because of their physical properties, PFCs may move easily with infiltrating water through some soil types, resulting in groundwater contamination. The limited number of studies regarding PFC migration suggest that PFCs are capable of entering groundwater from source areas (such as fire-training sites) and moving long distances. Analysis of water samples for PFOS and PFOA from four private wells located just to the east of the facility did not show the presence of either chemical. However, the wells are completed a significant distance below ground, and are in a side-gradient direction in terms of groundwater flow. The absence of PFCs in these wells does not rule out the possibility of PFC contamination in groundwater on or off of the site as a result of aerial deposition of PFCs and subsequent infiltration into groundwater, a transport mechanism that is thought to have occurred at other PFC facilities in the US.

Workers at the site have been exposed to PFCs through their work activities and through the facility's water supply. 3M has monitored workers at the facility for the presence of PFCs in their blood since the 1970s. Studies of PFC concentrations in blood serum have shown concentrations of PFOA of up to 115 parts per million (ppm). Epidemiological studies of workers at Cottage Grove have shown little apparent impact of PFC exposure on worker mortality. Epidemiological data for these chemicals is lacking for the general population.

Studies of PFCs in blood samples from the general population have shown that PFCs are ubiquitous in human blood, at concentrations much lower than seen in PFC production workers, and are not age-dependent. The estimated half-lives of PFOS and PFOA in humans is on the order of years. The source of exposure to PFCs in the general population is unclear, but is likely through a number of pathways including food, water, use of consumer products, or other environmental pathways. PFCs have also been found in the blood and tissues of various species of wildlife from around the world. The highest concentrations have been observed in bald eagles and mink in the Midwestern U.S. PFOS has been shown to bioconcentrate in fish.

Toxicological research on PFCs is ongoing. Animal exposure to PFCs at high concentrations can have adverse effects on the liver and other organs, and has caused the death of test animals (cynomolgus monkeys) for reasons that are not entirely clear. Exposure to high concentrations of PFOA over long durations has been shown to cause cancer in some test animals, although again the mechanisms are not clear. Developmental effects have also been observed in the offspring of pregnant rats exposed to PFCs.

The potential impacts on public health from perfluorochemical releases from the 3M Cottage Grove facility cannot be fully assessed by MDH at this time, because there are not sufficient environmental data available regarding PFC impacts from the facility in soil, groundwater, surface water, sediments, and biota. For this reason, MDH has recommended that additional investigation take place. Understanding the contribution of individual sources of PFCs to the environment is important, given the lack of information available about how the general population is exposed to PFCs, the long half-life of PFCs in humans, and their potential for toxicity based on animal studies. MDH will continue to work with the MPCA and 3M to investigate and assess PFC releases from the 3M Cottage Grove facility.

## **1. Purpose**

The manufacture and disposal of PFCs at the site has resulted in documented contamination of groundwater at the site. Potential contamination of soil, and of surface water and sediments in the adjacent Mississippi River remains to be investigated. Wastewaters containing PFCs were discharged to the river. PFCs have been detected in multiple on-site monitoring and production wells, and in the water supply system serving the facility. The Minnesota Pollution Control Agency (MPCA) Superfund Program has been overseeing site investigation and cleanup activities; because of other contamination issues the site was originally added to the Permanent List of Priorities, the state Superfund List, in 1985. 3M has been conducting various investigations and response actions under a consent order with the MPCA since that time. The MPCA staff requested that MDH review site documents prepared to date, the results of environmental monitoring conducted at the site, and information available on the toxicity of PFCs and their behavior in the environment in order to develop conclusions and recommendations regarding potential public health impacts from the site.

## **II. Background and History**

The 3M Company (formerly Minnesota Mining and Manufacturing Company) operates a facility on approximately 865 acres in the city of Cottage Grove, Minnesota. The facility has been in operation since 1947. The southeastern portion of the property has been used for a variety of industrial operations such as the manufacture of adhesive products, industrial polymers, and reflective road sign materials, and for research and development of similar products (Barr 1991). The facility also includes a permitted hazardous waste incinerator used to treat wastes generated at this and other 3M facilities. The remainder of the property has been for used recreation and farming, or simply left in a natural state. The site has been known variously as the 3M Cottage Grove Center and the 3M Chemolite Center. The location of the site is shown in Figure 1, and the site layout is shown on a recent aerial photo in Figure 2. Note that 3M uses a numbering system for the various buildings at the facility; the building numbers for the areas discussed in this report are shown in Figure 2.

Perfluorochemicals (PFCs), primarily perfluorooctanoic acid (PFOA) and one of its salts, ammonium perfluorooctanoate (APFO), as well as lesser amounts of related PFC products derived from perfluorooctanesulfonyl fluoride (POSF) have been manufactured at the site since approximately 1947 through an electrochemical fluorination process known as the Simons process (Abe and Nagase, 1982; Gilliland and Mandel 1993; Olsen et al 1998; 3M 1999a; Alexander 2001; OECD 2002). 3M voluntarily ceased production of PFCs at the site in 2002 (ERG 2004; 3M 2000a). Perfluorochemicals are a class of organic chemicals in which fluorine atoms completely replace the hydrogen atoms that are typically attached to organic hydrocarbon molecules (3M 2001a). Because of the very high strength of the carbon-fluorine bond, PFCs are inherently stable, nonreactive, and resistant to degradation (3M 1999a). The PFCs manufactured by 3M at the site were used in a variety of commercial and industrial products by 3M and other companies, including stain repellents (such as Scotchgard<sup>TM</sup>), surfactants, fire retardants and fire-fighting foams, and other chemical products.

The POSF production process through electrochemical fluorination yields about 35%-40% POSF, along with a mixture of byproducts and waste products of variable composition (3M 1999a; 3M 2000b). PFOA and its salts are typically produced in a similar fashion through a batch process (3M 2000c; EPA 2002). Volatile wastes and byproducts were vented to the atmosphere, and some byproducts were re-used in the manufacturing process. Waste tars from the PFC production process were at times disposed in an on-site pit, or later incinerated. Wastewaters containing PFCs from operations at the site have been discharged to the Mississippi River. Although wastewater from the site is routed through an on-site wastewater treatment plant prior to discharge to the river, many PFCs are resistant to treatment because of their chemical stability. One of the byproducts of the production of POSF is perfluorooctane sulfonate (PFOS), which is usually resistant to further degradation in the environment. It can also be produced by the subsequent chemical or enzymatic hydrolysis of POSF. 3M estimated that during POSF production at their Decatur, Alabama production plant, approximately 90% of the wastes generated were in the form of solid wastes (incinerated or disposed in landfills), 9% of the wastes were discharged as wastewater, and 1% in the form of air emissions (3M 2003b).



### Geology/Hydrogeology

The 3M Cottage Grove facility is underlain by fill materials and unconsolidated glacial deposits of sand, gravelly sand, and gravel terrace deposits associated with the adjacent Mississippi River. The thickness of these deposits ranges from approximately 20 feet in the northwest to more than 200 feet at the southern end of the site and in the stream-cut ravines along the eastern and western borders of the property. In the ravines, the upper bedrock formations have been partially or completely removed by erosion.

Beneath the glacial deposits, the first bedrock formation is the Prairie du Chien Formation, composed of dolomite (a magnesium-rich form of limestone). The upper portion of the Prairie du Chien has abundant solution cavities, but the lower portion tends to be more massive. Beneath the site, the bedrock has been uplifted on a series of faults and only the lower, more massive portion of the Prairie du Chien is present. The Prairie du Chien Formation overlies the Jordan Sandstone. Groundwater generally does not flow readily from the more massive, basal Prairie du Chien into the Jordan Sandstone, except where there are fractures or solution cavities. Beneath the Jordan Sandstone, the shaley St. Lawrence formation acts as a “confining layer” that inhibits the downward migration of groundwater to the underlying Franconia Sandstone. The cross-section in Figure 3 illustrates the geology underlying the site.

Two deeply incised glacial river valleys run from north to south along the eastern and western edges of the site. Intermittent streams run through the valleys. Erosion along these stream channels has created steep ravines on the southeast and southwest sides of the facility. A recent study by Mossler (2003) indicates the presence of a series of faults oriented northeast-southwest in this portion of Washington County, with associated minor faults oriented northwest-southeast. A pair of intersecting faults is reportedly present beneath the site (see Figure 4). Analysis of these fault systems by Barr Engineering (Barr, 2003) suggests there may be up to 50 feet of vertical off-set on the faults on the 3M property (see Figure 5). The northwest-southeast trending fault on the site appears to control the location of the stream valley in the southeastern portion of the site, where the ravine turns abruptly southeast before discharging to the Mississippi River.

The surface of the ground water, or water table, ranges from 60 to 100 feet below the ground surface and generally follows the surface topography. The water table is found in the glacial deposits near the river, in the Jordan Sandstone near the river bluffs, and in the Prairie du Chien Formation further from the river. The groundwater in the various formations is interconnected and is essentially one unit. The normal groundwater flow direction (i.e. when not influenced by pumping wells on-site) is towards the Mississippi River. Groundwater modeling by Barr (2003) suggests the faults and fractures in this area may have some influence on the pathways groundwater follows as it migrates toward the river. The model did not specifically evaluate faults on the 3M property, however it would be expected that once groundwater enters the faults, it likely flows parallel to the fault trace.

However, groundwater flow beneath the site is heavily influenced by the pumping of the facility’s high-capacity production wells. Some of these wells reportedly have been in operation since the 1940s. In 2002, 3M reported pumping just over one billion gallons of water from the

production wells on the property (DNR 2003). In previous years, an even larger amount of water was pumped from the aquifers beneath the site.

In fact, most of the groundwater from beneath the majority of the 865-acre site, and especially from the developed portion of the site, appears to be captured by the action of the production wells as shown in Figure 6 (ERG 2004). This figure is from a past groundwater model for the site developed for 3M. The source of the model, and the data and assumptions upon which it was created, were not available at the time this document was written. For example, it is not known whether the model incorporated pumping effects from the numerous nearby residential wells or included geologic features such as the intersecting faults recently identified in this area. These factors may affect the pathway of groundwater flow, but it is likely that most ground water that migrates beneath the site is captured by the facility production wells and only a small portion may discharge to the Mississippi River. One exception appears to be the southeastern-most portion of the site, where Sites D1 and D2 are located (see below). This area does not appear to be within the capture zone of the production wells and the groundwater beneath this area likely discharges to the Mississippi River.

As shown on Figure 7, there are approximately 100 private water supply wells located within one mile of the 3M property boundary. Most private and public wells in the area for which there is geologic information available are completed in the Jordan Sandstone. Because groundwater flows primarily to the south-southeast toward the Mississippi River, it appears that no private or public water supply wells on the north side of the river are located in areas downgradient of contaminant source areas.

#### Superfund Site History

The investigation and remediation activities conducted at the site under the MPCA Superfund program have generally centered around ten waste disposal areas originally identified by the MPCA and 3M (MPCA 1998). These activities, which were conducted under a consent order signed between the MPCA and 3M in 1985, were not focused on PFCs. The MPCA and 3M are currently negotiating an addendum to the existing consent order that will focus on the investigation of PFCs in all media at the site (David Douglas, MPCA, personal communication, 2004). The existence of the waste disposal areas (not all of which were related to PFC manufacture) was a primary reason the site was added to the state Superfund list. The locations of the waste disposal areas are shown in Figure 8. They are as follows:

#### Site D1: Hydrofluoric Acid Neutralization Pit

This site was used to neutralize hydrofluoric acid tars (containing unspecified fluorochemical by-products and hydrofluoric acid) with lime. Neutralization was thought to have been done in a concrete pit or vault, but this has not been confirmed. The tar materials in the pit were never directly sampled and analyzed for PFCs; instead hydrofluoric acid tars from the PFC production process were analyzed to determine if they were a hazardous waste as defined under federal and state regulations. Trace concentrations of metals were identified in the tars, but the neutralized tar material itself was considered to be non-hazardous. Although PFCs were detected in the

groundwater in this area, site D1 has not been fully characterized as to the magnitude or extent of PFC contamination.

Site D2: Sludge Disposal Site

This area was used for the disposal of sediments and sludge dredged from on-site wastewater treatment ponds, and may be up to four acres in size. Laboratory analysis of samples of the sludge material found elevated concentrations of numerous fluorinated compounds (including likely by-products of the PFC production process). Samples of the sludge and soil beneath the sludge showed lower levels of several volatile organic compounds (VOCs). This area has not been characterized with respect to PFCs.

Site D3: Ash Disposal Area

The location of this site was investigated using ground-penetrating radar, and no evidence of waste materials was found.

Site D4: Phenolic Waste Pit

This site was used for the disposal of a small process wastewater stream from Building 7 for a period of three years. The wastewater stream contained phenol and possibly formaldehyde. Part of Building 26 was built on top of this site, limiting infiltration of water through the former pit. While it was never formally investigated, it was believed that some biodegradation of the wastes would have occurred, and the construction of the building over the site would serve as an effective cap preventing human contact or migration of any remaining contaminants.

Site D5: Solids Burn Pit Area

This area is a concrete pit approximately 10 feet deep and 350 feet in diameter. 3M used the pit to burn off-spec products such as glass, tape, rubber, adhesives, rags, paper, wood, fiberglass, oily sludge material, plastics, and resins. The burning was occasionally fueled with waste solvents. The area has since been covered with several feet of fill. Soil borings drilled in this area found the presence of wastes, sludge, ash and cinders. Low levels of VOCs, such as toluene, ethylbenzene, trichloroethylene, and methylene chloride were detected in several soil samples collected from the borings; the area was subsequently given regulatory closure by the MPCA.

Site D6: Active Ash Disposal Area

This area is an inactive, MPCA-permitted waste disposal area for boiler ash and incinerator residues. Due to its permitted status, it has not been investigated under the Superfund program.

Site D7: Pit Burning Area

The history of this area is unclear. Three borings advanced in this area did not encounter waste materials, and soil sample analysis did not detect the presence of heavy metals or VOCs.

Site D8: Waste Disposal Area

This area is located along the bluff leading down to the Mississippi River. A variety of construction debris and other waste materials, including numerous drums, were disposed here by

dumping them over the edge of the bluff. An Interim Remedial Action (IRM) at Site D8 involved the removal of approximately 200 drums and drum carcasses (rotted drums). The drums were disposed in the on-site 3M incinerator. A composite sample of the soil beneath the drums showed no VOCs, but polychlorinated biphenyls (PCBs) were found at elevated levels. A composite sample of the waste materials in the drums contained various VOCs and PCBs. It is not known if samples were analyzed for fluorochemicals. Due to the extreme topography of Site D8, not all of the wastes were removed, and the site was covered and replanted.

#### Boiler Ash Fill Area:

This area is located on the western edge of the facility, in an area that is used for training on-site fire fighting personnel and for testing fire-fighting products (see Figure 8). Boiler ash from a coal-fired boiler, used to produce steam for heat and various industrial processes, was used for fill in this area (Barr 1991). Soil borings drilled in this area showed the boiler ash fill to be approximately one foot in thickness, and the volume was estimated at 850 cubic yards. Some of the boiler ash was exposed at the ground surface. Laboratory analysis of a sample of surface water that had pooled in the area showed elevated levels of metals, including antimony, arsenic, nickel, and vanadium. The ash was determined to be non-hazardous, and the area was covered with clean fill and vegetated.

#### Acrylic Acid Release Area:

In October of 1973, 3M discovered that approximately 17,000 gallons of acrylic acid had been released from an underground storage tank (UST) located adjacent to Building 7 (Barr 1991). The UST that was the source of the release was abandoned in 1986. This area was investigated by 3M, and no further action was required by the MPCA because the acrylic acid was thought to have degraded naturally.

#### Areas of PFC Production and Use

As stated previously, PFC production began (on a pilot scale) at the site around 1947; full-scale commercial PFOA production reportedly began in 1976. POSF-derived chemical production began in the 1960s. The main area for PFC production, storage, and testing was centered around Buildings 7, 15, 16, and 25, which are shown in Figure 2 (ERG 2004). The production of PFCs was phased out at the end of 2002. Wastes from the PFC production process were disposed in Site D1 and possibly Site D8. Wastewaters containing PFCs were routed through the on-site wastewater treatment plant before discharge to the river. Sludge from the wastewater treatment plant was disposed at one time in Site D2. PFC containing fire fighting chemicals were also tested on the west side of the facility in the area of Building 43.

In 2001, the chemical sewer lines running from various chemical production areas of the site to the wastewater treatment plant were upgraded and replaced (ERG 2003). Excavation of the old sewer pipes at the northeast corner of Building 15 (the PFC production plant) revealed that the pipes were corroded and had leaked. The soils in the base and sidewalls of the excavation had a strong phenolic odor. A composite sample of the sidewall soil showed low levels of metals, VOCs (trichloroethene (TCE) and 1,1-dichloroethane) and phenolic compounds. 3M also removed a portion of the interior floor from the northeast corner of Building 15 in response to

concerns over possible damage to the building foundation from releases of hydrofluoric acid. Soil samples were collected from borings placed around the interior trench. Analysis of the soil samples showed very low levels of metals, and one semi-volatile compound (butyl benzyl phthalate). The activities related to the sewer replacement in and around Building 15 indicate that releases to the soil (and possibly groundwater) of chemicals used in the PFC production process did occur while the PFC production plant was in operation. No analyses for PFCs themselves were conducted, however, so it is not clear if PFCs are present in soil and groundwater at Building 15.

In 1991, an air dispersion model was developed for VOC and inorganic emissions at the 3M Cottage Grove facility (Pace 1991). The emission points modeled included two 48-foot stacks at Building 15, the PFC production plant, where hydrogen fluoride emissions occurred. The emission rate used in the model was 0.38 pounds of hydrogen fluoride per hour of operation, with a stack exit velocity of 1,440 feet per minute at ambient (70° F) temperature. The horizontal extent and the estimated concentrations of hydrogen fluoride (both the 1986 annual average and the second highest 24-hour average in micrograms per cubic meter) predicted by the model are shown in Figures 9a and 9b. The results of the air dispersion model indicate that hydrogen fluoride emissions extended off-site in 1986.

The PFC production process would also have resulted in the release of some PFCs to the atmosphere, as mentioned previously. 3M estimated that 1,950 pounds of PFOA compounds were released to the air from vent stacks at the Cottage Grove facility in 1997, and that the releases occurred between 100 to 200 days per year (3M 2000c). Presumably, at least some of the PFOA compound releases to the air were from Building 15, or nearby buildings where PFCs were produced, handled, or used. Fugitive emissions of PFOA (both vapor and particulate) were also likely from the various operations, such as drum loading, reactor sampling, and drying operations (3M 2000c). The physical properties of PFOA and other PFCs are different from hydrogen fluoride, and their behavior once released to the air are likely to differ as a result. However, the air dispersion model results for hydrogen fluoride emissions shown in Figures 9a and 9b suggest that PFOA emissions (both particulate and vapor phase) from the Building 15 area may also have extended off the site property. Deposition of PFOA to the soil from these emissions may also have occurred.

#### On-Site Groundwater Monitoring and Use

Since investigation activities at the site began, at least 21 permanent monitoring wells have been installed at and around the site to evaluate groundwater quality (Figure 10). The monitoring well identifiers, unique well numbers, depth, and general locations are as follows:

<b>Well ID</b>	<b>Unique Well Number</b>	<b>Depth (feet)</b>	<b>Monitoring Well General Location</b>
MW-1	233567	200	Northern site boundary
MW-2	233568	192	East side of site
MW-3	233569	210	Center of site

MW-4	233570	200	South-central area of site
MW-5	233571	210	Northwest corner of site
MW-6	233572	219	West-central area of site
MW-7	233573	146	Northeast corner of site
MW-8	233574	173	Southwest area of site
MW-9	233575	104	West-central area of site
MW-10	233554	237	Southeast area of site
MW-11	233950	200	Southeast area of site
MW-12	233951	126	Southern edge of site
MW-13	233952	126	Southeast area of site, near ponds
MW-14	421705	60	D8 Area, southern edge of site, near PW-6
MW-15	431237	186	Southern edge of site
MW-16	431238	140	Southern edge of site
MW-17	570322	112	West-central area of site
MW-18	570323	91	West-central area of site
MW-19	612713	62	West-central area of site
MW-101	680685	100	D1 Area, southeast corner of site
MW-102	680686	96	D1 Area, southeast corner of site

Since the facility opened in 1947, 3M has installed eight production wells to serve the facility's potable water supply and to provide water for various industrial operations (Figure 10). They are as follows:

<b>Well ID</b>	<b>Unique Well Number</b>	<b>Date Completed</b>	<b>Depth (feet)</b>	<b>Casing Diameter (inches)</b>
PW-1	231867	1947	205	20
PW-2	231868	1948	202	20
PW-3	231869	1956	224	16
PW-4	231870	1958	275	16
PW-5	231871	c. 1960s	113	24
PW-6	229117	1970	143	24
PW-7	233576	c. 1980s	200	Unk.
PW-8	424131	1986	208	8

Four of the eight production wells (PW-2 to PW-5) serve the potable water distribution system, while two wells are used on a periodic basis for fire suppression (PW-1) and to supply non-contact cooling water to the 3M waste incinerator (PW-6; ERG 2004). Of the remaining two wells, PW-7 is used occasionally at the 3M on-site trap range and PW-8 supplies the guard shack.

In the past, low levels of VOCs including TCE, 1,1,2-trichloroethane, 1,1-dichloroethane, ethylbenzene, toluene, and methylene chloride have been detected in various monitoring and production wells at the southern end of the facility, specifically MW-4, MW-14, PW-5, and PW-

6, which are located in the vicinity of D8. Levels of these VOCs have only occasionally exceeded health-based drinking water criteria in the individual monitoring wells, and the distribution of the contaminants suggests that the sources of the VOC contamination are localized and not extensive (ERG 2001a, ERG 2001b). The concentrations of individual VOCs in PW-5, one of the wells that are used for the drinking water supply, have recently been less than approximately one microgram per liter ( $\mu\text{g/L}$ ). Such concentrations do not exceed applicable regulatory or health-based standards for a water supply system. The system is regulated and monitored by MDH as a public water supply. Exposure to VOCs in groundwater at the site does not appear to be a human health concern at this time.

#### PFC Monitoring at the Site

3M has been monitoring groundwater, production wells, the water distribution system, and wastewater treatment plant effluent for PFCs (primarily PFOS and PFOA) for a number of years. Data from monitoring wells, production wells, and the water distribution system are shown in Table 1, while effluent data from the wastewater treatment plant are presented in Table 2. The majority of the data is for PFOA alone, because it has been the focus of investigation activities at the site being conducted by 3M under a voluntary agreement with EPA (3M 2001b). Some samples were analyzed for PFOS, PFOA, and the 4-, 6-, and 7-carbon perfluorosulfonates and other acids. The 4-, 5-, and 6-carbon PFCs were likely found in the groundwater because they present in the PFC wastes that were disposed in several areas of the site. Much of the data were collected only in 2001, so information on long-term trends in the PFC concentrations in groundwater is not yet available.

The well monitoring results indicate that PFOS and PFOA are present in groundwater at the site in the D1 area (MW-101 and MW-102) and the D8 area (MW-14, PW-5 and PW-6). Levels of PFOS and/or PFOA exceed the MDH Health Based Values (HBVs) for PFOS and PFOA in these wells, sometimes by a factor of 100 or more. The HBVs represent a level of a contaminant in drinking water that MDH considers to be safe for human consumption over a lifetime. The HBVs were developed by MDH based on review of available toxicological information as of November 2002; neither the values themselves nor the toxicological inputs were derived by the EPA. The HBV for PFOS is  $1 \mu\text{g/L}$ ; the HBV for PFOA is  $7 \mu\text{g/L}$ . The derivation of the MDH HBVs for these two compounds and their toxicological basis can be found in Appendix 1. MDH has not developed HBVs for the other perfluorosulfonates and acids, mainly because of a lack of available toxicological information.

Detectable levels of PFCs (in some cases slightly above the HBVs) were also found in: MW-4 at the southern end of the facility on top of the bluff; PW-2 at the northern end of the facility; PW-4 northwest of the main facility; and in the water distribution system itself. The sample from the distribution system was collected from the cafeteria in Building 116. A very low level of PFOA (less than one  $\mu\text{g/L}$ ) was also found in MW-7 northeast (and upgradient hydrogeologically) from the main facility. Note that PFC data are not available for all of the monitoring and production wells at the site. 3M has proposed to collect a coordinated round of groundwater sampling from all of the available monitoring and production wells at the site. This would be very helpful in characterizing PFC contamination in groundwater across the facility. The available data

indicate, however, that groundwater in several areas of the site has been affected by past PFC production or disposal practices. This in turn is affecting the water wells serving the facility.

A groundwater model found in the site files suggests that much of the contaminated groundwater is likely captured by the pumping action of the production wells at the site, as shown in Figure 6, with the exception of the D1 and D2 areas, located just southeast of the area shown in the figure. The PFCs detected in the water distribution system lends support to this conclusion, although it is not possible to evaluate the validity of this model because the underlying data and assumptions used in its construction were not available at the time this document was written. Contaminated groundwater in the D1 Area most likely discharges to the Mississippi River, either directly or possibly via the intermittent stream in the ravine immediately north of the D1 Area.

The facility's water distribution system is used for potable water, and for various industrial processes. Bottled water has been provided to employees for drinking water for some time, however, and a GAC treatment system has been installed in the main cafeteria in building 116 to treat water used in food preparation and cleanup. Wastewater from these uses is collected in various sewer systems (see below) for treatment in the on-site wastewater treatment plant. The wastewater therefore contains PFCs from the groundwater contamination, and any PFCs picked up during the use of the water for production or other purposes throughout the plant.

Under its federal National Pollutant Discharge Elimination System (NPDES) permit (MN000149) the effluent from the wastewater treatment plant is monitored before discharge to the Mississippi River. Since 2000, 3M has regularly collected 24-hour composite samples of the treated effluent for analysis for PFOA. Limited data is available back to 1996 (see Table 2). Levels of PFOA have generally declined since 1996, with an overall high of 1,991µg/L detected in early 2000. With the phase out of PFOA production in late 2002, effluent concentrations of PFOA and PFOS should continue to drop. 3M also installed a large granular activated carbon (GAC) treatment plant at the site to remove organic contaminants (including PFCs) from the wastewater treatment plant effluent before discharge to the Mississippi River. It should also be noted that the effluent from a regional wastewater treatment plant (the Eagles Point plant, operated by the Metropolitan Council) located essentially within the grounds of the 3M Cottage Grove facility (see Figure 2) may also contain low levels of PFCs as has been found in limited studies at other wastewater treatment plants in the U.S. (see page 23).

For most chemicals, aerial deposition of a contaminant is not typically a pathway for groundwater contamination. However, given the physical properties and environmental behavior of PFOA and other PFCs it is possible. Air emissions of PFOA and/or other PFCs at production facilities in West Virginia and Alabama are suspected to have contributed to PFOA/PFC contamination of soil and groundwater from those facilities, in addition to other releases (West Virginia Dept. of Environment Protection 2003; Daikin 2004).

Because of the potential for past air emissions (and deposition) of PFOA to have extended off site, in December 2003 MDH staff collected water samples from four private residential wells located just east of the 3M Cottage Grove Facility for analysis for PFOA and PFOS by the MDH



laboratory. The locations of the four residential wells are shown in Figure 11, along with the approximate extent of air emissions of hydrofluoric acid predicted by the 1991 air model. All four wells are relatively deep (approximately 220 feet below grade). The results of the PFOA/PFOS analysis showed no detections of PFOA or PFOS above the laboratory detection limits of 1.0 µg/L and 0.5 µg/L, respectively, in any of the four wells. However, the absence of detectable PFOA or PFOS in the four deep wells sampled does not resolve the question of whether surface deposition and subsequent infiltration has occurred. The MDH laboratory does not have the ability to analyze for the 4-, 5-, or 6- carbon PFCs at this time.

#### Site Visit

On October 14, 2003 MDH staff visited the 3M Cottage Grove facility, along with representatives of the MPCA Superfund program. MPCA staff arranged the site visit for the purpose of becoming acquainted with the facility layout and areas of the facility where perfluorochemicals (PFCs) were manufactured and used, and where PFC wastes were disposed. 3M facility and corporate staff conducted the site visit, along with their lead environmental consultant for the facility (ERG).

The 865-acre site is located just south of the intersection of US Highway 61 and Washington County Road 19 in Cottage Grove, Minnesota, on the Mississippi River. Because the site is a chemical plant, it is a secure facility with a full perimeter fence and controlled entry. The facility is used for chemical manufacture, testing, product development, and for the incineration of hazardous chemical wastes. To the east of the facility are a golf course and residential development (River Oaks). To the south are the Burlington Northern Santa Fe Railroad main line and the Mississippi River. To the west are a regional wastewater treatment plant (the Eagles Point plant, operated by the Metropolitan Council), agricultural and rural residential land. To the north are US 61, scattered homes, and a regional park.

The site visit focused on the following areas: the fire training area, production wells PW-5 and PW-6, the PFC production area, the D1 land disposal area, the wastewater treatment plant outfall at the Mississippi River, and the wastewater treatment plant area.

#### Fire Training Area:

The fire training area is located below the main facility, near Building 43 (Figure 2). Facility employees are trained here in fire fighting through various mock situations, such as a chemical spill, a fire in a laboratory vent hood, or a leaking pipeline. Part of this area is underlain by a gravel-covered concrete pad with drains leading to a lined holding pond. The area appears to have been upgraded relatively recently. 3M staff indicated that the area was used for facility staff training purposes and to test fire suppressants containing PFCs (ERG 2004).

#### Production Wells PW-5 and PW-6:

These two production wells are located on the southern edge of the facility, close to the Mississippi River (see Figure 10). PW-5 feeds into the facility water distribution system, while PW-6 is only used for non-potable cooling water for the incinerator. Both PW-5 and PW-6 have detectable levels of PFCs, and a monitoring well located adjacent to PW-6 (MW-14) has

elevated levels of PFCs. A disposal site (D8) was located on the hillside just above PW-6 and MW-14. Apparently, construction debris and drums of waste materials were removed from this location during the mid-1980s. The wastes had reportedly been dumped over the edge of the hillside and buried sometime in the past. The main wastes identified at D8 were volatile organic compounds (VOCs); it is not known if PFC wastes were present as well. 3M has agreed to complete additional PFC monitoring in the area of PW-5 and PW-6.

#### PFC Production Area:

PFCs were produced in Building 15 for many years; the plant has now been shut down and is to be decommissioned. PFCs were used in the production of other compounds in Buildings 7, 16, and 25. These buildings are shown in Figure 2. Wastes from these processes were discharged to buried sewer lines that ran to the on-site wastewater treatment plant. These buried sewer lines have since been replaced with an upgraded system that is contained within a concrete trench open to the ground surface. There are numerous stacks and vents in the PFC production and use areas, and 3M staff confirmed that there were air emissions of chemicals (permitted by the MPCA) from these stacks.

#### D1 Area:

This area was used in the past for the disposal of PFC production wastes. It is located on the top of a narrow peninsula of land that extends southeast from the rest of the facility (Figure 8). From the top of the peninsula, the land drops off sharply to the south towards the railroad and Mississippi River. To the north the land drops towards a ravine, through which the wastewater treatment plant outfall stream runs. Another disposal site, D2, is located just west of D1. Two monitoring wells (MW-101 and MW-102) flank the D1 disposal site. These wells have shown the highest levels of PFOS so far detected at the site, and are located slightly downhill from the D1 area. According to 3M's consultant, no seeps or springs have been observed around the base of the peninsula or in the stream.

#### Wastewater Treatment Plant Outfall:

The output of the wastewater treatment plant is piped to an intermittent stream that runs through a ravine along the eastern edge of the facility. The output enters the stream through a pipe after exiting the smallest (and last) treatment pond just west of the D2 and D1 land disposal areas. There is a permanent effluent monitoring point there as well. Stormwater is also discharged at this point when necessary. The stream enters a small pond just north of the railroad tracks, passes under the railroad track bridge, and enters the Mississippi River, as shown in Figure 2. The stream is very clear, and vegetation and small fish could be readily observed in it.

#### Wastewater Treatment Plant:

The current wastewater treatment plant consists of various settling basins, biologic treatment vessels, and filters to handle four of the five waste streams at the facility (sanitary, organic wastes, inorganic wastes, and the incinerator process wastewater). Stormwater is not usually routed through the treatment plant, but can be in the event of a spill or accidental release. At the end of the treatment process the wastewater is piped into a series of holding ponds before discharge to the river, as described above.

3M has constructed a large granular activated carbon (GAC) treatment plant to augment its wastewater treatment operations and remove PFCs from the wastewater treatment plant effluent. The efficiency of the GAC for removing the PFCs from the waste stream has so far been in excess of 99%. The GAC treatment plant consists of 18 large GAC treatment vessels that are the final treatment step for the combined waste streams from the sanitary sewer, organic wastes, and inorganic wastes. A subset of the treatment vessels will be used specifically for treating the incinerator wastewater stream. The existing treatment ponds are to be abandoned and filled, with the exception of the largest one, which has been refurbished with a synthetic liner and will be used as a backup storage pond when needed.

#### Off-site Water Use and Sampling

As noted in the “Geology/Hydrology” section, there are approximately 100 private and commercial wells located within one mile of the 3M property boundary. In addition, the well field for the City of Cottage Grove is located approximately 1.5 miles northwest of the 3M property, and the well field for the City of Hastings is located approximately the same distance to the southeast, across the Mississippi River. Water samples from four residential wells located immediately east of the site were analyzed for PFOS and PFOA by the MDH lab (see Figure 11). Neither compound was detected in the sampled wells.

#### Public Comments

On June 24, 2004 a draft version of this document was released for public comment. Comments were received from EPA, MPCA, Washington County, the City of Cottage Grove, and 3M. The comments are attached as Appendix 2.

EPA provided several general comments, as well as suggestions as to specific language to describe EPA’s ongoing work with the perfluorochemical industry to investigate the sources, fate, and transport of PFCs in the environment. EPA did not review the document for toxicological accuracy, in part because a draft risk assessment for PFOA is not due until late 2004. The specific comments and suggestions made by EPA were incorporated into the document. The MPCA comments were mostly general in nature; MDH staff have addressed them by clarifying the text in several places described in the comments, including the description of past investigations at the site and the status of the consent order between the MPCA and 3M.

Washington County’s comments generally were in the form of recommendations to 3M for further investigation or disclosure of information relative to releases of PFCs and VOCs at the site. As the county’s comments appeared to reinforce MDH’s own recommendations and statements made in the text of the document, no further changes were made to the document itself as a result. The City of Cottage Grove comment letter simply expressed support for the recommendations made in the draft Health Consultation, including the need for continued monitoring.

3M submitted extensive comments on each section of the document. General comments from 3M on the conclusions and recommendations did not result in significant changes by MDH.

Specific comments regarding the text of the document were helpful in that they clarified certain historical facts regarding PFC production and disposal at the site; changes were made to reflect these comments. 3M provided missing information relative to certain monitoring and production wells at the site. 3M also provided several useful toxicological references that were not available at the time the document was first written, and these references have been included. Specific comments on toxicological issues were addressed with the major exception of the comments on the potential for developmental effects from exposure to PFOS (see 3M comments, page 12 in Appendix 2). This comment was apparently in response to MDH's statement on page 20 of this document that MDH may consider developmental effects when reviewing the current HBV for PFOS. Because MDH is not currently reviewing the PFOS HBV, this comment was not addressed.

### III. Discussion

Perfluorochemicals (PFCs), primarily perfluorooctanoic acid (PFOA;  $C_8F_{15}O_2H$ ) and one of its salts, ammonium perfluorooctanoate (APFO;  $C_8F_{15}O_2NH_4$ ), as well as lesser amounts of other PFCs such as perfluorooctanesulfonyl fluoride (POSF;  $C_8F_{17}SO_2F$ ) have been manufactured or used at the site since 1947. One of the byproducts of the production of POSF is perfluorooctane sulfonate (PFOS;  $C_8F_{17}SO_3^-$ ), which can also be produced by the subsequent chemical or enzymatic hydrolysis of POSF. These chemicals are used by 3M and other companies around the world in the production of stain repellents, lubricants, fire retardants and suppressants, and pesticides, and as industrial surfactants and emulsifiers.

The chemical structures of PFOA and PFOS make them extremely resistant to breakdown. As a result, they are persistent once released to the environment. On the basis of its physical properties, PFOS is essentially non-volatile, and would not be expected to evaporate from water (OECD 2002). If discharged to air (such as during production of POSF) it will rapidly deposit to soil and due to its low sorption tendency, once in soil it tends to remain there with the major loss due to run-off to surface water (DMER 1999). Infiltration of water could also carry it into the subsurface or into groundwater, however. In soil-water mixtures, PFOS has a strong tendency to remain in water due to its solubility (typically 80% in water and 20% in soil). PFOS does not easily adsorb to sediments, and is expected to be mobile in water at equilibrium (3M 2003b).

PFOA is slightly more volatile than PFOS, although it still has a very low volatility and vapor pressure (EPA 2002). PFOA is very soluble and completely disassociates in water; in aqueous solution it may loosely collect at the air/water interface and partition between them (3M 2003a).

In limited studies, PFOA has shown a high mobility in some soil types (EPA 2002). In an attempt to estimate the potential for long-range transport of PFOA released to the air, Franklin (2002; unpublished report on EPA's PFOA web site) stated that PFOA emitted to the air is likely to undergo dry or wet deposition within a few days, but could under certain conditions travel a distance of up to 800 kilometers from the source.

In a study of PFCs in groundwater at a former military fire-training site in Michigan, Moody et

al (2003) found PFOS concentrations up to 120 µg/L and PFOA as high as 105 µg/L near the original concrete pad used for the training. Concentrations of PFOS and PFOA in excess of the MDH HBVs were found in groundwater as far away as 500 meters from the pad. The facility was used for fire-training from 1952 until the early 1990s, and fire fighting foams containing PFCs were routinely used in training exercises. The results of the study indicate that PFCs in aqueous solution are easily capable of migrating into groundwater. They can travel extended distances with little or no retardation of the contaminants through adsorption to the aquifer substrate, and can persist for years after they were used at the ground surface. The 3M site contains a similar fire-training area where fire fighting foams containing PFCs were reported to have been used (ERG 2004). While the site studied by Moody et. al. has some similarities to the 3M fire-training site, actual site characteristics will determine the potential for PFCs to enter the groundwater and migrate away from the site. This has not yet been evaluated at the 3M fire-training site.

Because of the recent widespread interest in PFC compounds such as PFOS and PFOA, a great deal of toxicological, epidemiological, and environmental monitoring information has been published in government and industry reports and in peer-reviewed literature. Much of this research has been funded or conducted by 3M. Most recently, an analysis of the potential risk to the general population from exposure PFOA was published by Butenhoff et al (2004), and 3M has produced an updated environmental and health assessment of PFOS (3M 2003b). The following represents a brief summary of available information.

#### Summary of Toxicological Information

Animal studies have shown that PFOA and APFO (its ammonium salt) are easily absorbed through ingestion, inhalation, and dermal contact (EPA 2002; Kennedy 1985; Kennedy et al 1986; Kudo and Kawashima 2003). PFOS is also well absorbed orally, but is not absorbed well through inhalation or dermal contact (OECD 2002). In the past, workers at the 3M Cottage Grove facility were occupationally exposed to PFOA, and it is believed that dermal absorption of PFOA was significant (EPA 2002). Once absorbed, APFO disassociates to the PFOA anion. Both PFOA and PFOS are distributed and found mainly in the blood serum, liver and kidney (EPA 2002; Kudo and Kawashima 2003; OECD 2002). PFOA and PFOS are not metabolized, and are excreted in the urine and feces at different rates in various test animal species and humans. There also appear to be significant gender differences in excretion rates for PFOA in rats, but these differences have not generally been observed in higher animals and humans. The estimated half-life of PFOA in animals ranges from four hours in female rats and nine days in male rats to hundreds of hours in dogs (Kudo and Kawahima 2003). Half-lives of PFOS have been estimated at over 100 days in rats in a single-dose study, and 200 days in a sub-chronic dosing study in cynomolgus monkeys (OECD 2002). In a limited study of retired 3M workers, the mean serum half-life of PFOA was estimated to be 4.37 years, and the mean half-life of PFOS was estimated at 8.67 years (EPA 2002; OECD 2002).

Exposure to high levels of PFOA and PFOS is acutely toxic in test animals (Kudo and Kawashima 2003; OECD 2002). Chronic or sub-chronic exposure to lower doses of PFOA in rats typically results in reductions in body weight and weight gain, and in liver effects such as an

increase in liver weight and alterations in lipid metabolism (Kudo and Kawashima 2003). The liver appears to be the primary target organ of PFOA toxicity in rats, although effects on the kidneys, pancreas, testes, and ovaries have also been observed (EPA 2002). The effects on the liver may be more severe in aged rats (Badr and Birnbaum, 2004). Exposure to PFOA in rats results in a phenomenon in the liver known as peroxisome proliferation. This phenomenon is limited to rats and similar test animals, and is not observed in primates (or humans). Some of the adverse liver effects observed in rats (such as an increase in liver weight) that are in part attributed to peroxisome proliferation may not be seen in higher animals. Adverse liver effects in higher animals are likely the result of a different mode of action.

A 90-day study of relatively high-dose oral PFOA exposure in rhesus monkeys resulted in adverse effects on the adrenal glands, bone marrow, spleen, lymphatic system, and death in some animals (EPA 2002). A six-month study of oral PFOA exposure in male cynomolgus monkeys exposed to different doses of APFO showed toxicity (primarily to the liver) at even the lowest doses studied. Extreme toxicity was observed at the highest exposure level, prompting a modification of the dosage to prevent the death of the test animals (Butenhoff et al 2002). Even with the dosage adjustment, one test animal at the highest dose became extremely ill and had to be sacrificed. A similar condition developed in one of the lowest dose group animals. The toxicological mechanism for the apparent extreme adverse reaction in these two animals is unknown. A steady-state concentration of PFOA in the serum was reached within four to six weeks after dosing began; mean serum PFOA concentrations ranged from 77 parts per million (ppm) in the low dose group to 158 ppm in the high dose group (Butenhoff et al 2002). This study did demonstrate that the dose-response characteristics of APFO in this species of monkey are very steep – indicating that a small increase in dose can be associated with a significant increase in the number or severity of adverse effects.

Exposure studies of PFOS in rats have also demonstrated effects on the liver, weight loss, and death, with a steep dose-response curve for mortality observed (OECD 2002). In studies of PFOS exposure in rhesus monkeys, adverse effects included anorexia, convulsions, a marked decrease in serum cholesterol, and adrenal effects. Similar effects were observed in studies of cynomolgus monkeys. The adverse effects were no longer observed after a 52-week recovery period, and in fact some recovery was noted much earlier.

Some long-term animal studies suggest that exposure to PFOA (and possibly PFOS) could increase the risk of cancer of the liver, pancreas, and testes (Kudo and Kawashima 2003, EPA 2002, OECD 2002). The mechanism of potential carcinogenesis is unclear, but evidence suggests that the cancers are the result of tumor promotion (via oxidative stress, cell death, or hormone-mediated mechanisms) and not from direct damage to the genetic material within cells (genotoxicity). The tumors observed in rats may be a result of peroxisome proliferation, and may not be seen in higher animals or be of relevance in humans (Kennedy et al 2004).

Various reproductive studies of rats followed for two generations showed postnatal deaths and various developmental effects in offspring of female rats exposed to relatively low doses of PFOS and APFO (EPA 2002, OECD 2002). These studies demonstrate that exposure to

APFO/PFOA and PFOS can result in adverse effects on the offspring of rats exposed while pregnant.

At the request of the MPCA, in November 2002 MDH developed Health-Based Values (HBVs) for drinking water for PFOS and PFOA of 1 ppb and 7 ppb, respectively, based on existing toxicological information (liver toxicity; see Appendix 1). The HBVs represent a level of a contaminant in drinking water that MDH considers to be safe for human consumption over a lifetime. The HBV documentation in Appendix 1 states that reproductive and developmental effects occur at levels higher than doses associated with liver toxicity. However, recent studies on PFOS (Thibodeaux et al 2003; Lau et al 2003) suggest that developmental effects may also be of concern. These recent studies may lead MDH to examine developmental toxicity as a possible basis for the PFOS HBV, which could result in a different HBV for PFOS. MDH is awaiting further information or guidance from EPA before initiating a review of the HBVs for PFOS and PFOA. Note that MDH is also in the process of revising all HRLs to more directly account for childhood exposures, and this change could result in the lowering of all HBVs by a factor of three or four (see Appendix 1).

Also at the request of the MPCA, MDH staff developed interim Soil Reference Values (SRVs) for both PFOS and PFOA of 40 ppm and 200 ppm, respectively. The SRVs are soil evaluation criteria for protection of people from direct contact with contaminated soil through ingestion, skin contact, and inhalation of vapors and/or contaminated soil particles. Soil concentrations at or below the SRV are considered to be safe.

#### Summary of Epidemiological Data

The 3M Company has conducted a medical monitoring program of employees engaged in the manufacture of perfluorochemicals since at least the 1970s. The company initially measured total serum organic fluorine. In the mid-1990s, the company began measuring serum PFOA and PFOS when such analyses became available (Olsen et al 1998; Olsen et al 2003a; Olsen et al 2003b). A study of 3M employees at its Decatur, Alabama PFC manufacturing facilities showed a mean serum PFOS concentration of 1.32 parts per million (range 0.06 to 10.06 ppm) and a mean serum PFOA concentration of 1.78 ppm (range 0.04 to 12.70 ppm) in 263 employees. The mean concentrations in employees at 3M's Antwerp, Belgium facility were approximately 50% less (Olsen et al 2003b). There was no association between serum PFOS and PFOA concentrations and decreased serum cholesterol (or other common biological parameters) observed in this group of employees such as has been observed in animal studies. Exposure to PFOS and PFOA has been shown in test animals (including primates) to interfere with cholesterol metabolism and alter (usually lower) serum lipid and cholesterol concentrations.

A separate study of reproductive hormones in male 3M employees occupationally exposed to PFOA at the Cottage Grove facility showed no significant linear association between serum PFOA concentration and the measured hormones, although mean concentrations of one hormone (estradiol) were 10% higher in those employees (five in all) with a serum PFOA concentration above 30 ppm (Olsen et al 1998). This association was confounded by a high body mass index in the five employees, however. Serum PFOA concentrations in this study ranged from 0 to 115

ppm for the Cottage Grove workers. The higher serum PFOA concentrations observed in some workers in this study suggests that occupational exposures to PFOA at the Cottage Grove facility were higher than at the Decatur and Antwerp facilities, and/or that the exposures were of a longer duration. No association between serum estradiol and serum PFOA levels was observed for workers in 3Ms Decatur and Antwerp facilities.

Mortality of employees at the Cottage Grove facility has also been the subject of several epidemiological studies (Gilliland and Mandel 1993; Alexander 2001). In the earlier study, Gilliland and Mandel (1993) reported that the overall standardized mortality ratios (SMR) for 2,788 male and 749 female employees who worked at the facility for at least six months between 1947 and 1983 were 0.77 and 0.75, respectively (a value significantly below the expected rates). The SMR represents the ratio of the observed deaths in a study population over the expected deaths in a study population based on death rates in a non-exposed population of similar characteristics. This phenomenon, where the overall SMR is significantly below the expected rate for a similar, non-exposed population, is sometimes referred to as the “healthy-worker effect” in occupational studies. The study findings did show that male employees who worked in the PFOA production area for greater than 10 years had a 3.3-fold increase in mortality from prostate cancer. However, the low number of prostate cancers (four) in this group makes the findings tentative, and a later study by the same lead author (Olsen et al 1998) reported that only one of the four cases of prostate cancer occurred in a worker directly engaged in PFOA production. A separate study of workers at the 3M Decatur, Alabama facility who were primarily exposed to POSF/PFOS also showed an overall low SMR for all causes of death, but a higher than average risk of death from bladder cancer. This was due to three cases observed, again meaning that the findings may not be repeatable (Alexander et al 2003). There is no current toxicological evidence that suggests that the bladder is a critical target organ of PFOS (3M 2003b).

In a later study at Cottage Grove, Alexander (2001) looked at the mortality of 3,992 workers employed at the facility for at least one year prior to the end of 1997. The cohort was divided into three exposure groups based on their work history: definite PFOA exposure, probable PFOA exposure, and no PFOA exposure. It should be noted that, given the past exposure by workers to PFC contamination in the facility water supply, there may have been some exposure to PFOA even in the “no PFOA exposure” group. The results of this study showed that the overall SMR for all causes of death (0.85) for the workers was again well below the expected rate. No increase in prostate cancer was observed in this later study, but deaths from cerebrovascular disease were elevated in the definite PFOA exposure group. Once again, the low number of cases of cerebrovascular disease in this group (five) makes the findings tentative and difficult to interpret. Taken together, the results of these studies (three different findings of slightly elevated disease -different in each study - based on small numbers of cases) do not represent epidemiological findings of significance.

PFOS, PFOA, and other perfluorochemicals have been detected in human blood serum from adults and children in the general population at levels from 1/100 to 1/1000 of those seen in workers (Olsen et al 2003c, Olsen et al 2003d, 3M 2001c). In a study of 645 adult donor serum



samples from six Red Cross donation centers across the U.S., PFOS concentrations ranged from <4.1 ppb (the limit of detection) to 1,656 ppb. No substantial differences in PFOS concentrations in serum were observed with age of the donor. Serum PFOA concentrations ranged from <1.9 ppb to 52.3 ppb. A preliminary study of sera from 599 children ages 2-12 years from 23 different states showed PFOS concentrations ranging from 6.7 to 515 ppb, and PFOA concentrations ranging from <1.92 to 56.1 ppb. A study of elderly people in the Seattle area showed similar PFOS and PFOA serum concentrations compared to the rest of the population that has been studied so far (Olsen et al 2004). The source(s) of exposure to PFOS, PFOA, and other perfluorochemicals in the general population is unclear, but could include consumer products, environmental exposures, or other occupational exposures (3M 1999c). Analysis of blood samples collected in the early 1950s from army recruits show no PFOS (3M 1999c). Both PFOS and PFOA have been detected in samples of dust collected from household vacuum cleaner bags in Japan, indicating the indoor environment is a potential source of exposure (Moriwaki et al 2003).

Based on animal studies and available human epidemiological data for PFOA concentrations in blood serum, in a preliminary report in 2003 the EPA calculated a margin of exposure (MOE) range for PFOA for women of childbearing age and children of between 66 and 9,125 (EPA 2003). The MOE describes the relative difference between current measured human PFOA serum levels and serum levels determined in animal studies to be associated with adverse developmental effects. There are numerous uncertainties in such calculations as a result of intra- and interspecies differences, dose metrics used, and the choice of the animal model; EPA advises that they must be interpreted cautiously. The preliminary EPA report also may have seriously underestimated the serum PFOA concentrations in the rat study used to derive the MOE, making the low end of the MOE range too low. In a recent evaluation of the risk of PFOA exposure to the general population, Butenhoff et al (2004) calculated a MOE of between 1600 and 8900 for various toxicological endpoints, with a mean of 2100 based on the mean serum PFOA concentration in general population data. For PFOS, 3M has calculated a MOE range for non-occupationally exposed people of 310 to 1550 based on PFOS serum levels measured in the human population (3M 2003b).

#### Summary of Environmental Data

PFOS has been detected in the plasma and tissues of wildlife from across the globe, including seals, otters, dolphins, aquatic birds, bald eagles, polar bears, freshwater and saltwater fish, and reptiles (Giesy and Kannan 2001). The results of this study show that PFOS is widely distributed in the global environment. Levels of PFOS were higher in fish-eating and predatory animals than in their typical prey, indicating that PFOS may bioaccumulate as it moves up the food chain. Bald eagles from the Midwestern U.S. showed the highest levels of PFOS in plasma (up to 2,570 nanograms per milliliter), and mink from the Midwestern U.S. showed the highest levels in tissue (in liver; up to 3,680 nanograms per gram). Concentrations of other PFCs in wildlife samples, such as PFOA, are typically approximately ten times lower and are much less widely distributed (Giesy et al 2001).

Broader studies have found detectable levels of PFOS in surface waters, fish and bird blood and

livers, and human blood collected in Japan, with the highest levels observed in the waters and fish from heavily industrialized Tokyo Bay (Taniyasu et al 2003). A decreasing gradient of PFOS levels in aquatic invertebrates and two species of fish in an estuary and the North Sea was observed with distance from the port of Antwerp, Belgium (Van de Vijver et al 2003; Hoff et al. 2003). 3M operated a PFC manufacturing plant in Antwerp.

Estimated bioconcentration factors for PFOS in fish range from 200 to 1,124 in bluegills and carp (OECD 2002). Studies of APFO and PFOA have estimated that bioconcentration factors are quite low (1.8 in fathead minnows). Therefore, in contrast to PFOS, PFOA does not bioconcentrate through the food chain (EPA 2002).

In the United States, 3M researchers conducted a study of PFOA and PFOS levels in the Tennessee River both upstream and downstream of its facility in Decatur, Alabama (Hansen et al 2002). Analysis of 40 water samples showed that low levels of PFOS were present throughout the 80-mile section of the river studied. Concentrations increased from an average of 32 +/- 11 parts per trillion (ppt) upstream of the PFC manufacturing facility in Decatur to an average of 114 +/- 19 ppt downstream. Concentrations of PFOA were below the laboratory detection limits (25 ppt) upstream of the Decatur facility, but averaged 394 +/- 128 ppt downstream of the facility. The relatively consistent concentrations of PFOS and PFOA found in the Tennessee River suggest that there are no significant removal mechanisms (such as volatilization or adsorption to sediment) affecting their presence in the water. Boulanger et. al. (2004) studied PFOS and PFOA concentrations in sixteen water samples collected from Lake Erie and Lake Ontario. PFOS concentrations ranged from 21 – 70 ppt (mean 43 +/- 18 ppt) in the two lakes, while PFOA concentrations ranged from 27 – 50 ppt (mean 39 +/- 9 ppt). These concentrations were higher than those observed in the Tennessee River upstream of the 3M facility in Decatur. Ongoing studies (coordinated mainly by 3M) are designed to determine PFC concentrations in drinking water, food products, sediments, wastewater treatment plant effluent, sewage sludge, and landfill leachate in a number of cities across the U.S. (Battelle 2000; OECD 2002, EPA 2002). Four cities where PFCs are manufactured or used (supply cities), and two control cities were initially targeted. PFOS concentrations in wastewater treatment plant effluent ranged from 0.041 to 5.29 ppb while PFOA concentrations ranged from 0.040 ppb to 2.42 ppb. In dried treatment plant sludge the PFOS concentrations ranged from 0.2 ppb to 3,120 ppb and PFOA concentrations were from non-detect to 244 ppb. Drinking water samples showed maximum PFOS and PFOA concentrations of 0.063 ppb and 0.029 ppb, respectively; landfill leachate ranged from non-detect to 53.1 ppb for PFOS and non-detect to 48.1 ppb for PFOA. Surface waters ranged from non-detect to 0.138 ppb for PFOS and from non-detect to 0.083 ppb for PFOA; sediments ranged from non-detect to 1.13 ppb for PFOS and from non-detect to 1.75 ppb for PFOA. Data from the control cities were generally at the lower end of these ranges, with a few exceptions. More than 200 food product samples (green beans, apples, pork, milk, chicken, eggs, bread, fish, and ground beef) were also collected. PFOS was only detected in five samples, (one ground beef and four milk samples), at a maximum concentration of 0.852 nanograms per gram (ng/g). Only one of the four milk samples was from a control city, with the remainder from supply cities. PFOA was detected at concentrations up to 2.35 ng/g in two ground beef samples from control cities, two bread samples (from one control and supply cities), two apple samples

(supply cities), and one green bean sample from a supply city.

ERG, on behalf of 3M, has proposed a workplan conducting a facility-wide investigation of PFC releases at the site (ERG 2004). The purpose of the workplan is to:

- Define the extent and magnitude of on-site contamination resulting from the past site waste disposal practices of PFCs;
- Define the hydrology and geology of the site and the potential routes of exposure; and
- Provide information and data needed for consideration of response actions.

The workplan involves the collection of historical information on PFC production, use, and disposal, including releases to the environment, summarizing all available information regarding groundwater monitoring and production wells on the site. It also involves preparation of a groundwater flow model, and collection of groundwater samples for PFC analysis from all wells on the site. A further step will be to collect groundwater samples near the Mississippi River using push-probes in locations where PFCs were used or disposed, and finally preparation of a summary report.

EPA's Office of Pollution Prevention and Toxics, through an enforceable consent agreement (ECA) process undertaken with various manufacturers and users of PFCs (including 3M) and other interested parties, has been studying the extent, distribution, and fate of PFCs (primarily PFOA) in the environment associated with the manufacture, use, or disposal of PFCs or PFC containing products. All documents related to this undertaking are posted and available on an EPA web site ([www.epa.gov/edocket/](http://www.epa.gov/edocket/)) under docket number OPPT-2003-0012.

In this ECA process, EPA identified several needs for monitoring information, including monitoring in the vicinity of facilities currently manufacturing, processing, and using various PFCs. Three companies – 3M, Dyneon (a 3M company), and DuPont – participating in this process have indicated a willingness to enter into Memoranda of Understanding (MOU) with the EPA for monitoring on and around their respective fluoropolymer manufacturing facilities located in Decatur, Alabama and Washington, West Virginia. These MOUs are currently being negotiated. A fourth company, Daikin America, is undertaking an independent, voluntary monitoring program at its fluoropolymer manufacturing facility, which is co-located with the 3M/Dyneon plant in Decatur, Alabama. The 3M Cottage Grove facility has not been included in this effort to date because it is no longer producing PFOA on a commercial basis (M.F. Dominiak, EPA, personal communication, 2004). The phased-approach monitoring plan proposed by 3M for the 3M/Dyneon plant in Decatur, Alabama involves the following (in no particular order; Weston 2004):

- Monitoring of groundwater wells and plant effluent (on and off-site);
- Monitoring of surface water, sediments, aquatic organisms and fish in the adjacent Tennessee River;
- Air dispersion modeling of PFC emissions;
- Soil sampling (on and off-site);

- Sampling of terrestrial vegetation and vertebrates (on and off-site); and
- Monitoring of aquatic avian biota (on and off-site).

Some of the proposed monitoring has already been conducted, with other work proposed for 2004 and 2005. The results of the studies will be provided to EPA when completed. Similar monitoring (including air monitoring for PFCs) has been proposed for other PFC manufacturing sites. The proposed scope of this monitoring plan is broader than the scope proposed by ERG for the 3M Cottage Grove facility. Due to business data privacy concerns, the relative sizes of the two facilities in terms of the production quantities of PFCs are not available from 3M. However, there are many apparent similarities in terms of overall PFC production, site layout, past on-site waste disposal, discharge of PFC containing wastes to a major waterway (the Tennessee River in Decatur and the Mississippi River in Cottage Grove), and the length of time PFCs were produced (40+ years at Decatur and as many as 50 years at Cottage Grove). Based on these factors, a similar, phased scope of investigative work for the 3M Cottage Grove site may be needed to properly assess the potential impact of decades of PFC production and waste disposal. Some aspects of the Decatur workplan may not be applicable to the Cottage Grove facility. The MPCA has also stated that PFC production wastes from the Cottage Grove facility may have been disposed at other known 3M waste disposal sites in the Twin Cities area (MPCA 2004). If so, there is a potential for PFCs to have affected various media (soil, groundwater, or surface water) in these locations as well.

#### Child Health Considerations

ATSDR and MDH recognize that the unique vulnerabilities of infants and children make them of special concern to communities faced with contamination of their water, soil, air, or food. Children are at greater risk than adults from certain kinds of exposures to hazardous substances at waste disposal sites. They are more likely to be exposed because they play outdoors and they often bring food into contaminated areas. They are smaller than adults, which means they breathe dust, soil, and heavy vapors close to the ground. Children also weigh less, resulting in higher doses of chemical exposure per body weight. The developing body systems of children can sustain permanent damage if toxic exposures occur during critical growth stages. Most importantly, children depend completely on adults for risk identification and management decisions, housing decisions, and access to medical care.

Because the site is a secure chemical production and waste disposal facility, children are very unlikely to have been exposed to PFCs at the site itself. There are currently no data available to determine if children could have been exposed to PFCs off of the site property. If air emissions of PFCs extended off the site property, children who may have been living in areas beyond the site boundaries could have been exposed while production was occurring, or could be exposed through other environmental media. PFCs have been detected in blood samples of children from at least 23 different states.

## **IV. Conclusions**

The potential impacts on public health from perfluorochemical releases at the 3M Cottage Grove facility cannot be fully assessed by MDH at this time, because there are not sufficient environmental data available regarding PFC impacts from the facility in soil, groundwater, surface water, sediments, and biota. At this time perfluorochemical releases from the site represent an indeterminate public health hazard. There is a lack of information about how the general population is exposed to PFCs. PFCs have a long half-life in humans and animal studies indicate a potential for toxicity to the liver and effects on reproduction and development.

## **V. Recommendations**

1. Consideration should be given to developing and implementing a scope of investigation work that is generally similar to that developed by 3M for the Decatur, Alabama facility under their proposed voluntary agreement with the EPA (see pages 23-24). Some aspects of the Decatur workplan may not be applicable to the Cottage Grove facility, so a phased approach is recommended. The data from such an investigation are needed to understand the extent of PFC contamination from the facility in all media, and to assess its potential impact on public health.
2. 3M should continue to take action to ensure that workers at the Cottage Grove facility are not exposed to PFCs through the facility water supply at concentrations in excess of the MDH HBVs (currently being implemented by 3M).
3. While releases of PFCs to the Mississippi River are now being generally prevented by the installation of GAC treatment, 3M should continue to identify and reduce (or eliminate where possible) any other potential ongoing discharges of PFOS and PFOA to the environment from the facility.
4. Information should be gathered by 3M regarding any off-site locations where PFC processing wastes from the site were disposed in the past, and appropriate steps should be taken to investigate possible PFC releases from those locations.

## **VI. Public Health Action Plan**

MDH's Public Health Action Plan for the site consists of continued consultation with MPCA staff on the investigation of PFC releases at the site, distribution of this report, possible additional private well sampling, and participation in any planned public outreach activities.

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## **CERTIFICATION**

This 3M Cottage Grove Health Consultation was prepared by the Minnesota Department of Health under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR). It is in accordance with approved methodology and procedures existing at the time the health consultation was begun.

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Jeff Kellam  
Technical Project Officer, CAT, SSAB, DHAC  
ATSDR

The Division of Health Assessment and Consultation, ATSDR, has reviewed this public health consultation and concurs with the findings.

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Roberta Erlwein  
Chief, Cooperative Agreement Team, SSAB, DHAC, ATSDR

## **Appendix 1**

Derivation of MDH Health-Based Values and  
Soil Reference Values for PFOS and PFOA

# Memo



**Date:** November 20, 2002  
**To:** Douglas Wetzstein  
Dave Douglas  
**From:** Helen Goeden, Health Risk Assessment Unit  
**Phone:** (651) 215-0874  
**Subject:** Response to Request for Health Based Values and interim Soil Reference Values

---

This memorandum is in response to a request by the Minnesota Pollution Control Agency (08/21/02) for Health Based Values (HBVs) and interim Soil Reference Values (SRVs) for perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS).

There is limited published information on the toxicity of PFOA and PFOS. The MDH relied heavily on readily available toxicity summary information provided by 3M, EPA and the West Virginia Department of Environmental Protection. After reviewing this information the MDH modified the RfD and RfC values proposed by 3M.

### Health Based Values (HBVs)

<u>Chemical</u>	<u>CAS #</u>	<u>Endpoint</u>	<u>RfD</u> (mg/kg/d)	<u>HBV</u> µg/L
PFOA	3825-26-1	Liver	0.001	7
PFOS	2795-39-3/ 1763-23-1	Liver	0.0002	1

### Soil Reference Values (SRVs)

<u>Chemical</u>	<u>CAS#</u>	<u>Endpoint</u>	<u>RfD</u> (mg/kg/d)	<u>RfC</u> (mg/m <sup>3</sup> )	<u>Residential</u> <u>SRV (mg/kg)</u>	<u>Industrial</u> <u>SRV (mg/kg)</u>
PFOA	3825-26-1	Liver	0.001	2E-5	30	200
PFOS	2795-39-3/ 1763-23-1	Liver	0.0002	2E-5	6	40

**Toxicity Value Sources:** See Attachment II.

Based on information currently available we feel that the above values will provide an adequate level of protection from exposure to PFOA and PFOS in drinking water and direct exposure to PFOA or PFOS in soil; however, there is a degree of uncertainty associated with the HBVs and SRVs, and they should be considered provisional. The above criteria do not address impacts to groundwater as a result of soil leaching, food chain impacts or ecological impacts.

Please note that carcinogenicity studies in the rat have shown PFOA and PFOS to be potentially carcinogenic. However, at this time the available data are not sufficient to determine relevance to humans or for development of cancer potency values.

The data utilized in the derivation of the HBVs is provided in Attachment I. Standard assumptions of a 70 kilogram person with a drinking water ingestion rate of 2 liters per day, and a relative source contribution of 20 percent were used to calculate these values.

MDH is in the process of revising its Health Risk Limits for groundwater rule. The MDH is likely to recommend that the standard assumptions of 70 kilograms and 2 liters/day be replaced by a body weight and an intake rate more appropriate for children. If this recommendation is accepted and promulgated as rule, HBVs would likely decrease by a factor of 3 to 4.

The data utilized in the derivation of the SRVs is provided in Attachment II. The default exposure scenarios and target risk values presented in the MPCA's Draft Guidelines for the Soil-Human Health Pathway, Technical Support Document (Working Draft, January 1999) were utilized to calculate these values.

The MDH's authority to promulgate health risk limits under the Groundwater Protection Act is limited to situations where degradation has already occurred. Similarly, the HBVs and SRVs provided are intended to serve as interim advice issued for specific sites where a contaminant has been detected. As such, neither the HBVs nor SRVs are developed for the purpose of providing an upper limit for degradation.

cc: Larry Gust, MDH  
Anne Kukowski, MDH  
Jim Kelly, MDH  
Gerry Smith, MDH  
Shelley Burman, MPCA  
Luke Charpentier, MPCA  
Mary Dymond, MPCA  
Laura Solem, MPCA  
Michael Santoro, 3M  
John Butenhoff, 3M

# ATTACHMENT I

## DATA FOR DERIVATION OF GROUND WATER HEALTH BASED VALUE (HBV)

Compound Name: **Perfluorooctanoate (PFOA)**  
CAS #: **3825-26-1** (Oct. 16, 2002 personal communication with Dr. John Butenhoff, 3M)

LOAEL (*ingestion*): **3 mg/kg/day**  
Uncertainty Factor: **3000** (3 - interspecies; 10 - intraspecies; 10 subchronic-to-chronic; 10 LOAEL-to-NOAEL)

Modifying Factor: **1**  
RfD\*: **0.001 mg/kg/day**

Health effect: **Liver**

Relative Source Contribution (RSC): **20%**

Oral Slope Factor: **NA**  
Applied Risk Level: **NA**

$$\begin{aligned} \text{HBV} &= \frac{(\text{RfD, mg/kg/d}) (\text{RSC}) (1000 \text{ mg/mg})}{\text{Intake Rate (2 L per day/70 kg)}} \\ &= \frac{(0.001 \text{ mg/kg/d}) (0.2) (1000 \text{ mg/mg})}{0.029 \text{ L/kg/d}} = \mathbf{7 \mu\text{g/L}} \end{aligned}$$

### Data Sources:

1. EPA Revised Draft Hazard Assessment of Perfluorooctanoic Acid and Its Salts (Nov 4, 2002);
2. EPA Draft Hazard Assessment of Perfluorooctanoic Acid and Its Salts (Feb 2002);
3. 3M Lifetime Drinking Water Health Advisory for Perfluorooctane sulfonate (April 2002);
4. 3M Soil Screening Guidelines for PFOS (May 2002);
5. Subchronic Toxicity Studies on Perfluorooctanesulfonate Potassium Salt in Cynomolgus Monkeys. Seacat et al., *Toxicological Sciences* 68:249-264, 2002; and
6. 3M Soil Screening Guidelines for PFOA (March 2002).

\* Carcinogenicity studies in the rat have shown PFOA to be carcinogenic. However, at this time the available data are not sufficient for a quantitative assessment. Reproductive and developmental effects, based on studies in rats and rabbits, occur at levels higher than doses causing liver toxicity. However, due to rapid elimination in female rats (serum half-life of 1 day) it is unclear to what degree the fetuses and neonates were exposed. Ovarian tubular hyperplasia has also been observed in female rats at doses as low as 1.6 mg/kg/d (note: a NOAEL was not determined for this effect since effects were observed at the lowest dose evaluated). Women do not appear to have the same active secretory mechanism that exists in the female rat.



Compound Name: **Perfluorooctanesulfonate (PFOS)**  
CAS #: **2795-39-3 (potassium salt)**  
**1763-23-1 (free salt)**  
(Oct. 16, 2002 personal communication with Dr. John Butenhoff, 3M)

LOAEL (*ingestion*): **0.15 mg/kg/day**  
Uncertainty Factor: **1000** (3 - interspecies; 10 - intraspecies; 10 subchronic-to-chronic; 3 LOAEL-to-NOAEL)

Modifying Factor: **1**  
RfD\*: **0.0002 mg/kg/day**

Health effect: **Liver**

Relative Source Contribution (RSC): **20%**

Oral Slope Factor: **NA**  
Applied Risk Level: **NA**

$$\begin{aligned} \text{HBV} &= \frac{(\text{RfD, mg/kg/d}) (\text{RSC}) (1000 \mu\text{g/mg})}{\text{Intake Rate (2 L per day/70 kg)}} \\ &= \frac{(0.0002 \text{ mg/kg/d}) (0.2) (1000 \text{ mg/mg})}{0.029 \text{ L/kg/d}} = \mathbf{1 \mu\text{g/L}} \end{aligned}$$

Data Sources:

- 1) EPA Hazard Assessment and Biomonitoring Data on Perfluorooctane Sulfonate – PFOS (July 2000);
- 2) 3M Lifetime Drinking Water Health Advisory for Perfluorooctane sulfonate (April 2002);
- 3) 3M Soil Screening Guidelines for PFOS (May 2002);
- 4) Subchronic Toxicity Studies on Perfluorooctanesulfonate Potassium Salt in Cynomolgus Monkeys. Seacat et al., *Toxicological Sciences* 68:249-264, 2002; and
- 5) 3M Comments on Interspecies Uncertainty in Risk Assessment for PFOS.

\*Carcinogenicity studies in the rat have shown PFOS to be carcinogenic. However, at this time the available data are not sufficient for a quantitative assessment. Reproductive and developmental effects, based on studies in rats and rabbits, occur at levels higher than doses causing liver toxicity.

Date (Prepared or Modified): November 14, 2002  
Prepared by: H. Goeden

## ATTACHMENT II

### DATA FOR DERIVATION OF SOIL REFERENCE VALUE (SRV)

Compound Name:	<b>Perfluorooctanoate (PFOA)</b>
CAS #:	<b>3825-26-1</b> (Oct. 16, 2002 personal communication with Dr. John Butenhoff, 3M)
LOAEL ( <i>ingestion</i> ):	<b>3 mg/kg/day</b>
Uncertainty Factor:	<b>3000</b> (3 - interspecies; 10 - intraspecies; 10 subchronic-to-chronic; 10 LOAEL-to-NOAEL)
Modifying Factor:	<b>1</b>
RfD*:	<b>0.001 mg/kg/day</b>
RfC**:	<b>2E-5 mg/m<sup>3</sup></b>
Dermal Absorption:	<b>10% (MPCA Default for organic compounds)</b>
Health effect:	<b>Liver</b>
Hazard Quotient:	<b>0.2 (MPCA target risk value)</b>
Oral Slope Factor:	<b>NA</b>
Inhalation Unit Risk:	<b>NA</b>
Residential SRV:	<b>30 mg/kg</b>
Industrial SRV:	<b>200 mg/kg</b>

#### Data Sources:

- 1) EPA Revised Draft Hazard Assessment of Perfluorooctanoic Acid and Its Salts (Nov 4, 2002);
- 2) EPA Draft Hazard Assessment of Perfluorooctanoic Acid and Its Salts (Feb 2002);
- 3) 3M Lifetime Drinking Water Health Advisory for Perfluorooctane sulfonate (April 2002);
- 4) 3M Soil Screening Guidelines for PFOS (May 2002);
- 5) Subchronic Toxicity Studies on Perfluorooctanesulfonate Potassium Salt in Cynomolgus Monkeys. Seacat et al., *Toxicological Sciences* 68:249-264, 2002; and
- 6) 3M Soil Screening Guidelines for PFOA (March 2002).

\* Carcinogenicity studies in the rat have shown PFOA to be carcinogenic. However, at this time the available data are not sufficient for a quantitative assessment. Reproductive and developmental effects, based on studies in rats and rabbits, occur at levels higher than doses causing liver toxicity. However, due to rapid elimination in female rats (serum half-life of 1 day) it is unclear to what degree the fetuses and neonates were exposed. Ovarian tubular hyperplasia has also been observed in female rats at doses as low as 1.6 mg/kg/d (note: a NOAEL was not determined for this effect since effects were observed at the lowest dose evaluated). Women do not appear to have the same active secretory mechanism that exists in the female rat.

\*\* There is insufficient information on the toxicological effects of PFOA following inhalation exposure. PFOA is not considered to be a volatile chemical and therefore the inhalation exposure pathway is anticipated to be a minor pathway. 3M has suggested a RfC of 2E-5 mg/m<sup>3</sup> based on a generic exposure guideline for chemicals found to be carcinogenic in animals but with unknown relevance to humans. The CATT report generated a RfC of 1.1E-3 mg/m<sup>3</sup>. In the absence of information the provisional RfC suggested by 3M will be utilized for the development of an interim Soil Reference Value.

Compound Name: **Perfluorooctanesulfonate (PFOS)**  
CAS #: **2795-39-3 (potassium salt)**  
**1763-23-1 (free salt)**  
(Oct. 16, 2002 personal communication with Dr. John Butenhoff, 3M)

LOAEL (*ingestion*): **0.15 mg/kg/day**  
Uncertainty Factor: **1000** (3 - interspecies; 10 - intraspecies; 10 subchronic-to-chronic; 3 LOAEL-to-NOAEL)  
Modifying Factor: **1**  
RfD\*: **0.0002 mg/kg/day**

RfC\*\*:  
**2E-5 mg/m<sup>3</sup>**

Dermal Absorption: **10% (MPCA Default for organic compounds)**

Health effect: **Liver**

Hazard Quotient: **0.2 (MPCA target risk value)**

Oral Slope Factor: **NA**

Inhalation Unit Risk: **NA**

Residential SRV: **6 mg/kg**

Industrial SRV: **40 mg/kg**

#### Data Sources:

##### Data Sources:

- 1) EPA Hazard Assessment and Biomonitoring Data on Perfluorooctane Sulfonate – PFOS (July 2000);
- 2) 3M Lifetime Drinking Water Health Advisory for Perfluorooctane sulfonate (April 2002);
- 3) 3M Soil Screening Guidelines for PFOS (May 2002);
- 4) Subchronic Toxicity Studies on Perfluorooctanesulfonate Potassium Salt in Cynomolgus Monkeys. Seacat et al., *Toxicological Sciences* 68:249-264, 2002; and
- 5) 3M Comments on Interspecies Uncertainty in Risk Assessment for PFOS.

\*Carcinogenicity studies in the rat have shown PFOS to be carcinogenic. However, at this time the available data are not sufficient for a quantitative assessment. Reproductive and developmental effects, based on studies in rats and rabbits, occur at levels higher than doses causing liver toxicity.

\*\*There is insufficient information on the toxicological effects of PFOS following inhalation exposure. PFOS is not considered to be a volatile chemical and therefore the inhalation exposure pathway is anticipated to be a minor pathway. 3M suggested a RfCs of 2E-4 and 2E-5 mg/m<sup>3</sup> for PFOS and PFOA, respectively. The value for PFOA was based on a generic exposure guideline for chemicals found to be carcinogenic in animals but with unknown relevance to humans. PFOS appears to be carcinogenic in rats but it is not clear whether suggested mechanism of action is relevant to humans. In the absence of information the provisional RfC for PFOA (2E-5 mg/m<sup>3</sup>) suggested by 3M will be utilized for the development of an interim Soil Reference Value for PFOS as well.

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Prepared by: H. Goeden