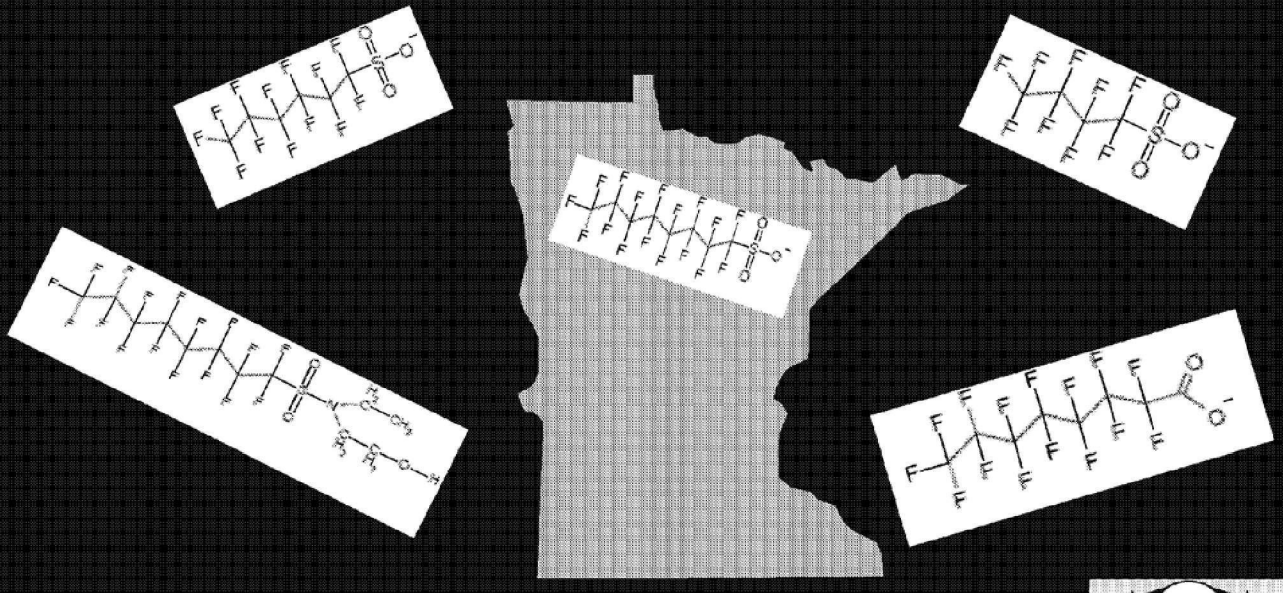
The presence and Distribution of Perfluorochemicals (PFCs) in Minnesota



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MET 0887473

Background of the Perfluorochemical (PFC) Problem

- This presentation focuses on perfluorochemicals (PFCs) manufactured by the Minnesota Mining and Manufacturing (3M) Company. The PFCs manufactured by 3M are used in the broad range of products and applications, and in consumer products by the 3M brand name Scotchguard.
- 3M was the sole manufacturer of this family of perfluorochemicals.

MET 0887474

Background of the PFC Problem…

- In 1997, a lab comparing 3M workers' blood to randomly chosen Red Cross samples found that the 3M PFCs were also present in the blood bank samples.
- 3M commissioned a number of studies to determine the extent of contamination of these PFCs in the environment.
- The initial study in 1999 by Michigan State University found PFOS in numerous animals worldwide, including human.
- In individual blood serum samples obtained from adults and children in various regions of the U.S., mean PFOS levels were approximately 43 ppb.

MET 0887475

Phase Out of PFOS

- 3M manufactured PFCs at plants in the U.S in Decatur, Alabama and Cottage Grove, Minnesota and in Europe in Antwerp, Belgium.
- In 2000 following a series of discussion with EPA, 3M announced that it would end production of the PFOS related PFCs.
- 3M began a phase out of PFOS related PFCs production and ceased this production at the Minnesota, Alabama, and Belgium facilities by the end of 2002.

MET 0887476

PBTs Characteristics of PFCs

- PFOS has been found to be ubiquitous in the environment in tissues of wild birds, wildlife, fish, and other animals, surface waters and sediments, sewage sludge, landfill leachates, and wastewater treatment effluents worldwide.
- PFOS is extremely persistent and does not bidodegrade or break down in the environment, and it is not metabolized in animals and humans.
- PFOS is bioaccumulative and has been shown to bioconcentrate in fish and other aquatic organisms.
- PFCs that were made in the 3M manufacturing processes eventually break down into PFOS in the environment.

MET 0887477

Concerns about of PFCs

- PFOS has been found to be persistent, bioaccumulative, and toxic to mammalian species.
- Animal studies show that PFOS is well absorbed orally and distributes mainly to the liver and blood.
- No further metabolism is expected. Elimination from body is slow and occurs mainly in the urine and feces.
- There are significant differences in the elimination half-life of PFOS in animals; in humans the mean half-life has been calculated at 8.67 years.

MET 0887478

PFCs Toxicity

- PFOS has been shown to cause moderate toxicity in the rat. Numerous studies on PFOS in rats and primates demonstrate that it is toxic to the liver.
- Adverse signs in 90 day rat studies include increase in liver enzymes, hepatic vacuolization and heptocellular hypertrophy, gastrointestinal effects, hematological abnormalities, weight loss, and convuolsions.
- Adverse effects in Rhesus Monkey studies include anorexia, emesis, diarrhea, hypoactivity, convulsions, atrophy of the salicvary glands and the pancreas, marked decreases in serum cholesterol, and lipid depletion in the adrenals.

MET 0887479

PFCs Carcinogenicity

- The potential carcinogenicity for PFOS was examined in a dietary 2 year bioassay in rats
  - A significant increase in the incidence of hepatocellular (liver) adenomas in males and the females at the highest PFOS dose occurred.
  - The female rats had a significant increase in combined hepatocellular adenomas and carcinomas.
  - There was a significant increased in follicular cell adenomas and combined thyroid follicular cell adenomas and carcinomas in the male rat recovery group at the high PFOS dose.

MET 0887480

Mortality Study

- In a mortality study of 3M workers at the 3M Decatur, Alabama plant, a 30 year retrospective evaluation:
- A stastically significant association between PFOS levels in workers blood and bladder cancer was reported.
- Stastical analysis of the mortality data indicated that workers who were employed in high exposure jobs were 13 times more likley to die of bladder cancer than the general population of Alabama.
- It was concluded that cancer of the bladder is considered a potentially significant yet uncertain endpoint in the analysis of risks from PFOS related subtances.

MET 0887481

Developmental Effects

- Postnatal deaths and other developmental effects were reported at low doses in offspring in a 2-generation reproductive toxicity study in rats.
- Developmental effects were also reported in prenatal developmental toxicity studies in the rat and rabbit, although at slightly higher dose levels.
- Significant decreases in fetal body weight and significant increases in external and visceral anomalies, delayed ossification, and skeletal variations were observed.

MET 0887482

More Toxicity Data

- PFOS has been tested on two species of bird:
  - The lowest acute dietary LC50 value of 220 mg/kg of food was determined in the test with the quail.
  - The lowest NOEC of 37 mg/kg of food for effects on body weight was, in contrast, obtained in the test with the duck.
- There are data on acute oral and contact toxicity tests on the Honey bee (*Apis mellifera*) using PFOS potassium salt:
  - These studies indicate moderate and high orders of toxicity of PFOS to bees when administered via these routes.

MET 0887483

PFCs Investigation in MN Environment

- The purpose of this investigation was to determine the extent of PFC contamination in MN, to further understanding of the behavior of PFCs in environmental media, to determine PFC concentration levels in order to assess risk, and to acquire PFC data necessary for development of any potential fish consumption advisory and discharge limitation.

- This investigation is related to the past and current discharge of PFCs from the 3M facility to the Mississippi River and disposal of its waste to landfills and WWTPs.

MET 0887484

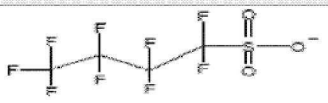
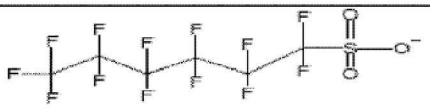
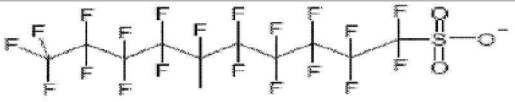
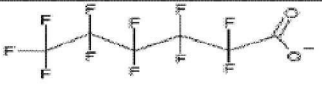
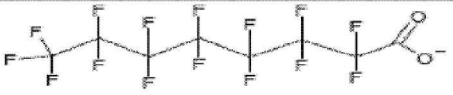
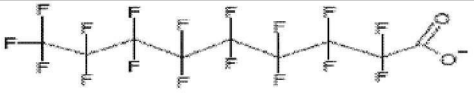
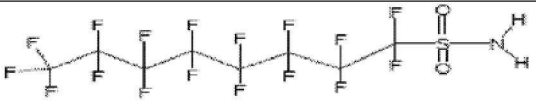
PFCs Study Areas

- PFC investigation consists of sampling and subsequent analysis of 12 PFCs in various environmental media:

1. Mississippi River
2. MCES Metro Wastewater Treatment Plant
3. Pine Bend Landfill
4. 3M Cottage Grove Plant
5. Washington County Landfill

MET 0887485

PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA, PFBS, PFHxS, and PFOS

Acronym	Name	CAS-number	Structure
PFBS	Perfluorobutane sulfonate	29420-49-3	
PFHxS	Perfluorohexane sulfonate	432-50-7	
PFOS	Perfluorooctane sulfonate	2795-39-3	
PFDS	Perfluorodecane sulfonate	67906-42-7	
PFHxA	Perfluorohexanoic acid	307-24-4	
PFHpA	Perfluoroheptanoic acid	375-85-9	
PFOA	Perfluorooctanoic acid	335-67-1	
PFNA	Perfluorononanoic acid	375-95-1	
PFOSA	Perfluorooctane sulfonamide	4151-50-2	

MET 0887486

Basis for PFC Study in Mississippi River

- The study was initiated to determine the impact of past and present PFC discharges on Mississippi River water and sediment related to the past decades of discharge of high amounts of PFCs from the 3M Cottage Grove plant to the river.
- Because of the extremely long term persistence of PFCs and the fact that these compounds do not degrade in the environment we expect that these compounds will reside in river sediments and other environmental media for an indefinitely long period.

MET 0887487

Mississippi River Water & Sediment Sampling

- sampling was conducted above, below, and proximate to the 3M Cottage Grove facility. Individual water and sediment samples were taken at 5 separate locations.
- This is the only study in Minnesota, and to our knowledge within the U.S. to date, that included analyses of samples for a complement of 12 PFC compounds.

MET 0887488

Historical 3M PFC Discharges

- Limited data is available for PFCs discharged to the Mississippi River from the 3M facility prior to 2002.
- Historical data provides some measure of PFCs 3M discharged prior to the C-8 PFC production phase-out which began in 2000.
- 3M could potentially have discharged about 50,000 lbs per year of PFC compounds to the Mississippi River.
- At times, during low flow years, the mixed river concentration of PFOS (perfluorooctane sulfonate) may have exceeded the recently established PFOS drinking water "standard" by the Minnesota department of Health of 1.0 ppb.

MET 0887489

PFC Concentrations (ng/L) in Mississippi River Water Samples

CLIENT ID	Miss-up	Miss-down #1	Miss-down #3	Miss-down #2	Cove (3M)	Cove-top
PFBA	<12.8	<12.7	<12.8	<12.9	5000.00	5530.00
PFPeA	<12.6	<12.5	<12.6	<12.7	1320.00	1560.00
PFHxA	<4.90	<4.87	<4.92	<4.93	1780.00	1970.00
PFHpA	<4.96	<4.93	<4.98	<4.99	<251	<251
PFOA	<4.88	35.30	<4.90	<4.91	3250.00	3650.00
PFNA	<5.30	<5.26	<5.31	<5.33	<268	<268
PFDA	<5.12	<5.09	<5.13	<5.15	<259	<259
PFUnA	<5.07	<5.04	<5.08	<5.10	<257	<257
PFDoA	<5.04	<5.01	<5.05	<5.07	<255	<255
PFBS	<5.02	<4.99	<5.03	<5.05	84800.00	89800.00
PFHxS	<5.04	<5.01	<5.05	<5.07	8230.00	9720.00
PFOS	5.14	14.50	<5.11	6.00	10800.00	18200.00
PFOSA	<5.10	<5.07	<5.11	<5.13	<258	<258
Total PFCs	**5.14**	**49.80**	**0.00**	**6.00**	**107080.00**	**121370.00**

MET 0887490

PFC Concentrations (ng/g dry wt) in Sediment Samples

Sample ID	Sed-Miss-up	Sed-Miss-down #1	Sed-Miss-down #2	Sed-Miss-down #3	Sed-Cove
PFPeA	<0.308	0.986	<0.320	<0.312	1.21
PFHxA	<0.299	0.755	<0.311	<0.302	2.28
PFHpA	<0.302	0.262	<0.315	<0.306	0.758
PFOA	<0.298	6.62	1.31	<0.301	18
PFNA	<0.323	0.333	<0.336	<0.327	0.671
PFDA	<0.312	1.13	0.49	<0.316	2.93
PFUnA	<0.309	0.437	<0.322	<0.313	1.73
PFDoA	<0.307	0.281	0.365	<0.311	2.47
PFBS	<0.306	1.74	<0.318	<0.310	49.8
PFHxS	<0.307	1.54	<0.320	<0.311	9.24
PFOS	1.57	27.9	8.26	1.69	99.4
Total PFC	**1.57**	**41.964**	**10.425**	**1.69**	**188.489**

MET 0887491

Results: PFC in River Water & Sediment

- The upstream river water sample containing PFOS at about 5 ppt is typical of background PFOS levels found in other studies worldwide.
- PFOS and PFOA were found in river water downstream of the 3M discharge (PFOS at 14 ppt and PFOA at 35 ppt).
- The PFCs levels in cove water sample which receives the 3M discharge are in the higher ppb ranges.These concentrations are comparable to the concentrations from fluorochemical plant discharges, and to the PFCs monitored in the 3M discharge.
- It is likely that PFCs in the water concentrate on the water surface micro layer due to their surface active properties.
- The concentrations of PFCs found in river sediments are relatively high compared to background, are uniquely associated with a PFC production facility discharge.

MET 0887492

Future Study Needs in Mississippi River

- A more extensive collection of river sediment cores is needed to characterize the levels of PFC contamination in the river sediments and the river cove sediments.
- Deeper sediment cores need to be collected, dated and analyzed.
- The bioavailability of PFC contaminated sediment needs to be evaluated, to determine potential impacts to aquatic life and wildlife.

MET 0887493

PFC Contamination in Fish

- PFOS is extremely resistant to environmental degradation. Once PFOS precursors degrade to PFOS, PFOS can be bioavailable and may enter the food chain.
- PFC compounds preferentially distribute and accumulate in livers and blood (plasma) in animals, including humans. No further metabolism by PFOS in animals is expected.
- Elimination is slow and the elimination half-life of PFOS differs from species to species.
- Unlike other PBTs, PFOS does not accumulate in fat tissue of organisms.

MET 0887494

PFOS Bioconcentrate in fish

- Laboratory studies in fish have shown that significant PFOS bioconcentration occurs.
- Studies on the bluegill sunfish found a BCF of 2796 for PFOS.
- For PFOS, BCF of 1100 whole fish, 5400 liver, and 4300 blood has been reported for rainbow trout.
- Concentration of PFOS in benthic invertebrates (amphipods & zebra mussels) were approximately 1000 times greater than the PFOS levels in the surrounding water.

MET 0887495

PFOS Bioaccumulates in Fish & other Animals

- PFOS is highly bioaccumulate with the reported BAF ranging from 6,300 to 125,000.
- For PFOS, estimated BAF of 830 for channel catfish, and 26,000 for largemouth bass has been reported.
- Very high concentrations of PFOS have been found in the liver and blood of higher tropic level predators that consume fish (polar bears, mink and birds).
- PFOS also significantly biomagnifies up the food chain. PFOS concentrations in predatory fishes are often 10 to 20 times greater than those in their prey species.

MET 0887496

PFOS Aquatic Toxicity

- A major route for PFOS into the food chain affecting and causing human PFOS blood levels may be through contaminated fish.
- The toxicity of PFOS has been studied in a variety of aquatic and terrestrial species, including aquatic plants, invertebrates and vertebrates and terrestrial invertebrates, birds and mammals.
- Toxicity data is primarily limited to the PFOS. Adverse animal effects range from growth inhibition, histopathological effects, atrophied thymus, change in species diversity in a microcosm, and mortality.

MET 0887497

Toxicity to Aquatic Organisms

PFOS have low to moderate toxicity to aquatic organisms:

- The lowest LC50 for fish is a 96-hour LC50 of 4.7 mg/l to the fathead minnow *Pimephales promelas* for the lithium salt.
- For aquatic invertebrates, the lowest EC50 for freshwater species is a 48-hour EC50 of 27 mg/l for *Daphnia magna*.
- For saltwater species, a 96-hour LC50 value of 3.6 mg/l for the Mysid shrimp *Mysidopsis_bahia*.

Long-term toxicity data for fish and aquatic invertebrates.

- The lowest NOEC for fish is a 42 day NOEC (survival) of 0.3 mg/l in an early life stage test with *Pimephales promelas* using the potassium salt.
- The lowest NOEC for aquatic invertebrates is a 35-day NOEC reproduction of 0.25 mg/l for *Mysidopsis bahia* using the potassium salt.

MET 0887498

PFOS Levels in Fish

- A review of the literature indicates that the maximum concentration of PFOS in fish liver found is about 1000 ppb.
- In a Great lakes Study smallmouth bass tissue (skinless fillets) were analyzed for PFOS at a range of 2.0 to 41.3 ppb
- In a study of fish from the Michigan waters of the Great Lakes, the following PFOS levels were reported in fish liver:
  - Chinook Salmon – 32-173 ppb (average 100 ppb)
  - Lake Whitefish – 33-81 ppb (average 67 ppb)
  - Brown Trout – range <17-26 ppb
  - Various species – range <7.7-120 ppb (average 43 ppb)

MET 0887499

PFCs in Mississippi River Fish

- Fish were collected from the Mississippi River in the vicinity of the 3M Cottage Grove plant and its
- discharge.
- Four different fish species were collected from two distinct ecological groups (benthivorous and piscivorous) from the study area.
- Fish collected were analyzed to determine PFC levels in the liver of the specimens.
- The fish sampling work done thus far should be considered Phase 1 of a multi-phase project.

MET 0887500

PFC Levels in Fish Liver Samples from Mississippi River (August 2004)

Samples	SMB - 1	SMB - 2	SMB - 3	SMB - 4	WB - 1	WB - 2
no/sex/age	1F&3M/2y	2F/3y	1F/4 y	1F/8 y	3F&1M/6y	1F/7y
UNITS	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)
PFBA	<3.76	<3.76	<3.88	<3.70	<3.88	<3.92
PFHxA	<0.360	20.2	<0.371	10.4	<0.371	<0.376
PFHpA	<0.365	<0.365	4.17	1.49	1.1	6.32
PFOA	0.551	<0.359	<0.370	0.489	1.27	<0.374
PFNA	<0.390	<0.390	<0.401	0.635	4.26	3.17
PFDA	13.1	25.5	18.1	63	19.4	11.2
PFUnA	26.1	34.5	21.2	31.2	6.95	5.03
PFDoA	25.9	21.9	21.4	84.7	4.15	4.6
PFTA	14	4.32	5.1	44.6	6.67	0.828
PFBS	NR	NR	NR	NR	NR	NR
PFHxS	<0.371	<0.371	<0.382	<0.364	<0.382	3.16
PFOS	1030	597	717	52500	1120	305
PFOSA	<0.363	<0.363	<0.374	481	<0.374	<0.379
Total PFCs	**1109.651**	**703.42**	**786.97**	**53217.514**	**1163.8**	**339.308**

MET 0887501

PFC Levels in Fish Liver Samples ....

Samples	Carp - 1	Carp - 2	Carp - 3	WE - 1	WE - 2
no/sex/age	2F&1M/6y	1F/7y	1F/8 y	1M/4y	1F/9 y
UNITS	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)	ng/g (wet)
PFBA	<3.70	<3.83	<3.62	<3.81	<3.74
PFHxA	<0.354	2.91	<0.346	<0.365	<0.358
PFHpA	0.969	<0.371	<0.351	<0.369	3.17
PFOA	0.662	<0.365	<0.345	0.651	<0.357
PFNA	1.5	0.89	0.817	<0.394	2.91
PFDA	6.54	4.99	2.86	13.6	8.41
PFUnA	1.66	3.21	3.18	5.5	3.17
PFDoA	1.73	1.82	1.14	2.29	<0.368
PFTA	5.39	0.455	0.408	3.31	2.17
PFHxS	<0.364	<0.377	0.88	<0.375	<0.368
PFOS	309	130	202	371	184
PFOSA	<0.357	<0.370	<0.349	<0.368	<0.361
Total PFCs	**327.451**	**144.275**	**211.285**	**396.351**	**203.83**

MET 0887502

Results – PFC in Mississippi River Fish

- Fish in the Mississippi River, collected in August 2004, demonstrate contamination with PFCs, predominantly PFOS.
- The PFOS concentrations found in fish livers are at relatively high levels and are indicative of exposure to a PFC contamination source, the 3M discharge .
- The impacts that these contaminated fish may have on wildlife and humans consuming these fish are unknown, which requires immediate and further study.
- The one smallmouth bass in this study contained an alarmingly high level of PFOS in liver, 52,500 ppb, and contained the highest concentration of any fish tested to date, and the second highest PFOS concentration for any animal species tested worldwide.

MET 0887503

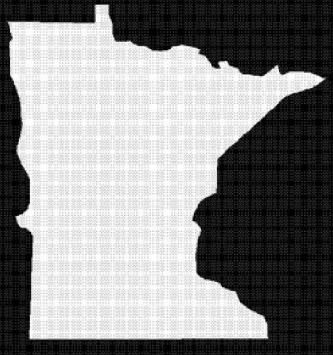
Future Study Needs for PFCs in Mississippi River Fish

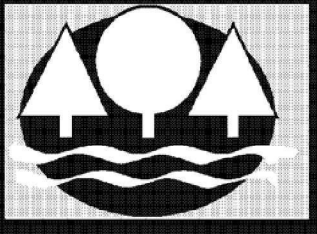
- More PFC fish analyses are required, including whole fish and fillet, in order to address the risk posed to humans and wildlife consuming contaminated fish.
- An evaluation should be done as to whether a fish consumption advisory is needed. A risk assessment should be conducted to determine the acceptable levels of PFC in fish.
- Other aquatic species including lower trophic levels should be analyzed and a model for bioaccumulation of PFCs should be developed.
- Fish should be collected in the river at greater distances downstream of the 3M discharge, including Lake Pepin, a deposition sink for organic pollutants.

MET 0887504

What is Next?

- More systematic long term biomonitoring environmental monitoring.
- More information on the toxicology and behavior of PFCs to enable a better estimation of risks associated with them.





THANK YOU FOR YOUR ATTENTION!!!!!!

MET 0887505