Environ Sci Pollut Res (2013) 20:1977–1992
DOI 10.1007/s11356-012-1275-4

PFOS and PFC releases and associated pollution from a PFC production plant in Minnesota (USA)

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Received: 30 March 2012 / Accepted: 22 October 2012 / Published online: 6 November 2012
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Abstract Perfluorooctane sulfonate (PFOS) and PFOS-related substances have been listed as persistent organic pollutants in the Stockholm Convention. From August 2012, Parties to the Convention needed to address the use, storage, and disposal of PFOS—including production sites and sites where PFOS wastes have been deposited—in their national implementation plans. The paper describes the pollution in Minnesota (USA) caused by the 3M Company at one of the largest per/polyfluorinated chemical (PFC) production facilities. From early 1950s until the end of 2002, when 3M terminated PFOS and perfluorooctanoic acid (PFOA) production, PFOS, PFOA, and other PFC production wastes were disposed around the plant and in local disposal sites. Discharges from the site and releases from deposits caused widespread contamination of ground and surface waters including local drinking water wells. Fish in the river downstream were contaminated with PFOS to levels that led to fish consumption advisories. Human exposures resulted from ingesting contaminated drinking water, requiring installation of water treatment facilities and alternate water supplies. The critical evaluation of the assessments done revealed a range of gaps in particular of human exposure where relevant exposure pathways including the entire exposure via food have not been taken into consideration. Currently, the exposure assessment of vulnerable groups such as children or Hmong minorities is inadequate and needs to be improved/validated by epidemiological studies. The assessment methodology described for this site may serve—with highlighted improvements—as a model for assessment of other PFOS/PFC production sites in the Stockholm Convention implementation.

Keywords PFC · PFOS production · Contaminated site · Landfill · Drinking water · Human exposure

Responsible editor: Philippe Garrigues

F. Oliaei and D. Kriens were former staff of Minnesota Pollution Control Agency (MPCA).

This paper belongs to the series of POPs contaminated sites edited by Weber R, Gaus C, Tysklind M (Weber et al. 2008).

Electronic supplementary material The online version of this article (doi:10.1007/s11356-012-1275-4) contains supplementary material, which is available to authorized users.

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Introduction

Most per- and polyfluorinated compounds (PFCs) are highly persistent chemicals. Several are highly toxic pollutants (Joensen et al. 2009; Lindstrom et al. 2011; Oliaei 2010; Stahl et al. 2011). Perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA), and other long-chained perfluorinated sulfonates and carboxylates bioaccumulate and biomagnify despite their water solubility (Conder et al. 2008; Martin et al. 2004).

In May 2009, PFOS, PFOSF, and related precursor substances were added to the Stockholm Convention listings and

officially became the first fluorinated persistent organic pollutants (Stockholm Convention 2009; www.pops.int). Consequently, PFOS and its related substances must, in future, be addressed globally in accordance with the provisions of the Convention. Currently, however, PFOS and other PFCs remain extensively used in industrial applications and consumer goods including impregnated paper, carpet, textiles, leather, furniture, paints, cleaning detergents, and cosmetics (Prevedouros et al. 2006; Stockholm Convention 2012a).

Furthermore, an extensive list of derogations and exemptions for the use of PFOS have been included in the Stockholm Convention listing. Countries need only register with the secretariat to allow these uses (Stockholm Convention 2009, 2012a, b). Therefore, PFOS will continue to be produced, used, and released into the environment, although hopefully at lower levels than previously as a result of lower production volumes and better life-cycle controls. Other PFCs, often with limited toxicity data, are increasingly being used as alternatives to PFOS/PFOA (Lindstrom et al. 2011; Stahl et al. 2011).

PFOS is still produced in at least three countries with one site in Germany (c. 10 tonnes/year) and Italy (with unknown production volume) and fifteen sites in China (100 to 250 tonnes/year) (Lim et al. 2011; Stockholm Convention 2012c; Zhang et al. 2012). While PFOS levels have fallen in many parts of the world, they have dramatically increased in others—most notably in China (Lim et al. 2011).

Paul et al. (2010) estimated that the total historic production of 96,000 tonnes of PFOSF generated about 26,500 tonnes of wastes. The former and future management of these (deposited) wastes at the production and formulation plants is vitally important. Furthermore, at the end of their product life, most PFCs end up in landfills (e.g., impregnated carpets, textiles, paper) where they are mobilized and released from mainly via leachates due to their high solubility (Busch et al. 2010; Weber et al. 2011; Huset et al. 2011). The remainder is released from plating industries or fire-fighting foam and contaminates ground water and surface waters (Antea Group 2011; Awad et al. 2011; Moody et al. 2000, 2003; Weber et al. 2010). PFCs ultimately end up in the oceans/sea (Yamashita et al. 2008). They are frequently detected in coastal areas (Sánchez-Avila et al. 2010; So et al. 2004; Theobald et al. 2011) at levels exceeding—often by an order of magnitude—the proposed maximum permissible concentration (MPC) for fresh waters of 0.65 ng/l (Moermond et al. 2010). Levels in the open waters of the Baltic are already around the MPC (Theobald et al. 2011).

It is estimated that to date only approximately 1 % of the total PFOS production has yet reached the sea (Paul et al. 2010). The continuous influx from rivers (Sánchez-Avila et al. 2010; Theobald et al. 2011) presents particular dangers for seas with low water exchange rates such as the Mediterranean and Baltic.

The assessment and management of PFOS and related substances are now regulated by the Stockholm Convention which has been ratified by 178 countries, although not yet by the United States. The Conference of Parties has made recommendations for risk reduction of PFOS (Stockholm Convention 2011; Electronic supplementary material), and guidance has been developed[1] to assist with inventory and management of PFOS and related chemicals (Stockholm Convention 2012a, b). The recommendations highlight the need for assessment of production, use, and end-of-life stages according to the life cycle principles. Notably, they emphasize the need to undertake "urgent investigations into landfills where waste from PFOS producers or from PFOS industrial users (paper, carpet, textile, chromium plating and other industries having used PFOS) are deposited."

The Stockholm Convention requires governments and their responsible competent authorities to develop management and monitoring concepts for the inventory, assessment, and management of key PFOS sources and stockpiles. This includes production plants and factories where PFOS and related substances have been used. Competent authorities play a key role in setting the framework to assess such sites, controlling these hazardous substances throughout their life-cycle, and to developing concepts to reduce releases from past and present production plants and other contaminated sites to ensure that exposures to humans and the environment are minimized (Fig. 1).

The Stockholm Convention recommendations promote the transfer of knowledge and technology, including capacity-building and good practice stories to support global efforts to reduce PFOS risks. Sharing methodologies for the assessment and remediation of PFOS production and other contaminated sites is an important example.

The 3M Company, with plants in the United States and Europe, was the primary global producer of PFOS and PFOS-related substances. In 2000, for example, 3M produced 3,300 tonnes at its plants (Oliaei et al. 2005) which was most of the total global production of PFOS (Paul et al. 2010). The company's facility in Minnesota (USA) was a major producer and has become one of the most studied in relation to pollution and contamination. 3M also produced PFOA at its Cottage Grove plant in Minnesota (Figs. 2 and 3) until late 2002, when it terminated production of eight-carbon PFOA and PFOS-related compounds. At that time, 3M reformulated its PFC chemistry to produce "four-carbon" perfluorinated compounds based on perfluorobutane sulfonate (PFBS) (OECD 2002). Generally, the longer the carbon chain length, the longer PFCs persists in the human body. The four-carbon PFBS is, on average, eliminated in just over 1 month, but PFOA takes 3.8 years and PFOS, 5.4 years. Perfluorohexane sulfonate (PFHxS), with six carbons, takes 8.5 years and is an exception to the rule

[1] The guidance and guidelines have not yet been approved by the conference of parties.

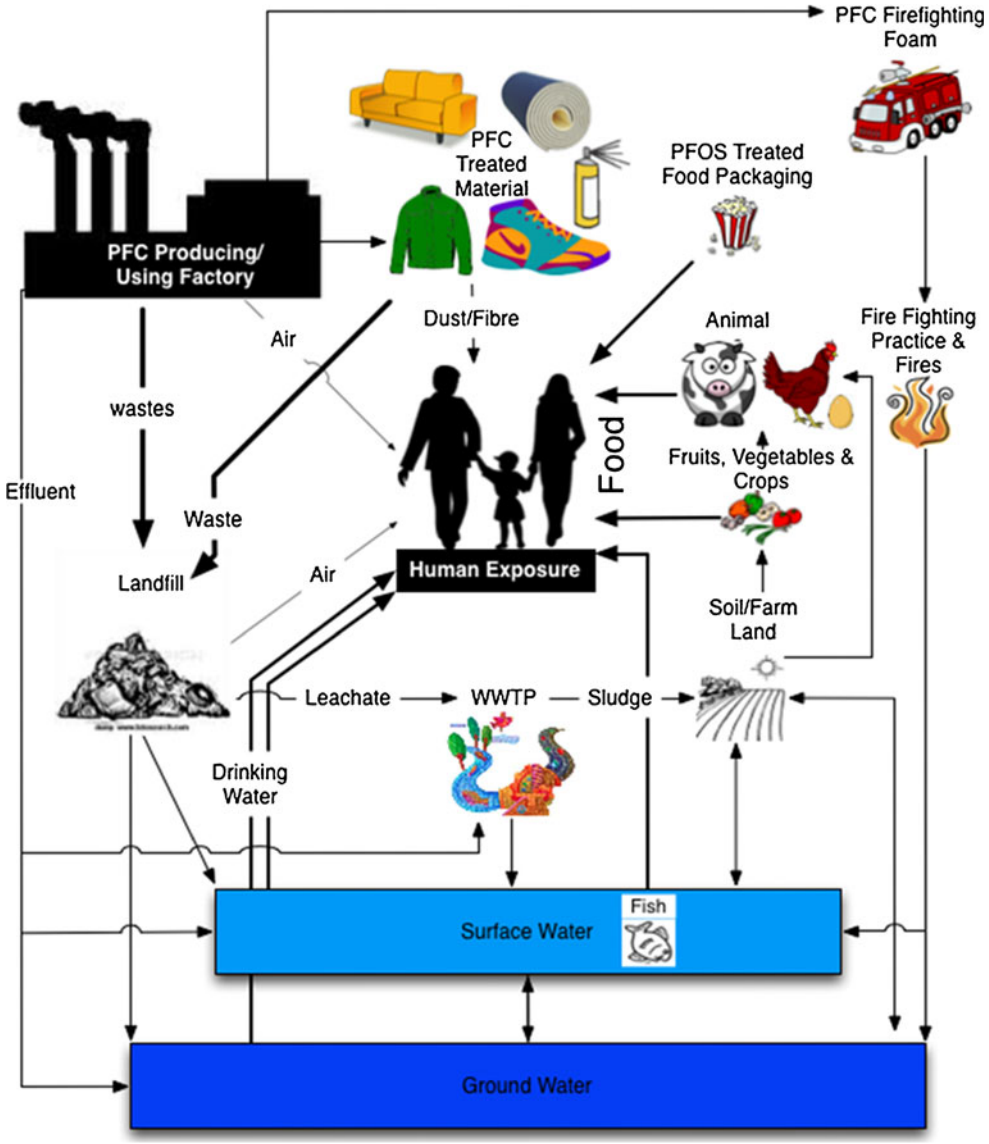

Fig. 1 PFC release from the technosphere and contamination pathways in the environment and exposure pathways to humans

(Betts 2007). 3M continues to produce and use the shorter-chain PFCs.

Over five decades of production from the 3M Minnesota PFC facility generated large quantities of PFC, including PFOS-containing wastes and sludges which were deposited at several sites in Minnesota. The Minnesota Pollution Control Agency (MPCA) began investigation of PFC contamination from these sites in about 2002. By 2006, Oliaei reported the MPCA's discovery and assessment of the exposure impacts on the local population from the facility and associated dumpsites releases—including the high levels of PFCs contained in the wastewater discharge to the Mississippi River—to the Minnesota State Senate (Oliaei et al. 2006). The pollution and associated exposures have been further assessed by the MPCA and others since that time. Remediation measures and further studies are ongoing.

This paper provides an overview of the releases and environmental contamination related to the 3M production facility in Minnesota. It describes the investigation approach taken by the MPCA and the Minnesota Department of Health (MDH), as the responsible competent authorities, and the consequences of the contamination of the wider environment (groundwater, sediments, surface water, and fish). The paper also highlights information gaps including those from the assessment of the site and the human exposure pathways (Fig. 1), taking into account the findings from the assessment of other PFC productions or contaminated sites.

The investigations of the Minnesota factory provide a case study illustrating how competent authorities might assess the pollution and fate of PFOS and related chemicals from a production facility. The methodology is also relevant to industries which used these substances. The assessment approach of the first study phase (phase I 2002 to 2006) is described in more detail (including materials and methods) in this paper as an example of how to initiate such an

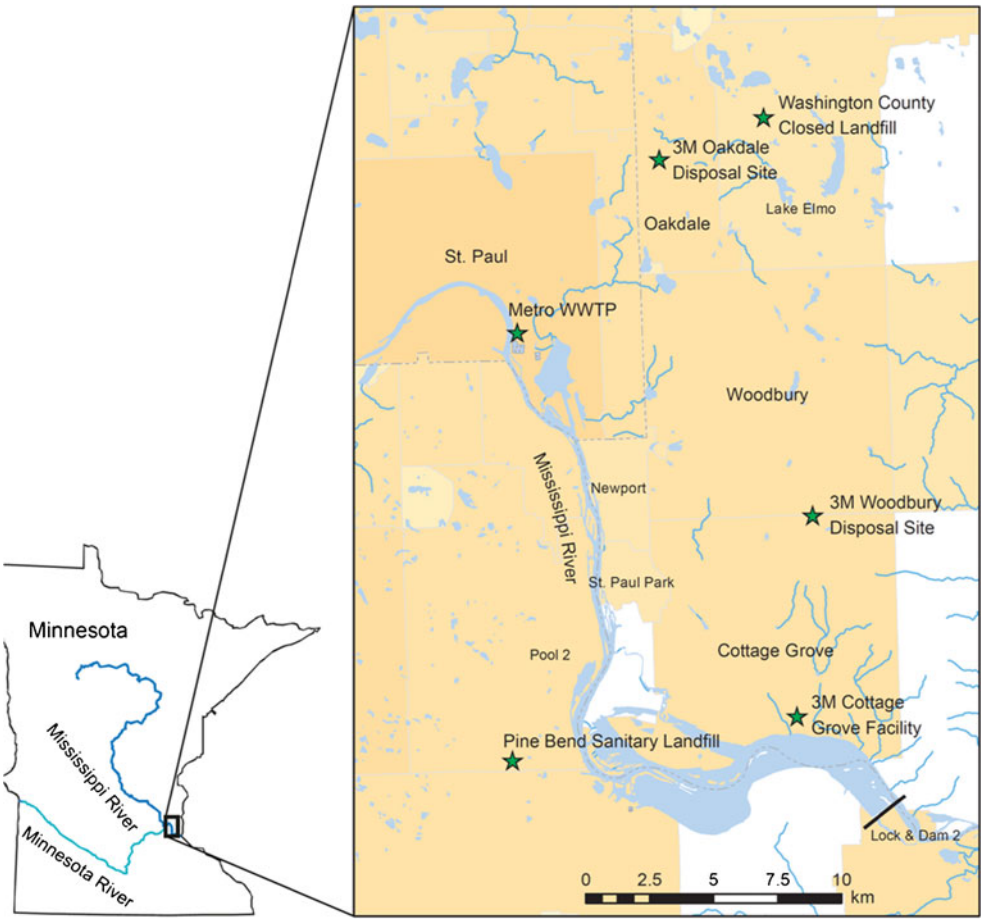

Fig. 2 Location of Twin City area within Minnesota and locations of production plant, landfills, waste water treatment plants, and Mississippi River pool 2 area

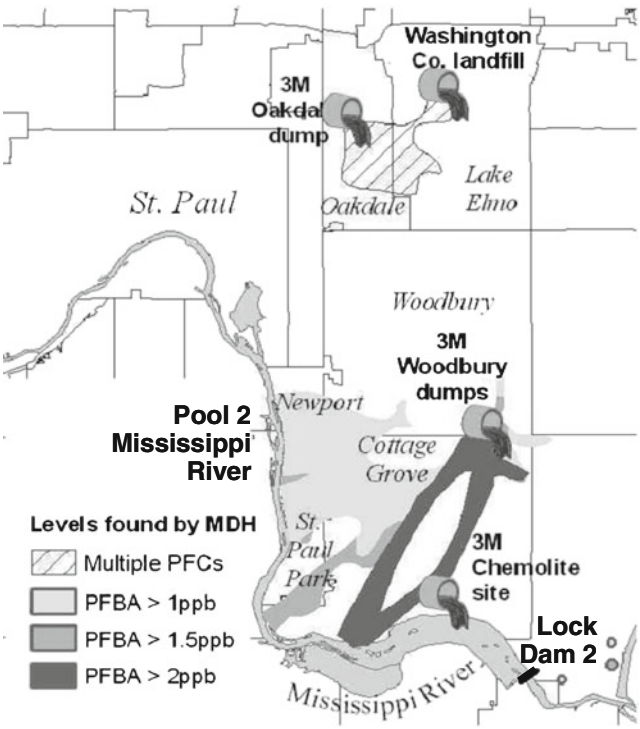

Fig. 3 Major PFOS/PFAS contaminated sites in Washington County and ground water contamination, Minnesota

assessment. For the subsequent assessments by MPCA, MDH, and other researchers, only key outcomes are included, but references and links to the relevant reports and publications are provided for further details.

Materials and methods for phase I 2002–2006

All samples (soil, sediment, landfill leachates, ground water, sewage sludge, landfill gas condensate, surface waters, and fish) were collected by MPCA staff using sampling methods developed specific for PFCs. The Minnesota Department of Natural Resources assisted the MPCA staff in fish sampling procedure. Analysis of 14 PFCs, including PFOS and PFOA, was performed by AXYS Analytical Ltd using liquid chromatography tandem mass spectrometry (LC-MS/MS), using approved methodologies for soils, water, fish, and other media (Oliaei et al. 2006). Quantification of PFCs was performed by isotope dilution method with isotope labelled standards. Instrumental analyses were performed by LC-MS/MS.

Water was analyzed using AXYS Method MLA060: analytical procedure for the analysis of PFCs in aqueous samples by LC-MS/MS. Soil samples were obtained by soil

borings. Soils were analyzed by AXYS PFC analytical method for soils.

Minnesota Department of Natural Resources staff assisted the MPCA staff with fish sampling procedure (Oliaei et al. 2006). In total, more than 200 fishes were collected from Mississippi River and Lake Superior. Fish blood was obtained by live caudal extraction. Fish were described by species and measured for length, wrapped in "pre-washed" aluminium foil, and frozen prior to shipment for analysis by AXYS Analytical Services Ltd. Fish weight, gender, length, age, and lipid content was performed by AXYS. Analysis of fish tissue was performed by AXYS method MLA-043, analytical procedure for the analysis of perfluorinated organic compounds in tissue samples by LC-MS/MS. Whole fish blood was analyzed by AXYS Method MLA-049, analytical procedure for the analysis of perfluorinated organic compounds in fish whole blood by LC/MS-MS. AXYS analyzed 12–14 PFC in all water and fish samples. The reporting level is the limit of quantitation, defined as the lowest non-zero calibration standard having accuracy of 100±30 %.

Results and discussion

The assessment and the outcome described below are structured according to the mass flow/life cycle of the contaminants:

- Contaminated production site and landfills,
- Releases from waste water treatment plants,
- Ground and surface water pollution,
- Drinking water and fish/food contamination, and
- Exposure to the population (Fig. 1).

The MPCA and MDH have established websites,[2] [3] with reports on their efforts and progress.

Contaminated production site and landfills

Following the MPCA investigation by Oliaei et al. (2006) and subsequent studies (MPCA 2008a, b; MDH 2012), four disposal sites have been evaluated for PFC contamination: the Washington County Landfill, the 3M Oakdale disposal site, the 3M Woodbury disposal site, and the 3M Cottage Grove production site (Figs. 2 and 3). The Pine Bend Landfill where sludges generated from the 3M wastewater treatment plant were deposited has also been studied.

Washington County closed landfill

The Washington County landfill was constructed without a liner or leachate management system. In spite of this, 3M disposed of PFC production wastes (and other industrial wastes) during the operational period from 1969–1975.

High levels of PFOS and other PFC contamination were found in the groundwater underlying the landfill in 2004 (Oliaei et al. 2006; Fig. 3). PFOA and PFOS concentrations in groundwater down-gradient were initially reported at 42,000 and 2,700 ng/l, respectively. These exceeded the then groundwater criteria of 7,000 and 1,000 ng/l and are much higher than the 2009 drinking water criteria of 500 and 300 ng/l (ATSDR U.S. Department of Health and Human Services 2009). Perfluorobutanoic acid (PFBA) was found to be highly mobile and was present in down-gradient groundwater at 1,170,000 ng/l. A drinking water criterion of 7,000 ng/l was later established for PFBA with the same value proposed for PFBS (as reviewed by Wilhelm 2010[4]). PFC migration into groundwater from the site also caused contamination of numerous down-gradient drinking water wells. This widespread contamination resulted in an MPCA program to provide alternate water supplies or individual activated carbon treatment systems.

A pump and treat system was installed in 1981 after volatile organic carbons (VOCs) had been found in groundwater below the site. This included a spray stripper system where contaminated groundwater was sprayed into the air to volatilize and remove the VOCs. The investigation revealed that ponded stripper water contained 1,700 ng/l PFOS, 15,000 ng/l PFOA, and 352,000 ng/l PFBA. These were lower levels than source groundwater used in spray stripping and suggested that PFC losses to the atmosphere occurred via aerosols and volatilization of PFCs during the spray stripping (Oliaei et al. 2006). PFCs were also found deep within the soil profile, likely due to the spray stripping system together with continuous migration over the then 25 years of operation (Figures S1 and S2 in the Electronic supplementary material). Landfill gas condensates collected from the landfill are treated at the main Twin Cities Minnesota metropolitan wastewater treatment facility.

The Washington County landfill is currently being remediated, with all the waste being moved into new landfill cells installed with double liners and leachate collection/leak detection systems. Completion is expected in October 2012.

[2] http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/index.html

[3] http://www.pca.state.mn.us/index.php/waste/waste-and-cleanup/cleanup-programs-and-topics/topics/perfluorochemicals-pfc/perfluorochemicals-pfcs.html

[4] Levels for other PFCs are perfluoropentanoate, 3,000 ng/l; PFHxA, 1,000 ng/l; perfluoroheptanoate, 300 ng/l; perfluorobutanesulfonate, 300 ng/l; perfluoropentanesulfonate, 1,000 ng/l; perfluorohexanesulfonate, 300 ng/l; and perfluoroheptanesulfonate, 300 ng/l, while the precautionary long-term lowest quality goal for all PFCs in drinking water is set to 100 ng/l (Wilhelm 2010).

Pine bend landfill

3M disposed of wastewater treatment plant sludges at the Pine Bend Landfill. The landfill has both lined and unlined areas. Leachates from the landfill contained high levels of PFCs with PFOA, PFOS, and perfluorohexanoic acid (PFHxA) in leachate up to 82,000, 31,000, and 29,000 ng/l, respectively, and total PFCs up to 178,000 ng/l. PFCs were also detected in groundwater, with higher levels in down-gradient wells (PFOS and PFOA at 110 and 1,600 ng/l, respectively), indicating migration of PFCs from the landfill to groundwater.

Gas condensate generated from landfill gases is collected and conveyed to leachate storage tanks, and this leachate is treated at the Twin Cities Minnesota main metropolitan wastewater treatment plant. PFOA, PFOS, and PFHxA in gas condensate were found at levels of 84,000, 30,000, and 38,000 ng/l, respectively, with total PFCs up to 194,000 ng/l (Oliaei et al. 2006). High PFC levels in gas condensate (Figure S3, Electronic supplementary material) suggest that PFCs could be released to the atmosphere through emission of landfill gases. This is consistent with results of elevated atmospheric PFC levels around landfills in Germany (Weinberg et al. 2011). The collected landfill gases are flared. We believe that this is the first study where PFCs have been analyzed in landfill gas condensates. To our knowledge, no study has been performed which evaluates the destruction efficiency of PFOS/PFOA and other PFCs in landfill gas condensates.

3M Oakdale disposal site

The Oakdale disposal site is an unlined dump with no leachate collection that overlies a relatively high groundwater table. 3M disposed of industrial and PFC wastes at this site between 1956 and 1960. A groundwater recovery system has been operating since 1985 to control shallow groundwater impacted by VOCs migrating from site. PFOS and PFOA were found at elevated levels in groundwater underlying the site in 2004. In 2005, four municipal wells from the City of Oakdale were also found to be contaminated with PFC that exceeded health-based drinking water criteria as assessed by MDH. It is likely that Oakdale residents had been drinking PFC contaminated water for many years. 3M entered into an agreement with the City of Oakdale to install a carbon treatment system to reduce the levels of PFOA and PFOS to below the MDH thresholds for PFOA and PFOS, and an activated carbon system was installed at a cost of about $2.5 million to treat the supply in late 2006. Levels are falling only very slowly, and as groundwater flow rates are generally slow, contaminated sites will cause problems by dispersing slowly and remaining present for decades (Eschauzier 2012).

The Oakdale disposal site is currently under remediation to include enhanced activated carbon groundwater recovery treatment together with limited excavation of higher level PFC-contaminated soils.

3M Woodbury disposal site

An August 1992 report "3M Woodbury, Minnesota Site History" estimated that 3M disposed of approximately 150,000 m^3 of scrap wastes, including waste adhesive, rolls of film, rags, resins, and off-specification materials, approximately 1,500 m^3 of liquid waste solvents (of which 750 m^3 was isopropyl ether), and 14,000 m^3 of wet scrap, at the 3M Woodbury disposal site (3M 2012). The site was used by the 3M St. Paul and Cottage Grove (Chemolite), Minnesota facilities between 1960 and 1966 (Weston 2007). A ground-water extraction system was installed at this site by 1973 since when extracted ground water has been pumped via pipeline to the 3M Cottage Grove manufacturing plant, where it is used as cooling and process water. In 2005, PFOS, PFOA, and other PFCs were detected in groundwater under the Woodbury site (Fig. 3). Remediation of the site is underway, with enhanced groundwater extraction and some excavation of contaminated soils.

3M Cottage Grove production facility

The 3M Center at Cottage Grove, Minnesota, formerly known as the 3M Chemolite plant is located adjacent to the Mississippi River (Figs. 2 and 3) and has been in operation since 1947. The plant produced PFOA- and PFOS-related fluorochemicals between about 1950 and 2002. Past methods of PFC waste disposal included disposal of PFC residuals and sludges along with other solid wastes, at several below-grade disposal areas within the plant site (3M 2012). All of these disposal areas were unprotected and unlined, thus allowing PFC to easily mobilize into the underlying groundwater (Fig. 3). Investigations by 3M in accordance with MPCA instructions found soils within these disposal areas to be highly contaminated with PFOS and PFOA. Groundwater underlying the site, which flows directly to the Mississippi River, was also found to contain very high levels of PFOS and PFOA.

The 3M site is currently being remediated with enhanced activated carbon groundwater treatment and excavation of the most contaminated soils in certain waste disposal areas. Some sediments in a river cove area receiving 3M wastewater discharge flows with high PFC levels will also be removed.

Waste water treatment plants

Water resources are a final sink for PFOS, PFOA, and other perfluorinated sulfonates and acids. The releases via waste

water treatment plants (WWTP) from industrial discharges as well as domestic wastewaters play a key role for the pollution of surface waters (Ahrens et al. 2009; Husset et al. 2008; Oliaei et al. 2006; Roads et al. 2008; Xiao et al. 2012). The 3M PFC facility in Cottage Grove was the primary pollution source of PFCs discharged by WWTPs to the Mississippi River in Minnesota. Municipal WWTPs, including the Minnesota Metro WWTP, discharged considerably smaller amounts:

Metro wastewater treatment plant

The Metro WWTP is the largest municipal WWTP in the Twin Cities metropolitan area and treats about 757,000 m^3 per day of wastewater, discharging its effluent to the Mississippi River. The Metro plant was chosen for the study because it treats the Pine Bend Landfill leachates, in addition to a wide range of industrial process wastewaters and domestic wastewaters likely to contain PFC residuals (Oliaei et al. 2006). The WWTP effluent was found to contain relatively low levels of PFOS and PFOA at 81 and 78 ng/l, respectively (Oliaei et al. 2006). PFOS and PFOA levels increased through the system, suggesting the degradation of precursor PFC to PFOS and PFOA. PFOS and PFOA levels in secondary sludge were 309 and 22 ng/g, respectively, with PFOS and PFOA in biosolids at 80 and 11 ng/g, respectively. Based on the limited substance flow analysis, it was estimated that about 10 % of the PFC load to the Metro WWTP stem from PFCs in the leachates of the Pine Bend Landfill. It is likely that PFCs in consumer products released from private households, and possibly other industrial sources, as well as runoff from contaminated soils (see below) represent a significant share of PFCs in the WWTP effluent from this plant.

The Metro WWTP disposes and treats sludges via incineration. Best available techniques sewage sludge incineration is normally operated at temperatures around 850 °C. But due to energy considerations, lower operation temperatures in sewage sludge incineration are often applied. Therefore, the destruction efficiency of the highly stable PFCs in sewage sludge incineration needs further assessment both here and in similar plants.

3M Cottage Grove wastewater treatment plant

The 3M WWTP at Cottage Grove treats organic process wastewaters from the 3M facility using a conventional activated sludge system followed by an activated carbon filtration system. In 2005, the total concentration of the 13 PFCs in the 3M WWTP final effluent to the river was 291,300 ng/l. PFOS and PFOA were 19,200 and 62,400 ng/l, respectively (Oliaei et al. 2006). The highest PFC levels in the effluent were for PFBA and PFBS at 80,600 and 104,000 ng/l, respectively, possibly reflective of the four-carbon PFC production that was substituted for PFOA- and PFOS-related PFC production at the end of 2002. PFOS and PFOA increased in concentration through the WWTP activated sludge system, likely due to degradation of PFOS and PFOA precursors, as observed in other studies (Dinglasan et al. 2004; Rhoads et al. 2008). Based on this limited analysis, it appears the activated carbon system was relatively efficient in removal of PFOS at 95 % but less so for carboxylic PFC with PFOA removal at 79 % and PFBA removal at 42 %. These removal rates are based on only one sampling campaign.

The 3M plant cooling water was used for non-contact cooling at the plant and was sourced from the 3M Woodbury Landfill pump-out system along with groundwater underlying the plant site together containing 30,460 ng/l total PFCs. The 3M WWTP discharges about 15,000 m^3 per day of cooling water and 15,000 m^3 of treated wastewater. Limited 3M discharge data prior to the 2002 termination of PFOA- and PFOS-related production indicate that very high levels of PFOS have been discharged to the river—with average PFOS levels of 1,403,000 ng/l during Jan–Mar 2001; 262,000 ng/l in Sept–Oct 2001; and 550,000 ng/l in Dec 2002. In 2007, MPCA conducted further measurements of PFCs in influent, effluent, and sludge at WWTPs across the state of Minnesota (MPCA 2008b). This study confirms earlier findings. The samples collected below the Metropolitan WWTP (MS/MN-19; Figure S1, Electronic supplementary material) and adjacent to a major chemical manufacturer showed higher PFC concentrations than samples collected upstream of this area. The survey also detected elevated PFOS at a WWTP receiving effluents from a chromium plating industry (Minnesota Pollution Control Agency 2008a, b).

In a recent study assessing a wide range of WWTPs in Minnesota, elevated levels of PFOS, PFOA, and PFHxA in influent have been found in 18 out of 37 WWTPs (49 %) (Xiao et al. 2012). Two WWTPs related to 3M sites were also found with a PFOS-dominated pattern and one with a PFOA-dominated pattern; however, both had influent below 100 ng/l PFC (Xiao et al. 2012). The highest PFOS release in this recent study came from a WWTP impacted by plating industry. Xiao et al. (2012) did, however, not report on the short-chain PFBA and PFBS which are main products/by-products at the production plant, and products have been major contaminants in the former monitoring with the lowest removal efficiencies (see above).

That the 3M Cottage Grove wastewater treatment plant has continued to release PFCs into the Mississippi River is officially documented by the National Pollutant Discharge Elimination System discharge monitoring report for the period January 2007 through July 2010 submitted by 3M (Minnesota Pollution Control Agency 2011). The average PFOS levels calculated from these data were 583 ng/l for 3M process wastewater discharge (SD001 in report) and

1,363 ng/l at 3M cooling water discharge (SD002 in report). PFOA averaged 2,989 ng/l at SD001 and 2,463 ng/l at SD002 for the same period.

Ground water and drinking water

Since 2004, PFOS and other PFCs have been found to have contaminated drinking water supplies in parts of the East Metro Twin Cities area as a result of mobilization and release of PFCs from the contaminated landfills. Over 1,200 private wells were sampled, along with more than 50 community wells (Kelly 2010). Numerous drinking water wells in the Lake Elmo area were found with PFC levels (PFOS, PFOA, PFBA) exceeding relevant health based drinking water criteria (USEPA 2009) and were placed on alternate water supply or fitted with activated carbon treatment systems. A performance evaluation on the removal of PFCs with point-of-use water treatment devices has been undertaken (Olsen and Paulsen 2008). PFBA is the primary pollutant in ground water contaminating large areas of the ground water (Fig. 2). It was ubiquitously found in private wells and has been detected in at least four community wells and therefore appears to be the most mobile PFC. Over 90 drinking water well advisories remain in effect for the region. Citizens have therefore been exposed to PFCs via ground and drinking water contamination exposure pathways (see below and Electronic supplementary material). PFC concentrations currently appear to be stable or trending downwards (Kelly 2010). Elevated serum concentrations of PFCs have been linked to contaminated drinking water supplies with evidence showing that even exposure to low levels of contamination can substantially increase total human exposure (Post et al. 2012). Chronic human exposure to PFOA-contaminated drinking water has been shown to increase the serum PFOA concentration, by approximately 100 times the drinking water concentration (Post et al. 2012). Serum levels of young children have shown even greater increases (Post et al. 2012). Post et al. (2012) calculates that drinking water concentrations of 1, 10, 40, 100, and 400 ng/L are predicted to contribute about 2.4 %, 20 %, 50 %, 71 %, and 91 % of total exposure, respectively, in populations with a background serum level of 4 ng/mL from non-drinking water sources.

The use of fire-fighting foams containing PFOS/PFC and the associated training sites are also known to have resulted in PFOS and other PFC contamination (Moody et al. 2000, 2003; Weber et al. 2010). The MPCA has initiated the assessment of fire-fighting training sites and fire accident sites where class B fire-fighting foams have been used (Minnesota Pollution Control 2008a, b).[5] By June, 2011, a good overview of these polluted sites had been established (Antea Group 2011). While some environmental contamination has been discovered in Minnesota via this source (Antea Group 2011), the contamination from the direct release of former 3M production and wastes is still the primary pollution source for ground and drinking water in Minnesota.

Mississippi River water and sediments

PFC were analyzed in Mississippi River water, sediment, and fish near to and downstream from the 3M PFOS/PFC production and wastewater treatment plant discharges in the first PFC assessment phase (Oliaei et. al. 2006) (Fig. 2).

PFOS and other PFCs in water

PFOS was detected at 6 and 15 ng/l in the river downstream of the plant and PFOA at 35 ng/l just downstream in pool 2. The surface water from a cove into which the 3M plant wastewater directly discharged contained PFOS, PFOA, PFHxS, and PFBS up to 18,200, 3,600, 9,700, and 89,800 ng/l, respectively, with total PFCs analyzed at 121,370 ng/l. Common duckweed (*Lemna minor*) in the cove area contained 264 ng/g PFOS and 405 ng/g total PFCs.

In 2009, PFOS and PFOA were determined by MPCA studies at higher levels in the river water, averaging 90 and 15 ng/l for PFOS and 94 and 17 ng/l for PFOA, at two stations just downstream of the 3M plant in Mississippi River pool 2 (Minnesota Pollution Control 2010a, b).

A more comprehensive assessment by USEPA of PFOS/PFCs in the Upper Mississippi River Basin on the Mississippi and Illinois rivers revealed an initial decrease in concentrations of PFCs, especially PFOS and PFBA, in river water downstream of the Minnesota metropolitan area followed by a steady increase in the total estimated mass flux. This suggested multiple sources of wastewater discharges and non-point sources in the Mississippi River basin downstream (Nakayama et al. 2010), in addition to the inflow from the 3M Minnesota PFC facility. It is notable that the PFBA levels in the river are a factor of a hundred greater than PFOA. A recent study in the Minneapolis area suggests that storm water runoff from industrial and commercial sources using PFC products may be a significant source of PFCs (primarily PFOS and PFOA) to the Metropolitan area lakes (Xiao et al. 2012).

PFCs were analyzed in the top 10 cm of sediment cores of the river and cove near the production plant. PFOS levels were at 1.6 ng/g in sediment core upstream of the plant, and 27.9, 8.3, and 1.7 ng/g in cores downstream of the plant. PFOS in the cove sediment core was 99 ng/g with total PFC concentration at 188 ng/g. Therefore, the cove sediments at the 3M plant may pose a continuing source of PFOS contamination to benthic organisms and fish.

[5] http://www.health.state.mn.us/divs/eh/hazardous/topics/pfcs/classbfoam.html

PFOS/PFCs in fish in Mississippi River and Minnesota lakes and sources

Fish tissue (fillets), blood, and livers were analyzed to determine whether fish PFC levels represented a source of risk for human consumption (Oliaei et al. 2006; Minnesota Pollution Control Agency 2009, 2010b). The fish monitoring efforts of the MPCA resulted in Fish Consumption Advisories for fish in pools 2 through 6 of the Mississippi River (Minnesota Department of Health 2009). This fish consumption advisory recommends eating no more than one meal of fish per week when PFOS levels in fish are above 40 ng/g and eating no more than one meal per month when PFOS levels are above 200 ng/g (Minnesota Department of Health 2009).

In the first survey, fish were collected from two areas (pools 2 and 4, Lake Pepin) in the Mississippi River near and downstream of 3M Plant in August 2004 and October 2005, respectively (Figs. 4 and 5). In pool 2, PFOS levels in 95 % of fish samples were above 40 ng/g of the later established fish advisory (Minnesota Department of Health 2008a, b) for one meal per week, and 38 % of fish were above 200 ng/g the criteria for one meal a month (Fig. 4), and this share also remained high for the following years (Fig. 6).

PFOS in fish collected in pool 4 approximately 60 km downstream of the PFC production plant contained lower levels of PFOS, yet all sampled fish still exceeded fish consumption guidelines of 40 ng/g while none of the sampled fish exceeded the 200 ng/g threshold (Fig. 5).

Very high PFOS levels were found in fish liver and fish blood in the first survey (Figures S4 to S6 in Electronic supplementary material). The PFOS level in a blood sample from a 1-year-old white bass in pool 2 was 29,600 ng/g. This is, to the best of our knowledge, the highest PFOS level found in any animal blood worldwide. PFOS was found up to 6,350 ng/g in the liver of a smallmouth bass. This is more than three times the highest PFOS levels found in fish livers (maximum, 1,800 ng/l) downstream of a site contaminated with PFOS from fire-fighting foam at Toronto airport (Awad et al. 2011).

Subsequent follow-up studies by the MPCA in 2008 and 2009 expanded PFC fish tissue analyses in the Mississippi River (Minnesota Pollution Control Agency 2009, 2010a, b). Fish were analyzed for PFAS over an approximate 160 km reach of the Mississippi River downstream of the 3M plant.

Certain species appear to accumulate higher concentrations of PFOS (smallmouth bass, bluegill, white bass, and freshwater drum) (Figs. 4 and 5). A similar observation was made by Delinsky et al. (2010). The typical pattern of bioaccumulation for organic pollutants appears to not be followed, and there was no correlation between age, weight, and lipid content and PFOS concentrations within fish species. There is also high variability in PFOS concentration within age classes for most fish species, especially freshwater drum (MPCA 2009). The reasons for these differential PFOS concentrations between and within species are unknown.

We performed statistical analysis (ANOVA) of fish PFOS levels in smallmouth bass, the most comprehensively analyzed species, for years 2004, 2005, 2006, 2008, and 2009 in the Mississippi River pool 2 areas close to the 3M plant, using the phase I and subsequent MPCA fish PFC data. We did not find a significant change in PFOS levels in smallmouth bass over this period ($p>0.05$). This is consistent with similar findings of MPCA on distribution of PFCs in fish from Minnesota lakes and rivers (Minnesota Pollution Control Agency 2010b). We also performed statistical trend analysis to assess for change in number of smallmouth bass exceeding 200 ng/g PFOS (the once-per-month fish consumption advisory limit) in pool 2 areas in proximity of the 3M plant and found no reduction or time trend in fish exceeding 200 ng/g PFOS (Pr $chi^2>0.4031$) (see Fig. 6). We did not conduct trend analysis for >40 ng/g PFOS in smallmouth bass since all fish tested exceeded 40 ng/g PFOS, the once per week fish consumption advisory, for all years in pool 2 the locations proximate to the 3M plant. Based on the study period, these findings suggest that reduction in PFC concentrations in the discharge from the 3M plant (and termination of PFC production in 2002) has not had an appreciable affect (reduction) on PFOS levels in fish (smallmouth bass) in proximity to the 3M plant yet.

Another recent study by USEPA of fish in the Mississippi River confirmed high PFC levels in Mississippi pool 2 with up to 2,000 ng PFOS/g (Delinsky et al. 2010). The data base from this study (type and number of fish) was however too scarce to compare, e.g., average levels.

A review for 3M by Exponent Company in 2011 suggested a statistically significant reduction of PFOS in 2011 versus 2009 for Mississippi River pool 2 fish smallmouth bass (Exponent 2011). However, this study compared only 2009 and 2011, which we believe would not be adequate to conclude (statistically) that a trend in fish PFOS contaminant levels is actually occurring, especially considering the high variability of PFOS concentrations in fishes. We did not have access to the exponent raw PFOS fish concentration data to include the data in our ANOVA and trend analyses.

Based on our statistical analysis of available fish raw data (as described above), we find no basis at this time for any reduction in the present level of fish. More robust contemporary data are needed to reach more firm conclusions on time trends.

There is uncertainty as to the relative contribution of PFOS sources responsible for these still-high levels of PFOS in fish close to and downstream of the 3M plant. A specific

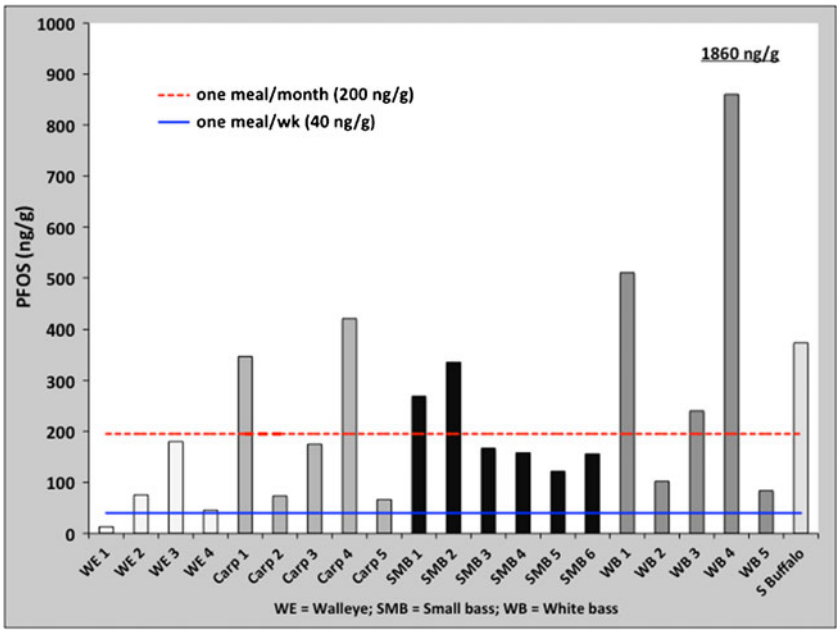

Fig. 4 Total PFOS (nanograms per gram) in fish fillets of different species in Mississippi River pool 2 (2005)

study would probably be needed to evaluate relative contributions of the possible PFOS sources such as the current 3M wastewater discharge mentioned above, the contamination of sediment reservoirs, or the run-off from soils or inflow from polluted ground water. Such a study could be a base to decide then on discharge limits or sediment remediation needs.

Fish in several lakes in the Metropolitan area were also found to contain high levels of PFOS, frequently above the 40 ng/g advisory level, and this also resulted in the imposition of fish consumption advisories (Minnesota Pollution Control Agency 2008a, b). A recent study showed that lakes in the non-metropolitan area of Minnesota further from the 3M facility had low PFOS levels, and fish collected from 52 of 59 lakes (88 % of lakes sampled) had PFOS levels below 3 ng/g (Delinsky et al. 2010). In that study, only PFOS concentrations from McCarrons Lake, located in the metropolitan area, and Zumbro Lake, with a specific point source, were above 40 ng/g (Delinsky et al. 2010) (see below).

A direct impact from 3M or related landfills via water pathway could be established for only a few of the contaminated lakes in the metropolitan area. The likely source of the PFOS contamination of Lake Elmo, for example, is the surface drainage from the Oakdale disposal site described above. Lake Elmo is also hydrologically connected to the Jordan aquifer, which in turn is contaminated by PFC

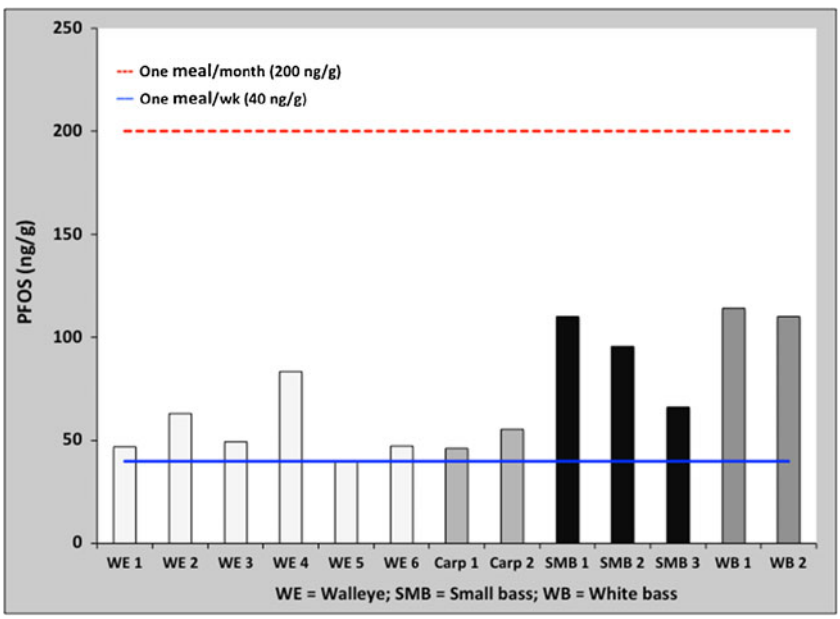

Fig. 5 Total PFOS and PFAS in fish fillets (nanograms per gram) in Mississippi River pool 4 (2005)

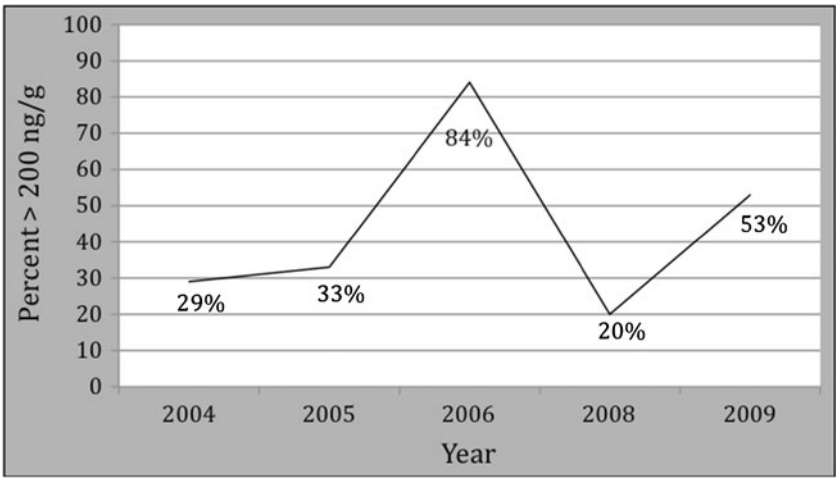

Fig. 6 Percent of smallmouth bass tested exceeding 200 ng/g (fish consumption advisory limit of one meal per month) in pool 2 proximate to 3M facility

releases from the Washington landfills associated with 3M. For most lakes in the metropolitan area, however, no direct connection from the 3M plant or related landfills via direct waste water pathway could be established (Minnesota Pollution Control Agency 2008a, b; Xiao et al. 2011). The lakes which have been affected by PFC contamination are mainly those within a radius of approximately 30 km of the 3M production plant and landfills. Contamination from historic 3M PFOS (precursor) air emissions and deposition to the lakes and soil with further run-off from soils with storm water to lakes appears to be a plausible contamination pathway of these lakes.

The importance of storm water run-off was recently established, and PFOA was found in all samples with the highest PFOS levels reported in storm water from an industrial site in Minnesota (Xiao et al. 2011). PFCs in storm water runoff from an industry using PFC chemicals were also found to be responsible for PFOS contamination of Lake Calhoun (MPCA 2008a, b; Xiao et al. 2011). McCarrons Lake, one of the two contaminated lakes in Delinsky study (2010), is located in the Minneapolis–St. Paul metropolitan area. Lake Zumbro, the other impacted lake, is approximately 100 km south of the 3M production plant. The likely source for the lake is a PFOS discharge from Pine Island plating plant into the Zambro River flowing into the lake. Additionally, the Rochester WWTP discharging upstream of the lake may have had an additional contribution, since PFOS has generally been found in municipal WWTP effluents (Husset et al. 2008; Ahrens et al. 2009).

The postulated pollution pathway of lakes via atmospheric deposition of PFC air emissions and additional runoff of such deposition imply soil contamination in the wider surrounding areas of PFC production plant. Data from the vicinity of a 3M plant in Zwijndrecht/Belgium (D'Hollander et al. 2011), a PFC factory in Wuhan/China (Wang et al. 2010), and PTFE/PFBS in Fuxian/China (Bao et al. 2011) reveal pollution in soil around PFC production factories. PFOS levels in three soil samples in Zwijndrecht (Belgium 3M factory) were between 21.3 and 33.7 ng/g while soils from other Belgium cities were mostly below 1 ng (D'Hollander et al. 2011). The 29 Belgium soils were sampled at sites where free-range chickens foraged. A significant positive correlation was found for PFOS concentrations in eggs and soil (Spearman's rank correlation, r=0.66, α=0.05). PFOS levels in eggs produced on the three contaminated soils in the vicinity of the Belgium 3M factory were high (110 to 3470 ng/g) (D'Hollander et al. 2011). This indicates that soils around the Belgium 3M plant are contaminated and were of relevance to human exposures through food pathways. Furthermore, measurements of rain water in Zwijndrecht/Belgium revealed high levels (61.4 to 119.7 ng/l) of PFOS while rain in other cities was mostly around or below 1 ng/l (D'Hollander et al. 2011). However, there is no comprehensive study on soil pollution or fate for human exposure for the Belgium 3M plant. There have also been no studies to date modelling potential PFC air emission pathways from the 3M Minnesota facility (or emission source such as the Washington County Landfill) to surrounding soils and surface waters and no assessment of potential impacts upon foods grown on any impacted lands. In one large area close the Washington County Landfill, vegetables are grown on many plots by Hmong families (Electronic supplementary material, Figure S7). The Minnesota Department of Health (2010) announced a research project on soil contamination for completion in 2011, but no data on this soil survey have yet been published.

In addition to soil pollution via atmospheric deposition pathway, the contamination of soils and lakes via application of contaminated sewage sludge or "bio-solids" and run-off needs to be assessed. The application of PFOS/PFOA and other PFC polluted sewage sludge has resulted in contaminated soils at other sites (Kroefges et al. 2007; USEPA 2012; Washington et al. 2010; Yoo et al. 2011) and via runoff; this has also contaminated surface water and drinking water reservoirs (Skutlarek et al. 2006; Kroefges et al. 2007). Sewage sludges are and have been applied as bio-solids in Minnesota, but no documentation is available. An

assessment of former application of sewage sludge, in particular from the 3M WWTP, would be important to assess the contribution to the contamination of soils and related ground water and surface water, as was performed in the case of Decatur in Alabama (USEPA 2012; Washington et al. 2010).

PFC levels in the population and exposure

The U.S. National Health and Nutrition Examination Survey (NHANES) data indicate that mean levels of PFOS, PFOA, and PFHxS in the general U.S. population older than 12 years declined between the sampling periods of 1999–2000 and 2003–2004 (Calafat et al. 2007). Presumably, the declines were due to the cessation by 3M of PFOS and PFOA production in 2002. Since 2003–2004, PFOS continues to show reductions in blood serum levels. However, PFOA, PFNA, PFDeA, and PFHxS in data from the Centers for Disease Control and Prevention show increases in blood serum concentration levels since 2003–2004, based on comparison with NHANES 2007–2008 data (Centers for Disease Control and Prevention 2012). PFNA increased by approximately 50 %, and PFDeA increased by 60 % over 4 years in NHANES.

To date, human exposure assessment (Fig. 1) in Minnesota has focused largely on drinking water (Minnesota Department of Health 2012) and primarily in the Metropolitan area (Minneapolis–Saint Paul). The Oakdale municipal well system, as noted above, was found to be contaminated with PFCs, and the MDH conducted a biomonitoring survey of 196 participants in households served by the city water supplies (Kelly 2010). This study found PFOS, PFOA, and PFHxS in all individuals and reported that PFOA blood levels were significantly associated with PFOA levels found in the drinking water. The PFOA geometric mean was 15.4 ng/mL (range, 1.6–177 ng/ml), about four times the NHANES[6] geometric mean of 3.9 ng/mL (range, 0.1–77.2 ng/mL). The PFOS geometric mean was 35.9 ng/mL (range, 3.2–448 ng/ml), as compared with a NHANES geometric mean of 20.7 ng/mL (range, 0.3–435 ng/ml). PFHxS geometric mean was 8.4 ng/mL (range, 0.32–316 ng/ml) as compared with NHANES geometric mean of 1.9 ng/ml (range, 0.2–82 ng/ml).

Another survey (Billot 2007, supporting information) reported PFC blood levels in residents from Oakdale, impacted by a 3M landfill (Fig. 2), at even higher levels and which significantly exceeded the U.S. population levels from the NHANES study. In 75 adults, the mean PFOS level was 54.4 ng/ml (range, 8.3–167 ng/ml), and mean PFOA was 36.9 ng/ml (range, 5.5–121 ng/ml). In ten children, the mean PFOS level was 51.0 ng/ml (range, 20.1–180 ng/ml), and mean PFOA was 32.3 ng/ml (range, 13.4–155 ng/ml) (Bilott 2007, supporting information). These mean levels were higher than the highest PFOS/PFOA levels in a Danish cohort study (PFOS maximum level of 45.2 ng/ml and PFOA maximum level of 7.5 ng/l). In the high PFOS–PFOA quartile group from this study, the male reproductive capacity was reduced and the median number of normal spermatozoa in their ejaculate was 6.2 million compared with 15.5 million in the group with lowest blood concentrations (Joensen et al. 2009).

PFOS and PFOA blood levels in residents affected by contaminated drinking water in the Minnesota East Metro area were found to be significantly higher than the general population as described above (Billot 2007, supporting information; Kelly 2010). It is also clear that other individuals living near PFC production sources and contaminated sites have much higher levels of PFCs in their blood serum. No epidemiological studies have been conducted in this affected population to assess any increases in illness incidence or possible physiological effects related to increased exposures to PFCs. Studies of PFC exposures, mainly PFOA, and health effects have been and are conducted for residents living near the DuPont Washington Works PFC plant near Parkersburg, West Virginia (USA), by the C8 Science Panel (http://www.c8sciencepanel.org/, Frisbee et al. 2009). In these studies, the panel found that higher PFOA and PFOS levels were each significantly associated with higher total cholesterol and LDL cholesterol; that higher serum levels of both PFOA and PFOS were associated with a higher risk of excessive uric acid in the blood (hyperuricemia); a small but clear linear association between PFOA and PFOS serum concentrations and ALT, a marker of liver injury; that thyroid disease (based on 61 cases) was positively associated with measured PFOA serum levels in children (with borderline statistical significance) suggesting that exposure during childhood to PFOS and PFNA may be capable of disturbing thyroid hormone levels; an association between cumulative blood levels of PFOA and thyroid disease occurrence in women; and that an increased risk for the more highly exposed in relation to malignant kidney and non-malignant kidney disease could possibly be due to PFOA (C8 Science Panel 2012a, b).

Given elevated levels of PFOS and PFOA found in the blood of East Metro Minnesota area residents together with the large numbers affected, appropriate health studies to evaluate possible health effects of PFOS/PFOA and other PFCs seem warranted.

Studies are also needed to assess whether greater exposures are occurring in particularly exposed minority groups. One example might be the Hmong who grow vegetables at sites located near the Washington County Landfill (Figure S7 in the Electronic supplementary material).

[6] NHANES concentrations likely exemplify U.S. "ambient" general population PFOA and PFOS levels, where individuals are not exposed to contaminated sources.

The human exposure investigations in Minnesota focus mainly on drinking water and the fish advisory. They do not adequately consider other exposure pathways, particularly food, which is normally considered to be the main PFC exposure route (Trudel et al. 2008; Vestergren and Cousins 2009) and which can be impacted by various pathways (Fig. 1), some highly relevant for contaminated areas around PFC producers. The initial soil and egg data from the Belgium 3M location exceed the European Food Safety Authority (EFSA) tolerable daily intake (TDI) (EFSA 2008) with exposure via eggs alone (D'Hollander et al. 2011). This highlights the need for further studies on the impact of soil contamination in the wider vicinity of the 3M facility in Minnesota and other PFOS/PFC production plants together with the related assessment of human exposure pathways (Fig. 1). In addition to soil-related exposure via eggs, exposure via fruits and vegetables can also be relevant, as PFOS and other PFCs can accumulate in plants and related fruits/vegetables (Fischer et al. 2009; Stahl et al. 2009; Weber et al. 2010). Also, cattle grazing on areas where PFC-contaminated sewage sludge has been applied has been demonstrated to be another important contamination pathway for the food chain at another 3M factory in Decatur (Renner 2008). These multiple exposure pathways related to PFC contaminated sites show that large gaps currently exists in the assessment of human exposure in Minnesota. All relevant exposure pathways need to be considered (Fig. 1) for an appropriate exposure assessment of the population around PFC production sites.

Settlement agreement and consent order (State of Minnesota 2007)

It is vitally important to establish legally binding management agreements between governmental authorities, the companies responsible for the pollution, and the owners (if different) for the environmentally sound management and remediation of polluted sites. For transparency, this should require the publication of progress reports available to the public.

In May 2007, 3M and the MPCA entered into a Settlement Agreement and Consent Order for the investigation, assessment, and clean-up of perfluorochemicals at contaminated sites in Washington County, in particular, former disposal areas at 3M Cottage Grove, Woodbury, and Oakdale disposal sites. In 2009, the MPCA approved clean-up plans for these sites, and the remediation at the four major sites began. Since July 2007, quarterly public progress reports have been supplied by 3M to MPCA, detailing progress on clean-up of the contaminated areas, health and toxicological studies, and other matters. Transparency in the approval of clean-up methods and reporting on progress is important to ensure public awareness, input, confidence, and support for the projects. There is still, however, no agreement to undertake epidemiological studies of the exposed population.

Conclusions

The basic assessment methodology described in this paper may serve—with consideration of the recommendations in Electronic supplementary material 1 and with improvements to fill the gaps which have been highlighted—as a model for assessment of other PFOS (and other PFC) production sites[7] in the implementation of the Stockholm Convention. Studies of the impacts of PFOS and other PFC production at the China and Belgium PFOS/PFC sites and data from the assessment of soils in the wider surrounding of the facility and areas where sludges have been applied can be used to plug the missing elements of the MPCA approach. A comprehensive assessment would therefore need to monitor the contamination levels of feed and food including eggs, vegetables, fruits, etc.

While the release vectors "waste water" and "solid waste" (production wastes and contaminated sludges) are reasonably well documented as important contamination pathways, the release vector "air" and associated pollution is less understood. This will therefore need further assessment for PFC production and industrial use, particularly considering that PFCs used today such as telomere alcohols are more volatile than the PFOA and PFOS. Also, the potential role in the pollution of lakes via "air-deposition to soil-run-off" and the alternative former pathway of "sludge application–soil-run off" and lake/ground water contamination need to be assessed/compared.

The studies and assessments illustrate that PFOS and other PFCs deposited at landfills may be easily mobilized via different pathways (leachates, ground water pollution/migration, and atmospheric releases) and that these result in wider environmental and, ultimately, human contamination. The remediation concept at the Minnesota site aims largely on containment of the pollutants. Although remediated PFC-containing wastes may now be deposited in hazardous waste landfills, these landfills will require long-term management, since PFOS, PFOA, and a range of other PFCs do not degrade or require extraordinary long periods to do so. They may often degrade to other more water-soluble PFCs (e.g., perfluorinated sulfonates or acids). Since PFOS and other PFCs will remain long beyond the landfill's engineering systems operational life, the renewal of lining systems and leachate management systems will burden future generations (Weber et al. 2011). Considering that PFOS and other highly persistent PFCs will eventually escape into the environment, the hazardous landfill approach is not necessarily protective in the long-term. Considering these challenges, very careful consideration will need to be given to how best to address both the estimated 26,500 tonnes of PFOS production wastes generated from global total historic PFOS production (Paul et al. 2010) along with the currently

[7] And sites where PFOS and other PFCs have been used in industries

generated PFC wastes. Any solution needs to be consistent with the obligations arising from the Stockholm Convention and consistent with the requirements of sustainable production.

For human exposure, only the drinking water pathway has been assessed, and fish advisories have been issued. Studies from other production sites or contaminated sites revealed that exposure to food (eggs, meat, or fruits/vegetables) are also relevant, and some have lead to exceeding the TDI for PFOS. Therefore, all relevant exposure pathways need to be assessed in Minnesota and for other production/contaminated sites. An integrated exposure and risk assessment near PFC-contaminated sites should include all potential relevant exposure/intake pathways (Fig. 1). No epidemiological study in Minnesota has yet been performed. This is important considering the findings of the C8 project and the negative impacts on, e.g., sperm quality (Joensen et al. 2009), and reduced fecundity (Fei et al. 2009) which have been found in cohort studies at lower contamination levels than those to which residents in the metropolitan area have been exposed. Appropriate studies are needed to better understand the range of potential health impacts to Minnesota East Metro residents including vulnerable groups such as children or groups such as the Hmong minority. Such studies should be considered a priority and integrated with the post-remediation monitoring of the production and disposal sites in order to reduce the harmful legacy of the 3M and other companies PFC pollution to a minimum.

Finally, the environmental concentration of short-chain PFC now often exceeds those of the longer-chain substances in water[8] and other media, yet there is very limited toxicological data for them, and currently no tolerable daily intake has been established (Gellrich 2013). Assessments of health risks should therefore also consider short-chain PFCs as these risks are currently not adequately evaluated.

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