DISCOVERY AND INVESTIGATION OF PFOS/PFCs CONTAMINATION FROM A PFC MANUFACTURING FACILITY IN MINNESOTA – ENVIRONMENTAL RELEASES AND EXPOSURE RISKS

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Introduction

Polyfluoroalkyl compounds (PFCs) are very persistent, and several are toxic pollutants[1]. In May 2009 PFOS and its precursors were added to the Stockholm Convention POPs list[2]. Therefore, PFOS contaminated sites need to be assessed in addition to direct PFOS exposures[3]. PFOS, PFOA, and other perfluorinated acids are present in water in ionic and highly soluble forms, with water resources as a primary final sink. A large part of PFCs are used in numerous consumer goods (e.g. impregnated paper, textiles, leather, furniture) and finally end up in landfills. Due to their high water solubility, PFCs are mobilized and released from municipal landfills[4].

The 3M Company was the primary global producer of PFOS-related PFCs, producing millions of pounds annually at its plants in the United States and Europe. In 2000 3M produced 7.33 million pounds at its plants in the United States and Europe[5]. 3M also produced PFOA at its Cottage Grove plant until the end of 2002 when it terminated production of PFOA and PFOS-related compounds. The production or use of other PFC-related compounds ("4 carbon PFCs") continues today[6]. In addition to residual or by-product releases during production, PFOS, PFOA and other PFXA are the ultimate breakdown products of a range of perfluorochemical. Significant amounts of wastes, residuals, and sludges were generated in production of PFCs and PFC containing products. An assessment from Minnesota Pollution Control Agency revealed that PFC wastes from the 3M production plant in Cottage Grove, Minnesota/USA had been deposited to a large extent in selected landfills and on the production plant property[7].

This paper describes the results of the first comprehensive investigation[7] of releases of past and currently produced PFCs from landfills, wastewater treatment plants, and the Minnesota PFC production plant, and the resulting contamination of the wider environment (groundwater, sediments, surface water, and fish) in Minnesota.

Materials and Methods

All samples (soil, sediment, landfill leachates, ground water, sewage sludge, condensate of landfill gas, fish) were collected by MPCA or Minnesota Department of Natural Resources staff.[7] Soil cores were obtained by soil borings. PFC analysis (up to 14 different PFCs including PFOS and PFOA)[7] was performed by AXYS Analytical Ltd using approved standard methodologies. Analysis and quantification of PFC was performed by LC-MS/MS.

Results and Discussion

The following summarizes the findings of this PFC investigation for selected study sites and environmental media in Minnesota that have been impacted by 3M PFC production in Minnesota.

Washington County Closed Landfill

The Washington County landfill (WCLF) is a 35 acre unlined closed landfill constructed without a leachate management system for prevention of groundwater contamination. During landfill operation from 1969–1975 3M disposed of PFC production wastes (and other industrial wastes). Landfill gases generated were not controlled until 1993 when a gas extraction system was installed. The WCLF is currently being remediated to install liners and leachate collection.

High PFC contamination was found in the groundwater around the landfill. Furthermore, PFCs migrating in groundwater from the site caused contamination of downgradient drinking water PFOA and PFOS in downgradient groundwater, at 42 ppb and 2.7 ppb, respectively, exceeded the pre-existing drinking water criteria of 7.0 ppb and 1.0 ppb, subsequently lowered to 0.5 and 0.3 ppb, respectively[8]. PFBA was found to be highly mobile, and present in downgradient groundwater at 1170 ppb. A drinking water criteria was later established for PFBA at 7.0 ppb, and the same value of 7.0 ppb is proposed for PFBS. Widespread well water PFC contamination resulted in a program that placed wells on alternate water supply or individual treatment systems (activated carbon).

Pursuant to a finding of VOC levels in groundwater below the site in 1981, a pump and treat system was installed that included a spray stripper system where contaminated groundwater was sprayed into the atmosphere to volatilize/remove VOCs for about 25 years. We found that ponded stripper water contained 1.7 ppb PFOS, 15 ppb PFOA, and 352 ppb PFBA, lower levels than source groundwater used in spray stripping, suggesting that PFC losses to the atmosphere may have occurred via aerosols and volatile PFCs during spray stripping. PFCs were found in deep soil profile, likely due to the spray stripping system and continuous migration over the 25 years operation. Landfill gas condensates collected are treated at the MCES wastewater treatment facility (see below).

Pine Bend Landfill (PBLF)

The Pine Bend Landfill PBLF received wastewater treatment plant sludges from the 3M production plant[7]. The PBLF has both lined and unlined areas. The leachates from PBLF contained significant PFC levels with PFOA, PFOS, and PFHxA in leachate up to 82 ppb, 31 ppb, and 29 ppb, respectively, with total PFCs up to 178 ppb. PFCs were also detected in groundwater, with higher levels in downgradient wells (PFOS and PFOA at 0.11 and 1.6 ppb, 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 leachate is treated at the Twin Cities Minnesota main Metro wastewater treatment plant (see below). This is the first study we are aware where PFCs were analyzed in landfill gas condensates. PFOA, PFOS, and PFHxA in gas condensate were found at unexpectedly high levels of 84 ppb, 30 ppb, and 38 ppb, respectively, with total PFCs up to 194 ppb. High PFC levels in gas condensate suggests that PFCs could be released to the atmosphere through emission of landfill gases. The collected landfill gases are finally combusted. Until today no study has been performed to evaluate the effectiveness of such relatively simple landfill gas combustion on the destruction efficiency of the highly stable PFOS/PFOA and other PFCs and possible associated PFC air releases.

Metro Wastewater Treatment Plant WWTP

The Metro WWTP is the largest municipal WWTP in the twin Cities metropolitan area and treats about 200 million gallons per day of wastewater, with effluent discharged to the Mississippi River. The plant uses a biological activated sludge process with sludge treatment. We chose the Metro plant for this study because it treats the PBLF landfill leachates in addition to a wide range of industrial process wastewaters and domestic wastewater. WWTP effluent contained relatively low levels of PFOS and PFOA at 81 and 78 ppt, respectively. PFOS and PFOA increased through the system, suggesting degradation of PFOS/PFOA precursor PFCs. PFOS and PFOA levels in secondary sludge were 309 and 22 ng/g, respectively, and PFOS and PFOA in biosolids at 80 and 11 ng/g, respectively. Based on the limited substance flow analysis we estimated that about 10% of the PFC load to the Metro WWTP stem from PFCs in the PBLF leachates. It is likely that PFCs in consumer products released from private households and possibly other industrial sources represents a significant share of PFCs in the WWTP effluent of this plant.
The Metro WWTP disposes and treats sludges via incineration. Best available technology (BAT) sewage sludge incineration is normally operated at temperatures around 850ºC. 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.

3M Wastewater Treatment Plant (WWTP)

The 3M WWTP treats organic process wastewaters using a conventional activated sludge system followed by an activated carbon filtration system. In 2005 we found that the total concentration of the 13 PFCs in the

3M WWTP final effluent to the river was 291,300 ppt. PFOS and PFOA were 19,200 and 62,400 ppt, respectively. The highest PFC levels in the effluent were for PFBA and PFBS at 80,600 and 104,000 ppt, respectively, possibly reflective of the 4 carbon PFC production that has substituted PFOA and PFOS related PFC production termination at the end of 2002. Also in this WWTP PFOS and PFOA increased in concentration through the WWTP activated sludge system, most probably due to (biological) degradation of PFOS and PFOA precursors. Our preliminary analysis indicated that the activated carbon system was relatively efficient in removal of PFOS at 95%, but less so for carboxylic PFCs with PFOA removal at 79% and PFBA removal at 42%, although these removals were based on only one sampling event.

The 3M plant cooling water, used for non-contact cooling at the plant, also contained PFCs totaling 30,460 ppt. The cooling water source is groundwater pumped from a barrier well system at another closed unlined landfill (3M Woodbury Landfill) where PFC production wastes were disposed in the past. The 3M WWTP discharges about 4 million gallons per day (MGD) of cooling water and 4 MGD of treated wastewater. Limited 3M discharge data prior to the 2002 PFOA and PFOS-related production termination indicate that much greater levels of PFOS were discharged to the river. In Jan-Mar 2001 and Sept-Oct 2001 the average PFOS discharged was about 1403,000 ppt and 262,000 ppb, respectively, and 550,000 ppb in Dec. 2002[9].

Mississippi River Water, Sediment, and Fish

PFCs were analyzed in Mississippi river water, sediment and fish near and downstream of the PFC plant and wastewater treatment plant discharges. PFOS were detected at 6 and 15 ppt in the river downstream of the plant. PFOA was at 35 ppt downstream. The surface water from a cove area that immediately receives the PFC plant wastewater discharge contained PFOS, PFOA, PFHxS, and PFBS up to 18,200 ppt, 3,600 ppt, 9,700 ppt, and 89,800 ppt, respectively, with total PFCs at 1221,370 ppt. Common Duckweed *(lemna minor)* in the cove area contained PFOS at 264 ng/g with total PFCs at 405 ng/g.

We analyzed PFCs in the top 10 cm of sediment cores of the river and cove. 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 PFCs at 188 ng/g. Therefore significant masses of PFOS in the cove sediment may pose a source and reservoir of PFOS to benthic organisms and bottom feeding fish.

Fish tissue (fillets), blood, and livers were analyzed to determine whether fish PFC levels represented a source of risk for human consumption. 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. Elevated levels of PFOS were found in fish, with 40 of 42 fish (fillets) exceeding a Minnesota Department of Health (MDH) guideline, established in 2006, that triggered a fish consumption advisory at 40 ng/g. Elevated PFOS levels were found in liver and fish blood. The PFOS level in one fish blood sample (a one year old White Bass) was 29,600 ng/g, which to our knowledge is the highest PFOS level found in any animal worldwide. PFOS was found at 6350 ng/g in the liver of a smallmouth bass, comparable to the highest PFOS levels found in fish liver worldwide. PFOS in fish collected farther downstream (pool 4) of the PFC plant contained lower levels of PFOS, but still exceeded fish consumption guidelines.

This study, as well as subsequent Minnesota studies[10,11] show that certain species (e.g. Smallmouth Bass, Bluegill, White Bass, Freshwater Drum) appear to contain the highest concentrations of PFOS. The study revealed that PFOS levels did not follow the typical pattern of bioaccumulation for organic pollutants that often increase with age, weight, lipid content, and trophic level. Species specific concentration factors may account for the large differences in PFOS concentrations for different species that reside in the same areas of water. The chemical and physical characteristics of PFCs, with high surface active properties, may affect exposure mechanisms and bioaccumulation, perhaps with higher exposures to surface feeding fish. Alternatively, for bottom feeders sediments may pose a more significant source of PFCs. These considerations need to be taken into account when human exposure risks are established.

From a landfill perspective, this study illustrates that PFCs deposited and released at landfills and a former production site are highly mobile and subject the wider environment to PFC contamination. Substance flows from landfills to leachates to wastewater plants and river, from landfills to groundwater, from landfill gases to atmosphere, or from contaminated ground water sprayed to the atmosphere, reveals multiple pathways in how deposited PFCs at landfills may end up in surface waters and fish, or perhaps in soils possibly posing contamination to vegetables. Human exposure and risk assessments around such contaminated sites to include all exposure pathways including fish consumption, drinking water, soil ingestion, fruit and vegetable consumption, and possibly - with respect to any landfill gas emissions - intake via inhalation near those sites, should be performed to assure adequate safeguards. Minority groups, where applicable, and who may have greater vulnerability of exposure due to their lifestyle and cultural attributes, should be considered.

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Disclaimer - Data used in this study/report was acquired during MPCA studies while the two of the authors are former MPCA staff. The MPCA was not involved with preparing this paper.