Some case studies of local pollution by perfluorinated acids and fluorotelomers in Japan

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Introduction

Perfluorochemicals (PFCs) such as perfluorinated alkyl sulfonates, carboxylic acids, fluorotelomer alcohols and fluorotelomer acids are used in a variety of consumer products to which humans come in contact on a regular basis. However, basic knowledge regarding physicochemical properties and information about sources of human exposures are not well understood, while much concern is focused on risks or hazardous effects. In order to evaluate the potential risk posed by PFCs, carefully designed studies addressing the sources of exposure, bioavailability, ecodynamics, pharmacokinetics and fate are needed. Production and use of these chemicals are under control by most of the industries but there exists some issues pertaining to the information on the production statistics, formulation types, usage, stockpiles of wastes and inventories of all perfluorochemical products in use. Despite the increase in the number of publications in the last five years, information regarding environmental contamination by local point sources are limited, except the reports by 3M Company in the USA. Our agency, AIST, in Japan initiated a research on PFOS, through funding by NEDO, in 2000. Annual meetings for discussion among the agency, PFOS consortium (PFCs producer/user industries) and the Ministry of Economy, Technology and Industry (METI) were held since 2003. As a result of these efforts supporting sustainable and reasonable use of PFCs in Japan, several cooperative projects between the fluorochemical industries and the AIST were initiated to describe case studies of local pollution by PFCs. These studies would help in the understanding of the fate of PFCs in the environment and to form a model for mitigating the releases for sustainable production and use of related compounds by industries. We summarize here three case studies of local PFCs discharge into the environment in Japan.

Case study one : Semiconductor manufacture

It well known that some of PFCs are used in a wide variety of high technology products, such as liquid crystal device (LCD) and semiconductors, for over two to three decades. High performance, photo-resistance of PFOS offers a unique property for its application in chip making. Until now, it is difficult to have a good replacement regent to PFOS for chip making. Based on the cost-benefit analysis, the use of PFOS for some important economic activity such as semiconductor industry (an exceptional use in some of closed plants) was permitted based on the significant new use rule (SNUR) in the USA. There is no such a rule in Japan, but most of the industries have shifted to use photo-resistance without PFOS, recently. This case study provides monitoring data from a semiconductor industry before the change (monitoring survey has been carried in 2003) and provide useful information regarding environmental release of PFCs from a chip making industry that used PFOS as a photo-resistant agent.

Concentration of PFCs in waste water, river water and coastal sea water collected near the semiconductor industry is shown in Figure 1. It is clear that around 30 ng/L of PFOS and 300 ng/L of PFOA were found in waste water from this industry. However, no significant concentrations in the river water were observed because of dilution. We have analyzed several types of exhaust gas from the industry and data are presented in Figure 1.

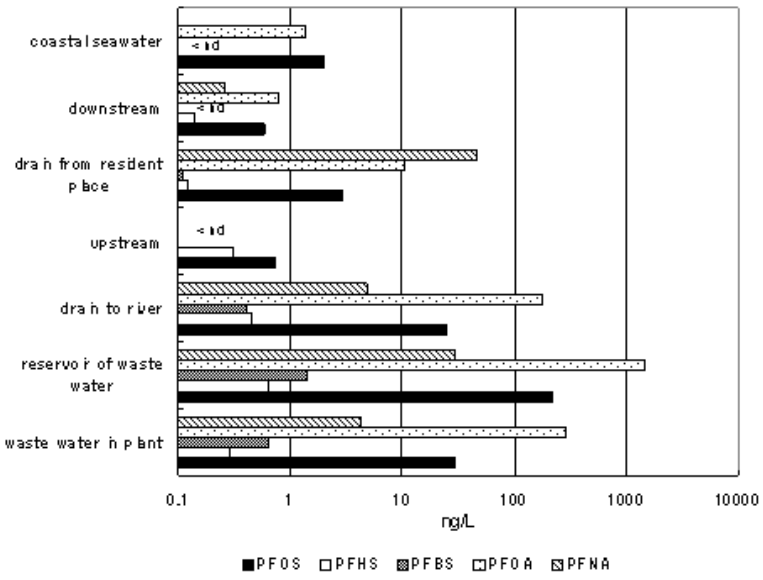

Figure 1 Concentration of PFCs in waste waters from a semiconductor industry and nearby waters

It is interesting to note that not only PFOS but also fluorotelomers and precursors were observed in air samples. It is worth to mention that there were no detectable levels of perfluorochemicals in exhaust gas after charcoal filter treatment.

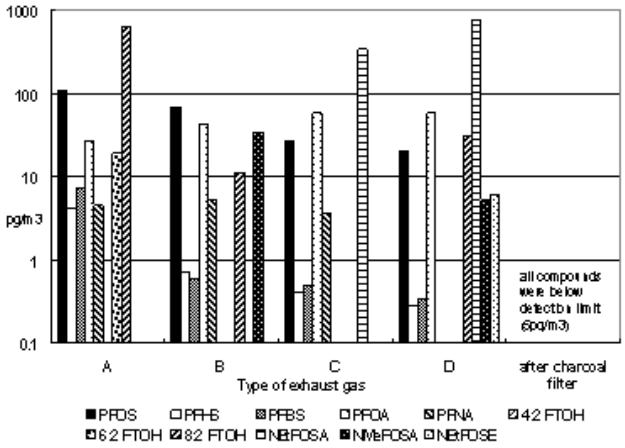

Figure 2 Concentration of PFCs in exhaust gas from several types of processes in a semiconductor industry.

Case study two : Fluoroplastics manufacture

There exists no data regarding PFC contamination arising from the production of fluoropolymer materials. However, considering a wide variety of use of fluoropolymer products, such as weather resistant rubbers, functional plastic materials, it is necessary to obtain information to enable insight into the inventory of PFCs in fluoropolymer materials. A monitoring survey of local point source pollution by PFCs from a fluoropolymer manufacturing plant was conducted in 2004 and 2005. The plant was located in an inland area but the waste water was discharged through a channel into a river. The river empties into coastal seawater. Maximum concentration of PFOA observed was 20 µg/L in a drain from the industry and all C4 to C8 sulfonates and C4 to C18 carboxyl acids were detected at significant levels.

Concentrations of these PFCs decreased to less than 10 ng/L after dilution in river water and water from some channels contained higher concentration than those reported above. This study would enable understanding of environmental kinetics of C4 to C18 perfluorinated carboxyl acids in environment.

Case study three : Unexpected release of fire fighting forms containing PFCs

On September 26, 2003, a magnitude (M) 8.3 offshore earthquake struck Hokkaido, Japan. The earthquake and ensuing tsunami injured hundreds of people and resulted in significant damage to port and coastal communities. Immediately following the earthquake, a major fire occurred at an oil storage facility of a refinery (Idematsu Kosan Company Ltd) located in the west part of Tomakomai, a Pacific coastal city in southern Hokkaido. Forty-five of the 105 oil storage tanks were damaged following the earthquake and resulted in the release of petroleum naphtha, which ignited accidentally. To extinguish two big fires after four days, more than 130,000 L of fire fighting foams (FFF) was delivered and at least 40,000 L was used. Detailed information regarding the type of FFF used was not available, but aqueous film forming foams (AFFF) have been used in the control of fuel-related fires. It was known that PFOS and related perfluorinated acids are a component of AFFF (1). Previous studies have reported on environmental contamination by PFCs due to accidental release of AFFF (2,3). Large amount of release of AFFF in Tomakomai oil refinery fire provided an opportunity to study environmental dynamics of PFCs in the environment. A monthly monitoring survey of the environmental levels of PFCs in the Tomakomai region was conducted since October 2003. Detailed results have been reported elsewhere (4). Estimated simulation of discharge of PFCs in AFFF was shown in Figure 3. The result from this survey was useful for understanding temporal storage of PFCs in cold environment such as snow and inland soil. It is also worth to mention that residence time of 90% of discharged PFOS was less than 30 days in coastal water that compared to longer time (less than 70% after 8 month) in soils of inland area.

It is clear that above information from several case studies are helpful to understand environmental kinetics of PFCs and enough data base of information about life cycle are necessary to make decision regarding sustainable use and development of functional material chemicals for high technology industries.

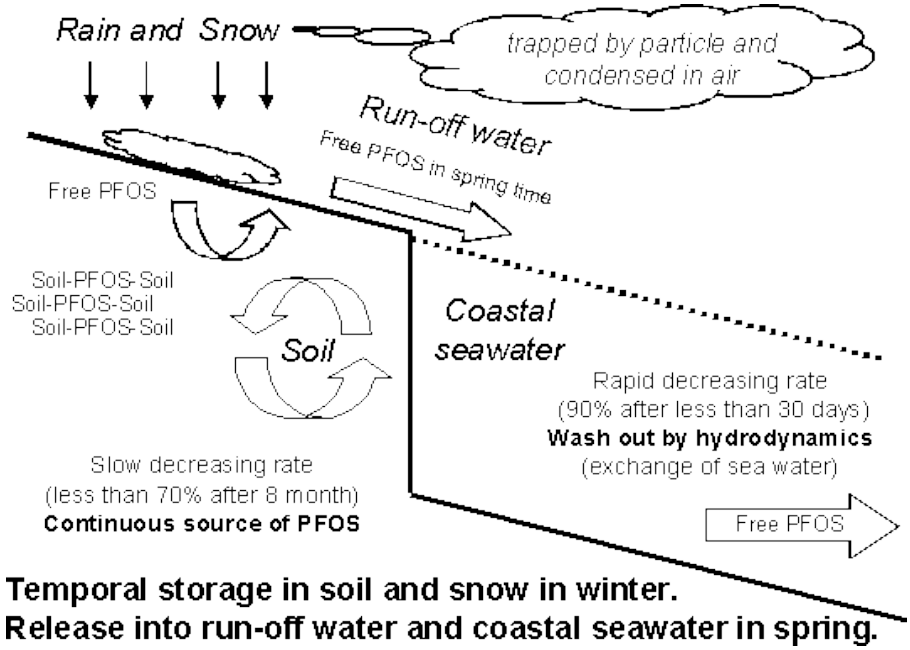

Figure 3 What is happening to perfluorochemicals released in Tomakomai after the fire?

References

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