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[redacted]entally Relevant Properties of 3M Fluorochemicals

Background

3M has manufactured fluorochemicals since the early 1950. During that time, and particularly since the mid 1970s, 3M has developed an understanding of the properties of these compounds. This document summarizes what we know with reasonable certainty about these compounds, and what we still need to learn.

Most of 3M fluorochemicals are made by a process called electrochemical fluorination. In this process, the hydrogen atoms on organic feed-stock compounds are electrochemically replaced with fluorine atoms. One of the most frequently used feed-stocks is n-octanesulfonylfluoride n-$CH_3(CH_2)_7SO_2F$ which is completely fluorinated to form perfluorooctanesulfonylfluoride ($CF_3(CF_2)_7SO_2F$; POSF). Conditions during the electrochemical process are rigorous and lead to many carbon chain rearrangements. Thus, during electrochemical fluorination, many byproducts and waste products are formed. Many of these products are volatile, such as perfluoromethane, and have been vented to the atmosphere. Others are high molecular weight and are disposed of as tars. Other byproducts are incompletely fluorinated and, after partially degradation in destructive stabilization processes, are discharged as water soluble fluorinated waste products. Still other byproducts, such as perfluorooctane, a perfluorocarbon or PFC, are sold as products. (A concern with PFCs It that they are very stable in the atmosphere and have high global warming potentials.) The electrochemical fluorination products and byproducts formed and sold are not pure, but are mixtures of branched and straight chains and the nature of these mixtures may vary somewhat from lot to lot.

POSF and some of its higher or lower molecular weight homologues are the starting compounds for many 3M fluorochemical products. Perfluorooctanoic acid and its homologues are also important 3M perfluorocompounds, but they are not intermediates. Some of the POSF derived products are relatively low molecular weight (~500 daltons) surface active materials and monomers. These POSF derivatives are most frequently fluoroalkylsulfonamides. They are used typically as low MW surfactants or they are joined with other

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monomers to form higher molecular weight oligomers and polymers with a mixture of fluorochemical and nonfluorinated portions. Frequently, ester linkages join the fluorochemical monomers to phosphates or to polymeric and oligomeric urethane or acrylate backbones. The resulting polymers are most frequently used to impart soil, oil, or water repellency to carpet, fabrics, and paper.

3M fluorochemical products are frequently made and sold as emulsions or solutions containing nonfluorochemical components as well as fluorocompounds. Much of the ecotoxicology data that 3M has is on these formulated products, and not on the individual fluorochemicals themselves.

What is Know

Perfluorochemicals are persistent. This is at least true of the perfluorinated portion of molecules that contain both fluorinated and nonfluorinated portions. This is true not only biochemically - no microorganisms have been found that can degrade perfluoroalkyl chains - but chemically as well. Perfluoroalkyl chains are not degraded in the chemical oxygen demand (COD) test. They degrade in high temperature total organic carbon (TOC) analyzers, but not in TOC analyzers that use very reactive chemical and ultraviolet degradation mechanisms. Due to this high stability, inexperienced analysts sometimes reach the misinterpretation that fluorochemicals are biodegradable because no detectable organic carbon remains in a product that contained perfluorinated moieties after biodegradation tests. To date, two carbon or larger perfluoroalkyl moieties have been found to be completely resistant to biodegradation under all aerobic and anaerobic conditions tested.

There is degradation of low molecular weight perfluorosulfonamide derivatives. For example, in vertebrates 2-(N-ethylperfluorooctanesulfonamido)-ethanol (N-EtFOSE-OH) is metabolized to N-ethylperfluorooctanesulfonamide and to other intermediates as it is degraded to form perfluorooctanesulfonate (PFOS). PFOS is not known to degrade further under any natural non-combustion conditions. In biodegradation tests, the biodegradation rates of perfluorosulfonamide derivatives can be slow but is sometimes measurable in laboratory studies. Laboratory tests suggest that the degradation of higher MW fluorochemical products is also slow. However, most of these tests have

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been conducted on formulated products that have other biodegradable components.

Perfluorochemicals are xenobiotic compounds. With the possible exception of perfluoromethane which may have some minor natural sources, all perfluorochemicals are man made and thus new to the biosphere. Some, the ionic and polymeric POSF derivatives, do not have the properties of semi-volatility and fat solubility of other xenobiotic materials of concern, e.g. DDT and PCBs that lead to their distribution and bioconcentration in the biosphere. Perfluorochemicals have properties different from other organic compounds. Most important in addition to their stability is that they may be simultaneously hydrophobic and oleophobic. As a result, many of the quantitative structure activity relationships (QSARs) used to predict properties of other organic molecules do not apply as well to fluorochemicals. Again, this can lead to inaccurate properties estimations by inexperienced practitioners.

Some fluorochemicals have significant biological activity. This is most easily illustrated by the fact that at least two POSF derivatives are used as insecticides. One of these products, PFOS, is the expected "final degradation product" of POSF derived products. Their toxicity varies over a wide range. One fluorochemical surfactant has an LC_{50} to Mysid shrimp of 10 ug/L while other low molecular weight fluorochemicals have aquatic organism LC_{50}s greater than 1000 mg/L. A typical aquatic LC_{50} for a low molecular weight POSF derivative might be in the range of 30 mg/L. High molecular weight derivatives typically have very low toxicity.

Fluorochemicals can bioaccumulate. POSF derivatives have been found in fish at mg/Kg levels near a fluorochemical manufacturing facility. PFOS, the final POSF derivative degradation product, has been found at ug/Kg levels in eagles, at locations well away from major manufacture or application sites.

μg/g

ng/g

Fluorochemicals are being released to the environment. Low molecular weight POSF derived compounds are used directly as surfactants, e.g., in firefighting foams. Fluoro-polymers and fluoro-oligomers are washed off carpets and fabrics during laundering and carpet cleaning. They are both tracked and vacuumed off carpets. Fluorochemicals are present in wastewater from 3M manufacturing facilities and from customer facilities applying 3M products to paper, fabrics and carpets. Some low MW fluorochemicals are released from fluorochemical-treated paper products during microwave cooking or as these products degrade as litter.

Questions that Remain.

What are the major sources of fluorochemical exposure through the natural environment? How much of human and ecosystem exposure is due to releases from 3M plants, from the application of 3M products, and the releases from use and disposal of 3M products? What happens to fluorochemical products released from treated products? For example, how much low molecular fluorochemical is released to the air or water as fluorochemical polymers pass through municipal waste water treatment systems. What is the distribution of fluorochemicals throughout the biosphere: Near manufacturing and treatment sites; Near municipal waste water treatment systems; In remote areas away from manufacture or usage sites? How and in what forms are fluorochemicals transported through water and the atmosphere? Could POSF or other fluorochemical derived from PFOS interfere with important ecosystem functions at concentrations that exist today, or that could exist in the future?

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Environmental Exposure

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Research Plan for 3M Fluorochemicals [redacted]

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Needs:

It is not clear how 3M fluorochemicals move in the environment or if they might have ecological impact. These chemicals have different properties than hydrocarbons and chlorinated hydrocarbons that are the foundation of our understanding of chemical fate. Therefore 3M scientists cannot extrapolate from limited data available. 3M needs more data. A combination of properties and monitoring information is needed similar to that derived for the first hydrocarbons and chlorinate hydrocarbons studied by environmental scientists.

The research planned includes laboratory tests to determine toxicity and fate properties, and field monitoring to determine the extent of environmental contamination. The monitoring and laboratory results will be used in models or used to compare with modeling results. This will help us understand how these chemicals move in the environment, and what tests or measurements should be done next. When appropriate data is available, risk models will be used to estimate risk.

Testing:

The testing has been prioritized based on: Which chemicals are being found in the environment; The highest production level chemicals; and Data availability. The utility of older data is limited because the exact nature of the chemicals tested is not known, because of omissions, or because advanced analytical techniques were not available. Also these chemicals have properties that make some testing problematic. These properties were sometimes not taken into account in early tests.

The testing for certain properties of some chemicals have been sequenced. This was done to allow the results of the first test to dictate the need for the second test or how best to do the second test.

The prioritization and sequencing has only been done for a couple of steps because the results of the laboratory tests and field monitoring will be used as input for planing the next phase of testing. Table 1. lists the chemicals currently of most interest, the properties to be tested, their priority, and sequence.

Monitoring:

A comprehensive monitoring plan has not yet been developed. Currently, pioneer sampling of the environment is underway. Samples close to sources are being evaluated to see if 3M can detect the chemicals there before looking farther afield. It is expected that 3M will detect the chemicals in these samples, and that has been the case close to a manufacturing site. Early results indicate the concentrations drop off rapidly with distance from the site. Next 3M will do more intensive sampling.

3M is also looking at the end of food chains for the chemicals. Pioneer sampling found one of the chemicals in continental birds (eagles) but not pelagic birds (albatrosses). 3M will broaden the number of samples and species, and 3M will move down the food chain and sample fish.

Because these chemicals are used in many homes and can be washed off of textiles and sewered. Sewage and effluent will be monitored to see if this could be a significant release to the environment.

As 3M scientists proceed with their pioneer monitoring, they are developing an overall testing and monitoring plan with consultants. These plans are helping to organize thoughts, give guidance and provide a structure to the concepts that is easily communicated.

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