

Perfluorooctanoate in air near a manufacturing facility fence line: Comparing modeled and monitored values

Mary Kaiser¹, Catherine A Barton¹, Larry E Butler¹, Charles J Zraecki¹, Miguel A Botelho¹

¹DuPont

Introduction

The aim of this study was to measure and predict perfluorooctanoate transport in ambient air. Sampling was performed at the fence line of a fluoropolymer manufacturing facility using OSHA Versatile Sampler (OVS) tubes that speciate between the particulate and vapor phases. High-volume impact samplers were used to determine particle size distribution (PSD). Perfluorinated compounds are gaining increased attention from the scientific community, based on their environmental persistence and prevalence. In 1999 Moody reported the presence of perfluorinated compounds in groundwater impacted by fire-fighting exercises that were concluded years before the analyses were conducted(1). Hansen reported that human sera contained low concentrations (viz., ppb) of perfluorinated organic molecules [e.g., perfluorooctane sulfonate (PFOS); perfluorooctanoic acid (PFOA)] in the general population(2). Other reports showed those low levels of these and similar compounds could be found in wildlife and in the environment(3,4,5). These reports led to questions about the mechanism for local and long-range transport of these compounds. Techniques for determining perfluorinated compounds in air are still developing. The determination of fluorine-containing compounds in air has been generally limited to charcoal adsorption followed by Wickbold torch determination of total fluorine(6) or measurements of volatile hydrofluorocarbons, chlorofluorocarbons, or chlorofluorocarbons, either directly or after adsorption, via gas chromatography(7-14). In 2002 Martin reported a method for the collection and determination of nine fluorine-containing neutral compounds by high-volume air sampling followed by extraction and then gas chromatography mass spectrometry(15). Shoeib investigated perfluoroalkyl sulfonamides in indoor and outdoor air(16). Stock reported data from a six-city sampling campaign in North America where both perfluorinated alcohols and amides were found(17). Organofluorine compounds have unusual physicochemical properties that make them difficult to quantify in the environment(18,19). Perfluorocarboxylic acids are especially difficult since the perfluorinated moiety is hydrophobic with $-CF_2-$ groups forming a stiff backbone; whereas, the carboxylic acid end is quite polar and hydrophilic. Because of their unique properties, perfluorocarboxylic acids such as PFOA are commonly used as fluoropolymer polymerization aids and surfactants (20). Perfluorinated surfactants are also quite stable(21). The exceptionally strong C—F bond makes PFOA stable to pH extremes, redox reactions, and elevated temperature. These same properties make PFOA difficult to determine since most analytical techniques for organic compounds rely on the more or less predictable behavior of hydrocarbons and their oxygenated derivatives. The presence of many C—F bonds often renders these predications unreliable. OVS tubes have been shown to be successful for industrial hygiene monitoring(22) and were expected to perform well in field applications. Monitored values from the fence line were compared with results from air dispersion modeling for the purpose of understanding the model's predictive capability for PFOA. High-volume sampling was also conducted at the fence line using cascade impactors. The use of impactors allowed the determination of the particle size distribution and the associated concentration of PFOA as a function of particle size at each monitoring location.

Materials and Methods

OVS Tube Sampling Methodology: Six sampling events using the OVS sampling system were conducted over a ten-week period from November 1993 to January 2004. During each sampling event, one sample was taken at the five locations along the fence line plus an additional sample taken at a spot co-located near the sampling position predicated to have the highest concentration based on historical air dispersion model data. The events were scheduled so that samples were collected at least 6-days apart and that both weekday and weekend patterns were monitored. One field blank per event was also taken with each sample set. OVS tubes with a nominal 0.3micrometer quartz fiber filter were used for all events. These tubes are uniquely designed to simultaneously capture particulates/aerosols, and vapors. The tubes contain a quartz fiber filter to trap aerosols and particulate matter, and a two-section sorbent bed of XAD resin to capture vapors. **High-Volume Impactor Sampling Methodology:** The (PSD) measurement was accomplished by means of a cascade impactor, an inertial particle classification device, attached

to a standard high volume sampler base. At each location, sampling equipment consisted of a Tisch Model 235 High Volume Cascade Impactor. The complete sampler consisted of the 5-stage impactor head attached to a high volume-sampling pump. The impactors were calibrated in accordance with EPA methods and operated in accordance with the manufacturer's instructions(23). Material from each of the collection stages was analyzed separately to determine the mass of PFOA for each particle cut size. Flow rates and run time were recorded so that actual sampling rate during the sampling period could be determined allowing for the stage cut size to be properly adjusted. Model Description: The Industrial Source Complex Short Term Model (ISCST3) was used to conduct air dispersion modeling. ISCST3 is a steady-state Gaussian model recommended by the U.S. EPA. It is included in the "Guideline on Air Quality Models" which is codified as Appendix W to 40 CFR Part 51(24). It is appropriate for modeling of pollutant emissions from multiple, industrial-type sources subject to significant building downwash. The downwash algorithms in the ISCST3 model provide a representation of the aerodynamic downwash of a stack plume caused by complex building configurations typical of industrial facilities. Analytical Methodology: The analysis was performed on the extract with a HP electrospray mass spectrometer using a method similar to that published recently (25).

Results and Discussion

OVS tube sampling showed PFOA in airborne emissions was present in the particulate form, with no material detected in the vapor portion of the sampling tube. Sampling results from OVS tubes and high volume samplers were consistent in measuring the highest sampled concentrations downwind of the prevailing wind direction. A comparison of measured to modeled PFOA concentrations showed the ISCST3 model did not under-predict where there was a quantifiable concentration for comparison. On average the model over-predicted ambient air concentrations by approximately 6 times and showed that the direction of major transport was in the direction of the prevailing wind (from the SW to the NE), demonstrating agreement with monitoring results. High volume sampling using cascade impactors also allowed the determination of a PSD for PFOA at the fence line. This determination showed that less than 6% of the particles were larger than 4 μm in size, while almost 60% of the particles were below 0.3 μm . High volume sampling also provided concentrations of PFOA at four fence line locations where OVS tube sampling had occurred. Results of both sampling methods agreed in points of maximum and in their general concentration range.

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