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Characterizing Perfluorooctanoate in Ambient Air near the Fence Line of a Manufacturing Facility: Comparing Modeled and Monitored Values

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ABSTRACT

In order to improve our understanding of the nature, measurement and prediction of salts of perfluorooctanoic acid (PFOA) in air, two studies were performed along the fence line of a fluoropolymer manufacturing facility. First, a six-event, 24-hr monitoring series was performed around the fence line using the OSHA versatile sampler (OVS) system. Perfluorooctanoate concentrations were determined as perfluorooctanoic acid (PFOA) via liquid chromatography and mass spectrometry. Those data indicated that the majority of the PFOA was present as a particulate. No vapor-phase PFOA was detected above a detection limit of approximately $0.07 \mu\text{g}/\text{m}^3$. A follow-up study using a high-volume cascade impactor verified the range of concentrations observed in the OVS data. Both studies aligned with the major transport direction and range of concentrations predicted by an air dispersion model, demonstrating that model predictions agreed with monitoring results. Results from both monitoring methods and predictions from air dispersion modeling showed the primary direction of transport for PFOA was in the prevailing wind direction. The PFOA concentration measured at the site fence over the 10-week sampling period ranged from 0.12 to $0.9 \mu\text{g}/\text{m}^3$. Modeled predictions for the same time period ranged from 0.12 to $3.84 \mu\text{g}/\text{m}^3$. Less than 6% of the particles were larger than $4 \mu\text{m}$ in size, while almost 60% of the particles were below $0.3 \mu\text{m}$.

IMPLICATIONS

The ability to model PFOA in ambient air resulting from manufacturing facility emissions is critical to understanding its near-field transport and potential local exposure resulting from that transport. Evaluating a model that is readily available and currently supported by U.S. Environmental Protection Agency is also important. If the current model conservatively predicts ambient air concentrations, that result would suggest to regulatory agencies and industry that it can be used in ongoing programs to evaluate near-field exposure and transport of PFOA.

These studies are believed to be the first published ambient air data for PFOA in the environment surrounding a manufacturing facility.

INTRODUCTION

Perfluorinated compounds are gaining increased attention from the scientific community, based on their environmental persistence and prevalence. In 1999, Moody and Field¹ reported the presence of perfluorinated compounds in groundwater impacted by fire-fighting exercises that were concluded years before the analyses were conducted. In 2001 Hansen et al.² reported that human sera contained low concentrations (namely, ppb) of perfluorinated chemicals (e.g., perfluorooctane sulfonate and perfluorooctanoic acid [PFOA]) in the general population. Other reports showed that 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 analyzing 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 fluorine⁶ or measurements of volatile hydrofluorocarbons or chlorofluorocarbons, either directly or after adsorption, via gas chromatography.^{7–14} In 2002, Martin et al.¹⁵ reported on 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 (GCMS). In 2004, Shoeib et al.¹⁶ investigated perfluoroalkyl sulfonamides in indoor and outdoor air. Stock et al.¹⁷ reported data from a six-city sampling campaign in North America where both perfluorinated alcohols and amides were found.

Organofluorine compounds have unusual physicochemical properties that make them difficult to quantify in the environment.^{18,19} Perfluorocarboxylic acids are especially difficult because the perfluorinated moiety is hydrophobic with $-\text{CF}_2-$ 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, because 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 predictions unreliable.

The objective of this study was to advance the state of science for measuring and predicting PFOA transport in ambient air. Sampling was performed at the fence line of a fluoropolymer manufacturing facility using Occupational Safety and Health Administration Versatile Sampling (OVS) tubes that speciate between particulate and vapor phases. OVS tubes have been shown to be successful for industrial hygiene monitoring²² 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 predictive capability of the model 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.

EXPERIMENTAL METHODS

Air Dispersion Modeling

DuPont conducted air dispersion modeling of PFOA emissions from its Washington Works facility located near Parkersburg, WV, in the Ohio River valley (see Figure 1). Modeling was conducted to predict 24-hr ambient air concentrations of PFOA resulting from actual plant emissions that occurred during six sampling events during the period of November 5, 2003, through January 16, 2004. The predicted PFOA values were then compared with concurrent samples taken during the sampling events.

Emissions Inventory. The following emission inventory information was assembled for 15 individual site sources to conduct the air quality modeling: (1) stack locations; (2) stack heights; (3) stack diameters; (4) hourly stack gas exit temperatures; (5) hourly stack gas flow rate; (6) detailed plant layout, including all building dimensions; and (7) hourly PFOA emissions.

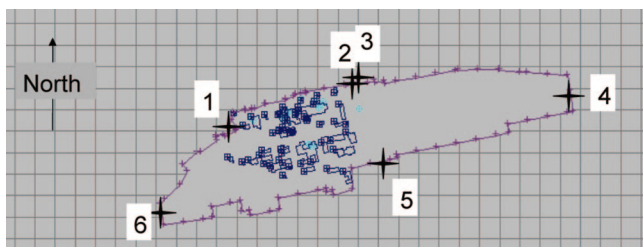


Figure 1. Receptor locations.

Site-specific operational data were used to relate production data to stack emissions levels using a production correlation factor. Through a combination of actual stack monitoring (for vents with highest emissions) and mass balance estimates (for vents with very small emissions), a factor was established for each PFOA emission point to estimate the quantity of emissions released at a given production rate. This factor was combined with production data to calculate PFOA emissions from each source on an hourly basis during each 24-hr sampling event.

Meteorological Data. On-site meteorological data for the period November 5, 2003, through January 16, 2004, were used in this study. These data are from a well-maintained, on-site meteorological observing system. The system included a thermistor-type (resistance change) temperature detector and a capacitance humidity sensor. Wind speed was measured with a 3-cup anemometer, and wind direction was measured with a rotating wind vane. Solar radiation was determined using a pyranometer. Collected data used in the modeling analysis consisted of hourly average wind speed, hourly average wind direction, and hourly average ambient air temperature, as well as hourly stability class. Stability class was determined using the horizontal standard deviation of wind direction and the scalar wind speed, as described in Section 6.4.4 of U.S. Environmental Protection Agency (EPA) "Meteorological Monitoring Guidance for Regulatory Modeling Applications."²³ Concurrent twice-daily upper air data from the upper air observation station located in Dayton (near Wilmington), OH, were used along with on-site surface temperatures to obtain hourly mixing depths. Missing data and measured wind speeds of <1 m/sec were treated consistent with the recommendations made in EPA Meteorological Monitoring Guidance. An anemometer height of 9.14 m was used for the modeling analysis. This dataset was broken down into six 24-hr datasets to correspond with the sampling events. Information about wind speed and direction for each of the datasets was plotted on wind roses, as shown in Figures 2 through 7. These wind roses depict the direction from which the wind originates. For instance, in Figures 3 and 4, the wind is

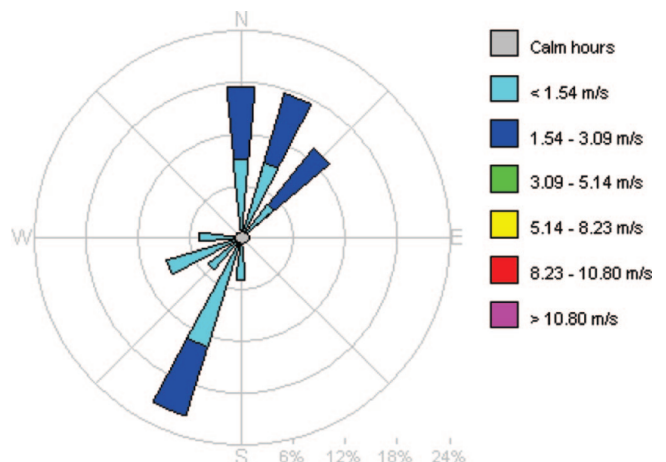


Figure 2. November 5, 2003, sampling.

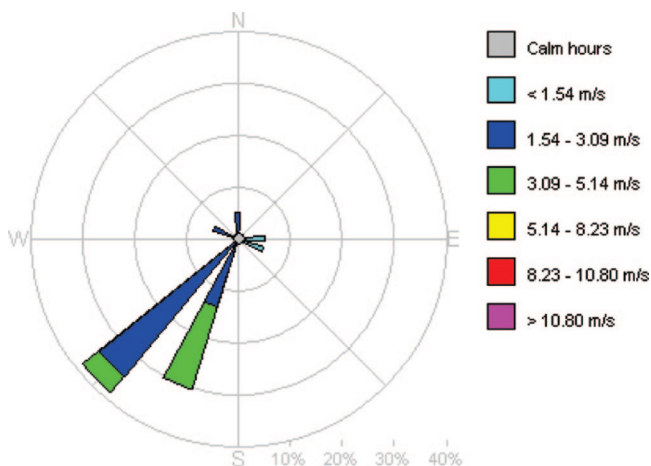


Figure 3. November 11, 2003, sampling.

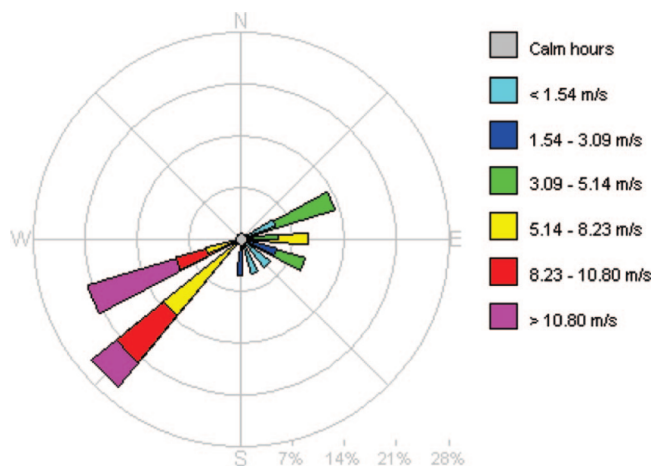


Figure 5. December 10, 2003, sampling.

predominantly blowing from the southwest toward the northeast.

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 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. Refined ISCST3 modeling was conducted using the sequential hourly meteorology from the on-site observation facility, as described above.

The area surrounding Washington Works is primarily nonurban. EPA procedures classify land use within 3 km of the site by the Auer method.²⁵ Review of U.S. Geological Survey maps, aerial photographs, and site visits clearly indicated that the area is well more than 50% nonurban. Significant terrain features surround the Washington Works facility on both sides of this river valley. Although all of the modeling was conducted at

receptor locations within the river valley, terrain elevations were considered in the modeling analysis.

Receptor Selection. Model prediction locations (receptors) were placed at the exact coordinates of the perimeter sampling locations. A total of five discrete receptors were used in this modeling analysis. These receptors are shown in Figure 1. (Receptors 2 and 3 were colocated and represent a single receptor location.) A survey team used the global positioning system to identify latitude, longitude, and Universal Transverse Mercator (UTM) coordinates of each sample location. The above-ground elevation of the intake tubing was measured at 1.09 m. This elevation was accounted for in the ISCST3 model.

Modeling Procedures. The most recent version of ISCST3 (version 02035) was used in the model verification study. All of the model options were set to EPA regulatory default version of ISCST3. The model was run in the rural mode, because the land area in the immediate vicinity of Washington Works is >50% rural. Any effects of aerodynamic downwash caused by structures adjacent to each modeled stack were included in the ISCST3 modeling analysis along with a summary of the building downwash

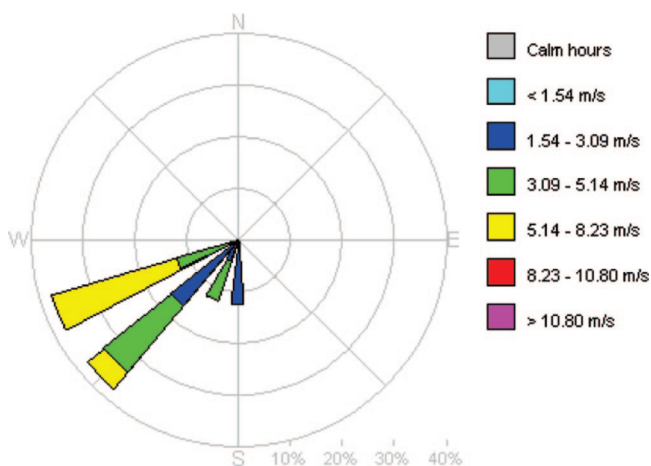


Figure 4. November 29, 2003, sampling.

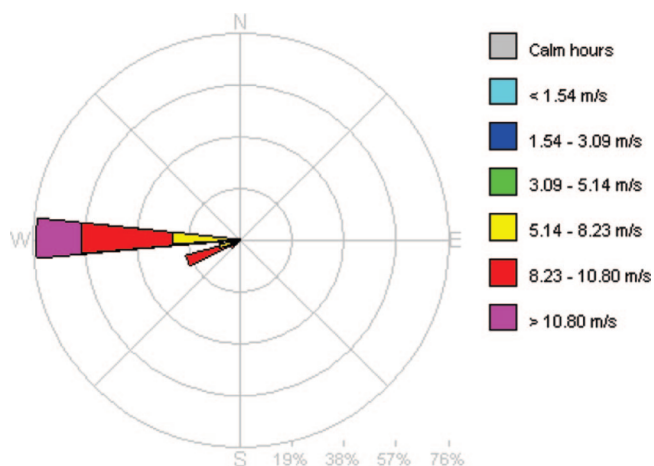


Figure 6. December 11, 2003, sampling.

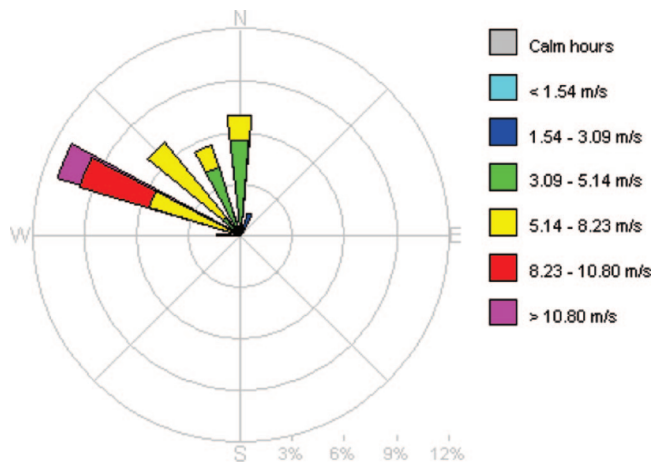


Figure 7. January 15, 2004, sampling.

input files. Air quality dispersion modeling was conducted on an hour-by-hour basis using the on-site meteorological data described above. The PFOA modeling results were summarized for 24-hr averaging time periods to simulate the duration of each field-sampling event. ISCST3 can simulate vapor and particle emissions. For this modeling program, there was no significant difference in ambient air predictions when emissions were assumed to be a gas versus results when the actual particle size distribution was used and emissions were assumed to be in particle form. The reason that results were essentially the same is that fence line receptors are close enough to emission sources, and particle sizes are small enough such that no significant plume depletion would have occurred at the fence line.

Each of the short-term sampling events commenced at 7:00 a.m. and ended at 7:00 a.m. on the following day. This was done so that each of the events would coincide with the work shift schedule at Washington Works. Likewise, the dispersion modeling was also conducted in the same time frame, and 24-hr average concentrations occurring during that time period were calculated.

Sampling Methods

OVS Tube Sampling Methodology. Six sampling events using the OVS sampling system were conducted over a 10-week period from November 2003 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 collocated near the sampling position predicted to have the highest concentration based on historical air dispersion model data (stations 2 and 3). The events were scheduled so that samples were collected at least 6 days apart and so that both weekday and weekend patterns were monitored. One field blank per event was also taken with each sample set.

Occupational Safety and Health Administration Versatile Sampling (OVS) tubes with a nominal 0.3- μ m quartz fiber filter were used for all events (SKC). This tube is uniquely designed to simultaneously capture particulates/aerosols, and vapors. The tube contains a quartz fiber filter to trap aerosols and particulate matter and a two-section sorbent bed of XAD resin to capture vapors.

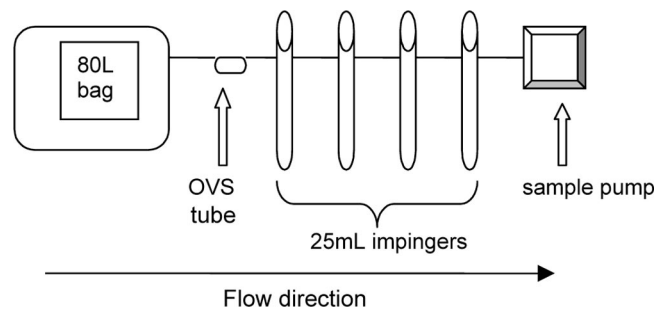


Figure 8. Laboratory apparatus for PFOA transport in OVS tubes.

A Universal PCXR4 sample pump (SKC) was used at each location and connected to a continuous source of electrical power. After calibration, airflow was set to ~ 1 L/min and recorded and checked. The tubes were removed from the pump after 24 hr, capped, and shipped overnight at ambient temperature to the laboratory.

A key feature of the OVS tube is its design to allow speciation between particulate/aerosol matter and vapors. Because this distinction provides important insight into the nature of PFOA in air, a laboratory transport test was conducted to verify the ability of the tube to separately measure particles and vapor. Specifically, the transport study was run to demonstrate that if PFOA vapor were present, it would be transported and adsorbed on the XAD resin beads. For this study, PFOA was heated above its boiling point to force the material into the vapor phase in air. To start, 2 grams of PFOA (Oakwood Products) were placed on the bottom of a 25-mL midget impinger (SKC). A schematic representation of the laboratory apparatus is shown in Figure 8. During the study, PFOA was seen to deposit on tubing and other cold internal surfaces of the vaporizer, and there was also some loss through the laboratory hood. Consequently, a mass balance of material added versus material recovered was not possible. The impinger was placed in a silicone oil bath and the inlet nozzle connected to an air supply. The air supply was an SKC Universal sample pump, Model 224-43XR, which is a factory-calibrated flow meter. The exit nozzle was connected to an 80-L Tedlar sampling bag. The airflow was set at 250 mL/min, and the temperature of the oil bath was set to 230 $^{\circ}$ C. When the bag was almost full, the valve of the bag was closed. The bag was then connected in series to the filter side of the OVS tube, followed by a midget impinger sampling train consisting of two midget impingers with 10-mL of water each, an empty midget impinger, and a desiccant impinger followed by a sample pump. The water impingers served as a final trap for any vapor-phase PFOA exiting the OVS tube. The valve of the bag was opened and the pump set at ~ 1 L/min flow for 1 hr. The OVS tube and the water samples were analyzed for PFOA. The data indicated (Table 1) that if a vapor were present, it would have been transported and adsorbed on the XAD resin of the OVS tube.

Table 1 data show that a small portion of PFOA was measured in the first chamber, either on the filter or on the glass tube. This mass represented $\sim 7\%$ of the total mass captured on the tube. Approximately 93% of the total mass was captured on the XAD-2 resin. It was

Table 1. Transport of PFOA vapor.

Quantity of PFOA Trapped in Transport Test (μg)	
OVS filter	24.2
OVS absorbent section 1	309
OVS absorbent section 2	11.7
Impinger 1	0.34
Impinger 2	0.09

concluded that, although a small portion of the PFOA was found in the first chamber, the majority of the mass was captured in the chambers designed to collect vapor. This finding demonstrates that if a vapor were present in ambient air, a reasonable majority of the vapor could pass through the filter and be captured in appropriate compartments, rendering the ability of the tube to speculate the presence of a vapor acceptable. Table 1 also shows that only 0.43 μg was detected in the final traps (impingers). These results indicate that the OVS tube media effectively adsorbed PFOA that was present in the air, that is, 99.9% of the PFOA present was adsorbed in the OVS tube, with $\sim 0.1\%$ exiting the tube and absorbed in the traps.

High Volume Impactor Sampling Methodology. High volume sampling was conducted in March 2004 during a 72-hr period at locations 1, 2, 3, and 5, shown in Figure 1. Locations were selected to represent areas of the predicted maximum ambient air concentrations, according to air dispersion modeling. Two samplers were colocated (at stations 2 and 3) to provide information about sampling precision. One background sampler was located at station 5 to collect predicted upstream concentrations, assuming that wind patterns follow predominant directions in the valley.

The particle size distribution (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 rented from RAMCON Environmental. The complete sampler consisted of the five-stage impactor head attached to a high-volume sampling pump. The impactors were calibrated in accordance with EPA methods²⁶ and operated in accordance with the manufacturer's instructions.²⁷ 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 the actual sampling rate during the sampling period could be determined allowing for the stage cut size to be properly adjusted. Actual sample flow rates averaged between 1162.7 and 1367.7 L/min (41.06 to 48.3 ft^3/min) for the four sample locations.

To determine the retention efficiency of the filter paper used for the high-volume cascade impactor, a 1- μg spike (10 μL of 100.7 $\mu\text{g}/\text{mL}$ in acetone) of PFOA was applied to five 47-mm circles of filter paper cut from the

Table 2. Retention of PFOA on Whatman #41 filter paper vs. time at 10.5 L/min.

Time (hr)	Volume (m^3)	Mass Spiked (μg)	Mass Detected (μg)	% Retention (compared with detected mass at time zero)
0	0	0	0.02	NA
0	0	1.01	0.82	NA
24	15	0	0.02	NA
24	15	1.01	0.75	91
48	30	0	0.03	NA
48	30	1.01	0.53	65
72	45	0	0.03	NA
72	45	1.01	0.52	63

Notes: NA indicates not applicable.

larger paper used in the impactor. The circles were contained in a standard filter cassette (SKC, Inc.). The spiked cassettes were allowed to air dry and then placed in series with air first passing through an unspiked filter paper cassette then the spiked cassette. The data are reported in Table 2. Results indicate that 91% of the PFOA was retained during the first 24 hr, with losses of up to 37% by the end of the 72-hr sampling period. It can be concluded that a small amount of PFOA may be lost during high-volume sampling, resulting in sampling concentrations that may somewhat underestimate actual ambient air concentrations. However, this potential can be minimized by limiting the sampling duration to ≤ 24 hr, when retention would be expected to be $>90\%$.

Analytical Methodology. The OVS tube was disassembled into fraction A (plastic retaining ring and filter), fraction B (first section of XAD resin beads and the first polyurethane foam filter), and fraction C (second section of XAD resin beads and the second polyurethane foam filter). Each fraction was placed into individual vials and then spiked with 50 μL of a 10- $\mu\text{g}/\text{mL}$ solution of nonadecanofluorodecanoic acid (surrogate; Sigma Aldrich). To each vial was added 950- μL of methanol (EM Science). The vial was agitated two to three times over a period of 30 min. The solvent was then extracted using a disposable Pasteur pipette to a labeled 2-mL clear high-performance liquid chromatography (LC) vial for LC/MS determination. (The PFOA water method is similar to one published previously.²⁸)

The analysis was performed on an HP 1100 series electrospray mass spectrometer (Agilent) with a 2-mM ammonium acetate and methanol gradient (0 time, 70% ammonium acetate; 6 min, 10% methanol; 12 min stop; posttime 4 min) at 0.3 mL/min. A 5- μL aliquot was injected onto a Betasil C_{18} column (2 mm \times 30 mm, 3 μm ; Thermo Hypersil-Keystone) at 35 $^\circ\text{C}$. Ions 369 (m/z; PFOA) and 469 (m/z; surrogate) were monitored. A six-point (nonzero) linear calibration curve was used for quantitation. The standards were measured both at the beginning of the run sequence and interspersed throughout the run. For the initial run (6 points) and the combined initial and interspersed set (12 points), the correlation coefficient (R) was ≥ 0.992 (coefficient of

determination, $R^2 \geq 0.985$). A matrix control sample fortified with PFOA was included with a blank with each set of samples. Fortification and surrogate recoveries falling within 75–125% were considered acceptable. Samples in which no peaks were detected (i.e., signal:noise ratio <3:1) at the corresponding retention times were reported as not detected. Samples in which peaks were detected at the corresponding analyte retention time but less than the lowest concentration of the calibration standards (50 ng/mL) were reported as not quantifiable. The limit of quantitation for this method was 50 ng/mL (or 50 ng/fraction). Method blanks did not contain analyte at levels greater than the limit of quantitation.

Filter paper samples were placed in 50-mL polypropylene centrifuge tubes and fortified and air dried, if needed. Forty milliliters of water were added, then the tube was capped and shaken overnight (12–24 hr) on a wrist-action shaker. The tubes were removed from the shaker and centrifuged at ~5000 rpm for ~10 min. The supernate was decanted into another 50-mL polypropylene centrifuge tube. C_{18} solid-phase extraction cartridges (Waters) were preconditioned by passing 10 mL of methanol and then 5 mL of water through each. The sample was then loaded onto the cartridge and the eluate discarded. The column was then washed with 40% methanol in water and the eluate discarded. The cartridge was then eluted with ~5 mL of 100% methanol. Five milliliters of the eluate were collected in a 15-mL polypropylene centrifuge and transported for LC/MS analysis, as above.

RESULTS

A summary of ambient air results from the OVS tube sampling and corresponding modeling predictions are presented in Table 3. Colocated samples from stations 2 and 3 were identical for four of the six sampling events, and differed by $0.01 \mu\text{g}/\text{m}^3$ for one sampling event. (Colocated samples were not comparable for one event because of a pump malfunction at station 3.) Field blanks registered no detectable background contamination for the six samples used in this study. (Note that the field blank from one round of sampling taken during the 10-week period did register contamination. It appears that an actual sample may have been inadvertently mislabeled as the field blank. But, because that mistake could not be confirmed, results from this round were discarded, leaving the six remaining sample results used for the study.) Sample spike recoveries were within the acceptable range of 75–125% for all six sampling events.

Twenty-eight useable pairs of modeled/monitored results were generated. Results show that at no time did the model underpredict the concentration of PFOA in air, as compared with quantifiable monitored values. Rather, in all of the cases the modeled value either overpredicted or was in agreement with the measured value. Note that model overprediction is a more desirable outcome than underprediction, because it results in a conservative estimate of air concentrations when considering potential exposure. A comparison of monitored and modeled values yields the observations described below.

Table 3. Summary of fence line results for modeling and monitoring.

Event	Date	Receptor Location	Modeled Value, $\mu\text{g}/\text{m}^3$	Monitored Value, $\mu\text{g}/\text{m}^3$	Overprediction
1	11/05/03	AMS-1	0.00	<0.14	—
2	11/11/03	—	0.23	<0.14	1.6
3	11/29/03	—	0.00	<0.14	—
4	12/10/03	—	1.28	0.3	4.3
5	12/11/03	—	0.00	<0.12	—
6	1/15/04	—	0.00	<0.14	—
1	11/05/03	AMS-2/3	1.79	0.075	23.9
2	11/11/03	—	3.84	0.9	4.3
3	11/29/03	—	3.00	0.7	4.3
4	12/10/03	—	0.83	0.3	2.8
5	12/11/03	—	0.11	<0.14	—
6	1/15/04	—	0.00	<0.17	—
1	11/05/03	AMS-4	0.10	<0.14	—
2	11/11/03	—	0.00	<0.14	—
3	11/29/03	—	—	^a	—
4	12/10/03	—	0.02	<0.12	—
5	12/11/03	—	1.02	<0.14	7.3
6	1/15/04	—	0.03	<0.14	—
1	11/05/03	AMS-5	0.01	<0.14	—
2	11/11/03	—	0.21	<0.14	1.5
3	11/29/03	—	0.00	<0.14	—
4	12/10/03	—	0.00	<0.14	—
5	12/11/03	—	0.00	<0.14	—
6	1/15/04	—	0.53	0.3	1.8
1	11/05/03	AMS-6	0.02	<0.14	—
2	11/11/03	—	0.00	<0.14	—
3	11/29/03	—	0.00	<0.14	—
4	12/10/03	—	0.10	<0.12	—
5	12/11/03	—	—	^a	—
6	1/15/04	—	0.00	<0.14	—

^aPump failure; no sample collected.

Modeled values overpredicted measured values 32% of the time (for 9 of the 28 cases.) On average, the model overpredicted by approximately six times, with a range of 1.5–7.3 for all but one case. In one case, the model overpredicted 24 times the measured value. This larger overprediction may be a result of low wind speeds and changing wind directions that occurred throughout the 24-hr period and are apparent from the wind rose for that day (see Figure 2).

Modeled values are in agreement with sampling results that measured below the quantifiable limit. For 19 of the 28 cases, or 68% of the time, the monitored value was below the quantifiable limit, and the model predicted a concentration that was also below the quantifiable analytical value.

Results from high-volume sampling were used to calculate a PSD and to determine ambient air concentrations at the facility fence line. The average PSD is shown in Table 4. The overall mass concentration of PFOA for the 3-day test period is shown in Table 5.

Field blanks showed no detectable background contamination. Colocated samples from stations 2 and 3 differ by $0.007 \mu\text{g}/\text{m}^3$ (~7%), showing acceptable precision in the sampling methodology. Measured concentrations are consistent with predicted model results that show

Table 4. Average particle size distribution for PFOA at fence line.

Particle Diameter, μm	Mass Fraction %
>4.0	5.6
1.7	12.9
0.8	9.2
0.5	7.2
0.3	5.3
<0.28	59.8

station 5 as the predominant upwind location and stations 2 and 3 as the predominant downwind location. The concentration range at each sample location compares favorably to previous 24-hr sampling collected using OVS tubes, considering that samples were collected on different days.

At station 1, the majority of OVS tube results were below a quantitation limit of $\sim 0.07 \mu\text{g}/\text{m}^3$ for the particulate fraction; the high volume sampler measured $0.0099 \mu\text{g}/\text{m}^3$, which is also $< 0.07 \mu\text{g}/\text{m}^3$. (Note that the quantitation limit for the high volume sampler was two orders of magnitude lower than for the OVS tube, because the sampling flow rate was > 1000 times higher, allowing a greater volume of air to pass through the sampler.)

At collocated stations 2 and 3, both samplers showed maximum concentrations for perimeter monitoring. OVS tube results showed detected levels for six of the eight sampling events with all of the results ranging from < 0.07 to $0.9 \mu\text{g}/\text{m}^3$; the high-volume sampler measured 0.1030 , which registers in this range of values.

At station 5, the majority of OVS tube results were below a quantitation limit of $\sim 0.07 \mu\text{g}/\text{m}^3$ for the particulate fraction; the high-volume sampler measured $0.0034 \mu\text{g}/\text{m}^3$, which is also $> 0.07 \mu\text{g}/\text{m}^3$.

DISCUSSION

This study provides insight into both sampling and modeling methods for PFOA-like compounds in air. OVS tube sampling showed that 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 at stations 2 and 3, downwind of the prevailing wind direction. A comparison of measured to modeled PFOA concentrations showed that the ISCST3 model did not underpredict where there was a quantifiable concentration for comparison. On average, the model overpre-

Table 5. Mass concentration of PFOA for 72-hr high-volume sampling.

Station	Mass Concentration ($\mu\text{g}/\text{m}^3$)
Station 1	0.0099
Station 2	0.1099
Station 3	0.1030
Station 5	0.0034

dicted ambient air concentrations by approximately six times and showed that the direction of major transport was in the direction of the prevailing wind (from the southwest to the northeast), demonstrating agreement with the 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 $< 6\%$ of the particles were $> 4 \mu\text{m}$ in size, whereas $\sim 60\%$ of the particles were $< 0.3 \mu\text{m}$. High-volume sampling also provided concentrations of PFOA at four fence line locations where OVS tube sampling had occurred. The results of both sampling methods agreed in points of maximum and in their general concentration range.

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