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EPA Comments on DuPont's Proposed Air Modeling Approach to Verify the Modeled Results, and Use the Results to Determine Where to Sample Ground Water (as presented to EPA on October 27, 2003).

EPA has reviewed the DuPont presentation on air modeling verification and has prepared comments based on our understanding of the proposed approach, as presented on October 22, 2003. DuPont presented their approach to verifiying that their intended use of ISCST3 will alone adequately serve as a direct pointer for where there would be the most efficient underground water monitoring. At the October 22, 2003 meeting, EPA experts in the Office of Pollution Prevention and Toxics, the Office of Research and Development,the Office of Air Quality Planning and Standards from Headquarters, Research Triangle Park, North Carolina, Ada, Oklahoma, and Athens, Georgia all stated that they believe soil sampling, especially in the first few inches above the area the ISCST3 suggests highest air levels, is a more reliable means of verifying that the air model is accurately predicting where to sample ground water than air sampling alone. DuPont stated it intended to use the verification, i.e. limited air sampling, at one place (Washington Works) to suffice for verifying the model's applicability elsewhere without further site specific verification via additional sampling. EPA's experts disagreed with this approach, stating that the model would need to be calibrated to the other sites. Our comments are grouped into three sections in this document: 1) Comments on DuPont's proposal to evaluate the ISCST3 model to determine maximum air; 2) Comments on DuPont's suggested proposal for using the modeled air concentrations to determine where ground water monitoring will be performed; and 3) Comments on DuPont's modeling/measurement approach. The Agency's comments appear below.

1. DuPont's proposal for evaluation of ISCST3 model to determine maximum air concentrations (emphasis on particles)

- Use ISCST3 to develop concentration gradients (based on annual data)
- Monitor at 5 locations within fenceline (cardinal ordinates plus two locations with highest modeled concentration)
- Collocated air sampler at highest location to provide estimate of sampler precision
- One field control sample for a total of 7 samples each period to estimate error associated with blank material
- Monitor for 7 different periods over 6 weeks
- Sampling inlet approximate to breathing zone
- Sample collection protocol following NAMS/SLAMS every sixth day timeframe
- Analyze samples and provide data to EPA within approximately 18 weeks

Potential issues

- Sampling regime needs to be revisited to ensure that sample collection occurs during periods where maximum concentrations are anticipated at the collocated site. Since this

effort is to evaluate the usefulness of the model in lieu of status and trends, sampling back-to-back days might be more appropriate in lieu of every 6th day sampling.

- Sampling on a fixed every sixth day regime may result in sampling during rain events or other conditions that might result in increased numbers of sampling non-detects
- Sampling on a fixed calendar basis in lieu of a meteorological/industrial process basis might result in sampling occurring when the plant emissions are lowest or when meteorological conditions are not favorable related to the fixed sampler layout
- The proposed activity is intended to provide model evaluation and not status and trends data. The sampling design and schedule needs to be reconsidered to ensure it focuses on the primary objective.
- Sampling and analyzing a couple of back-to-back maximum day events early would provide early input for the usefulness of this activity, and opportunities for adjustments, in lieu of sampling 7 events and then trying to interpret the completed results
- Sampling within the fenceline is a good first approach, but it does not provide the corresponding data to evaluate the usefulness of employing this model for assessing exposures outside the fenceline
- The possibility of long range transport of particulates is not considered with this approach.
- Field and lab spikes should be included to demonstrate analyte recoveries and potential interference from handling, storage, and shipping.
- If the ambient air model results presented are an accurate representation of the expected air concentration field, there is a good probability that the size and nature of the air monitoring data set proposed will be inadequate to verify the model predictions. Sites 2 and 3 are duplicates, and sites 4, 5 and 6 would be expected to have little or PFOA in the air. Consequently, the ability to estimate magnitudes of concentration are based primarily on repeated measures in time at two sites, not 6.
- A total of 35 samples is characterized as a very large number of samples for the analysis but this number is only large when taken as a whole. However, they will only be sampling from 35 locations at selected company boundary locations according to a compass points (N-S-E-W). Therefore, they will only have seven data points per location and no data beyond the facility boundary. It would appear that for their statisticians to validly reject the null hypothesis (i.e., accept that model results "match" measured samples) would require several additional sampling locations at greater distances than those proposed and would require seasonal effects be considered as well (e.g., wind speeds, directions, precipitation, barometric pressure changes, etc.). This would greatly delay final study results because data collection could be extensive, could greatly delay obtaining final study results because data collection would essentially take a year to complete. However, they are asking EPA to accept their conclusions to what appears to be an inadequate study. Additional information on the statistical analysis that will be utilized in this study would be helpful in understanding the power of the analysis.
- The emissions estimate will be based on production volume capacity data. This is an important parameter. Additional information is needed to understand how well the capacity data predict the actual emissions, and to determine whether this is an acceptable

method for this purpose.

2. DuPont's Suggested Proposal for Using the Modeled Air Concentrations to Determine Where Ground Water Monitoring Will Be Performed

- Using the Washington Works data, DuPont observed that there was an apparent correlation between the modeled (sampled) air concentration data and the measured groundwater results from the extensive network of wells at the Washington Works facility
- DuPont suggests, once the ISCST3 model is evaluated for the Washington Works, that this model could be used at the other facilities to estimate ambient air concentrations without the need for confirmatory air measurements
- DuPont suggests that the modeled air concentrations (based in part on measured data) could be used as a first assessment for selecting areas for conducting ground water monitoring
- Use this methodology to determine if and when to sample groundwater at all 4 fluoropolymer manufacturing facilities.

Potential Issues

- The initial assessment of the data provided by DuPont does not allow EPA to directly assess the correlations/relationships among the Washington Works air, soil, and groundwater measurements (modeled values). This may result in EPA not fully understanding the timing and sequencing of the air, soil, and groundwater sample results, i.e., when were the air samples collected in time relationship with the water samples; what data is available to demonstrate the phased or total wash-out of the PFOA from the soil to the groundwater.
- Groundwater samples containing some of the higher concentrations of PFOA were collected in locations where air concentrations were predicted to be relatively low. Likewise, some groundwater samples containing some of the lower concentrations of PFOA were collected in locations where air concentrations were predicted to be relatively high.
- Factors associated with each industrial plant/location (meteorological conditions, industrial processes, sampling site plan, soil type, etc.) may adversely influence the key modeling parameters if model sensitivity testing and/or some confirmatory monitoring is not performed to evaluate the robustness of the model for each specific site.
- Sampling the ambient concentrations without parallel results from other key environmental parameters does not allow the direct assessment of the usefulness of using the air concentration data to directly determine locations for ground water sampling The ambient air modeling, as presented at the 10/22/2003 meeting, is insufficient to justify or support a monitoring program whose goal is to establish the source of contaminated ground water in the vicinity of the Washington Works manufacturing facility. Without

surface soil sampling to establish that PFOA is derived from an aerial source, the actual PFOA source of contaminated ground water would remain an uncertainty. Using some variation of the air dispersion model to locate monitoring wells may be useful, but not in the manner which has been proposed.

- No scientific justification was presented at the 10/22/2003 meeting as to why air concentration is, in their opinion, a good predictor of ground-water concentration for PFOA. They noted a coincidental co-occurrence of predicted contaminated ambient air and contaminated ground water, but has not established the source of PFOA in ground water. There was no technical information or discussion of a route of transport from the contaminant source (alleged to be Washington Works) to the ground water (in the Little Hocking well field) which would circumvent transport through the soil, or unsaturated zone consistent with their assertion that ambient air concentrations are better predictor of the location of contaminated ground water than soil concentrations. Lack of detections in soil samples cited in support of their position that soils should not be sampled, can be logically attributed to field methods used to sample soils which did not target surface soil samples.
- The map presented at the meeting represented the estimated average annual ambient concentrations for only a single unspecified year (2002?). They indicated verbally that other years showed very different patterns, perhaps due to mitigation?? They provided no information on how model inputs reflected that mitigation or if wind patterns change substantially from year to year (very possible). Note also that no information was presented on the stack heights and historical discharges, the discharge rate, or the pattern of particulates deposited in relation to total (gaseous plus particulate) PFOA concentrations. It is impossible to know the validity of the air modeling with virtually no information on the inputs presented.
- Year-to-year as well as or day-to-day variability in ambient air concentrations was hinted at but not demonstrated. One can speculate that high annual mean air concentrations around the plant would be associated with stationary air, or temperature inversions, rather than with atmospheric conditions likely to move the chemical off site.
- The variability in deposition pattern of PFOA associated with stack emissions would be expected to be a critical parameter in determining the source of PFOA contaminated ground water (presuming the Washington Works is the sole PFOA source). Neither the proposed air sampling nor the annual concentrations presented would be adequate to determine the source with adequate certainty. The air dispersion simulations should be altered to consider variations in emission rates with varying meteorolgical conditions and then dispersion model should be used to determine where soil sampling should take place. The soil sampling could then be used for well location. Using the yearly average meteorological conditions may not actually provide a location of maximum deposition. The location of maximum deposition will depend on a combination of simultaneously occurring processes, namely the emission rate and the prevailing meteorological conditions that occur during that particular emission. If emissions are constant throughout the year, then perhaps the average yearly meteorological conditions may be appropriate. However, if there are substantial day-to-day or seasonal variations in the

emission rate throughout the year, then using the average meteorological condition would be inappropriate. It such a case, it would be preferable to create daily deposition contour maps each using the daily emissions rate for individual emission sources and the corresponding daily meteorological. It may also be worthwhile to check evening vs. day meteorological conditions and day vs. evening emission rates. Integrating these maps would create an overall contour map, such that a more appropriate location for maximum deposition could be obtained. The location determined by these integrated maps should be used to give an indication of where soil sampling should take place. Soil sampling should occur across a large enough transect that the maximum location of deposition could be determined (assuming that there is a single area of maximum deposition). Wells could then be located in this area. Note that soil sampling across a wide swath should be much more economical than the expense of drilling a well in an inappropriate area.

3. Comments on the modeling/measurement approach.

DuPont suggests a 0.1 microgram/cubic meter detection rate based on a 1 liter/min flow rate. This would result in ~150 ng of analyte if fully extracted:

0.1 microgram/m3 * 1 liter/min *1 m3/1000 liters * 1440 mins in a day = 0.144 micrograms

0.144 micrograms * 1000 nanogram/1 microgram = 144 nanograms

Of course, there are dilution and matrix factors that influence the actual extract concentration, i.e., the final volume the extraction was reduced down to for the purposes of analyses.

Potential Issues

- This would suggest ~150 nanograms are available for analysis
- EPA experiences picogram levels of detection with LC/MS technology, additional orders of magnitude in sensitivity.
- However this difference may result from differences in EPA understanding in the instrumentation and estimates of precision and accuracy associated with both the sampling and analytical instrumentation.