REVIEW OF DATA ASSESSMENT REPORT AND SCREENING LEVEL HUMAN EXPOSURE ASSESSMENT

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Overall comments:

Review of the three assessment documents (1) Data Assessment Report, (2) Screening Level Human Exposure Assessment, and (3) Future Data Needs Assessment Report, submitted by 3M Company to the U.S. Environmental Protection Agency in response to the Charge to evaluate 'Are current PFOA environmental releases and sources of those environmental releases from the Site and the presence of PFOA in environmental media on and around the Site sufficiently understood so that pathways of migration and exposure to PFOA associated with the Site are adequately characterized and assessed on a screening level basis?

The data assessment report presents a comprehensive survey of PFOA in a variety of environmental matrices to assess human exposures. PFOA environmental releases and sources of environmental releases from the Site have been assessed. The presence of PFOA in environmental media on and around the Site has been determined. Pathways of migration and exposure to PFOA associated with the Site have been characterized. Major emphasis has been placed in identifying the distribution of PFOA in soils on the Site and in surface waters near the Site, particularly in the Tennessee River/Wheeler Reservoir. For important environmental media, adequate samples have been collected to identify distribution of PFOA in on-site soils and water from the Tennessee River. However, for other environmental media either sample size is small, not statistically representative, not well planned, or were not collected; details for some such issues are discussed below. The sampling strategy is reasonably planned for addressing the major issues, to address questions pertaining to the on-site contamination. The analytical techniques used to determine PFOA in environmental media, accuracy of the data and the overall data quality is appropriate. The analytical method used for certain biota samples (hispid cotton rat) has a very high limit of quantitation (1 μg/g), which is not justified. The overall interpretation and analysis of the data are logical; a few minor issues and concerns are discussed below.

The number of samples collected for certain environmental media/matrix is not adequate and not systematic. Statistical treatment of the data is missing. For many of the samples and locations, only one sample has been collected in time and this does not represent seasonal or biological variations. For example, only four off-site soils have been collected for this study and all of the 4 off-site soils have contained detectable concentrations of PFOA. It is conceivable that PFOA contamination is widespread in soils around the Site and more soil samples need to be collected to characterize the sources and pathways.

Based on the results, it is concluded that the ingestion of groundwater and WestMorgan/East Lawrence municipal water by the residents is the major source of PFOA exposure in this region. The conclusions are logical and are adequately substantiated. Overall, tremendous effort has been put into planning, organizing and executing this work; vast majority of the information presented is technically and scientifically sound. These three reports address the charge fully. The data gaps have been clearly identified and a few additional needs are addressed in the comment below for consideration to be addressed in Phase 3.

PRIMARY QUESTIONS:

Notations used - *Report 1*: Data Assessment Report; *Report 2*: Screening Level Human Exposure Assessment Report

Clarifying Questions Assignment #4

1. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented?

Air:

The section 3 of the data assessment report and the section 2 of the screening level human exposure assessment describe conceptual model of PFOA transport and migration and sources and pathways of PFOA migration. These sections address the overall goal of the report – i.e., to characterize the presence of PFOA in environmental media on and around the Site and for transport pathway characterization. The report indicates that the production of PFOA began in 1999 and was discontinued in 2000. Dyneon facility at Decatur has used PFOA until 2004. It was acknowledged in the report that during the facility's operation, there were air emissions (page 3-6 report 1). There are currently no known air emissions from the manufacturing process (page 3-11, report 1). The report mentions that volatilization from surface soil is a minor or negligible pathway for PFOA transport (page 3-11, report 1). It has been indicated that PFOA is a non-volatile or semivolatile compound and at typical soil pH levels, PFOA is present in an anionic form. For these reasons, the report indicates that, no air monitoring was performed on or around the site.

Available data in the literature suggest that (including data collected near other PFOA production facilities) air emissions can be a major source of contamination in the areas surrounding production facilities (Davis et al., 2007, Chemosphere 67, 2011). The protonated form of PFOA and the salts (e.g., ammonium or potassium salts) of PFOA sublime at room temperature and these forms can be transported atmospherically (Kaiser et al., 2005, J.Chem. Eng. Data 50, 1841). The vapor pressure of free acid form of PFOA is 10 mm Hg at 25°C. The anionic form of PFOA can be converted into acid form under acidic environmental conditions (the sludge is acidic and the soil incorporated with sludge is expected to be acidic). PFOA, in its acid form, has a vapor pressure high enough (2.25 Pa at 20°C) to be volatile and partition into air. Air-water flux studies of PFOA have shown net volatilization from surface waters (Kim and Kannan, 2007, ES&T 41, 8328). Particulate deposition from air emissions to soil and the subsequent transfer of PFOA through the soil was determined to be a source of PFOA contamination of

groundwater (Pautenbach et al., 2007, J. Toxicol. Envl. Health, 70, 28-57). Inhalation has been identified as a pathway of PFOA exposure in humans.

Although no significant current stack emission of PFOA is expected at the 3M facility, stack releases from the past production activities (including on-site incineration of wastes), evaporation/volatilization from on-site WWTP, evaporation from inactive landfill area, evaporation from soils in the former sludge incorporation area, evaporation from surface waters (section 4.7.3 report 1), off-site locations such as Morgan Co/City of Decatur Landfill, and BFI landfill can contribute to PFOA contamination of air. Evaporation or volatilization from such contaminated surfaces can be a source of human exposures. Air-water, air-soil, plant-air and sludge-air partitioning need to be addressed to evaluate the exposure pathways. Sludge from active PFOA production years in 1999 and 2000 have been sent to Morgan Co. landfill and these landfills are expected to release PFOA into the atmosphere.

Occurrence of PFOA in the background surface soils around the facility and in the off-site soils and in vegetation samples suggests that airborne emissions have contributed to the sources of contamination. Air emissions have been identified in several sections of the report. The section 2.1.1 of report 2 has identified that air emission had occurred during the past manufacture and use on-site. The section 2.1.1.1 discussed about historical air emissions (page 2-6 to 2-8), and identified that "the potential exists for PFOA to occur in on-site and off-site air through several transport mechanisms". However, page 2-4 of the report 2 mentions that volatilization of PFOA from soils is not likely a significant pathway. This assumption is not adequately justified. Inhalation can be a potential exposure pathway of human exposure in on-site and in off-site locations where sludge has been land-filled. Furthermore, evaporation from historically contaminated soils can contribute to human inhalation pathway of exposures. Use of ground water, that contain PFOA, for irrigation of field crops and subsequent evaporation of PFOA can contribute to air emissions and exposures in humans. Therefore, air monitoring is required for both on-site and off-site locations. Air monitoring and collection of data for PFOA in air should be performed during different seasons to evaluate the influence of temperature (summer) on air levels of PFOA.

Clarifying Questions Assignment #4

2. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented?

Biota:

The section 3.2 of the data assessment report describes sources and pathways of migration of PFOA. Soil, groundwater, surface water, sediment, and air have been identified as major pathways of migration of PFOA from the Site. Biota have not been identified as a pathway of migration in this report, although potential exists that biota can play a role in the transport of PFOA from the Site. It has been mentioned in the report that the data for biota were not intended for screening level human exposure assessment, but the data are for use in characterizing the presence of PFOA in on-site biota. In comparison with media such as air, water, soil and sediment, contribution by biota as a pathway of migration of PFOA is limited. Seasonal migration of fish from the contaminated areas to other locations, movement of small and large terrestrial mammals

in and around the Site can result in migration of PFOA from the Site to other locations. The former sludge incorporation area appears to be frequented by several species of birds (page 2-22, report 1), shrews, rabbits, and white-tailed deer. The small mammal community provides prey for apex predator species. Food chain transfer of PFOA can be another pathway of biological transport of PFOA from the Site. Hispid cotton rats, which are the dominant species of small mammals found on-site, are preyed upon by hawks, owls, foxes, coyotes, bobcats, and snakes. Selection of preys from the Site can contribute to biological migration of PFOA from the Site. Several public hunting areas have been identified within 3 miles around the Site. The hunting of game animals including white-tailed deer, wild turkey, rabbit, quail, and migratory water fowl have been occurring in this area. Collection of baseline data for PFOA in the tissues of game animals is needed to evaluate the extent of contribution by the biological medium in the transport of PFOA. Foraging by game animals on the Site can acquire PFOA which can be transferred in the human food chain.

Selected species of vegetation from the Site has been analyzed for the presence of PFOA and were found to contain detectable concentrations of PFOA. Cotton and wheat have been cultivated on the former sludge incorporation area. To a lesser extent (page 2-21, report 1; page 2-3, report 2), soybeans and rye have been harvested and used as animal feed. This could have contributed to exposure in cattle and therefore, the human food chain. Nevertheless, the agricultural usage of the sludge incorporation area is currently discontinued. Although the role of vegetation in the migration of PFOA is limited, given the lack of use of vegetation from the Site for human activities, the data collected for vegetation on-site can be used to calculate soil-vegetation transfer coefficients of PFOA.

Overall, the major pathways of migration of PFOS from the Site are air, water (both surface and groundwater), soil, and sediments. The potential for biological migration of PFOA exists, but this pathway is expected to be relatively small. A baseline survey of PFOA levels in certain migratory species would be helpful in understanding the extent of biological migration of PFOA.

Clarifying Questions Assignment #8

3. ***Are the monitoring data sufficient to quantify exposures?***
   a. ***Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environment medium?***

Biota:

The major biological samples analyzed for screening level human exposure assessment are fish, represented by channel catfish and large mouth bass. Data for fillet samples have been used in the exposure assessment. Samples were collected from six locations in the Tennessee River including Bakers Creek. A total of 120 fish samples have been analyzed as 10 samples/species/location. Asiatic clams have been collected and analyzed from the six sampling sites, but the data were not used in screening level human exposure assessment. Similarly, PFOA has been detected in fish wholebody homogenates from several locations, but were not included in screening level human exposure assessment. PFOA was more frequently found in wholebody than in fillet. This suggests that tissues

other than fillet accumulate PFOA. Earlier studies have shown great concentrations of PFOA are found in liver and blood. The method of preparation of fillet can vary depending on the consumer and presence of traces of blood in fillet can increase exposure levels. The method of preparation of fillet is not discussed in this report.

The data for PFOA in fish is limited to two species. Although of the species are at the higher trophic level in the foodweb, accumulation of PFOA in fish can vary depending on the species. Wheeler Reservoir provides habitat for a variety of sport fish including crappie, walleye, striped bass and black bass. It has been stated that several other fish species such as crappie, blue catfish, black bass, sunfish, striped bass, and spotted bass are commonly harvested in Alabama (page 7-23, report 2). The popularity of the Wheeler Reservoir and Bakers Creek for fishing suggests that ingestion of recreationally caught fish may be a route of potential exposure to PFOA. Therefore, data for PFOA in major edible fishes from the area is needed to comprehensively evaluate exposure from seafood harvested in the Tennessee River and Bakers Creek. The report has identified this issue as a data gap and addressed as an uncertainty in the exposure assessment (page 9-5; report 2).

Farmer and agricultural product ingestion pathways (page 5-16 report 2): Twenty eight agricultural parcels have been identified within 1 mile of the 3M facility. Agricultural commodities in this region include field crops and livestock. Corn and soybean are commonly cultivated. The potential exists for farmers and individuals who ingest homegrown vegetables and livestock raised in the area to be exposed to PFOA in the vegetables and meat and dairy products. Cattle have been found to be grazing at these farms and exposure of vegetation to air-borne PFOA or from irrigation of groundwater containing PFOA, can result in grass/crop-cattle-human food chain migration of PFOA. Therefore, PFOA data for field crops (grains such corn, soybean, etc), hay, fodder grasses, cattle and poultry tissues (blood or milk or meat or eggs) is required to evaluate exposures through this terrestrial food chain.

Ingestion of homegrown vegetables is an exposure pathway identified in the report (page 5-13, report 2). However, lack of data precluded from exposure assessment for this pathway. The use of Kow model, as mentioned in this report (page 5-16, report 2), is not appropriate to model PFOA levels in vegetation. Instead, data for vegetation obtained from on-site vegetation samples (or from background vegetation samples) can be used to estimate soil-vegetation concentrations of PFOA. This can be used to estimate concentrations in vegetation from off-site locations, in the absence of measured data.

The potential pathways could be considered in future data collection efforts if it is shown that they could result in a significant level of exposure, e.g., locally grown meat, milk, eggs and produce, locally grown vegetables, fruits, livestock forage, silage and pasture grass. These data gaps have been identified in the report (page 10-2; report 2).

Clarifying Questions Assignment #10

5. ***Other than the EPCs, were the assumptions and exposure input parameters for each combination of pathway and receptor appropriate?***
    a. ***Was bioavailability of PFOA in the various exposure media (e.g., soil and sludge) addressed appropriately?***

Dermal absorption factor has been used to represent the fraction of PFOA that is assumed to penetrate the skin following dermal contract with soil or sediment containing PFOA (unitless). The value has been taken from Fasano et al. (2005; Drug and Chemical Toxicology, 28, 79-90) and it is 0.00048. This parameter has been used in the calculation of exposures in recreational boaters, residential soil exposures, trespasser soil exposures, construction/utility worker exposures, and groundskeeper/maintenance worker exposures.

Dermal permeability coefficient (Kp) has been used as a measure of the movement of PFOA across the skin and into the bloodstream and is expressed in units of centimeter per hour (cm/hr). The Kp value has been obtained from Fasano et al. (2005) and it is 9.5E-07 cm/hr (i.e., 0.00000095 cm/h). This parameter has been used in the calculation of exposures from scenarios that involve contact with surface waters.

Application of these factors in the calculation of exposure assessment has resulted in non-conservative estimates for exposure values. Fasano et al. 2005, from where the factors have been obtained, describe an in vitro study of human epidermal cells dosed with 20% aqueous solution of ammonium perfluorooctanoate. The permeability of concentrated solution of PFOA, because of its surfactant properties, is expected to be low. However, under typical pH conditions, as found in the Tennessee River, PFOA is expected to present predominantly in dissociated, anionic, form. The permeability of anion is expected to be different from the form of PFOA salt tested under the in vitro conditions by Fasano et al. (2005). Furthermore, the permeability factors derived for high dose exposures (i.e., % level) may not be applicable to the low level exposures from contaminated water or soil (nanogram level). Because PFOA is present at low ng/L concentrations in water and in dissolved form, it is appropriate to use water permeability coefficient rather than PFOA permeability coefficient. Water is the vehicle for PFOA (under swimming or dermal contact related exposures) and water permeability coefficient for human skin is 0.0015 cm/h (Fasano et al., 2002; Toxicology In Vitro, 16, 731-740). Use of water permeability coefficient instead of the factor derived by Fasano et al (2005), will increase the exposure doses by four orders of magnitude. Bioavailability of PFOA can be influenced by several factors and can be different from what was found under in vitro conditions. Extrapolation of factors derived from a single in vitro study and from high dose exposure scenario requires application of a safety factor or uncertainty factor for use in exposure assessments.

A recommendation:

Biomonitoring studies of human populations around the facility would eliminate several uncertainties associated with extrapolation of data for exposure assessment (bioavailability, ingestion rate, etc). Selecting populations living within 2 or 3 mile radius for the biomonitoring study and a reference population for comparison would help in identifying the extent of exposures in populations living around the site. However, it is acknowledged that such data may not be directly helpful in risk assessments.

SECONDARY QUESTIONS:

Question 1. Are the data and information presented in this report relevant to the Screening Level Exposure Assessment and of sufficient quality, quantity, objectivity, utility, and integrity? Were sufficient samples of each environmental medium

collected? Were the analytical procedures and levels of quantitation and detection adequate? Does the assessment adequately characterize the presence of PFOA associated with the Site?

Response to this question can be found as the overall comments on page 1.

Question 4. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented?

Surface water:
Both on-site and off-site surface waters have been collected to evaluate the pathways of migration of PFOA from the Site. Water samples from drainage ways, ponds, ditches, and outfalls have been sampled. The Tennessee River and Bakers Creek have been sampled systematically at various transects and along the river. Concentrations of PFOA in the on-site surface water samples are in the range of ng/ml to several hundreds of ng/ml (page 6-7; report 1). Only one wastewater effluent from the on-site WWTP was analyzed and this can be a major pathway of PFOA to the Tennessee River. Data for the on-site WWTP effluent are not reported. Data from this effluent can be useful to model the loadings and fate of PFOA into the Bakers Creek and the Tennessee River. Additional samples at different time periods need to be analyzed. The surface water data in general are adequate to understand the pathways of migration of PFOA. A clear gradient in PFOA concentrations along the Tennessee River downstream of the facility is evident.

Sediment:
Sediment samples have been collected from most locations where surface waters were collected. Both on-site marsh and pond sediments and the Tennessee River/Bakers Creek sediments have been analyzed. Sediment samples have been collected along the contamination gradient in the Tennessee River, downstream of the 3M facility. Concentrations of PFOA in sediments have been relatively low; this may imply that the major pathway of migration of PFOA is by water currents or atmospheric transport. Based on the data, it appears that the number of sediment analyzed is adequate to evaluate the pathways of migration of PFOA from the Site.

Question 8. Are the monitoring data sufficient to quantify exposures?
a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environment medium?

ii. Ground water. Data from off-site monitoring of PFOA in groundwater is limited to a single round of samples. A more robust set of groundwater data would enhance the confidence in an EPC used to represent potential residential exposure to groundwater. <u>This has been identified as a data gap in the report.</u> Because all of the groundwater

samples analyzed in this study contained PFOA, it is important to expand the survey to evaluate the extent of contamination on a regional basis.

iii. Surface water. A systematic and comprehensive survey of surface waters including the Tennessee River water, municipal water supplies from both upstream and downstream (of the facility) locations have been conducted. The data are adequate for screening level human exposure assessment.

NEIL SASS RESPONSES

CLARIFYING QUESTIONS RELATED TO THE DATA ASSESSMENT REPORT

Please answer the clarifying questions in light of the Charge, the definitions given above, and the full MOU text. As you do this, consider whether the Assessments fully address the Charge or if further work is needed.

1. Are the data and information presented in this report relevant to the Screening Level Exposure Assessment and of sufficient quality, quantity, objectivity, utility, and integrity? Were sufficient samples of each environmental medium collected? Were the analytical procedures and levels of quantitation and detection adequate? Does the assessment adequately characterize the presence of PFOA associated with the site?
2. Are the characteristics of the on-site and off-site locations evaluated in this assessment described in a sufficient level of detail to understand potential human exposure pathways? These characteristics include, for example, land use patterns, characteristics of the local population, habitats, and general physical conditions.

I believe that the on-site and off-site locations have been described in sufficient detail to understand the placement of PFOA injected into fields and the drainage patterns over and through the soil layers to be able to assess the fate of PFOA in the environment. The flow of surface and groundwater, its source, route, and destination have been determined and sampling has occurred in appropriate areas to enable clarification of contaminant levels for which risk assessments may be performed.

3. Have the nature of the soil, sub-surface geological, sedimentary, and hydrological conditions been adequately described for the purposes of assessing pathways of migration?
4. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented?
    a. Soil
    b. Groundwater
    c. Surface water
    d. Sediment
    e. Air
    f. Biota
    g. Wastewater treatment sludge and biosolids

CLARIFYING QUESTIONS RELATED TO THE SCREENING LEVEL HUMAN EXPOSURE ASSESSMENT REPORT

Site Conceptual Model

5. Does the site conceptual model adequately characterize sources associated with the site and exposure pathways linking these sources to on-site and off-site human receptors?
6. Have all appropriate receptors been identified? Do they include potentially highly exposed populations?

Section 5 of the SLHEA report documents potential human exposures to PFOA from various sources on and around the 3M property. On-site receptors include groundskeepers/maintenance workers, construction/utility workers and trespassers, as well as exposure scenarios. These I believe to be adequate for the assessment of exposure risk. I was unable to locate any classification under which plant workers themselves, other than the abovementioned, were included and would consider them to potentially be at risk from some type of exposure.

Children were classified in the 1 to 6 year old range. While this range may be appropriate, depending upon the possible mode of toxicity of perfluoro- compounds, it may be more appropriate to extend the range for children to 15 years of age.

7. Do the selected exposure scenarios sufficiently cover the situations, behaviors, and conditions under which receptors are likely to be exposed?

Generally, exposure scenarios cover situations and behaviors under which receptors might be exposed. However, there are always exceptions. I.e., fishing (Sec 5.2, SLHEA) is said to be on a catch and release basis; what evidence exists to show that this rule is obeyed?

There is also analytical detail provided for the levels of PFOA in the fish, clams, hispid cotton rats, and vegetation on the 3M site. There is reference to the presence of agricultural operations, including growth of corn, soybeans, beef and dairy cattle in areas adjacent to the Decatur facility, as well as in areas around which deposition of contaminated material may occur. I saw no analytical data that could indicate uptake by any of these products, e.g., milk, or agricultural crops that may result in an exposure of individuals both locally and at some distance from the facility. This also includes references to residential vegetable gardens (Sec. 5.3.2.2 SLHEA), a venue under which exposure may occur.

Elements of Exposure Analysis and Utilization of Data

8. Are the monitoring data sufficient to quantify exposure?
    a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media?
        i. Soil
        ii. Groundwater

iii. Surface water

iv. Sediment

v. Biota

It was mentioned that pokeweed (*Phytolacca americana) was present and contained quantifiable levels of PFOA*. It would be interesting to know the frequency of ingestion by members of the local population.

b. Of the data available to the authors, did they select the right data sets to quantify exposure? Should they have considered any of the data excluded from the analysis?

Sec. 5.3.2.7 addresses wild game available in the seven-county area, yet no data were provided to indicate that any of these could serve as a source of exposure. Other risk assessments with which I have been involved (e.g., USACHPPM – ANAD Chemical Demilitarization Facility) have posited potential exposure levels from sources such as deer, wild turkey, etc, based upon levels detected in soil, ground- and surficial waters and vegetation. The Weston report stated that ingestion of harvested gain occurs in the 7-county area, but not from the vicinity of the Decatur facility and, therefore, does not constitute an exposure scenario. This contention may be difficult to support

9. Were the data used appropriately to calculate exposure point concentrations (EPCs)?

a. Did the authors define reasonable exposure points that represent locations associated with current and future exposure?

I believe that the Weston report did enumerate sufficient and accurate data points to enable characterization of current and future exposure scenarios.

b. Are the data sufficient to understand the presence and concentration of PFOA in environmental media at each exposure point?

Sec. 5.3.4.1, Residential Scenario 3 includes potential exposures from inhalation of PFOA in dust, incidental ingestion of PFOA in soils, dermal contact, and consumption of and direct contact with PFOA in potable water, and ingestion of homegrown vegetables. However, this latter source has not been quantified nor uncertainty determined due to problems with the chemical properties of PFOA and the lack of empirical data needed to quantify these pathways (Sec. 5.3.4.5.) I believe that this could actually serve as a significant source of exposure to some populations, albeit on a seasonal basis.

c. Were EPC calculations and other statistical manipulations (e.g., treatment of results below detection limits, field duplicates, and qualified data) of these data performed accurately and appropriately?

I believe that the calculations performed were sufficient to assess exposures. I would have liked to have seen the methods used to isolate, analyze and quantitate PFOA in various media types, as well as QA/QC data on these methods, vis-à-vis, limit of detection and limit of quantitation.

d. Do the data indicate that there are exposure points other than those identified in this assessment?

See 8.b. and 9.b. above.

10. Other than the EPCs, were the assumptions and exposure input parameters for each combination of pathway and receptor appropriate?

a. Was bioavailability of PFOA in the various exposure media (e.g., soil and sludge) addressed appropriately?

I believe the bioavailability of PFOA from the various media types were addressed appropriately.

b. Have the appropriate age groupings been defined?

Children were classified in the 1 to 6 year old range. While this range may be appropriate, depending upon the possible mode of toxicity of perfluoro- compounds, it may be more appropriate to extend the range for children to 15 years of age.

c. Are the selected receptor characteristics and exposure patterns (i.e., duration, frequency, and intensity) the most appropriate for use in this assessment?

Weston used the "Reasonable Maximum Exposure" to develop a conservative estimate of potential exposures of various targets via multiple routes, durations of exposure. The General Equation (p.7-2, SLHEA) provides a workable means of quantifying the potential exposure to PFOA. I believe that results, using the parameters described in Sec. 7.2, provide an extremely conservative estimate of exposure levels, possibly in the 9th + decile range. Therefore, any calculated value might exceed the actual exposure by a significant amount.

d. Were the doses averaged over the appropriate time interval?

With the exception of categorizing a child in the 1-6 y.o. range, rather than extending this to an older age, e.g., 15 y.o., the time intervals appear appropriate. Again, data for the possible exposure to construction or utility workers for the 3M facility was estimated to be approximately one year under the presumption that these workers were employed by outside contractors. I saw no mention of possible exposure to full-time 3M workers other than the groundskeeper/maintenance worker or the duration of their tenure at the Decatur facility.

e. Overall, are the input data and assumptions valid and appropriate for all receptors?

In spite of a lack of definitive data expressing possible exposure to some segments of the potential target population, I believe that the overestimation of the potential risk to other segments of the population would permit extrapolation of a valid risk to those overlooked individuals.

The estimates of fish consumption do not fit with the hypotheses utilized by the State of Alabama. It was presumed that the mean daily consumption was 97 g/day (3.42 oz; range = 0.6 g/day [0.021 oz/day] – 895 g/day[31.57 oz/day]) in actuality, Alabama uses

meal consumption values of 8 oz (226.8 g) wet weight = 6 oz (170.09) cooked weight for fish meals.

11. Were the appropriate exposure pathways selected for quantifying dose? Was the justification for excluding exposure pathways from dose estimation reasonable?

Appropriate scenarios and pathways were selected to enable determination of exposure for the general population in and around the Decatur facility. I am not sure whether the same scenarios could be applied to areas further remote from the actual source of contaminant (e.g., surrounding other landfill areas and adequate characterization of ingestion of PFOA from residential scenarios from where contaminant may be leached or be found in processed waters.)

12. For exposure pathways for which the data did not allow quantitative assessment, did the authors present a qualitative or semi-quantitative description of exposure?

No, the authors dismissed exposures in areas for which data were not collected or developed.

Uncertainty Analysis and Data Needs to Remedy Uncertainty

13. The authors describe data needs for exposure pathways that were not quantified in this assessment. Do you agree with recommendations for further sampling and analysis designed to facilitate quantification of these other exposure pathways on a screening level basis? Do you have other recommendations for data collection, modeling and other analyses, and exposure pathway quantification?

I concur with the proposals cited in the Future Data Needs Assessment Report.

14. Were all the significant sources of uncertainty identified and characterized? Are the authors' conclusions regarding the significance and impact of the uncertainties on the resulting assessment conclusions appropriate (See Table 9-1)? Given uncertainties, what is the likelihood that actual exposures have been over-estimated or under-estimated?

I believe that the scenarios, estimates, and uncertainties will result in an over-estimation of level of risk of exposure. The provision of additional data will verify/disprove the adequacy of the exposure estimates.

CLARIFYING QUESTIONS RELATED TO THE FUTURE DATA NEEDS ASSESSMENT REPORT

15. Does this Assessment identify additional data and/or other appropriate information necessary? Please identify any critical data gaps or potential pathways for exposure you feel have not been identified.

At this stage, I believe the Phase 3 plan will fill remaining gaps I have identified, pending review of the data and incorporation of said data into existing estimates.

16. Does the Phase 3 Work Plan Outline contain all of the technical elements required for gathering the proposed additional data?

Technical clarification: p. 2-19, Data Assessment Report states that fish consumption advisories have been issued for the Indian Creek and Huntsville Spring Branch for bigmouth and small mouth drum. This is incorrect. The advisories have been issued for buffalofish (*Ictiobus sp.*) rather than freshwater drum (*Aplodinotus grunniens.*

RESPONSE TO PEER CONSULTATION CLARIFYING QUESTIONS

C. J. NEWELL APRIL 8, 2008

CLARIFYING QUESTIONS RELATED TO THE DATA ASSESSMENT REPORT

2. *Are the characteristics of the on-site and off-site locations evaluated in this assessment described in a sufficient level of detail to understand potential human exposure pathways? These characteristics include, for example, land use patterns, characteristics of the local population, habitats, and general physical conditions.*

PRELIMINARY COMMENTS PRIOR TO MEETING

This question appears to be directed at the completeness and overall level of detail provided in Section 2 of the Data Assessment Report, titled "Environmental Settings." Section 2 discusses the following topics: site location, topography/drainage, geology, hydrogeology, demographics/land use, and the environmental setting of the Former Sludge Incorporation area.

There is considerable detail on each of the key topics listed above. There are a few questions/issues where additional environmental setting data (or clarifications of the existing data) would be helpful:

- A more detailed topographic map for evaluating stormwater drainage flow is needed. Although the drainage flow arrows on Figure 2-2 are instructive, there are specific questions I had regarding on-site stormwater flow direction from the various sludge incorporation fields to off-site (e.g., do any of the Sludge Incorporation Fields drain into Goose Pond and/or the Avenue A ditch?). Although some of the subsequent figures have grey-line topography, it is not labelled and difficult to interpret. A topographic map that shows the elevation of the drainage ditches and swales would be useful to evaluate the conclusion that the residuum and epikarst units discharge into the on-site drainage system on the southwest portion of the plant.
- Data showing the maximum depth of the Tennessee River/Wheeler Reservoir would be useful to support the conclusion that northerly flowing groundwater in all three units discharges to this system.
- Table 2-10 shows sludge applied by field. A companion table showing the total amount of sludge applied per year, if available, would be helpful to assess loading rates over time and might be helpful to assess the spatial pattern of off-site groundwater concentrations.
- More information regarding the "City Boundary" information on Figure 2-2 would be helpful. For example, is the City Boundary immediately to the west of the 3M facility part of Decatur?
- Minor Point: The text and title of Figure 2-5 indicate that the bedrock elevation is posted on the map; however, the legend states the data are "Groundwater Elevations." Is the legend incorrect?

CLARIFYING QUESTIONS RELATED TO THE DATA ASSESSMENT REPORT

3. *Have the nature of the soil, sub-surface geological, sedimentary, and hydrological conditions been adequately described for the purposes of assessing pathways of migration?*

PRELIMINARY COMMENTS PRIOR TO MEETING

This question refers to the completeness and level of detail regarding the physical environment of the study area in terms of soils, geology, and hydrology. These data are presented in several sections of the Data Assessment Report.

In general considerable data has been collected regarding the soil, geology, and hydrology of the study area. There are areas where additional information would be helpful, or where I had questions that might be clarified by further review. Key issues/questions are summarized below:

- Are there any hydraulic conductivity data for the residuum or shallow bedrock units?
- A short summary of the dye test for the epikarst unit (location, test design, results) would be helpful.
- Why are there no wells in the northern portion of the site that are screened in the epikarst unit (see Figure 2-8)?
- Data showing the bottom elevation of the surface drainage and the surface water elevation range in the Wheeler Reservoir/Baker Creek would be useful to evaluate the groundwater discharge patterns for the residuum and epikarst units (see Question 2 response).
- What is the vertical gradient for groundwater at the site? Does it change much across the site? What information was used to conclude that there is "...restricted downward vertical movement between the three groundwater zones" at certain locations (page 2-15, Data Assessment Report).
- More information about the surface water hydrogeology would be helpful, such as a summary the flow regime in the river (e.g., discharge statistics) and if available, the residence time of Wheeler Reservoir.
- Where is off-site well in the marsh (well OSM) screened? What were the typical flowrates for this well during the time it was operated? Is it possible to estimate a capture zone for this well while it was operated?
- The Future Data Needs Assessment Report concluded that the following data needs had been identified for off-site groundwater, off-site soil, and surface water/sediment:
    - Additional off-site groundwater sampling events at existing (and new wells)
    - Follow-up investigation of off-site water supply wells
    - Additional off-site monitoring shallow bedrock wells located northwest, west, southwest, and east of the site to determine groundwater direction in these areas
    - Analysis of surface water and sediment samples collected in Dec. 2006 but not included in the current reports

CLARIFYING QUESTIONS RELATED TO THE FUTURE DATA NEEDS ASSESSMENT REPORT

16. Does the Phase 3 Work Plan Outline contain all of the technical elements required for gathering the proposed additional data?

PRELIMINARY COMMENTS PRIOR TO MEETING

This question refers to the Phase 3 Work Plan Outline, a one-page summary of the key elements to be included in the Work Plan. I had no major comments. One minor question is why in Section 3, Groundwater, Soil, and Biota each have there own subheadings (Section 3.1, 3.2, 3.3) but Surface Water and Sediment appear to be lumped under Section 3.4 "Additional Activities". Is this because the Phase 3 Surface Water and Sediment tasks are relatively minor compared to Groundwater, Soil, and Biota?

CLARIFYING QUESTIONS RELATED TO THE SCREENING LEVEL HUMAN EXPOSURE ASSESSMENT REPORT

Elements of Exposure Analysis and Utilization of Data

1. Are the monitoring data sufficient to quantify exposure?
    a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media?
        ii. Groundwater

PRELIMINARY COMMENTS PRIOR TO MEETING

Most on-site groundwater concentrations appear to be significantly higher than the off-site groundwater concentrations presented in the Data Assessment Report. Some of this relatively high concentration groundwater from the source areas appears to have migrated slightly off-site in at least one location (i.e., well OSM, the off-site well that was pumped to provide water to pond at the Wetlands Edge Nature Center) (see Figures 5-1 and 5-17). Well OSM was not included in the off-site groundwater EPC calculations, presumably because of the artificial gradient created by the well.

Another relatively high-concentration well (Well 136R, located in the southwest corner of the facility, is screened in a unit that may have an off-site flow gradient at this location (see Figure 2-8).

Linda S. Lee Response to Phases I and I Reporting

1. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented? (*question 4 in clarifying questions*) - **Soil,** *Groundwater,* Surface water, Sediment, *Air* ,Biota, and **Wastewater treatment sludge and biosolids**

Sampling of the various media done in Phase I with the follow up of additional samples in Phase II appears to have captured much of the contamination patterns but there are still some issues that need some or better resolution. Much of the additional characterization needed is noted in the Future Data Needs Assessment Report. Of greatest importance that was noted is a better characterization of the PFOA concentrations and flow gradients of the shallow water-bearing zones. In addition, I believe some additional soils samples with depth may need to be taken in relation to the former sludge incorporation area as needed to better assess some of the flow gradients in the upper two water-bearing regions. It would also be informative to have a few samples taken form the off-site swamp area, which it appears no sampling was done. It is not clear what wildlife or people access this swamp area has.

Concerns on PFOA levels present in other off-site areas and media as it relates to personal gardens, farms, and animal production farms should be addressed. It would seem getting surface soils samples for this assessment would be adequate since if concentrations are not presenting soils above background then there is likely not going to be an issue with the vegetation, meat, or milk produced around theses soils.

2. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media? Are the monitoring data sufficient to quantify exposure? (*question 8 in clarifying questions*)
    a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media? – **Soil,** *Groundwater,* Surface water, Sediment, and Biota
    b. Of the data available to the authors, did they select the right data sets to quantify exposure? Should they have considered any of the data excluded from the analysis?

Even with the request of some additional data needs, the authors generally used a conservative approach in assigning EPCs and using these values to determine RMEs.

Miscellaneous comments related to the above questions:

The former sludge area, which in general has the highest PFOA levels of all media tested to date, compromised 575 acres of land of which some was sold to Daikin. Originally field 7 (not sampled– on Daikin property) was that was sold, so only Field 14 never had sludge applied, thus a good assessment of PFOA levels expected if contamination modes are limited to aerosol and dust transport and irrigation water. Sludge (1 to 3% solids) was supposedly only subsurfaced injected about 1 foot below the surface and never land applied; however, considerable contamination does exist above that zone for many of the soil samples (especially in Fields 8b,

10, and 11a). The latter suggests one of several possible explanations or a combination them: (1) subsurface injection was not as deep as thought, which can occur if the person operating the injector is traveling at higher speeds than recommended, or given the condition of the soil, soil texture (clayey soils with a high moisture content, which appears to be the case for many cores), and injection rate, the liquids could have routinely bubbled back up into the surface profile; (2) substantial amounts of run off occurred, which in some cases, but not all, may have been a significant contribution; (3) tilling practices although tilling usually disturbs no more than the top 10 inches of soil; (4) dust transport and deposition (transport of aerosols formed during irrigation), although based on the concentrations from Field 4 samples, this contamination mode would not lead to the concentrations observed in some of the surface soils; and/or (5) long term irrigation with PFOA-contaminated water. Data from Field 14 samples indicates modes 4 and/or 5 coupled to leaching were operating on the control field, which would explain low levels throughout the soil column. The area is no longer cropped (thus no longer tilled), but is naturally vegetated, but it is not clear when the cropping and tilling practices stopped.

Even more interesting, is that these high concentrations are from sludge that was applied before PFOA production was commenced at the 3M facility; report states that PFOA production started in 1999 and was phased out in 2000, but the practice of subsurface injection of sludge was only until 1998. This indicates that the levels in the soils now (which have dissipated some since that time) are from the small (relative to PFOA production) amounts of PFOA that was used in the production of other things or present in impurities of the other perfluorochemicals.

In some cases in the Data Assessment Report values were reported as NR due to lab QA/QC criteria not being made; however, values for theses same samples are latter reported (and they are always high), in the SLHEA Report. I am assuming that although both reports have the same date (January 2008) that SLHEA report, which had to be prepared after the data assessment report, included results from soils that were re-analyzed.

3. Other than the EPCs, were the assumptions and exposure input parameters for each combination of pathway and receptor appropriate? (*question 10 in clarifying questions*)
    a. Was bioavailability of PFOA in the various exposure media (e.g., soil and sludge) addressed appropriately?

It appears that bioavailability of ingested material was assumed to be unity, which is a safe conservative approach and may be the case for such a soluble chemical.

I have some questions regarding the dermal absorption factors used, which were cited to Fasano et al, 2005. This is not my area, but I do question if the salt form (counter ion) of PFOA impacts its transport across membranes. Fasano et al (2005) use an ammonium PFOA form in their studies, which is not likely to be the form present in the soil that may adhere to the skin since any ammonium applied to the soil will be converted to other forms (non-cation forms) of nitrogen or have long been dissipated by various processes. Having said, this, I have not done a sensitivity analysis to see how much this value impacts the final RMEs for the scenarios that involve this mode of exposure.

Mike Jayjock Big X Questions and Responses

5. Does the site conceptual model adequately characterize sources associated with the site and exposure pathways linking these sources to on-site and off-site human receptors?

One of the fundamental assumptions of the conceptual model for source characterization is that the PFOA is essentially nonvolatile. I have a question and concern about this assumption.

It is clear that PFOA has nonionic surfactant properties and is a weak acid in aqueous systems. That is it tends to accumulate on the air/water interface when it exist in aqueous volumes and its predominant chemical form is as an associated (*i.e.,* non-ionized) molecule. Thus, one might conclude that most of the PFOA is on the surface of any aqueous system and that vast majority of its molecules will be associated or protonated in aqueous systems with neutral or acidic pH. As such, one would assume that there might be a very significant expression of the vapor pressure of PFOA from these systems. That is - because it is mostly on the surface and not ionized it should be at least partially, if not readily, available to evaporate.

Given a vapor pressure of 4.2 Pa the full expression or saturation vapor pressure of PFOA is approximately 40 ppm v/v (675 mg/m^3) in normal atmospheric air at 25C which is not an insignificantly level of volatility for any material. Thus, my concern is that the assumption of no PFOA volatility in reports by Weston may be missing a significant route and source of exposure and depuration from the site. It would appear to me that this assumption could come into question and this, of course, could affect the overall assessment.

In briefly researching this issue on the Internet I have been able to find a report from Europe: *PFOA in Norway TA-2354/2007* issued by the Norwegian Pollution Control Authority (SFT). This 77 page report is dated December 2007 and available online at: http://www.sft.no/publikasjoner/2354/ta2354.pdf . An Adobe PDF file of this report is also available from Jayjock (PFOA in Norway 2007.pdf). Within this document there are referenced reports of significantly higher pKa (more association or protonation of the weak acid) and actual measured volatility of PFOA in the headspace over water.

While I certainly agree that the octanol/water partition coefficient (Kow) is essentially unmeasureable; the vapor pressure of the compound over water may not be. It would certainly appear to be worthwhile to check out the referenced work in the Norwegian publication and otherwise revisit the assumption of nonvolatility. Unfortunately, the references within this report at not straightforward citations and it may take some further investigational effort to get at them.

Other comments below outline potential missing parts for the conceptual model.

7. Do the selected exposure scenarios sufficiently cover the situations, behaviors, and conditions under which receptors are likely to be exposed?

For the most part the reports' treatment of exposure scenarios appears to be quite extensive. The scenarios as outlined reveal considerable thought and a reasonable level of care. I did, however, find myself asking certain questions as I read the description of the analysis.

For example, it is stated in section 5.1 of the Screening Level Human Exposure Assessment Report (SLHEA) that although the former sludge area fields have no trespassing signs posted they are not fenced; thus, there is the possibility of trespassers accessing the area. The question in my mind is: Could there be any gathering, hunting or trapping activity within these fields that would result in trespassers become exposed. This might include capturing game for ingestion? The only potential activities for trespassers listed in Section 5.2.1.3 are "walking and bird watching".

Relative to any examination of PFOA in game species the report advises: "

> "... ingestion of harvested game is common in the seven-county study area but not in the immediate vicinity of the Decatur facility. Therefore, exposure to harvested game was not considered further in the SLHEA." (page 5-9)"

In addition to any game potentially captured by trespassers in the former sludge area and areas immediately adjacent to it, I wonder about game that feeds in these area and then goes considerable distance off-site to be hunted, captured and eaten. Birds are particularly mobile and dove and quail are listed as favorite hunted species for the area. Birds also typically ingest dirt and small bits of gravel from sites to aid their digestion and these sites are often in areas where the soil has been disturbed.

These questions (and perhaps news ones) will have a clearer voice when we have an opportunity to visit the site and ask for more specific information.

10. Other than the EPCs, were the assumptions and exposure input parameters for each combination of pathway and receptor appropriate?
    a. Was bioavailability of PFOA in the various exposure media (e.g., soil and sludge) addressed appropriately?
    b. Have the appropriate age groupings been defined?

It would appear that appropriate age groupings were used in some of the scenarios (*e.g.,* the area of fish consumption). Dividing those exposed into two groups; that is, young children (3-5 years and adults (>18 years) appears to make sense. However, from what I could determine within the report, it seems that the tacit assumption is that all on-site (Tables 7-13 and 7-14) and off-site marsh area trespassers are adults and depending on the circumstance this may not be true. Indeed, from my experience, given a reasonably opportunity, children (of 18 years of age or less) are more likely to be extensively roaming in such areas.

My sense is that children should be included in all scenarios where there is a reasonable possibility for their existence within the scenario because of their special vulnerability. This specific issue was addressed in a 1997 Presidential Executive Order: http://yosemite.epa.gov/ochp/ochpweb.nsf/content/whatwe_executiv.htm .

An excerpt from this order advises:

> "A growing body of scientific knowledge demonstrates that children may suffer disproportionately from environmental health risks and safety risks. These risks arise because: children's neurological, immunological, digestive, and other bodily systems are still developing; children eat more food, drink more fluids, and breathe more air in proportion to their body weight than adults; children's size and weight may diminish their protection from standard safety features; and children's behavior patterns may make them more susceptible to accidents because they are less able to protect themselves."

c. Are the selected receptor characteristics and exposure patterns (i.e., duration, frequency, and intensity) the most appropriate for use in this assessment?

d. **Were the doses averaged over the appropriate time interval?**

This question highlights the inextricable connection between the exposure assessment and effects assessment in the ultimate determination of human health risk. Indeed, the appropriate time interval for the measurement of "average" exposure over that period is very much a function of the residence time and the response of that material in the body.

For example, if a material causes its biological damage quickly and is gone from the body in a short time then how we both measure its exposure and test its toxicity become critical. Assume that a material has a half-life of a few minutes in the body then spreading or apportioning the daily dose of this material over 24 hours in an inhalation toxicology protocol will give very different results than if the animal got the same amount in 4 or 3 or 1 hour's inhalation exposure that day. The same dose of this quick acting material would do much more damage amassed in a bolus dose of a few minutes or even an hour or two than spread over 24 hours.

This reality has obvious implication relative to the dosing scheme for toxicity testing but more important for our purposes is that it also advises as to which exposure sampling intervals are appropriate and useful.

That is, if a material causes its biological damage and is gone from the body in a relatively short period of time then a long-term sampling and averaging times are inappropriate and dangerous for the above-mentioned reasons.

On the other hand, if the biological half-life of the compound is longer than a few months then relatively high spikes of exposure occurring within a year or more are most likely not significant from a health impact perspective. What is important from a chronic toxicity perspective for these types of compounds is, of course, the weighted average

over a significantly longer time period. Some of the mathematical details of this reality are presented in the references below by Roach and Rappaport.

The biological half-life of PFOA in humans is remarkably long and reported to be 3.8 years (http://www.chem.utoronto.ca/symposium/fluoros/). Thus, assuming that the concentration encountered by people during short term exposure do not cause any specific acute effect, using a long term averaging time interval for assessing exposure is completely appropriate.

REFERENCES:

Roach, S.A.: A More Rational Basis for Air-Sampling Programs, American Industrial Hygiene Journal, vol 27, pp 1-12, 1966.

Rappaport, S.M.: Smoothing of Exposure Variability at the Receptor - Implications for Health Standards, Annals of Occupational Hygiene, vol 29, pp 201-214, 1985.

Rappaport, S.M. and R.C. Spear: Physiological Damping of Exposure Variability During Brief Periods, Annals of Occupational Hygiene, vol 32, pp 21-33, 1988.

14. Were all the significant sources of uncertainty identified and characterized? Are the authors' conclusions regarding the significance and impact of the uncertainties on the resulting assessment conclusions appropriate (See Table 9-1)? Given uncertainties, what is the likelihood that actual exposures have been over-estimated or under-estimated?

With the possible exceptions of some of the potentially important and missed scenario specifics mentioned above, the authors did a very credible job of identifying the uncertainties.

The critical impact of uncertainty is born of a lack of knowledge and this basic unawareness is truly the bane of any risk assessor. When we admit that "we don't know what we don't know" it makes it extremely difficult to render even qualitative conclusions about the nature of its effect. For example, relative to the author's conclusions regarding the significance and impact of the uncertainty as presented in Table 9-1 I would argue that when the information is so uncertain that even the DIRECTION of the uncertainty is unknown then its magnitude should also be declared unknown and thus (in the spirit of precaution) potentially high.

My feeling is that the overall level of actual exposure to PFOA has been under-estimated; however, my "feelings" are not a credible and objective risk assessment. In my experience a single unaccounted source of source of exposure could be a very significant contributor to the exposure of some subpopulation of interest. In my younger days I have been surprised on a number of occasions. Indeed, there is no substitute for data and careful and comprehensive analysis.

Assuming some or all of the issues identified above are adequately addressed then I believe that a reasonable degree of confidence would be warranted that the estimated exposures for the vast majority of potential exposed persons would be below the actual exposures for those individuals.

KIRK KESSLER RESPONSES

CLARIFYING QUESTIONS RELATED TO THE DATA ASSESSMENT REPORT

Please answer the clarifying questions in light of the Charge, the definitions given above, and the full MOU text. As you do this, consider whether the Assessments fully address the Charge or if further work is needed.

1. **Are the data and information presented in this report relevant to the Screening Level Exposure Assessment and of sufficient quality, quantity, objectivity, utility, and integrity? Were sufficient samples of each environmental medium collected? Were the analytical procedures and levels of quantitation and detection adequate? Does the assessment adequately characterize the presence of PFOA associated with the site?**

Kessler Response:

(It is noted this reviewer would prefer to have completed an analysis of the data reported in the Data Assessment Report (DAR) through the use of Geographic Information System (GIS) examination of the data. GIS files were not available to this reviewer by the time of this preliminary assessment of the report – thus the response to Clarifying Questions should be considered as potentially partial and subject to update at a later time.)

The DAR contains data and information that are relevant to the Screening Level Exposure Assessment (SLERA), and in addition other data are presented but as noted are not included in the SLERA. The DAR could be clearer as to the rationale for collecting the additional information that was omitted from the SLERA.

The overall quality, objectivity, and utility of the data were sound and sufficient for the purpose of determining a representative Exposure Point Concentration (EPC) within the SLERA. This reviewer has other comments related to the completeness of the site assessment as related to the ability to evaluate the transport and fate of perfluorooctanoic acid (PFOA) at the subject site – these potential deficiencies would not affect the EPC or the SLERA in general, but rather would materialize at a later stage of the risk characterization process. As such these comments are appended to the end of this review (Attachment 1).

The quantity of data for some media seems excessive (e.g., soils from the Fields), if data were simply being collected to characterize a representative EPC. The excessive amount of soils data is true for both surface and moreover subsurface soils. This reviewer presumes the detailed vertical distribution profiling of PFOA in the subsurface soils is for the purpose of some subsequent evaluation of the transport and fate characteristics of PFOA, for little is made of this data within the DAR. Indeed, these data are simplified into a single mean concentration for each sample location. Another question concerning the excessive quantity of data is related to the abundance of field duplicate <u>and</u> laboratory replicate analyses. This is especially true for water matrix samples where both duplicate and replicate analyses were conducted at a 100% level. The DAR does not seem to utilize these duplicate/replicate samples in an analysis of field and/or laboratory variability – this reviewer's qualitative evaluation of the duplicates suggest a relatively low degree of variability (which is generally true for a water matrix sample compared to a solid matrix sample) and as such, in hindsight

perhaps this amount of field duplication and laboratory replication was excessive and unnecessary. A more rigorous analysis of these data seems appropriate to avoid unnecessary analytical testing in any future phase of work.

The integrity of the data and information presented in the DAR are generally adequate for use in the SLERA, with the possible exceptions noted below:

- *The lack of sample size of 10 or more for some of the sample categories results in a conservative measure of the EPC, represented by the maximum detected PFOA concentration within that sample category. In these cases the mean or median concentration of the sample is typically significantly lower than the maximum. This point is further discussed in the review of the SLERA (Clarifying Question 9b).*
- *Some of the water matrix samples may have been affected by high suspended solids content in the sample (assuming, as noted in the documents, PFOA is often sorbed to the solid phase particle). This issue seems especially prevalent to the river pore water samples, and to some of the groundwater samples. Typically such interference would result in a false positive (or exaggeration) of the PFOA concentration in the water matrix sample. This reviewer's qualitative evaluation of the correlation between suspended solids concentration and PFOA concentration shows no apparent bias; a more rigorous evaluation is suggested however.*

The analytical procedures and laboratory quantitation level are judged to be adequate. Indeed very few samples are expressed as undetected below the quantitation level.

The presence of PFOA associated with the site is adequately characterized for the purpose of supporting the SLERA. Comments regarding the quality and thoroughness of the overall site characterization are appended to this set of Clarifying Questions (Attachment 1).

2. **Are the characteristics of the on-site and off-site locations evaluated in this assessment described in a sufficient level of detail to understand potential human exposure pathways? These characteristics include, for example, land use patterns, characteristics of the local population, habitats, and general physical conditions.**

Kessler Response:

See Attachment 1 for specific points raised during the review of the DAR. It is difficult to judge the adequacy of the assessment in terms of the overall site characteristics and ability of apply these characteristics to the understanding of an exposure pathway, for the DAR is lacking in terms of detailed evaluation and discussion in many instances. Potential deficiencies include:

- *issues related to the hydrogeologic site characterization and PFOA plume distribution (supported by the hydrgeologic characterization); and*
- *leaching characteristics of the soil, especially within the sludge applied to the Fields area of the site.*

3. Have the nature of the soil, sub-surface geological, sedimentary, and hydrological conditions been adequately described for the purposes of assessing pathways of migration?

Kessler Response:

The DAR contains mention of supporting studies regarding the assessment of migration pathways, such as dye trace studies, fracture trace studies, and sediment transport modeling although these studies are not provided nor are the study conclusions necessarily stated in the DAR. It is as if the DAR is limited to presenting the studies related to characterizing the concentration of PFOA in the various environmental media, for the purpose of supporting the derivation of the EPC on the SLERA document.

4. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented?
    a. Soil
    b. Groundwater
    c. Surface water
    d. Sediment
    e. Air
    f. Biota
    g. Wastewater treatment sludge and biosolids

Kessler Response:

The pathways of migration of PFOA from these media have been adequately considered, with the exception of the leaching of soil (and sludge formerly applied to the Fields) to groundwater. Direct measurement of the leaching characteristics was not performed, but rather inferred based on the general association of high PFOA levels in soil to high PFOA levels in the underlying groundwater. This association could simply be a result of differences in the original sludge characteristic applied to the different areas of the site, and the slow (ongoing) dewatering of the porewater contained in the original sludge,

CLARIFYING QUESTIONS RELATED TO THE SCREENING LEVEL HUMAN EXPOSURE ASSESSMENT REPORT

Site Conceptual Model

5. Does the site conceptual model adequately characterize sources associated with the site and exposure pathways linking these sources to on-site and off-site human receptors?
6. Have all appropriate receptors been identified? Do they include potentially highly exposed populations?

7. Do the selected exposure scenarios sufficiently cover the situations, behaviors, and conditions under which receptors are likely to be exposed?

Elements of Exposure Analysis and Utilization of Data

8. Are the monitoring data sufficient to quantify exposure?
    a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media?
        i. Soil
        ii. Groundwater
        iii. Surface water
        iv. Sediment
        v. Biota

Kessler Response:

Instances where the EPC was assigned as the maximum concentration characterized for a given medium, owing to small sample size, likely over-predicts the true exposure. Additional sampling and recalculation of the EPC may be warranted for such instances.

Also, it appears from Figure 6-6 in the SLERA that the EPC calculated for the Middle Reach of Wheeler Reservoir contained samples from both the Middle Reservoir and onsite areas outside the river proper. These data should be segregated for the purpose of characterizing the exposure.

    b. Of the data available to the authors, did they select the right data sets to quantify exposure? Should they have considered any of the data excluded from the analysis?

Kessler Response:

See comment above regarding the possible mixing of samples from the plant site proper and the Middle Reservoir.

9. Were the data used appropriately to calculate exposure point concentrations (EPCs)?
    a. Did the authors define reasonable exposure points that represent locations associated with current and future exposure?
    b. Are the data sufficient to understand the presence and concentration of PFOA in environmental media at each exposure point?

Kessler Response:

Data were used appropriately in the derivation of the EPC. This reviewer has commented previously herein on the possible overstatement of the EPC for media of small sample size, where the EPC defaults to the maximum detected concentration of PFOA in that media.

c. Were EPC calculations and other statistical manipulations (e.g., treatment of results below detection limits, field duplicates, and qualified data) of these data performed accurately and appropriately?

d. Do the data indicate that there are exposure points other than those identified in this assessment?

10. Other than the EPCs, were the assumptions and exposure input parameters for each combination of pathway and receptor appropriate?

    a. Was bioavailability of PFOA in the various exposure media (e.g., soil and sludge) addressed appropriately?

    b. Have the appropriate age groupings been defined?

    c. Are the selected receptor characteristics and exposure patterns (i.e., duration, frequency, and intensity) the most appropriate for use in this assessment?

    d. Were the doses averaged over the appropriate time interval?

    e. Overall, are the input data and assumptions valid and appropriate for all receptors?

11. Were the appropriate exposure pathways selected for quantifying dose? Was the justification for excluding exposure pathways from dose estimation reasonable?

12. For exposure pathways for which the data did not allow quantitative assessment, did the authors present a qualitative or semi-quantitative description of exposure?

Uncertainty Analysis and Data Needs to Remedy Uncertainty

13. The authors describe data needs for exposure pathways that were not quantified in this assessment. Do you agree with recommendations for further sampling and analysis designed to facilitate quantification of these other exposure pathways on a screening level basis? Do you have other recommendations for data collection, modeling and other analyses, and exposure pathway quantification?

14. Were all the significant sources of uncertainty identified and characterized? Are the authors' conclusions regarding the significance and impact of the uncertainties on the resulting assessment conclusions appropriate (See Table 9-1)? Given uncertainties, what is the likelihood that actual exposures have been over-estimated or under-estimated?

CLARIFYING QUESTIONS RELATED TO THE FUTURE DATA NEEDS ASSESSMENT REPORT

15. **Does this Assessment identify additional data and/or other appropriate information necessary? Please identify any critical data gaps or potential pathways for exposure you feel have not been identified.**

Kessler Response:

The Future Needs document mentions additional surface water and sediment samples have been collected but not reporting in the documents (results were obtained apparently too late for incorporation) – it is unclear if the intent of the samples is to re-examine the data with respect to the EPC.

The installation and sampling of additional monitoring wells and re-sampling of existing wells will improve the understanding of the distribution of PFOA in this media. Additional hydraulic head measurement points will also improve the understanding of groundwater flow. Of potential major significance however is the possibility of preferential groundwater flow pathways (conduit flow) in the Epikarst system – such pathways may not be expressed in the normal mapping of a potentiometric surface. Additional dye trace study may be prudent, although it is impossible to judge the absolute need for this work without the benefit to past dye trace study at the site.

16. **Does the Phase 3 Work Plan Outline contain all of the technical elements required for gathering the proposed additional data?**

Kessler Response:

The Work Plan Outline should also contain a technical element of an integrated analysis of all currently available information related to groundwater, to support the number and locations of additional monitoring wells and perhaps other form of groundwater investigation. For example, the presently characterized distribution of PFOA in the groundwater should be examined with respect to such factors as fracture traces, overlying soils concentrations, and potentiometric surfaces (for the three hydrogeologic layers).

Kirk Kessler Attachment 1

Data Assessment Report

Page	Comment
2-9	Mention of pumping tests, fracture trace analyses - where is the data & interpretation?
2-12	Mention of dye trace analyses - where is the data & interpretation? Possible misinterpretation of potentiometric surface & groundwater flow characteristics.
Figure 2-4	Fracture traces - why haven't they been identified in the main study area (Fields)? They could be of primary importance in discerning the groundwater flow characteristic in this area.
Figures 2-6 to 2-8	Potentiometric surfaces are typically not so "complicated". Recharge/infiltraiton from Fields seems evident.
2-14	SW drainageway is interpreted as "intercepting flow" of residuum and epikarst groundwater. If so, surface water should be evident in the drainageway. Perhaps trough is subsurface only - secondary permeability feature.
2-15	Does the PFOA plume distribution match the key findings expressed in the report (no evaluation of the plume distribution is mentioned)? Also, why weren't the main plant site wells tied into the investigation?
3-7	Surface Transport - stated pathway was characterized by collection of surface soil samples in drainages, and transport models were used to model sediment transport. Model detals not provided. Why not measure transport direct by sampling of mobilized sediment (storm water event sampling)?
3-8	Leaching - again, why the indirect measure of this pathway (soil & groundwater sampling). Why not run TCLP/SPLP to measure leaching potential?
3-11	Uptake [sediment] - fish sampling did not include lower trophic level fish or benthos (prey species). This would be important to discern influence of diet versus environment regarding the PFOA levels characterized in the higher trophic level finfishes.
4-6	Why is groundwater sampled with a PE bailer, rather than current EPA method of low-flow purge & sample? Was there excess turbidity in the sample due to bailer use?
4-29	SW samples included unfiltered + filtered sample to assess sorbed fraction of PFOA - were data assessed in this manner?
4-29	Report presumes pore water to be groundwater (based on flownet analysys); lock & dam control of pool elevation may affect GW-SW interaction on this scale such that the river loses water to the shallow aquifer at high pool stages.
4-30	Flownet analysis is mentioned - where is this presented in the report?
Figure 5-2	Explain reason for elevated PFOA in two of the plant site wells (310R; 327R). Are local sources hypothesized (high conc. in soil for 327R)?
Figure 5-15	Note: whole body tissue concentrations are higher than fillet concentrations. Bass seem to have higher concentrations compared to catfish. Are these trends expected?
6-2	Key Hydrogeologic Finding in the report state "restricted downward vertical movement between the three groundwater zones". Note the hydraulic head measurements that consistently demonstrate a downward gradient, more pronounced in the Fields areas. Head differences are typically in excess of 10ft across the well clusters.
6-4	There is no discussion of the consistent pattern of downward head gradients between the 3 hydrogeologic zones, with respect to groundwater flow characteristics.
6-4	Was there any attempt to contour PFOA concentrations in groundwater (either two dimensionally for three dimensionally)?
6-6	Subsurface Soil - comment is made that detection of PFOA throughout entire thickness of soil column down to the water table, demonstrates PFOA has leached from the soil. An alternative explanation could be the PFOA is largely the result of porewater released from the slurry (only 1-3% solids content) and migrating vertically - this is not the same as leaching. Has a correlaton evaluation been attempted between PFOA concentration, soil moisture content, and observed presence of slurry materials?
6-7	Detection of 924 ppb PFOA in vegetation suggests rather significant uptake characteristic; was vegetation cleansed prior to sample collection?

Screening Level Human Exposure Assessment Report

Page	Comment
2-9	Data gap noted - uncertainty is expressed in the SLERA as to the uptake mechanism of PFOA to finfish. Sampling of prey items (benthos; lower trophic fish) could address the uncertainty.
4-1	Soils (also Figure 4-1) - clarify definition of "surface soils"; Data Assessment Report states samples collected from 0-3 inches and 3-6 inches, whereas here it is stated as 0-6 inches.
Figure 4-4	Shows inadequacy of sediment sampling in the river - all data are lumped into general category of "Wheeler Reservoir - Middle Reach" with concentrations spanning nearly 3 orders of magnitude. Sampling design seems generally to be directed/biassed, not systemmatic or random. Concentration gradient, if present, cannot be identified from this sampling design.
6-2	The high percentage of field duplicates and lab replicates seems excessive. Were these data analyzed in detail for sample/lab variation?
Table 6-10	Note effect of small sample size on eggageration of EPC - low n (<10) forces use of Max Conc. which is considerably higher than mean or median.
Table 6-11	Note effect of small sample size on eggageration of EPC - low n (<10) forces use of Max Conc. which is considerably higher than mean or median.
Figure 6-1	Explain basis for individual exposure units for each Field, given the lack of pathway limitation (no fencing or boundary). EPC for the entire area might be more representative of the exposure.
Figure 6-6	Middle Reach of Wheeler Reservoir sediment data set is shown to include onsite (upland) sediment locations. Reservoir data set should be limited to the river setting.

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8 April 2008

To: Menzie-Cura and Associates, Inc.
2 West Lane
Severna Park, Maryland 21146

Subject: Review of Documents Regarding PFOA Environmental Releases, 3M-Dyneon Plant, Decatur, Alabama (*EPA Docket ID Number EPA-HQ-OPPT-2004-0112*) - Written Comments

Dear Sirs:

I have reviewed the three documents submitted by 3M Company and Dyneon, LLC to the Peer Consultation Group assembled by Menzie-Cura and Associates, Inc. as follows:

1. *Data Assessment Report, DM Decatur, Alabama Facility, PFOA Site-Related Environmental Monitoring Program,* Prepared by Weston Solutions, Inc. (W.O. 02181.129.081.0001), January 2008, 7 Sections, 7 Appendices.

2. *Screening Level Human Exposure Assessment Report, PFOA Site-Related Environmental Monitoring Program,* Prepared by Weston Solutions, Inc. (W.O. 02181.129.081.0001), January 2008, 12 Sections, 5 Appendices.

3. *Future Data Needs Assessment Report, PFOA Site-Related Environmental Monitoring Program,* Prepared by Weston Solutions, Inc. (W.O. 02181.129.081.0001), January 2008, 13 p.

Upon review, I have assembled my preliminary comments in the attached report. These are submitted for consideration at the forthcoming meeting of the PFOA Peer Consultation Group in Decatur, Alabama on 16-17 April 2008.

I look forward to participation in the peer consulting process and to productive discussions on this important matter.

Sincerely,

Ernst H. Kastning, Ph.D.
Professional Hydrogeologist
Retired Professor of Geology
Radford University (Virginia)

Review of Documents Regarding PFOA Environmental Releases, 3M-Dyneon Plant, Decatur, Alabama

(EPA Docket ID Number EPA-HQ-OPPT-2004-0112)

Written Comments

Ernst H. Kastning, Ph.D.

8 April 2008

General Comments About the Investigations

As a hydrogeologist, I have scrutinized the groundwater, soil-water, and surface-water aspects of the documents. In general, I find that the studies performed to date, within the scope of the Memorandum of Understanding, are well done and that the conclusions reached are consistent with the data collected. The hydrostratigraphic units (soil, sludge incorporation layer, residuum, epikarst, and limestone bedrock) are well defined. Water levels from monitoring wells, analysis of subsurface structural features, and concentration levels of perfluorooctanoic acid (PFOA) in various horizons and components of the hydrogeologic environment are well documented and illustrated in the summary tables and maps that accompany the reports. The results and conclusions are clear and logical, based on the data gathered in the studies.

However, there are some additional studies that should be done in order to further provide answers to the "Charge" as it is stated in the MOU. As work moves forward, beyond the findings and recommendations of the Peer Consultation Group, there are some important investigations relative to the groundwater flow at the site and its environs that need to be considered (*see* below).

As discussed in Section 2 of the Data Assessment Report, the site and surrounding land are underlain by carbonate rock, specifically the Tuscumbia Limestone. This unit has developed significant karst, particularly in the topmost zone of the limestone, the epikarst. There is also evidence of karstification in the bedrock below the epikarst, as described in the report. Specifically, some fractures have been widened by dissolution, producing openings that can hold and transmit significant amounts of water.

Despite good summaries and conclusions drawn from the data at hand, I find some lingering concerns. These are based on my familiarity with karst processes and environmental assessments in karst terranes. It is a well-known fact among scientists that have extensively studied karst in great detail that this is a medium unlike others. Whereas characterization of other types of aquifers (*e.g.* porous-media aquifer such as sand and sandstone, fractured crystalline rock such as granite) are relatively routine, karst requires special attention. There are few aquifers as difficult to characterize as those in karst, and the techniques used in the analysis of karst often differ from those used elsewhere.

Important Tenets of Karst Hydrology

There are three types of porosity in sedimentary rock; primary, secondary, and tertiary. **Primary porosity** encompasses all pores that were formed during the depositional phase, when sediments accumulated. Primary porosity can become much reduced with time as sediments compact, original minerals recrystallize, and minerals dissolved in circulating groundwater are precipitated in pores as fillings. Generally speaking, as carbonate rocks age, they become much denser and have little or no primary porosity. This is the case with the Tuscumbia Limestone of Mississippian age that underlies the 3M/Dyneon site in Decatur.

Secondary porosity is the result of tectonism. Brittle, lithified materials (rocks) are subject to external stresses caused structural deformation, isostatic adjustment, and denudation of overlying materials through erosion. This results in fractures such as joints, faults, and bedding-plane partings. In dense, crystalline carbonate rock such as the Tuscumbia Limestone, fractures may be the only avenues for circulation of groundwater.

Groundwater (which is typically slightly acidic) circulates within a fracture-medium aquifer from points of recharge to points of discharge through an integrated network of intersecting fractures. This water will slowly dissolve soluble bedrock it comes in contact with it and this, in turn, leads to enlargement of fractures. Fractures become wider and perhaps higher and enlongated. These enlarged openings are collectively termed **tertiary porosity**. A typical mature aquifer in karst has a significant amount of tertiary porosity. This may have evolved into an efficient flow system, where the openings intersect and are well-integrated into a three-dimensional network.

Difficulty of Studying Hydrogeology of Karst Aquifers

Porosity in soluble rock (primarily carbonate rock such as limestone, dolostone, and marble, sulphate rock such as gypsum and anhydrite, and halite) consists largely of secondary and tertiary porosity. Flow paths are confined to fractures (including joints, faults, bedding-plane partings) and the rock between fractures is usually devoid of water.

Data derived from wells and borings in karst may potentially lead to non-conclusive or vague conclusions. The reason is that bedrock aquifers in karst are anisotropic and heterogeneous. A viable assessment of hydrologic conditions in karst would need numerous borings to serve as piezometers or water-quality monitoring wells.

Wells and boreholes may not intersect secondary and tertiary porosity (fractures, bedding-plane partings) in a representative way, particularly when relatively few wells are drilled over a large area. Data derived from investigative wells in karst often lead to crude estimates of the true nature of the flow systems. This includes information obtained from down-hole geophysics, water-level measurements (piezometers), and pump (a.k.a. aquifer) tests. These shortcomings are well documented in the applied karst literature, including reports of the U.S. Environmental Protection Agency.

Dye-Trace Studies

Reference was made to dye-trace studies performed on the site, in the vicinity of the chemical plant. This work was briefly mentioned on page 2-12 of the 3M Data Assessment Report (January 2008) and cited from a report by Weston Solutions prepared in 2003. Specific results of the tracings were not included in the three documents sent to the Peer Consultation Group in 2008. It would be instructive to see where the dye was introduced and where it was detected, with respect to both the hydrostratigraphic horizons described and tested and the length and direction of the interpreted paths of flow. This information can then be interpreted in context with flow nets that could be constructed from potentiometric data like those summarized in Figures 2-6, 2-7, and 2-8. This could then be compared to a contour map of the bedrock surface for additional interpretation. (Incidentally, Figure 2-5 is titled as "Bedrock Topography," yet the blue contours are identified in the Legend as "Groundwater Elevation Contour (feet above mean sea level)." This figure needs to be corrected in order to eliminate confusion.)

Dye-trace studies are highly recommended by hydrologists who specialize in groundwater studies of karst terranes. It is universally agreed that tracer studies are the best technique for determining avenues of groundwater flow and migration in karst. They are the highly reliable and relatively inexpensive. A well-designed dye-tracing program may definitively characterize the extent of groundwater drainage systems and identify connections between zones of recharge and discharge. To perform such studies requires places where dye can be injected (*e.g.* naturally sinking streams, artificial flushing of water into sinkholes, wells, etc.) and places of discharge where dye detectors can be placed (*e.g.* springs, surface waters, other wells).

Recommendations

The Future Data Needs Assessment Report suggests actions for Phase 3 of the site evaluation. I agree wholly that additional sampling should be carried out over the course of this follow-up study, especially with regard to water samples.

This last report, however, does not mention the possibility of performing dye-trace studies. I find this to be a glaring omission, as would most researchers who work in karst

I strongly recommend a well-designed program of dye tracing at the Decatur site. This would include a careful prior inventory of potential points for dye injection as well as identifying natural receptors and discharge points (springs, wells, and the like). These studies should include traces on the site property as well as on adjacent lands. Surface water (ponds, streams, the Tennessee River/Wheeler Reservoir and Bakers Creek) and existing wells should be included where possible. It is important that a dye-tracing program in karst be performed by individuals or companies that specialize in, or have an established history with studies in karst. There are about a dozen well-known specialists and consultants in the United States that have extensive experience with dye tracing in karst terranes.

PRIMARY QUESTIONS ASSIGNED TO J.H. DRIVER
(see yellow highlighted questions/text)

Preliminary Draft
April 08, 2008

8. Are the monitoring data sufficient to quantify exposure?
    a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media?
        i. Soil
        ii. Groundwater
        iii. Surface water
        iv. Sediment
        v. Biota
    b. **Of the data available to the authors, did they select the right data sets to quantify exposure? Should they have considered any of the data excluded from the analysis?**

RESPONSE:

Based on a preliminary review, the authors of the "Screening Level Human Exposure Assessment Report, January 2008" have selected and utilized the appropriate available monitoring results to inform the potentially exposed human receptor calculations for the scenarios evaluated (note: exposures associated with the 3M site, for purposes of the SLHEA, are defined as "current exposures and the potential for future exposures from the presence of PFOA in environmental media as a result of current or past manufacturing activities at the site, but not exposures that may have occurred in the past"). The monitoring data utilized was appropriately based on measurements collected as part of the "Phase 2 Work Plan" which was specifically designed to address "current exposures" via PFOA measurements in various environmental media at the 3M site. Thus, other data available, i.e., historical data from Phase 1 monitoring efforts, were only used to inform Phase 2 data collection. The author's correctly focused on the Phase 2 data. Page 3-3 of the January 2008 SLHEA report provides a list of on-site and off-site media analyzed (e.g., one-site and off-site soils, on-site vegetation, fish tissue from two species in the Tennessee River) that could be (and were) used to inform quantitative estimates of possible on-site and off-site exposure pathways and routes.

9. Were the data used appropriately to calculate exposure point concentrations (EPCs)?
    a. Did the authors define reasonable exposure points that represent locations associated with current and future exposure?
    b. Are the data sufficient to understand the presence and concentration of PFOA in environmental media at each exposure point?
    c. **Were EPC calculations and other statistical manipulations (e.g., treatment of results below detection limits, field duplicates, and qualified data) of these data performed accurately and appropriately?**
    d. Do the data indicate that there are exposure points other than those identified in this assessment?

RESPONSE:

Based on a limited quality assurance check of EPC (defined as the 95% upper confidence limit of the average concentration to which an individual would be exposed in any given exposure unit during the assumed exposure duration and frequency) calculations and other reported statistics, it appears that these were performed accurately and appropriately. A summary of EPCs used in the exposure assessment, along with data distributions are provided in Tables 6-8 through 6-14. Appendix E also provides output of EPA's ProUCL software program which allows the user to calculate distribution-specific upper confidence limits (UCLs), as well as non-parametric UCLs for data that do not approximate a specific distribution. UCLs were calculated only for datasets with a sample size (n) greater than or equal to 10. The maximum sample concentration was used as the EPC for datasets with less than 10 samples. Non-detect values present in a dataset were given a proxy value of ½ the LOD (early Exygen lab results) or LOQ (3M lab and later Exygen lab results). In the event that not quantifiable (NQ) values were present in a given dataset, a proxy value of the arithmetic mean of the LOQ and LOD was used. NDs or NQs represented a small portion of the PFOA data sets (see "Frequency of Detection" listed in Tables 6-1 through 6-7); thus, their impact on EPC calculations is expected to be minimal.

10. Other than the EPCs, were the assumptions and exposure input parameters for each combination of pathway and receptor appropriate?
    a. Was bioavailability of PFOA in the various exposure media (e.g., soil and sludge) addressed appropriately?
    b. Have the appropriate age groupings been defined?
    c. **Are the selected receptor characteristics and exposure patterns (i.e., duration, frequency, and intensity) the most appropriate for use in this assessment?**
    d. Were the doses averaged over the appropriate time interval?
    e. **Overall, are the input data and assumptions valid and appropriate for all receptors?**

RESPONSE

The selected receptor characteristics and exposure patterns were appropriate and reasonable for use in the SLHEA. It is important to note that exposure (and absorbed dose) estimates and their associated duration, frequency and magnitude or intensity evaluated must be relevant to the "time-to-effect" (and associated dosing regimen) for the toxicological endpoints of interest. Simply stated, chronic toxicological effects and the normalized, e.g., mg/kg/day, no-adverse-effect-level or NOAEL resultant from long-term repeat dosing studies (often via the oral route), would be compared to estimates of lifetime average daily exposures or doses (e.g., total dose across relevant routes). In contrast, if a "short-term" toxicological endpoint and NOAEL was relevant to consider, i.e., the time to adverse effect in the toxicology study is short, e.g., several days to several weeks, a shorter-term time averaging period would be appropriate to estimate potential average daily dose estimates. The short-term absorbed dose estimates would be divided by the short-term NOAEL to derive short-term Margins of Safety or Margins of Exposure. Risk estimation and characterization is not part of the SLHEA or the scope of the peer review. However, it is important that the exposure metrics estimated (and their associated "patterns" or duration, frequency and intensity) are relevant to the risk characterizations being made.

Overall, the input data and assumptions reported in the SLHEA are valid and appropriate for described receptor populations, given that the deterministic "screening-level" exposure assessment, as presented, is focused on subchronic to long-term average daily exposure and absorbed dose metrics.

12. **For exposure pathways for which the data did not allow quantitative assessment, did the authors present a qualitative or semi-quantitative description of exposure?**

RESPONSE

The January 2008 SLHEA report acknowledges data limitations for some media evaluated (e.g., off-site soil and off-site groundwater data sets). The SLHEA (see 9.2.2) acknowledges the likely conservative bias in the exposure estimates provided for those scenarios evaluated, e.g., residential groundwater. The SLHEA report also discusses routes of exposure not quantified (see section 9.5), e.g., consumption of locally grown meat, milk, produce, and other fish species. The lack of PFOA data was cited as the reason for not considering these potential sources of exposure. The SLHEA could be further expanded to discuss other potential exposure sources and pathways, e.g., locally grown produce, house dust, and comment further, at least qualitatively, or the likely magnitude of their potential contribution. The SLHEA also discuss potential "aggregate" exposure patterns (combination of absorbed dose estimates, e.g., the same individual could be exposed to soil and groundwater in a residential setting and via contact with former sludge incorporation area fields. This particular combined exposure scenario was evaluated. Other combinations could be considered and discussed qualitatively, or evaluated quantitatively. However, the probability of any other aggregate exposure combinations considered should also be acknowledged and described, at least qualitatively.

Boulanger Review of PFOA Site-Related Assessment Documents

General Comments

After reviewing the Data Assessment Report and the Screening Level Human Exposure Assessment Report, I generally feel that the presented reports are a good attempt to begin understanding and characterizing human exposures to PFOA from the site. My general comments identify additional areas where more clarification or information is necessary, including:

- Data Quality of Exygen Results. Have inter-laboratory studies been performed to validate Exygen's methods? What methodologies were used to extract the samples and were surrogates or internal standards employed during the analyses?
- Past PFOA Production and Usage. What were the past PFOA usage and/or production rates at the site?
- Current On-Site Fluorochemical Production. Are other fluorochemicals currently being produced on-site? Can currently produced fluorochemicals degrade to PFOA (precursors present)?
- Air Quality Data. Outdoor and indoor air quality data are missing from the reports. There are no measured reports of gaseous or particulate PFOA air concentration data for on-site or off-site samples.
- Groundwater Plume Magnitude. What is the extent of groundwater contamination moving off site? How extensive are groundwater plumes originating from the site?
- Human Biomonitoring Programs. There was no data presented to characterize blood levels for workers or the general population.
- Daikin Facility. The presence of the Daikin facility in such close proximity to the site is problematic. How should current production and emissions from the Daikin facility be considered into this assessment?

- Storm Water Runoff. Storm water PFOA concentrations during runoff events is not currently discussed in presented reports
- Homegrown Fruits, Vegetables, and Dairy Products. Additional information is necessary for PFOA exposures from homegrown fruits and vegetables. The lack of this information is recognized in the reports and an assessment of PFOA in homegrown fruits and vegetables should be completed as part of future phases. Any local dairy production should also have dairy products analyzed for PFOA content.
- Other Fluorochemical Compounds. Are compounds capable of degrading to PFOA present in any of the measured environmental media? Has any screening for other fluorochemicals been completed on-site or off-site?

Specific Comments

1. *Are the data and information presented in this report relevant to the Screening Level Exposure Assessment and of sufficient quality, quantity, objectivity, utility, and integrity? Were sufficient samples of each environmental medium collected? Were the analytical procedures and levels of quantitation and detection adequate? Does the assessment adequately characterize the presence of PFOA associated with the site?*

While sufficient data exists for most of the presented routes of exposure, not all exposure routes are fully characterized. Missing data includes: gas and particulate phase outdoor air quality information for both on-site and off-site locations; gas and particulate phase indoor air quality information for both on-site and off-site locations; monitoring data for additional off-site groundwater locations needed to assess the magnitude of the PFOA groundwater plume originating from the site; storm water on-site, storm water migrating off-site; and human biomonitoring for workers and the general public for PFOA blood concentrations.

4. Have the pathways of migration of PFOA from the following environmental media to other environmental media been adequately considered and represented?

c. Surface Water

The presented PFOA surface water quality data begin to satisfactorily characterize potential routes of exposure to surface waters from on-site and off-site locations based upon the information presented in the Data Assessment and SLHEA Reports. Once the site visit is completed, however, there is a possibility that additional sampling locations could be identified and evaluated. Additionally, PFOA concentrations in storm water are not currently presented. Having PFOA storm water concentration data will allow for the characterization of PFOA release from the site to surrounding off-site water bodies during storm events.

Surface water data is presented in the body of the report without a detailed description of sample extraction methods or instrumental analytical information (at least as I can recall). Also, information concerning analytical method validation studies or inter-laboratory comparison results is not given for surface water PFOA analysis or for PFOA analysis in any other media. Without the validation studies, the quality of the resulting concentration data is hard to evaluate. Because the risk assessment performed and presented in the SLHEA report is data intensive, any error that may have been introduced to the concentration data because of analytical methodologies or data quality is critical to consider.

Finally, are any other fluorochemicals present in surface water that could degrade to form PFOA?

g. Wastewater treatment sludge and biosolids

Limited data is presented characterizing PFOA concentrations in local WWTP sludges and biosolids. Additional clarification of existing disposal methods for local WWTP sludges and biosolids containing PFOA should be given within the reports.

5. Does the site conceptual model adequately characterize sources associated with the site and exposure pathways linking these sources to on-site and off-site human receptors?

The following pathways of exposure, missing from the SLHEA report and Data Analysis package, are important to characterize for on-site and off-site exposures:

- On-site outdoor air quality PFOA exposures
- On-site indoor air quality PFOA exposures
- Off-site outdoor air quality PFOA exposures
- Off-site indoor air quality PFOA exposures
- On-site storm water runoff exposures
- Off-site storm water runoff exposures
- Additional off-site groundwater exposure information
- Soil exposure in residential areas (caused by deposition)
- Exposure to other fluorochemicals present in environmental media that can transform to PFOA in-vitro

8. Are the monitoring data sufficient to quantify exposure?

a. Are the data representing each environmental medium sufficient to support the exposures that were quantified in the assessment? Are data needed for other environmental media?

iii. Surface water

With the exception of storm water PFOA concentration data, the other presented PFOA surface water data are likely sufficient to support the exposure analysis for PFOA as long as no other fluorochemicals that can degrade to PFOA are present in the analyzed surface water samples. However, the quality of the presented data is

still in question. Therefore, additional information that could help validate the analytical results and rule out precursors would increase my comfort levels and allow for a more detailed analysis of the reported data's quality.

In my opinion, a more complete SLHEA could result from additional data from the following environmental media:

- On-site outdoor gas and particulate phase PFOA air concentrations
- On-site indoor gas and particulate phase PFOA air concentrations
- Off-site outdoor gas and particulate phase PFOA air concentrations
- Off-site indoor gas and particulate phase PFOA air concentrations
- On-site storm water runoff PFOA concentrations
- Off-site storm water runoff PFOA concentrations
- Additional off-site groundwater sampling locations
- Residential soil sampling in Decatur and across Tennessee River (caused by deposition)
- Human biomonitoring for PFOA blood concentrations for workers and the general public
- Analysis of other fluorochemicals that could degrade to PFOA across environmental media

b. of the data available to the authors, did they select the right data sets to quantify exposure? Should they have considered any of the data excluded from the analysis?

I was surprised that the authors selected to eliminate PFOA volatilization from the conceptual model without a sufficient body of information of PFOA gas phase air concentrations. I was also surprised that other fluorochemicals that are known to degrade to PFOA were not evaluated across environmental matrices.

15. Does this assessment identify additional data and/or other appropriate information necessary? Please identify any critical data gaps or potential pathways for exposure you feel have not been identified.

Yes, to some degree. I feel inclusion of homegrown fruits and vegetables is an important pathway to consider. Additionally, measuring any impact on local agriculture would also be helpful, especially if any dairy products are locally produced (and consumed). I also agree with other proposed work detailed in the Future Data Needs Assessment Report. In addition to topics presented in this report, I also recommend adding:

- On-site outdoor gas and particulate phase PFOA air concentrations
- On-site indoor gas and particulate phase PFOA air concentrations
- Off-site outdoor gas and particulate phase PFOA air concentrations
- Off-site indoor gas and particulate phase PFOA air concentrations
- On-site storm water runoff PFOA concentrations
- Off-site storm water runoff PFOA concentrations
- Residential soil sampling across the Tennessee River (caused by deposition)
- Human biomonitoring of PFOA blood concentrations for workers and the general public
- Information on concentrations of other fluorochemicals that can degrade to PFOA across environmental matrices

16. Does the Phase 3 work plan outline contain all of the technical elements required for gathering the proposed additional data?

No. The Future Data Needs Assessment Report that I was given a copy of does not discuss the Phase 3 work plan in any detail. Currently the Phase 3 work plan outline spans page 13 and is vague. I may, however, be missing this final section of the report in my copy (although from examination of the table of contents, it really does appear to terminate early).