Health Consultation

JANUARY 5, 2002 AIR RELEASE
DIOXINS IN RESIDENTIAL SOIL

DIAZ CHEMICAL CORPORATION
(A/K/A FMC C/O DIAZ CHEMICAL C/O FMC)

VILLAGE OF HOLLEY, ORLEANS COUNTY, NEW YORK

EPA FACILITY ID: NYD067532580

MARCH 1, 2006

U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES
Public Health Service
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation
Atlanta, Georgia 30333

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Prepared by:

New York State Department of Health
Center for Environmental Health
Under Cooperative Agreement with the
U.S. Department of Health and Human Services
Agency for Toxic Substances and Disease Registry
Division of Health Assessment and Consultation

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SUMMARY

In November 2003, the New York State Department of Health (NYS DOH) and Agency for Toxic Substances and Disease Registry (ATSDR) published the final public health assessment (PHA) about the potential health risks from the January 5, 2002, accidental release of 2-chloro-6-fluorophenol (CFP) from Diaz Chemical Corporation. Several people who commented on the PHA noted the lack of direct measurement of dioxins as a deficiency, because of reports that dioxins can be produced during the manufacture of chlorinated phenols such as CFP. In response to these comments, the remaining portions of seven soil samples that were originally collected in January 2002 for CFP analysis were tested by NYS DOH for polychlorinated dibenzo-*p*-dioxins (dioxins) and similar compounds known as polychlorinated dibenzofurans (furans).

We evaluated the dioxin and furan toxicity of the samples using methods from World Health Organization (WHO) and the United States Environmental Protection Agency (US EPA) by calculating Toxicity Equivalents (TEQs). NYS DOH compared the TEQs to the ATSDR Action and Evaluation Guidance Values, and levels in background soils as measured in urban and rural soils by other scientists. We also compared the dioxin and furan results to the measured CFP concentrations and qualitatively evaluated the results as they relate to distance from the Diaz facility.

The TEQs for the seven NYS DOH soil samples ranged from 0.06 parts per billion (ppb) to 0.10 ppb using one method of calculation (substituting ½ detection limit for non-detects) and from less than 0.01 ppb to 0.03 ppb using another method (substituting "0" for non-detects). The TEQs are less than the ATSDR Action Guideline of 1.0 ppb. Some of the TEQs are within the range of the ATSDR's Environmental Media Evaluation Guideline (EMEG) of 0.05 ppb to 1.0 ppb. The TEQs measured in these soil samples are consistent with the TEQs measured in background soils for urban areas, and higher than those measured in rural areas. A general trend of higher TEQ levels and higher 1,3,6,8-tetrachlorodibenzo-*p*-dioxin (1,3,6,8-TCDD) levels is found in the soil samples that have higher levels of the CFP. In general, the higher levels are in the samples closest to the facility. 1,3,6,8-TCDD is the tetrachlorinated dioxin congener found in the highest concentration in a sample of the wash liquid of the vessel after the CFP release. Low levels of dioxins and furans, especially 1,3,6,8-TCDD, may have been associated with the release. The levels of the TEQs for the soils are consistent with ATSDR's site category of No Apparent Public Health Hazard.

The TEQs found in NYS DOH samples are consistent or slightly higher than the TEQs found in two other sampling programs, one conducted by US EPA in June 2003 and the other conducted by the New York State Office of the Attorney General (NYS OAG) in December 2004. Neither of these two sampling efforts found TEQs above the ATSDR Action Guideline of 1.0 ppb, which also is the US EPA action guideline. The data from the seven NYS DOH samples are consistent with a trend of higher TEQs near Diaz. The more extensive US EPA data set shows that, in general, the properties further away from Diaz have lower mean TEQ values than the properties closer to Diaz. However, this trend does not always hold true. In some cases, the mean TEQ for properties further away are higher than the mean TEQ for a property closer. In summary, none of the three sampling programs (NYS DOH, US EPA, and NYS OAG), although there are differences in methodology and the date of sampling, have any results above the ATSDR 1.0 ppb Action Guideline.

BACKGROUND AND STATEMENT OF ISSUES

On January 5, 2002, the Diaz Chemical Corporation facility in the Village of Holley, Orleans County, New York, accidentally released into outdoor air a mixture consisting primarily of toluene, water (steam), and 2-chloro-6-fluorophenol (CFP) from a storage vessel. The New York State Department of Health (NYS DOH) and Agency for Toxic Substances and Disease Registry (ATSDR) prepared a Public Health Assessment (PHA) that included the results of environmental and biological sampling and a summary of the health issues resulting from this release (NYS DOH, 2003).

During the public comment period on the draft PHA, several people requested soil testing for polychlorinated dibenzo-*p*-dioxins (dioxins) and polychlorinated dibenzofurans (furans), because dioxins can be produced during the manufacture of chlorinated phenols and dioxins are environmentally persistent and toxic. In response to the public comments, NYS DOH analyzed the remaining portions of 7 soil samples (originally collected for CFP analysis in January 2002) for dioxins and furans.

After the accidental release from the storage vessel, the vessel was washed with toluene to recover any remaining product. A sample of this material was analyzed. It contained CFP and a number of other compounds, including dioxins and similar compounds known as furans. The dioxin found in the highest concentration in this sample was 1,3,6,8-tetrachlorodibenzo-*p*-dioxin. At the time, soil and other environmental samples were not analyzed for dioxins and furans.

United States Environmental Protection Agency (US EPA) and the New York State Office of the Attorney General (NYS OAG) also sampled for dioxins. In the spring/summer of 2003, US EPA collected a large number of soil samples from throughout the Village of Holley for analysis of many different contaminants, including dioxins. This effort provided more spatial coverage than did the NYS DOH sampling. The results of this work were provided to NYS DOH in August 2005. In December 2004, NYS OAG collected soil samples from six locations for laboratory analysis of dioxins and furans, and 6 samples using a bioassay method, called CALUX. The results of this work were reported to homeowners and provided to NYS DOH in September 2005. NYS OAG samples had limited spatial coverage, similar to the NYS DOH sampling.

The first draft of this health consultation (HC) was publicly released in September 2004, prior to NYS DOH receipt of data from NYS OAG and US EPA. For that reason, the September 2004 draft HC did not contain the US EPA and NYS OAG data. Additionally, this document contains the comments from the public on the September 2004 draft HC, as well as the NYS DOH responses (Appendix B). However, neither the public comments nor the additional data from US EPA and NYS OAG changed the conclusions made in the September draft.

DISCUSSION

A. Environmental Data Evaluation Methodology

There are 210 different polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzo furans. Commonly, the 210 different dioxins and furans are referred to as dioxins. The different dioxins and furans are called congeners. The most studied and most toxic of these is 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin (2,3,7,8-TCDD). The remaining individual dioxins and furans are not equally toxic. Because the dioxins and furans generally affect the body in similar ways, scientists describe approximately how toxic each one of these chemicals is by comparing what is known about its toxicity to that of 2,3,7,8-TCDD. The toxicity of a mixture of these chemicals is estimated by expressing the amount of each dioxin and dibenzofuran as if each were 2,3,7,8-TCDD and adding these amounts to produce a value called toxicity equivalents (TEQs). The factors (toxicity equivalency factors or TEFs) used to calculate TEQs have been derived by groups of experts convened by US EPA (US EPA, 2000) and the World Health Organization (WHO) (Martin Van den Berg *et al.*, 1998). ATSDR identifies two guidance values for dioxin and furan contaminated soils: an evaluation level and an action level. These levels are guidance and are not standards that are established by law or regulation. The evaluation level is a concentration greater than 0.05 parts per billion (ppb) (in TEQs) but less than 1.0 ppb. If a value is in this range, site-specific factors, including, but not limited to, bioavailability, ingestion rates, pathway analysis, soil cover, climate, other contaminants, community concerns, and background exposure are considered in a deliberative process to assess the nature and extent of exposure. The action level is a concentration greater than 1.0 ppb TEQ. If the 1.0 ppb ATSDR Action Level is exceeded, then ATSDR advises that consideration of action to reduce exposures should occur. A copy of the guidance is available at www.atsdr.cdc.gov/dioxindt.html.

B. Environmental Sampling and Exposure Pathways

On January 14-15, 2002, NYS DOH collected seven soil samples from a depth of 0 to 4 inches for analysis of CFP and related compounds. The sampling locations were selected to be downwind of the plume and to include areas with and without visible contamination. Five samples were collected from properties on Jackson Street, one sample from South Main Street, and one sample from a property on Perry Street. After analysis of a portion of each sample for CFP and other similar chemicals, the remaining samples were stored in sealed containers and refrigerated.

Portions of each stored soil sample were analyzed by NYS DOH at Wadsworth Center. The portions of the samples analyzed for dioxins and furans were stored at the laboratory from January 2002 until the spring of 2003 when the decision was made to analyze them for these compounds. The sample extracts were passed through several clean-up steps that removed compounds that may have interfered with the measurement of the dioxins and furans by the

chemical analyzers. The instrument used to measure the dioxins is called a high-resolution capillary gas chromatography mass spectrometer.

There are 17 different dioxins and furans with chlorines in the 2,3,7, and 8 positions (e.g., 2,3,5,7,8-pentachlorinated dibenzo-*p*-dioxin and 1,2,3,5,7,8-hexachlorinated dibenzo-*p*-dioxin are just two of the 17 possible total) and all of these were measured. As described previously, the dioxins and furans with chlorines in the 2,3,7, and 8 positions are those that contribute to the calculation of the dioxin TEQ. In addition, 1,3,6,8-tetrachlorinated dibenzo-*p*-dioxin (the dioxin found in the storage vessel) was quantified. The results of the wash sample analysis are provided in Appendix A. Detection limits ranged from 0.005 to 0.17 nanograms per gram (ng/g). A ng/g is equivalent to a ppb.

We did not measure brominated dioxins and furans. Although some citizens identified brominated dioxins as a potential concern, we did not evaluate them because quantitative standards are available for only a few congeners, and laboratory synthesis of additional brominated standards is not feasible. Additionally, our sampling was based on evaluating the effect of the January 5, 2002 CFP release.

Other sampling data that we received (August and September 2005) since the first draft of the health consultation (in October 2004) include the results from separate efforts by US EPA and NYS OAG. Environmental sampling conducted by US EPA in June 2003 included 256 soil samples for dioxin and furan analysis. Their sampling program had between 2 to 11 samples from each of 29 different properties. The NYS OAG work included samples from 6 different locations and included laboratory analysis using traditional methods similar to those used by US EPA and NYS DOH, and also analysis using a bioassay method called CALUX. The CALUX analysis was done to help provide information about brominated dioxins and furans. Both the US EPA and NYS OAG sampling programs included locations on Jackson Street properties, with the US EPA also including other areas of Holley. The analytical work for both efforts included congener specific work that allowed for calculations of TEQs.

As previously described, ATSDR's guideline suggests that when dioxin values are between 0.05 ppb and 1.0 ppb, the health assessor should look at the extent of contamination, whether the surface soils are easily accessible to children and adults, how often (daily, weekly, monthly) and for what length of time would exposure be likely. We followed this guidance and concluded that a risk assessment was not needed, because the additional US EPA and NYS OAG data showed that the extent and level of contamination was low.

C. Environmental Data Evaluation (Results)

In all of the soil samples, many dioxin and furan compounds (congeners) are not present or are present at a level too low to be detected. The detection limit is the lowest level of a congener that the laboratory can detect. When calculating TEQs, an assigned value must be used for any congener not detected. Two commonly used approaches are: (1) that there is no congener present and thus the amount is zero; and (2) that the congener is present and the amount is equal to one half the detection limit. The results of calculating TEQs using these two methods are presented in Table 1. Since dioxin and furan congeners were often not detected in this data set,

the calculated TEQs differ, depending on which method is used (Table 1). Both methods have been presented so the reader can see how the methodology affects the values. The calculation of the US EPA TEQ values is a little more complex than either of the two methods described above because they reported values for congeners below their detection limits. The use of these values in this method that generally gives results somewhere between the two methods (ND=0 or ND=1/2 detection limit or DL) used by NYS DOH and NYS OAG reported in Table 1.

The highest NYS DOH TEQ resulting from either of the two methods is 0.1 ppb and is below the ATSDR Action Guideline of 1.0 ppb. The 0.1 ppb TEQ occurred when congeners not detected are assumed to be present at one half the detection limit. This method clearly results in the higher TEQ values. Many of the values are slightly above (e.g. 0.056 and 0.058 ppb) the ATSDR Evaluation Guideline of 0.05 ppb, but lower than the ATSDR Action Guideline of 1.0 ppb. The highest TEQ that is calculated for the samples, assuming the value for non-detects is zero, is 0.03 ppb; none of these values are greater than the ATSDR Evaluation Guideline of 0.05 ppb. None of the NYS OAG samples have a TEQ that exceeds either of the ATSDR guidelines. In general, the NYS OAG TEQ values are about a factor of ten lower than the NYS DOH TEQs. This is also true for the mean TEQs calculated for each of the properties listed in Table 1. None of the mean TEQs exceed either the ATSDR Action or Evaluation Guidelines. However, one, of the more than two hundred fifty individual soil samples that are used to calculate the mean TEQs, exceeds the 0.05 ppb ATSDR Evaluation Guideline.

NYS OAG also collected six samples for analysis using a bioassay method called CALUX (US EPA, 2005). This method estimates the TEQ of contaminants such as dioxins (including brominated dioxins, chloro-bromo-dioxins, 1,3,6,8-TCDD and others), furans and dioxin-like compounds in soil based on a measurement of the biological activity of the sample. The results from these analyses showed low levels, all below the ATSDR Action Guideline, with one sample above the Evaluation Guideline. Further comparison of the results from this method to results from the other analyses is difficult because the bioassay is a new technology and there are relatively little available data. Given the CALUX results are consistent with the other results, all below the ATSDR Action Guideline, we do not provide further discussion of this nontraditional analysis in this public health consultation.

Table 1. TEQs of Dioxins in Soil from Samples Collected from Properties in Holley, New York.

US EPA RESULTS			NYS DOH AND NYS OAG RESULTS		
Map Location[1]	Number of Samples	Avg US EPA TEQ (ppb)[2]	Map Location[1]	TEQ ND = 0 (ppb)[3]	TEQ ND = ½ DL (ppb)[4]
EPA-1	11	0.00419			
EPA-2	10	0.00144			
EPA-3	11	0.00558	OAG-D[5]	0.00445	0.00446
EPA-4	11	0.00265			
EPA-5	10	0.00330	DOH-D[6], DOH-F	0.007, 0.004	0.063, 0.056
EPA-6	11	0.00887			
EPA-7	10	0.00380	DOH-C	0.013	0.074
EPA-8	11	0.00272	OAG-E	0.00442	0.00442
EPA-9	2	0.00209			
EPA-10	2	0.00005			
EPA-11	11	0.00604	DOH-A, DOH-B	0.034, 0.013	0.100, 0.068
EPA-12	10	0.00798			
EPA-13	10	0.00294			
EPA-14	2	0.00025			
EPA-15	2	0.00004			
EPA-16	2	0.00028			
EPA-17	11	0.00287			
EPA-18	11	0.00346			
EPA-19	11	0.00053			
EPA-20	10	0.00200	OAG-B, OAG-C	0.000656, 0.000744	0.000928, 0.000816
EPA-21	11	0.00110			
EPA-22	10	0.00415	DOH-E	0.005	0.058
EPA-23	10	0.00514			
EPA-24	11	0.01372	OAG-A	0.00456	0.0046
EPA-25	11	0.00323			
EPA-26	10	0.00324			
EPA-27	10	0.00509			
EPA-28	3	0.00267			
EPA-29	11	0.01086			
			DOH-G	<0.001[7]	0.056
			OAG-F	0.00105	0.00113

ATSDR Action Guideline: 1.0

ATSDR Environmental Media Evaluation Guideline (EMEG): Greater than 0.05 to less than 1.0

[1]Map location corresponds to properties shown in Figure 1.
[2]Average EPA TEQs represent the average of the respective samples collected by EPA from that property; TEQ: Toxic Equivalency Factor; ppb: parts per billion.
[3]The TEQ values were calculated by using a value of zero for congeners that were not detected.
[4]The TEQ were calculated using one-half the detection limit for congeners that were not detected.
[5]OAG is an New York State Office of Attorney General sample.
[6]DOH is a New York State Department of Health sample.
[7]The symbol "<" means the quantity is less than the presented value.

Table 2 presents the mean TEQ for the three sampling efforts, as well as rural and urban comparison values taken from US EPA's dioxin reassessment report (US EPA, 2000). Included is the range of the mean TEQ found in background soils for both rural and urban environments (US EPA, 2000). The TEQs are taken directly from the US EPA document, except that they are converted from part per trillion concentrations to part per billion concentrations. According to US EPA, all but one of the reported TEQs are calculated using the value of zero for dioxins or furans not detected. The mean TEQ for the seven NYS DOH soil samples is within the range of the mean TEQ from the urban studies and higher than the maximum mean concentration reported for natural/rural background soils. The mean for both US EPA and NYS OAG also follow this trend, but are more consistent with the background data for rural soil.

Table 2. Comparison of the Holley Mean TEQ Values to Mean Values from Background Studies (all values are in ppb).

NYS DOH Diaz Sample Mean TEQ	US EPA Diaz Sample Mean TEQ[2]	NYS OAG Diaz Sample Mean TEQ	Comparison Data Urban[1]	Comparison Data Natural/Rural
0.011	0.0044	0.0027	0.00221 - 0.021	0.00012 - 0.0057

[1] The comparison data are taken from Table 3-14 of the US EPA September 2000 Exposure and Human Health Reassessment of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin (TCDD) and Related Compounds document. The values presented are the minimum and maximum mean value reported from the different studies. Either US EPA or the authors of the original study characterized the data as rural or urban. US EPA presented the background TEQ values based on using zero for non-detects for most of the studies. One result was presented using one half the detection limit.

In summary, the TEQ results for each of the soil samples are less than the ATSDR Action Guideline. Depending on the method used to calculate the TEQ, a few of the NYS DOH sample TEQs are within the range of the ATSDR Evaluation Guideline, similar to the background levels for soils in urban areas and higher than the levels in rural areas. None of the NYS OAG results (Table 1), and the mean TEQ per property calculated from the US EPA data (Table 1), exceed ATSDR Evaluation or Action Guidelines. One of the more than two hundred fifty individual US EPA results is slightly above the ATSDR Evaluation Guideline, and all are below the Action Guideline.

The predominant dioxin in the toluene wash sample from the storage vessel that ruptured on January 5, 2002 is 1,3,6,8-TCDD. Diaz expressed concern that the solvent used to wash the vessel, toluene, already contained low levels of dioxin and that it was potentially the source of the dioxins found in the wash sample. The dioxin 1,3,6,8-TCDD was in five of the seven NYS DOH soil samples (Table 3). In general, higher 1,3,6,8-TCDD concentrations are in the samples that have higher concentrations of CFP. These results suggest that the 1,3,6,8-TCDD was part of the release and that the 1,3,6,8-TCDD was part of the mixture of chemicals in the storage vessel prior to the toluene wash.

Table 3. The Measured Soil Concentrations of 1,3,6,8-TCDD and CFP for Each of the Seven NYS DOH Soil Samples.

Sample Location	1,3,6,8-TCDD (ppb)[1]	CFP (ppb)
A	0.276	8900
B	0.077	2000
C	0.123	960
D	0.049	520
E	0.027	470
F	<0.01[2]	9.3
G	<0.01	5.3

[1] ppb is parts per billion.
[2] The symbol "<" means the quantity is less than the presented value (the detection limit).

In general, higher levels of TEQs and 1,3,6,8-TCDD are in the NYS DOH samples collected closer to Diaz than the samples further away (Figure 1). Samples A and B are from locations closest to the plant. Samples C, D, and F are from properties on Jackson Street, Sample E is from property on South Main bordering Jackson Street, and Sample G is from a property on Perry Street.

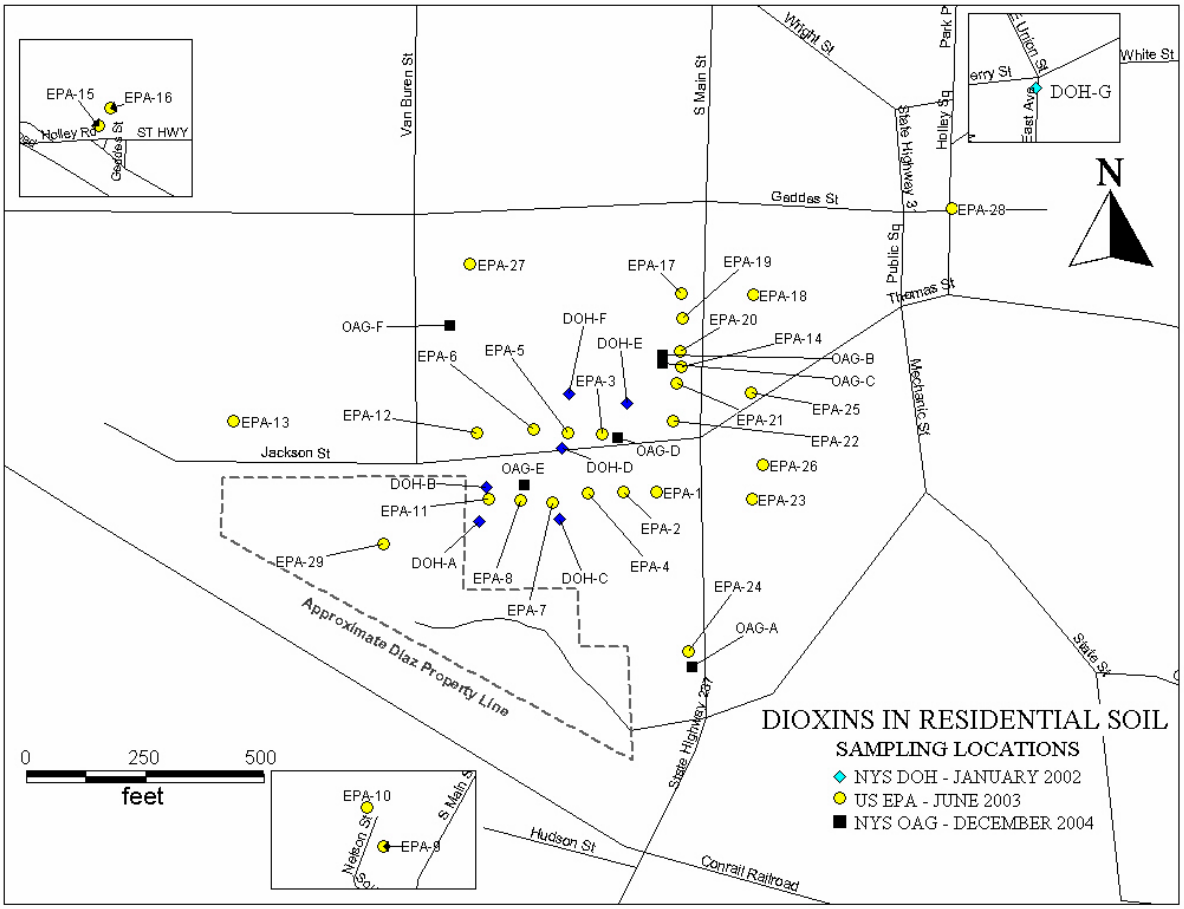

Figure 1. NYS DOH, US EPA and NYS OAG Soil Sampling Locations.

Figure 2. A Graph of the Distance from the Center of a Sampled Property to the Nearest Point along the Diaz Property Boundary Compared to the Mean US EPA TEQ.

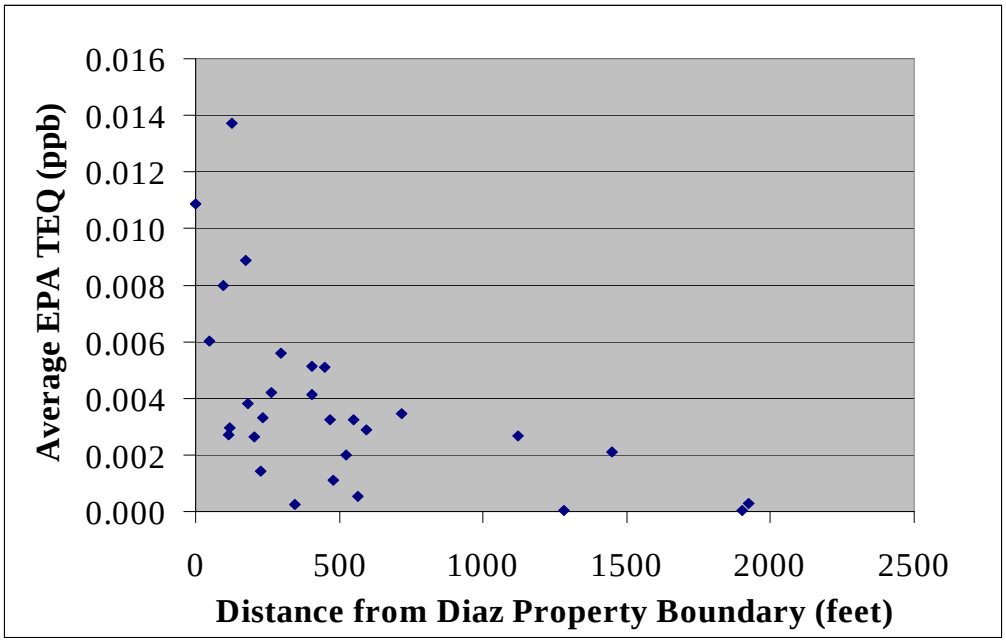

Figure 2 is a graph of the mean TEQ for the 29 properties sampled by US EPA, compared to the distance from the center of that property to the nearest part of the Diaz property boundary. The resulting graph suggests a relationship between a property's distance from the Diaz site and the property's mean TEQ. The relationship is that the mean TEQ decreases with distance. The graph shows that some properties closer to the Diaz Property have a mean TEQ lower than some properties further away, but overall the trend is a decreasing mean TEQ with increasing distance.

CONCLUSIONS

1) The concentration of dioxins (as TEQs) for each NYS DOH, US EPA, and NYS OAG soil sample was less than the ATSDR Action Guideline of 1.0 ppb. These levels are consistent with ATSDR's category of No Apparent Public Health Hazard.

2) A few of the NYS DOH samples exceed the ATSDR Evaluation Guideline of 0.05 – 1.0 ppb when the TEQs are calculated using a value of one half the detection limit for dioxin and furan congeners not detected. TEQs between 0.06 ppb and 0.1 ppb are calculated using this method. For the same samples, assuming a value of zero for non-detects, none of the calculated TEQs exceed either of the ATSDR Guidelines. NYS OAG results did not exceed either the ATSDR Action or Evaluation Guideline, only one of the 250 US EPA samples slightly exceeded the ATSDR Evaluation Guideline (0.05 ppb to 1.0 ppb), none exceeded the Action Guideline (1.0 ppb). The mean TEQ for all of the US EPA samples collected from each property were all below both ATSDR guidelines.

3) The average TEQ concentration for the NYS DOH soil samples is less than or similar to the average TEQ concentrations that are reported in studies on urban background soils, but higher than concentrations reported in studies on rural soils. NYS OAG and US EPA results also showed this trend, but are lower and more consistent with the rural background.

4) In general, the 1,3,6,8-TCDD concentrations, TEQ values, and CFP concentrations are higher in the NYS DOH samples collected closer to Diaz. A factor of ten difference in TEQ values exists between some samples collected near Diaz versus samples collected further away from Diaz. This trend was true for CFP as well. The same general trend is shown for the TEQs calculated for US EPA and NYS OAG samples.

5) In general, higher 1,3,6,8-TCDD concentrations (the TCDD found in the greatest concentration in the storage vessel wash sample) are in the NYS DOH samples that have the higher concentrations of CFP. This suggests that the CFP release included this dioxin, and that the 1,3,6,8-TCDD found in the wash sample is from the CFP release.

RECOMMENDATIONS

No further action is needed based on the existing data. NYS DOH does not plan any additional sampling or laboratory analyses for dioxins and furans.

PUBLIC HEALTH RESPONSE PLAN

NYS DOH (August 31, 2005) mailed a letter to the community to provide an update of ATSDR and NYS DOH activities at the Diaz Chemical Corporation Site. The letter summarized completed and ongoing activities and commits to providing the Holley community with additional progress reports approximately twice a year or as documents are released. A revised update of the ATSDR and NYS DOH activities at the Diaz Chemical Corporation Site will be sent to interested parties along with the final version of this health consultation.

FOR MORE INFORMATION

If you have any questions, please contact any of the people listed below.

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REFERENCES

Agency for Toxic Substances and Disease Registry. **1998**. Toxicological Profile for CHLORINATED DIBENZO-p-DIOXINS (Update). Prepared by Research Triangle Institute for U.S. Department of Health and Human Services, Public Health Service.

DeRosa, C., Brown, D., Dhara, R., Garrett, W., Hansen, H., Holler, J., Jones, D., Jordan-Izaguirre, D., O'Connor, R., Pohl, H., and Xintaras, C. **1997**. Dioxin and Dioxin-Like Compounds in Soil, Part II: Technical Support Document for ATSDR Interim Policy Guideline. *Toxicology and Industrial Health*. 13 (6): 769-804.

New York State Department of Health and the Agency for Toxic Substances and Disease Registry. **2003**. Public Health Assessment: Diaz Chemical Corporation January 5, 2002 Air Release. CERCLIS NO. NYD067532580. 133 pp.

U.S. Environmental Protection Agency. **2000**. Exposure and Human Health Reassessment of Tetrachloro-p-Dioxin (TCDD) and Related Compounds. Washington, DC: National Center for Exposure Assessment, Office of Research and Development EPA/600/P-00/001Bc

U.S. Environmental Protection Agency. 2005. "Technologies for the Monitoring and Measurement of Dioxin and Dioxin-like Compounds in Soil and Sediment."

Van den Berg, M., Birnbaum, L., Bosveld, A.T., Brunstrom, B., Cook, P., Feeley, M., Giesy, J.P., Hanberg, A., Hasegawa, R., Kennedy, S.W., Kubiak, T., Larsen, J.C., Van Leeuwen, F.X., Liem, A.K., Nolt, C., Peterson, R.E., Poellinger, L., Safe, S., Schrenk, D., Tillitt, D., Tysklind, M., Younes, M., Waern, F., Zacharewski, T. **1998**. Toxic equivalency factors (TEFs) for PCBs PCDDs, PCDFs for humans and wildlife. *Environ Health Perspect*. 106(12): 775-792. http://ehpnet1.niehs.nih.gov/members/1998/106p775-792vandenberg/vandenberg-full.html

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CERTIFICATION

The New York State Department of Health has prepared this Public Health Consultation under a cooperative agreement with the Agency for Toxic Substances and Disease Registry (ATSDR). It is in accordance with approved methodology and procedures existing at the time the Public Health Consultation was initiated. Editorial review of this health consultation was conducted by the cooperative agreement partner.

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Technical Project Officer, CAT, SPAB, DHAC

The Superfund Site Assessment Branch (SSAB), Division of Health Assessment and Consultation (DHAC), ATSDR has reviewed this Public Health Consultation and concurs with its findings.

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Team Leader, CAT, SSAB, DHAC, ATSDR

APPENDIX A

Table from 2003 ATSDR PHA
Diaz Chemical Corporation January 5, 2002 Air Release

Appendix A

Results of Dioxin and Furan Analysis of Toluene Wash Solution of Residue Remaining in Storage Vessel after Material Release and Calculation of Toxicity Equivalent (TEQ) Concentration (Table is taken from November 2003 Public Health Assessment).

Detected Dioxins and Furans[1]	Concentration (ppt)[2]	Dioxin Concentration/ CFP Concentration[3]	Maximum Amount of CFP Found in Soil (ppb)[4]	Estimated Amount of Dioxin in Soil (mcg/kg)[5]	TEF[6]	Estimated TEQ[7] Concentration in soil (ppb of Dioxin equivalents)
1,2,3,4,7,8-hexachlorodioxin	20	1.54E-10*	8900	1.37E-6	0.1	1.37E-7
1,2,3,4,6,7,8-heptachlorodioxin	40	3.07E-10	8900	2.73E-6	0.01	2.73E-8
octachlorodioxin	40	3.07E-10	8900	2.73E-6	0.0001	2.73E-10
octachlorofuran	20	1.54E-10	8900	1.37E-6	0.0001	1.37E-10
non-2,3,7,8 congener tetrachloro dioxin	127000	0	0	0	0	0
non-2,3,7,8 congener pentachlorodioxin	11000	0	0	0	0	0
non-2,3,7,8 congener hexachlorodioxin	910	0	0	0	0	0
non-2,3,7,8 congener heptachlorodioxin	150	0	0	0	0	0
non-2,3,7,8 congener tetrachlorofuran	240	0	0	0	0	0
non-2,3,7,8 congener pentachlorofuran	110	0	0	0	0	0
Total TEQ	2.4[8]					1.376E-7

1: The following compounds were tested for but not found at a concentration above the detection limit of either 10 or 20 nanograms per liter: 2,3,7,8-tetrachlorodioxin; 1,2,3,7,8-pentachlorodioxin; 1,2,3,6,7,8-hexachlorodioxin; 1,2,3,7,8,9-hexachlorodioxin; 2,3,7,8-tetrachlorofuran; 1,2,3,7,8-pentachlorofuran; 2,3,4,7,8-pentachlorofuran; 1,2,3,4,7,8-hexachlorofuran; 1,2,3,6,7,8-hexachlorofuran; 2,3,4,6,7,8-hexachlorofuran; 1,2,3,7,8,9-hexachlorofuran; 1,2,3,4,6,7,8-heptachlorofuran; 1,2,3,4,7,8,9-heptachlorofuran; Total hexachlorofuran; and Total heptachlorofuran.

2: Concentration reported by NYSDOH laboratories at the Wadsworth Center from analysis of the wash sample as parts per trillion (ppt).

3: The dioxin concentration/2-chloro-6-fluorophenol (CFP) concentration is calculated by taking the dioxin concentration provided in Column 2 and dividing it by the CFP concentration in the Storage Vessel wash reported by NYSDOH laboratories at the Wadsworth Center as 130 grams per liter (130,000,000,000 ng/L).

4: The maximum amount of CFP found in soil was 8900 parts per billion (ppb) (2003 Public Health Assessment, Appendix A, Figure 5A).

5: The estimated amount of dioxin found in soil (Column 5) was calculated by multiplying Column 3 and Column 4.

6: TEFs (toxicity equivalence factors) are from the World Health Organization (Van den Berg et. all, 1998). Because other congeners are less toxic than 2,3,7,8-TCDD, TEFs are used to estimate the 2,3,7,8-TCDD concentration that would have the same toxicity as the mixture of congeners seen. TEFs above zero exist only for the 2,3,7,8-substituted dioxins and furans; other dioxins/furans that do not have 2,3,7,8 substitution do not contribute to dioxin toxicity and thus the TEF equals zero.

7: The TEQ (toxicity equivalent or dioxin equivalent) was determined by multiplying Column 5 and Column 6.

8: The total toxicity equivalents of the wash solution was calculated by multiplying corresponding entries in Column 2 by Column 6 and summing.

*It is sometimes convenient to express large or small numbers in scientific notation. For this table, scientific notation is expressed as E, as in 1.54E-10 (meaning 1.54×10^{-10} or 0.000000000154). The number following the E is called the "exponent," or the "power of ten." For a positive exponent, it represents the number of times the number before the E is multiplied by 10. For a positive exponent, it represents the number of times the number before the E is divided by 10. To simplify, the sign of the exponent tells which way the decimal point moves; positive exponent moves the decimal point to the right, and a negative one moves it to the left. The magnitude of the exponent tells how many positions to move.

APPENDIX B

Summary of Public Comments and Responses

Appendix B
Summary of Public Comments and Responses on the 2004 Draft Dioxin Public Health Consultation.

This summary was prepared to address comments and questions on the public comment draft of the Diaz Chemical Corporation January 5, 2002 Air Release Dioxins in Residential Soil Public Health Consultation (PHC). The public was invited to review the draft during the public comment period, which ran from the release of the document in October 2004 to November 26th, 2004. Many similar comments were received and therefore combined to reduce redundancy. Some statements were also reworded for clarity. If you have any questions about this summary, you can contact the New York State Department of Health's (NYS DOH) project manager for the site at the toll-free number: 1-800-458-1158, extension 27714.

Comment #1: Many of the comments ask for more dioxin testing. They requested more testing because brominated dioxins were not evaluated, the extent and direction of sampling was limited, the residents are still fearful, the "precautionary principle" needs to apply because of the potential for low level chronic exposures, and that there are contaminants other than dioxins that need to be evaluated.

Response #1: Dioxins were tested in soils in response to the comments on the November 22, 2002 draft Public Health Assessment (PHA) for the January 5, 2002 Accidental Release of 2-Chloro-6-Fluorophenol (CFP) from the Diaz Chemical Facility, Village of Holley, Orleans County. We predicted that the levels of chlorinated dioxins and furans in the release would be low based on an analysis of a sample of the wash of the ruptured vessel. However, we agreed to dioxin testing because this was a predicted value and because of the repeated expression of concern about dioxins, including concern about possible past dioxin emissions unrelated to the CFP release.

We analyzed samples that had not been subjected to weathering since the CFP release by analyzing archived portions of the soil samples that were collected in January 2002 for CFP analysis. We believe that these samples give us the best data for evaluating whether chlorinated dioxins were part of the release. Five of the soil samples we collected were from properties down wind of Diaz during the CFP release, and two were from more distant locations. The resulting data provide information on the levels of dioxin and furan concentrations in the soils, regardless of whether or not they were from the January 2002 release.

We also have included the United States Environmental Protection Agency's (US EPA) and the New York State Office of the Attorney General's (NYS OAG) data in this report to provide more information. These data were not available at the time the October 2004 public comment version of the dioxin PHC was released. These additional data provide more geographic coverage than the NYS DOH January 2002 sampling. US EPA collected more than 250 samples from a total of 29 properties, about 10 samples per property. The mean TEQ for these individual properties did not exceed either the ATSDR Action or Evaluation Guidelines. One of the more than

250 samples exceeded the ATSDR Evaluation Guideline, but not the Action Guideline. None of the NYS OAG results exceeded either ATSDR Guideline.

The issue of brominated dioxins and other compounds has been raised because of other processes at the plant and the large amount of bromine used by the facility. The January 2002 release was documented and confirmed to be CFP and so our objective was to evaluate the samples for chlorinated dioxins. Based on the CFP release, chlorinated dioxins were the most likely dioxins to be formed. It also was not possible for us to evaluate the brominated dioxins and furans except for a limited few because of the lack of analytical standards. Analytical standards for many brominated dioxins and furans do not exist and without them, accurate measurement of the amount of these compounds is not possible. The NYSOAG used the CALUX assay to address the brominated dioxins/furans. Based on the results of this test, the findings of the health consultation do not change. In summary, our evaluation of the dioxins is based on responding to the impact from the January 5, 2002 release.

The data from the NYS DOH, US EPA and NYS OAG are consistent with the ATSDR's classification of no apparent public health hazard. With these results for about 300 samples, no additional sampling is planned.

Comment #2: Who defined Holley as an "Urban" area? The Holley dioxin values appear to be elevated compared to background. Testing is needed to determine why Holley is an anomaly and higher than other communities. Is there deposition from Niagara?

Response #2: The September 2004 draft Public Health Consultation references dioxin and furan background data from the 2002 US EPA Reassessment of Dioxins for both urban settings and rural settings. The PHC provides both sets of information as a reference for the reader. The PHC does not describe Holley as either rural or urban. Holley is neither a rural area nor is it an urban area. However, reference data are only available for rural and urban areas.

The dioxin TEQs for three NYS DOH samples taken immediately adjacent to the facility are elevated compared to rural background values from US EPA. These three samples fall within the urban background values. The remaining four NYS DOH samples are consistent with the background range for rural areas. We believe that the data suggest that Holley is not different from rural background except for those samples immediately adjacent to Diaz. As noted in the document, dioxin levels approach background as you move farther from the Diaz site.

Dioxins and furans can be found in many communities. Other potential sources of dioxins reportedly exist in addition to Diaz. House fires, burning of household waste and even wood or oil burning can produce dioxins and dibenzofurans. A home at 13 Jackson Street reportedly had a structure fire; one would expect this to be a local source. Review of the data shows that the samples furthest from Diaz (E, F and G) have levels in the range of values reported for rural background, and therefore Holley

as a whole is consistent with the levels of dioxins found in similar communities. Only samples (A, B and C) very close to Diaz have levels of dioxin above background, but these samples still have TEQ levels below the 1.0 ppb action level.

Comment #3: How can NYS DOH close this issue of human health and safety before the property owners have received vital US EPA test data on dioxins? All decision making on determining health risks in Holley must be stayed until all data are available for evaluation.

Response #3: The September 2004 draft PHC stated that NYS DOH and ATSDR would review US EPA's dioxin and furan data when they became available. That has happened and they are included in this report. We have drawn conclusions in this report based on the data from three sampling efforts (NYS DOH, US EPA, and NYS OAG). If more data become available, we will look at that data as well.

Comment #4: Why did it take 11 months to inform the community there were dioxins in the explosion of January 5, 2002? Why did it take the DOH almost 3 years to inform "Interested Parties" there are dioxins and furans in our property soil?

Response #4: The initial work focused on the release of CFP. All of the evidence, including company records and sampling data, suggested that CFP was the main contaminant of concern. Our initial evaluation presented in the November 2002 draft PHA suggested dioxins and furans were not a significant part of the January 5, 2002 release. After hearing and receiving comments on the draft document, we agreed to do additional work in response to people's concerns. We then asked property owners permission to analyze their samples for dioxins and furans. We also have tried to coordinate our efforts with those of the June 2003 US EPA sampling so that the dioxin data became available all at once. All of these steps resulted in the health consultation about dioxins being released in October 2004.

Comment #5: There is a need for a public meeting and more outreach.

Response #5: This PHC was prepared to answer specific concerns voiced by the community about dioxins in soil from Diaz. We do not feel at this time that the limited scope of this document constitutes the need for a formal public meeting. However, NYS DOH staff are available, to talk about the results of this PHC or any activities related to Diaz. If you have any questions for NYS DOH, you may contact Lloyd Wilson at 1-800-458-1158, extension 27714, or, for ATSDR, Greg Ulirsch at 1-888-422-8737.

NYS DOH (August 31, 2005) mailed a letter to the community to provide an update of ATSDR and NYS DOH activities at the Diaz Chemical Corporation Site. The letter summarized completed and ongoing activities and commits to providing the Holley community with additional progress reports approximately twice a year or as documents are released.

Comment #6: Health concerns have not been addressed. Test data has revealed numerous combinations of hydrocarbons, metals, dioxins and furans. Many of the chemical and metals found are known carcinogens. Many of the chemicals and metals cause birth defects, damage to immune systems, liver, kidney, and hormones. All chemicals and chemical combinations, all metals in air, soil, ground water and household dust must be addressed in any decision-making process to determine the health risk posed on the community and its future generation.

Response #6: The NYS DOH and ATSDR are taking a multidisciplinary, multi-exposure pathway, coordinated approach to addressing health concerns at the Diaz site. The agencies are focusing on the major chemicals of concern (CFP and dioxin) and conducting epidemiological activities to evaluate potential health effects related to these or other chemicals released by the Diaz facility. The NYS DOH and ATSDR released a Public Health Assessment (PHA), two Public Health Consultations (one of which is this one about dioxins in soils) and several other information sheets describing potential exposures and health risks to chemical contamination from the Diaz facility. The PHA focused on the risks associated with exposure to CFP from the January 5, 2002 accidental release; however, other Diaz chemicals are described in this document. NYS DOH and ATSDR are preparing a Public Health Consultation on groundwater and the soil vapor intrusion pathway for chemicals discharged by Diaz into the groundwater.

As described in the NYS DOH August 2005 status of on-going activities letter, NYS DOH has several on-going epidemiologic activities in response to potential exposures from the Diaz Chemical Facility and community concerns. NYS DOH offered enrollment in the NYS Volatile Organic Chemical (VOC) registry. Participants in the registry will be contacted approximately every two to three years, for a period of ten years, to track changes in demographic data.

In addition to the registry, NYS DOH is conducting a cancer incidence investigation and a review of birth defects in the Village of Holley. This work will evaluate if the cancer and birth defect diagnoses in the Village of Holley are occurring at higher, lower or the same level as would be expected for a typical community in New York of the same size and age. A summary of this work and a status report on the registry is expected in the winter of 2005/2006.

In summary, NYS DOH and ATSDR have evaluated many different chemicals and epidemiologic evaluations are on-going to evaluate if any unusual health outcomes are being experienced by the residents in the Village of Holley.

Comment #7: TEQs should be calculated using ½ the detection limit when a dioxin congener is not detected as per ATSDR guidance.

Response #7: The HC presents the TEQs calculated both with non-detects equal to zero and with the non-detects equal to one half (1/2) of the detection limit. One reason that both values are presented is to show how the methodology affects the

TEQ values. Also, US EPA presents their summary of the background data using zero for non-detects, others may not. For these reasons we present the TEQ calculated both ways.

Comment #8: Testing is needed to the south and east because the highest values were there.

Response #8: The January 5, 2002 CFP release, as characterized by visible staining, went to the northeast. Therefore, soil sampling was targeted in these areas of greatest staining. The soil samples that we analyzed were originally collected to measure the CFP levels as a result of the release and NYS DOH reported the data from this work in February 2002 and in the November 2003 PHA. Our purpose for the current dioxin and furan analyses was to follow up on what dioxins may have been associated with the January 5, 2002 release. The data from the CFP and dioxin sampling do show higher levels of CFP and total dioxin TEQs in the soil samples next to the facility in the northeast direction.

In December 2004 the NYS OAG collected a sample from a location to the east of Diaz near US EPA's sample location 24, which was sampled in June 2003. The NYS OAG sample showed levels very similar to the results found at many properties, while the US EPA result was the highest of the US EPA results. Both the NYS OAG (0.0046 ppb) and the US EPA (0.01372 ppb) results are below the ATSDR Action level of 1.0 ppb. Given the more recent NYS OAG data and because both results are below the 1.0 ATSDR Action Guideline action and the ATSDR Environmental Media Evaluation Guideline (EMEG) of 0.05 ppb, no further testing is planned.

Comment #9: A comparison of the predicted TEQ (see Appendix A (1.376E-7)) value in the soil of the sample with the highest CFP level found from the November 2003 PHA and the mean TEQ (0.011 ppb) from this sampling experience shows that there are about 80,000 times more dioxin than predicted (See Appendix 1). This discrepancy should be explained.

Response #9: We agree that the predicted TEQ was lower than the TEQ measured by orders of magnitude. One of the reasons we agreed to do the dioxin analyses was because we only had estimated concentrations expected from the CFP release. The discrepancy between the actual and predicted concentrations could exist for a number of reasons. Two possible reasons are that there is another source(s) of dioxin or our estimate in the PHA was too low. The predicted value of dioxin is based solely on the CFP release, but it is possible that other releases occurred from Diaz as well as other sources that contained low levels of dioxins. Other sources, such as the reported use (see Response 2) of burn barrels and a fire that destroyed a home at 13 Jackson Street, may be contributing to the levels of dioxins and furans found. It is not possible to determine the origin of the dioxins in the soils. Another reason our estimated dioxin value may be too low is that our predicted dioxin concentration was based on the assumption that the CFP to dioxin ratio was constant in both the wash solution of the ruptured vessel and in the soil samples. This assumption requires that

the environmental fate and transport (e.g. volatilize into air, degrade in sunlight, leach into water) of dioxins and CFP be the same. This may not be true. Regardless of the reason for the discrepancy between the measured and estimated levels, the measured and estimated are below the ATSDR Action Guideline.

Comment #10: Dioxins were in the toluene rain and not just associated with the CFP. Using CFP as a measure of dioxin contamination is not appropriate because dioxins were in the toluene as well.

Response #10: Assuming toluene, CFP and dioxins were all part of the same droplet, as they probably were, the ratio of the CFP to dioxin, if the fate and transport properties are similar, can be used to estimate dioxin. The issue of fate and transport as it relates to our estimate is discussed in our Response to Comment #9.

Comment #11: The PHC should describe main sources of exposure to dioxins and furans. The comment included a copy of a published article that described the relative importance of different routes of human exposure.

Response #11: Comment 11 included a reference to a published article that describes food as being an important source of exposure to dioxins. There are several published articles that suggest food is the predominant source of human exposure; many of these papers are included in the US EPA 2002 Reassessment that we reference in this PHC. The reference provided suggests that ingestion of food is probably the most significant route of exposure to dioxins for the majority of the public. This, however, does not preclude the need to investigate whether other routes of exposure may be of more importance for site specific circumstances.

Comment #12: The PHC suggests that the 1,3,6,8- tetrachlorinated dibenzo-*p*-dioxins (TCDD) found in the soil is associated with the CFP release on January 5, 2002. The 1,3,6,8-TCDD was most likely a contaminant in the toluene used to wash the vessel after the release.

Response #12: The comment is so noted.