STATE OF DELAWARE
DEPARTMENT OF NATURAL RESOURCES
AND ENVIRONMENTAL CONTROL
DIVISION OF AIR AND WASTE MANAGEMENT
391 LUKENS DRIVE
NEW CASTLE, DELAWARE 19720-2774

WASTE MANAGEMENT SECTION
SITE INVESTIGATION &
RESTORATION BRANCH

TELEPHONE: (302) 395-2600
FAX: (302) 395-2601

May 10, 2007

Mr. Roger Malatesta
3617-A Silverside Road
Wilmington, DE 19801

Re: Response to your email on May 3rd regarding the remediation and development of the Hercules Tract (aka Delaware National) Site

Dear Mr. Malatesta:

Secretary Hughes has asked me to response to your May 3rd email regarding the Hercules Tract/Delaware National Technical Assistance Site ("Hercules"). As you may be aware, the Delaware Department of Agriculture reviewed the pesticide/fertilizer logs for Hercules and has stated that the logs do not indicate the misapplication of these chemicals at this Site. Due to this finding, DNREC does not have jurisdiction over this Site. However, DNREC has entered into a Memorandum of Understanding with New Castle County Government to ensure that the technical and substantive requirements of the Hazardous Substance Cleanup Act are met at Hercules.

The Department understands your concern regarding the potential for dioxins to be present at Hercules. The Department and Toll Brothers, Inc. have looked into the merit of this concern and concluded that sampling for dioxin compounds is not technically warranted at this Site. This conclusion was reached only after extensive review of published documents in addition to direct communication with other federal and state cleanup programs. The attached memorandum, dated May 1, 2007, summarizes this conclusion.

Thank you for your concern over this process and if you have any other questions or concerns with this Site, please feel free to contact Kathleen Stiller-Banning or me at (302)395-2600.

Sincerely,

Timothy T. Ratsep
Program Manager

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Enclosure

pc: John Hughes, Secretary
James D. Werner, DAWM - Director
Kathleen Stiller-Banning, SIRB – Program Manager II
Stephen Johnson, SIRB – Project Officer
Barbara Smith, EPA – Region Three

Delaware's good nature depends on you!

Good work Steve. I know this is only a brief summary of the work you've done to ensure the site investigation & cleanup are fully protective.

Memorandum

To:	James D. Werner, Director of Air & Waste Management
Through	Kathy Stiller Banning, Program Manager II KSB 5/2/07 Tim Ratsep, Program Manger I TCR 5/1/07
RE:	Recommendation concerning sampling for dioxin[1] at Hercules Golf Course
From:	Stephen F. Johnson, PE SFJ 5/1/07
Date:	May 1, 2007

4 MAY 2007

The purpose of this memo is to respond to questions and comments presented to the Site Investigation and Restoration Branch (SIRB) at the public meeting held on March 21, 2007. The meeting concerned the cleanup and development of the Hercules Golf Course in New Castle County. A copy of the comment regarding dioxin sampling is attached to this memo.

After an extensive review of the existing literature and information, the SIRB recommends against sampling for dioxin. The SIRB's reasoning is summarized in the *Findings* and *Conclusions* below.

The SIRB recognizes that decisions of this nature are not made on a purely technical basis and that there may be other reasons to proceed with a sampling program. Dioxin is frequently "featured" in the news media and has extreme negative associations for most people. Three examples are the recent dioxin poisoning of Viktor Yushchenko, the industrial accident at Seveso, Italy and, notoriously, dioxin in Agent Orange used by the US Air Force in Vietnam.

Dioxin is also in the news because it is controversial in the scientific world. There is a wide range of expert opinion on its toxicity and carcinogenicity. Judging by information available on the world wide web, new dioxin studies are frequently greeted with charges of "junk science" by those who have formed differing conclusions. The dioxin debate combined with the strong feeling against the re-development of the Hercules site makes for a contentious issue. Therefore, the SIRB recognizes that there unusual public relations aspects to both dioxin and this specific project that may support sampling.

A caution: if the decision is made to sample for dioxin, then it should not establish a precedent to perform similar sampling at other sites. Sampling for dioxin should always be a site by site decision. If sampling does occur, the sampling plan should consider that dioxin is ubiquitous in the environment. Care should be taken to establish a background data set to which the site information can be usefully compared.

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[1] Dioxin is the name of a family of over 200 related compounds which vary significantly in toxicity. The most toxic form is 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD). Concentrations of complex mixtures of dioxins are usually stated as Total Toxic Equivalentcy (TEQ) to TCDD.

Findings

The SIRB pursued two lines of inquiry to address the comments concerning dioxin:

- First the SIRB examined available published documents on the chemical dioxin, its environmental persistence, presence in herbicide and presence in soil as a result of herbicide application. Among other sources, the SIRB relied on a summary document compiled by its contractor, the environmental consulting company, CDM. The CDM report is attached as a useful and readable summary. It is also thoroughly referenced.

- Second, the SIRB inquired through an extensive network of federal and state site cleanup programs as to the regulatory practice in other jurisdictions pertaining to testing for dioxin at golf courses and other herbicide application sites.

Dioxin contamination in commercial weed killer
Various authorities confirm that dioxin compounds may be present in 2,4,-D. Its presence in 2,4,5-T has been repeatedly confirmed and contributed to the ban of 2,4,5-T. The process used to produce 2,4,5-T was apparently more likely to produce dioxin as a by-product. Since 1990, the presence of dioxin in 2,4-D has been limited to 1 ppm by federal regulation.

Weed killer use at Hercules Golf Course
2,4-D application is noted in Hercules Golf Course pesticide application logs that go back to 1970. The logs do not show any use of 2,4,5-T. However, 2,4,5-T was banned for use on turf grass in 1970, so logs do not cover the period when it could have been legally used. The SIRB found one turf management magazine recommending use of 2,4,5-T to control clover (Daniel). If 2,4,5-T were ever applied to the golf course, it was prior to 1970.

Dioxin persistence
Dioxin is frequently described as a persistent compound. However, there is a difference between dioxin accumulation in the food chain and dioxin in the environment. When a herbicide is applied to green plants, most of the dioxin that may be present in it sticks to plant matter where it is photo-degraded and never reaches the soil (Nathan). Soil tests taken over a ten year period in an Agent Orange test area showed a 99% reduction in dioxin concentrations in soil (Young).

The SIRB reviewed a report on dioxin sampling along a pipeline in Alaska that received documented treatment with 2,4,5-T containing herbicides between 1955 and 1970 (USACE). Sampling occurred in 2003. None of the 23 sample results exceeded the State of Alaska's risk based cleanup of 39 ng/kg. Four were between 3.9 ng/kg and 39 ng/kg. (The SIRB's guidance gives a screening concentration of 4 ng/kg [parts per trillion]).

Practices in other states
The SIRB has not found a single instance in which a state or federal cleanup program required testing for dioxin at a golf course site due to herbicide application. Several experts and experienced program managers explicitly stated that they had never heard of this being done. This is significant given that inorganic contaminants in golf course soil are receiving heightened attention in the site cleanup field. However it should also be noted that agricultural chemicals are excluded from most state cleanup programs.

The commenter referred specifically to the State of Oregon's "Guidance for Evaluating Residual Pesticides on Lands Formerly Used for Agricultural Production" as requiring dioxin testing (Oregon). In fact, the guidance recommends sampling for dioxins in cases where 2,4,5-T is known to have been applied. Known applications of 2,4-D are reviewed individually. The Oregon web page does not list any cleanup sites where dioxin contamination in soil was caused by herbicide application, either 2,4-D or 2,4,5-T.

The SIRB did find two instances of dioxin testing on golf courses at US Air Force bases, but both had suspected dioxin sources off the golf course and were not related to the usual application of herbicides.

Conclusions

In the opinion of the SIRB, the weight of evidence is that dioxin released during the application of herbicide would not persist at significant levels in soil for the 37 years since 1970. More recent applications of 2,4-D (rather than 2,4,5-T) would have had very little or no contamination by dioxin.

The remedial action proposed for the inorganic contaminants, soil removal and blending, would be reasonably expected to reduce the volume and concentrations of any dioxins that might be present on the site.

The SIRB found no regulatory precedent in other jurisdictions to require sampling for dioxin at a golf course due to herbicide application.

References

Daniel WH, 1953. *The use of 2,4,5-T for clover control in turf.* Southern California Turf Culture Volume 3, Number 3. July 1953.

Karch NJ, DK Watkins, AL Young and ME Ginevan, 2004. *Environmental fate of TCDD and Agent Orange and bioavailability to troops in Vietnam.* Organohalogen Compounds 66:3689-3694.

Oregon Department of Environmental Quality Land Quality Division. 2006. Guidance for Evaluating Residual Pesticides on Lands Formerly Used for Agricultural Production. DEQ-06-LQ011.

Young AL and M Newton. *Long overlooked historical information on Agent Orange and TCDD following massive applications of 2,4,5-T-containing herbicides, Eglin Air Force Base, Florida.* Environ Sci Pollut Res Int 2004;11(4):209-21.
http://www.ncbi.nlm.nih.gov

US Army Corps of Engineers (USACE) Alaska District Materials Section Engineering Services Branch. 2004. *Chemical Data Report: Herbicide Residue Survey, Haines-Fairbanks Pipeline, Alaska.* January 2004.

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Delaware National Golf Course
(a.k.a. Hercules Road Property)

In an e-mail dated March 22, 2007 and a conference call on March 27, 2007, the Delaware Department of Natural Resources and Environmental Control (DNREC) requested Camp Dresser & McKee Inc. (CDM) to review background information on the production of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and the potential of dioxin contamination in these herbicides. In addition, DNREC requested information on typical application rates for these herbicides on turf and possible resulting dioxin concentrations in soil. Finally DNREC requested investigation of the persistence of dioxins after 2,4-D and 2,4,5-T degrades or dissipates and a short list of references for the assessment of health risks due to low concentrations of dioxin in soil and airborne dust. CDM's review is presented in the following sections.

1.0 Background

1.1 2,4-D

2,4-D is the most widely used herbicide in the U.S. and worldwide, and has been in use for over 60 years. 2,4-D controls a broad spectrum of broadleaf weeds, such as carpetweed, dandelion, cocklebur, horseweed, morning glory, pigweed, lambsquarters, ragweed, shepherd's purse and velvetleaf with little to no effects against grasses in agricultural crops such as wheat, corn, rice, soybeans, potatoes, sugarcane, fruit and nut trees. It also controls weeds in turf grass and invasive species in aquatic areas. 2,4-D is also widely used in mixtures with other herbicides to provide weed control in forestry, orchards and non-crop areas and for the control of aquatic weeds, such as water hyacinth, bulrush, bladderwort, water lily and Eurasian water milfoil (Pesticide Action Network 2006, Industry Task Force 2007).

2,4-D is categorized in the phenoxy group of herbicides and is a synthetic form of the auxin (plant hormone). Plant injuries induced by the application of 2,4-D include growth and reproduction abnormalities, especially on new growth. Symptoms may appear on young growth almost immediately after application, but death may not occur for several weeks (Industry Task Force 2007).

Initial tests of 2,4-D were conducted in 1944 on a lawn infested with dandelions; the dandelions were selectively killed with no injury to the turf grass. Additional studies were conducted on a golf course also showing exceptional weed control. In 1945, a developmental program was conducted with the United States Golf Association and on turf grass of the National Capital Park Service including the White House lawn. During the same year, 2,4-D was first extensively tested on crops at various state agricultural experiment stations (Industry Task Force 2007). 2,4-D was introduced commercially in 1946 (Industry Task Force 2007) and is produced by many different companies around the world (Pesticide Action Network 2006).

EPA/600/P-03/002F (2006) 2,4,5-T was used in the U.S. for a variety of herbicidal applications until the late 1970s through early 1980s, and was used primarily (approximately 41% annual usage) in the control of woody and herbaceous weeds on right of ways. Other uses were forestry (28% of usage), rangeland (20% of usage), and pasture (5% of usage) practices.

In 1970, EPA suspended the home and garden, commercial and ornamental turf, and aquatic weed control/ditch bank uses of 2,4,5-T. In 1979, EPA ordered emergency suspension of the forestry, rights-of-way, and pasture uses of 2,4,5-T. In 1983, EPA cancelled the sale of 2,4,5-T for all uses (EPA 2006) due to the presence of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (details in Section 3).

2.0 Application of 2,4-D and 2,4,5-T

2.1 2,4-D

Application rates of 2,4-D vary due to its different formulations and use as an individual herbicide, or in mixtures containing other herbicides. Several other factors may influence the amount of 2,4-D applied such as season, size of the treatment site, type of weeds, nature of the application site (roadside weed control, golf courses, rangeland, household use, etc.) and means of application (e.g., aerial and ground).

In the EPA document entitled *Reregistration Eligibility Decision* (RED) *for 2,4-D*, EPA 738-R-05-002 (2005), a 2,4-D master label was developed by the 2,4-D Task Force. The volumes on the label represent the maximum application rates for agricultural and non-agricultural uses. As per the regulatory guidance, all registrants must conform to the master label rates.

As per the U.S. EPA RED for 2,4-D guidance document, a required application rate for ornamental turf grass is specified. Application rates of 2,4-D to ornamental turf range from 2.0 to 4.0 pounds (lbs) acid equivalent per acre per year. However, 2,4-D registrants agreed to reduce the amount from 2.0 to 1.5 lbs acid equivalent per acre with a new maximum yearly rate of 3.0 lb acid equivalent per acre. In addition, as per the National Agricultural Pesticide Impact Assessment Program's (NAPIAP) report on Phenoxy Herbicides 2,4-D application on turf grass areas, on average, is applied once per year (EPA 2005).

A suggested application rate for turf grass using Agrisolutions brand commercial herbicide 2,4-D LV4 (contains 66.2% 2-ethylhexyl ester of 2,4-D) range from 2 to 4 pints per acre; the higher dose for use on deep-rooted weed species (CDMS 2007). In this example, the actual weight of 2,4-D used to create the solution contains 3.8 pounds of 2,4-D per gallon which would equate to 0.475 pounds per pint.

2.2 2,4,5-T

2,4,5-T was applied alone or as mixtures with other herbicides in the form of solutions, dispersions, or emulsions in water. Because use of 2,4,5-T has been banned in the U.S. for over 20 years, recommended application rates for the herbicide were unavailable.

The 1995 estimate for dioxin emissions from 2,4-D, taken together with National Science Academy (NAS) estimates for 2002/2004 releases from other sources of dioxin in the U.S., suggest that 2,4-D applications to land ranks 7th (2.6% of all dioxin sources) behind backyard burning (57%), sewage sludge application (6.9%), residential wood burning (5.7%), coal-fired utilities (5.4%), diesel trucks (3.2%), and secondary aluminum smelting (2.6%) in terms of dioxin emissions. Since 1942, the manufacturing processes for 2,4-D and its chemical intermediate, dichlorophenol, has been modified and those modifications decrease the chance that 2,3,7,8-TCDD and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PCDD) are formed during the manufacturing process (cited on page 83 of EPA 2005).

In a study conducted by Cochrane *et al.*, (1981) as cited on the International Program on Chemical Safety (1988) website, samples of 2,4,-D esters and amine salts manufactured in Canada were analyzed for dioxins. Results of the investigation showed that eight of nine esters and four of seven amine salts were found to be contaminated with dioxin. 2,4-D esters showed considerably higher dioxin levels than the amine salts ranging from 210 to 1752 nanograms per gram (ng/g); dioxin concentration in amine salts ranged from 20 to 278 ng/g. In addition, another study investigating dioxin in a German manufactured 2,4-D formulation showed that it contained 6.8 ng/g of 2,3,7,8-TCDD (IPAC 1988) .

It is difficult to determine the amount of residual dioxin, if any, as a result of the application of 2,4-D as information on the subject is limited. Effective in 1990, the EPA required that all 2,4-D be synthesized to reduce dioxin impurities to less than 1 part per million (ODEQ 2006). In addition, as cited in U.S. EPA's *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000 in 1995* (2006), domestic manufacturers of 2,4-D have been undertaking voluntary actions to reduce the dioxin content of the product.

3.2 2,4,5-T

Dioxins formed during the synthesis of 2,4,5-T were the result of a combination of high temperatures in the presence of starting materials. In contrast, the manufacturing process for 2,4,-D uses much lower temperatures. If dioxins are formed during the manufacturing process, they will be present in the final technical grade product because they are not destroyed under manufacturing conditions (CPMRA 2006).

During the time 2,4,5-T was manufactured, the amount of 2,3,7,8-TCDD present in the herbicide varied greatly, and was dependant on the temperature control and purification efficiency of the manufacturing process. 2,4,5-T formulations manufactured and used in the 1960s may have contained as much as 100 mg/g or 10 percent 2,3,7,8-TCDD (IPCS 1988).

A 1975 study involving 10 lots of a commercial herbicide containing 2,4,5-T showed 2,3,7,8-TCDD concentrations ranging from 10 to 40 micrograms per kilogram (μg/kg) (Lewert, 1976 as cited in EPA 2006). In another study, conducted by the EPA, 16

In aquatic environments, photochemical decomposition, volatilization and biodegradation of 2,4,5-T appear to be the dominant removal mechanisms. The aquatic near surface half-life for direct photolysis has been calculated to be 15 days during summer at latitude 40 degree (HSDB 2007).

4.3 Dioxin

As cited in U.S. EPA's *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000* (2006) chlorinated dioxins are highly persistent compounds under normal environmental conditions, especially when adsorbed on soil and sediment. Dioxins are slow to degrade with half-lives ranging from years to several decades depending on the compound. It has been reported that the most toxic form of dioxin, 2,3,7,8 TCDD, may have a half life of approximately one year in soil, but may persist in the environment for over twelve years. Due to their lipophilic nature and resistance to metabolism, dioxins tend to persist and bioaccumulate in fatty tissue of humans and animals.

This document (EPA 2006, page 11-11) also states that although actual data were not available on the amount of 2,3,7,8-TCDD originally applied as a contaminant of the 2,4,5-T, best estimates indicated that less than 1% of the applied 2,3,7,8-TCDD remained in the soil after 14 years. It was suggested that photodegradation at the time of and immediately after aerial application was responsible for most of the disappearance. However, once incorporated into the soil, the data indicated a half-life of 10 to 12 years. Paustenbach *et al.*, (1992) concluded that the half-life of 2,3,7,8-TCDD in soils at the surface might be 9 to 15 years and the half-life below the surface could be 25 to 100 years.

The Paustenbach *et al.*, 1992 paper also states that microbial and chemical degradation of 2,3,7,8-TCDD under virtually all soil conditions is negligible. Due to its very low water solubility, most of the dioxin occurring in water will adhere to sediments and suspended silts. It tends to adhere to soil if released to land and is not likely to leach to groundwater. Two processes which may be able to remove dioxin from water and soil are evaporation and breakdown by sunlight. Dioxin is generally resistant to microbial breakdown, and exhibits great tendency to accumulate in aquatic life from algae to fish. (EPA 2007)

5.0 References for the Assessment of Health Risks

This section contains a short list of references for the assessment of health risks due to low concentrations of dioxin in soil and airborne dust per DNREC's request.

- Agency for Toxic Substances and Disease Registry, 1998. Toxicological Profile for Chlorinated Dibenzo-*p*-Dioxins. UD Department of Health and Human Services, Public Health Service, Atlanta, GA. http://www.atsdr.cdc.gov/toxprofiles/tp104.pdf.

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Extension Toxicology Network (EXTOXNET). 1993, Cornell University Cooperation Extension Pesticide Management Education Program (www.pmep.cce.cornell.edu/profiles/extoxnet/24d-catan/24d-ext.html).

Hazardous Substance Databank (HSDB). 2007. National Library of Medicine's TOXNET System. (www.toxnet.nlm.nih.gov)

Health Canada Pest Management Regulatory Agency, 2005. Proposed Acceptability for Continuing Registration; Re-evaluation of the Lawn and Turf Uses of 2,4-Dichlorophenoxy acetic acid (2,4-D).

Industry Task Force (Industry Task Force) II on 2,4-D Research Data. 2007. On-line www.24d.org.

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National Cancer Institute (NCI), 2003. De Roose, AJ, SH Zahm, KP Cantor, DD Weisenburger, FF Holmes, LF Burmeister and A Blair. Integrative assessment of multiple pesticides as risk factors for non-Hodgkin's lymphoma among men. Occup Environ Med 60(9):p. E1.

Oregon Department of Environmental Quality (ODEQ). 2006. Guidance for Evaluating Residual Pesticides on Lands Formerly Used for Agricultural Production. DEQ-06-LQ-011. ODEQ Land Quality Division Cleanup Program. January 2006.

Pesticide Action Network North America (PAN). 2006. Version 7.1 of PesticideInfo (www.pesticideinfo.org).

Paustenback DJ, RJ Wenning, V Lau, NWHarrington, DK Rennix, and AH Parsons, 1992. *Recent developments on the hazards posed by 2,3,7,8-tetrachlorodibenzo-p-dioxin in soil: Implications for setting risk-based and industrial sites.* J Toxicology and Environmental Health 36:103-149.

United States Environmental Protection Agency (EPA). 2005. Reregistration Eligibility Decision for 2,4-D. EPA 738-R-05-002. U.S. EPA Prevention, Pesticides and Toxic Substances (7508C). June 2005.

MLCA Statement to DNREC at Public Meeting on Hercules Tract Remediation Plan

Good Evening, my name is Bill Dunn and I'm President of the Milltown-Limestone Civic Alliance, the civic umbrella group that represents the area in which the Hercules Tract is and is proposed for residential development by Toll Brother's Builders. Based on the change in use, we took an interest in the development of this property shortly after it was announced to the community by Councilman Tansey and the County Land Use department back in the Fall of 2003. By January 2004, we had helped to establish what we call the Hercules Working Group to study and review Toll Brother's plans for the property and evaluate how those plans may impact the surrounding existing communities. Soon after the working group began to meet, we realized that State and Local elected officials were equally interested in how this plan might develop.

As everyone is aware, the environmental issues surrounding this property have become one of the two major concerns we all seem to have with Toll's plans. Also, we all could agree that Toll and their environmental engineering firm, Brightfield and Associates, have made significant efforts to evaluate this property, yet woefully inadequate for a 50+ year old golf course in which homes will be built and children will play.

I find it astounding that anyone who makes a living studying environmental issues could find the Remedial Action Plan as it exists today, if implemented, would adequately protect the present and future residents of the area. Some may think that is pretty strong language to describe all the work that has been done by Brightfield and others, but when discussed amongst our technical group of PhD's and technically degreed members of the community, the sentiment was that the testing was far to quickly focused on arsenic as the primary marker of the problems on the property and if it was remediated, all other contaminants would be resolve as well.

It's probably best at this point that I touch on a few of many questions that we have been developing. Hopefully, from the few that I'll be mentioning here, DNREC and others will quickly understand that the community is interested in getting answers to substantive issues that have yet to be adequately addressed.

1) DNREC has made it perfectly clear that they believe that this site does not qualify as a HSCA regulated site. But to help New Castle County out with the fact that they do not have environmental engineers on their staff, under a Memorandum of Understanding that has yet to be finalized, will act as a contracted agent to evaluate Toll and Brightfield's remediation plan based on HSCA regulations and standards.

Why isn't DNREC and/or the County requiring that Toll Brother's obtain insurance to provide the community with guaranteed legal recourse if the plan is poorly carried out and the contamination is spread to the surrounding communities during clean-up? Under normal HSCA-qualifying remediation, at the end of the clean-up process, the State and DNREC accepts legal responsibility for any future environmental problems tied to previous contamination. In this situation, the public doesn't have those assurances and Toll Brother's parent company, if the costs of settling any law suites got to great, could allow the local LLC to collapse and go bankrupt, leaving the community with no avenue for restitution.

2) In a county with one of the highest cancer rates in the nation, how is the community's best interest being served by permitting the mixing of soil with concentrations of arsenic more than three times the permissible limit, with soil of lower concentrations of arsenic until the overall ground has concentrations is below 11mg/Kg of soil? Don't get me wrong, I know how it represents Toll Brothers best interest. I just don't know how it represents the communities?

Lastly) Why is it that having log book entries confirming that 2,4-D, a dangerous and sometimes banned pesticide, was applied to the golf course and also, that Hercules was one of two major producers 2,4,5-T, another dangerous and now banned pesticide, and which Hercules would have likely applied it to their own golf course before the early 70's ban on it's use, that DNREC has not asked for and Brightfield has not done any testing for dioxin, that was a residual by-product in the production and application of these chemicals?
In an Oregon Department of Environmental Quality report providing guidance for Evaluating Residual Pesticides on Land Formerly Used for Agricultural Production dated January 2006, they recommend sampling for dioxins when either one of these pesticides has been used. In the Hercules log book we have records dating back to the '70's that 2,4-D was applied. But it wasn't until the 90's that the EPA began to require that the producers of 2,4-D reduce the level of dioxin in their product to less than 1 part per million. Although it is known that 2,4-D and other pesticides breakdown over time, it is also known that the original dioxin by-product is significantly more stable in soil and deteriorates at a dramatically slower rate. In turn, it's easily conceivable that either one of the original chemicals would be undetectable, but the dioxin would remain.

I could go on for over an hour asking questions developed by our technical group, but really wouldn't get to the point that needs to be made. Why is it a group of generally, technically qualified community members are telling our State's environmental protection agency what they should be doing to protect us? We're disappointed that DNREC has not taken a more proactive roll in identifying the problem and making sure their corrected. Also, not being an expert in environmental issues, I don't understand why Brightfield didn't recommend to their client that they evaluate the property for dioxin and readily known hazards from heavy pesticide use?

Finally, none of us from the community attests to being an authority in environmental engineering, nor do we want to. But of the people that have a technical background and/or work in the chemical research field, we find it surprising that someone of authority in this process isn't aware of what we believe to be extreme hazards associated with the improper clean-up of this property and that recommended clean-up standards seem to be based more on financial commitment than community protection.

Based on the lack of technical specificity, no testing for dioxin, lack of legal recourse for the community, lack of complete containment of processing and subsequent dust potential, we are in no way comfortable with the present remediation plan and will do everything we can to stop it's implementation until adequate safeguards are added to protect the present and future community. In many respects, the development of this golf course is a precedent setting situation and in some other respects we have found the systems set forth to protect the community disappointing.

Thank You,

Delaware National Golf Course (a.k.a. Hercules Road Property)

In an e-mail dated March 22, 2007 and a conference call on March 27, 2007, the Delaware Department of Natural Resources and Environmental Control (DNREC) requested Camp Dresser & McKee Inc. (CDM) to review background information on the production of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) and the potential of dioxin contamination in these herbicides. In addition, DNREC requested information on typical application rates for these herbicides on turf and possible resulting dioxin concentrations in soil. Finally DNREC requested investigation of the persistence of dioxins after 2,4-D and 2,4,5-T degrades or dissipates and a short list of references for the assessment of health risks due to low concentrations of dioxin in soil and airborne dust. CDM's review is presented in the following sections.

1.0 Background

1.1 2,4-D

2,4-D is the most widely used herbicide in the U.S. and worldwide, and has been in use for over 60 years. 2,4-D controls a broad spectrum of broadleaf weeds, such as carpetweed, dandelion, cocklebur, horseweed, morning glory, pigweed, lambsquarters, ragweed, shepherd's purse and velvetleaf with little to no effects against grasses in agricultural crops such as wheat, corn, rice, soybeans, potatoes, sugarcane, fruit and nut trees. It also controls weeds in turf grass and invasive species in aquatic areas. 2,4-D is also widely used in mixtures with other herbicides to provide weed control in forestry, orchards and non-crop areas and for the control of aquatic weeds, such as water hyacinth, bulrush, bladderwort, water lily and Eurasian water milfoil (Pesticide Action Network 2006, Industry Task Force 2007).

2,4-D is categorized in the phenoxy group of herbicides and is a synthetic form of the auxin (plant hormone). Plant injuries induced by the application of 2,4-D include growth and reproduction abnormalities, especially on new growth. Symptoms may appear on young growth almost immediately after application, but death may not occur for several weeks (Industry Task Force 2007).

Initial tests of 2,4-D were conducted in 1944 on a lawn infested with dandelions; the dandelions were selectively killed with no injury to the turf grass. Additional studies were conducted on a golf course also showing exceptional weed control. In 1945, a developmental program was conducted with the United States Golf Association and on turf grass of the National Capital Park Service including the White House lawn. During the same year, 2,4-D was first extensively tested on crops at various state agricultural experiment stations (Industry Task Force 2007). 2,4-D was introduced commercially in 1946 (Industry Task Force 2007) and is produced by many different companies around the world (Pesticide Action Network 2006).

EPA/600/P-03/002F (2006) 2,4,5-T was used in the U.S. for a variety of herbicidal applications until the late 1970s through early 1980s, and was used primarily (approximately 41% annual usage) in the control of woody and herbaceous weeds on right of ways. Other uses were forestry (28% of usage), rangeland (20% of usage), and pasture (5% of usage) practices.

In 1970, EPA suspended the home and garden, commercial and ornamental turf, and aquatic weed control/ditch bank uses of 2,4,5-T. In 1979, EPA ordered emergency suspension of the forestry, rights-of-way, and pasture uses of 2,4,5-T. In 1983, EPA cancelled the sale of 2,4,5-T for all uses (EPA 2006) due to the presence of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD) (details in Section 3).

2.0 Application of 2,4-D and 2,4,5-T

2.1 2,4-D

Application rates of 2,4-D vary due to its different formulations and use as an individual herbicide, or in mixtures containing other herbicides. Several other factors may influence the amount of 2,4-D applied such as season, size of the treatment site, type of weeds, nature of the application site (roadside weed control, golf courses, rangeland, household use, etc.) and means of application (e.g., aerial and ground).

In the EPA document entitled *Reregistration Eligibility Decision* (RED) *for 2,4-D*, EPA 738-R-05-002 (2005), a 2,4-D master label was developed by the 2,4-D Task Force. The volumes on the label represent the maximum application rates for agricultural and non-agricultural uses. As per the regulatory guidance, all registrants must conform to the master label rates.

As per the U.S. EPA RED for 2,4-D guidance document, a required application rate for ornamental turf grass is specified. Application rates of 2,4-D to ornamental turf range from 2.0 to 4.0 pounds (lbs) acid equivalent per acre per year. However, 2,4-D registrants agreed to reduce the amount from 2.0 to 1.5 lbs acid equivalent per acre with a new maximum yearly rate of 3.0 lb acid equivalent per acre. In addition, as per the National Agricultural Pesticide Impact Assessment Program's (NAPIAP) report on Phenoxy Herbicides 2,4-D application on turf grass areas, on average, is applied once per year (EPA 2005).

A suggested application rate for turf grass using Agrisolutions brand commercial herbicide 2,4-D LV4 (contains 66.2% 2-ethylhexyl ester of 2,4-D) range from 2 to 4 pints per acre; the higher dose for use on deep-rooted weed species (CDMS 2007). In this example, the actual weight of 2,4-D used to create the solution contains 3.8 pounds of 2,4-D per gallon which would equate to 0.475 pounds per pint.

2.2 2,4,5-T

2,4,5-T was applied alone or as mixtures with other herbicides in the form of solutions, dispersions, or emulsions in water. Because use of 2,4,5-T has been banned in the U.S. for over 20 years, recommended application rates for the herbicide were unavailable.

The 1995 estimate for dioxin emissions from 2,4-D, taken together with National Science Academy (NAS) estimates for 2002/2004 releases from other sources of dioxin in the U.S., suggest that 2,4-D applications to land ranks 7th (2.6% of all dioxin sources) behind backyard burning (57%), sewage sludge application (6.9%), residential wood burning (5.7%), coal-fired utilities (5.4%), diesel trucks (3.2%), and secondary aluminum smelting (2.6%) in terms of dioxin emissions. Since 1942, the manufacturing processes for 2,4-D and its chemical intermediate, dichlorophenol, has been modified and those modifications decrease the chance that 2,3,7,8-TCDD and 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PCDD) are formed during the manufacturing process (cited on page 83 of EPA 2005).

In a study conducted by Cochrane *et al.*, (1981) as cited on the International Program on Chemical Safety (1988) website, samples of 2,4,-D esters and amine salts manufactured in Canada were analyzed for dioxins. Results of the investigation showed that eight of nine esters and four of seven amine salts were found to be contaminated with dioxin. 2,4-D esters showed considerably higher dioxin levels than the amine salts ranging from 210 to 1752 nanograms per gram (ng/g); dioxin concentration in amine salts ranged from 20 to 278 ng/g. In addition, another study investigating dioxin in a German manufactured 2,4-D formulation showed that it contained 6.8 ng/g of 2,3,7,8-TCDD (IPAC 1988) .

It is difficult to determine the amount of residual dioxin, if any, as a result of the application of 2,4-D as information on the subject is limited. Effective in 1990, the EPA required that all 2,4-D be synthesized to reduce dioxin impurities to less than 1 part per million (ODEQ 2006). In addition, as cited in U.S. EPA's *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000 in 1995* (2006), domestic manufacturers of 2,4-D have been undertaking voluntary actions to reduce the dioxin content of the product.

3.2 2,4,5-T

Dioxins formed during the synthesis of 2,4,5-T were the result of a combination of high temperatures in the presence of starting materials. In contrast, the manufacturing process for 2,4,-D uses much lower temperatures. If dioxins are formed during the manufacturing process, they will be present in the final technical grade product because they are not destroyed under manufacturing conditions (CPMRA 2006).

During the time 2,4,5-T was manufactured, the amount of 2,3,7,8-TCDD present in the herbicide varied greatly, and was dependant on the temperature control and purification efficiency of the manufacturing process. 2,4,5-T formulations manufactured and used in the 1960s may have contained as much as 100 mg/g or 10 percent 2,3,7,8-TCDD (IPCS 1988).

A 1975 study involving 10 lots of a commercial herbicide containing 2,4,5-T showed 2,3,7,8-TCDD concentrations ranging from 10 to 40 micrograms per kilogram (μg/kg) (Lewert, 1976 as cited in EPA 2006). In another study, conducted by the EPA, 16

In aquatic environments, photochemical decomposition, volatilization and biodegradation of 2,4,5-T appear to be the dominant removal mechanisms. The aquatic near surface half-life for direct photolysis has been calculated to be 15 days during summer at latitude 40 degree (HSDB 2007).

4.3 Dioxin

As cited in U.S. EPA's *An Inventory of Sources and Environmental Releases of Dioxin-Like Compounds in the United States for the Years 1987, 1995, and 2000* (2006) chlorinated dioxins are highly persistent compounds under normal environmental conditions, especially when adsorbed on soil and sediment. Dioxins are slow to degrade with half-lives ranging from years to several decades depending on the compound. It has been reported that the most toxic form of dioxin, 2,3,7,8 TCDD, may have a half life of approximately one year in soil, but may persist in the environment for over twelve years. Due to their lipophilic nature and resistance to metabolism, dioxins tend to persist and bioaccumulate in fatty tissue of humans and animals.

This document (EPA 2006, page 11-11) also states that although actual data were not available on the amount of 2,3,7,8-TCDD originally applied as a contaminant of the 2,4,5-T, best estimates indicated that less than 1% of the applied 2,3,7,8-TCDD remained in the soil after 14 years. It was suggested that photodegradation at the time of and immediately after aerial application was responsible for most of the disappearance. However, once incorporated into the soil, the data indicated a half-life of 10 to 12 years. Paustenbach *et al.*, (1992) concluded that the half-life of 2,3,7,8-TCDD in soils at the surface might be 9 to 15 years and the half-life below the surface could be 25 to 100 years.

The Paustenbach *et al.*, 1992 paper also states that microbial and chemical degradation of 2,3,7,8-TCDD under virtually all soil conditions is negligible. Due to its very low water solubility, most of the dioxin occurring in water will adhere to sediments and suspended silts. It tends to adhere to soil if released to land and is not likely to leach to groundwater. Two processes which may be able to remove dioxin from water and soil are evaporation and breakdown by sunlight. Dioxin is generally resistant to microbial breakdown, and exhibits great tendency to accumulate in aquatic life from algae to fish. (EPA 2007)

5.0 References for the Assessment of Health Risks

This section contains a short list of references for the assessment of health risks due to low concentrations of dioxin in soil and airborne dust per DNREC's request.

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United States Environmental Protection Agency (EPA). 2005. Reregistration Eligibility Decision for 2,4-D. EPA 738-R-05-002. U.S. EPA Prevention, Pesticides and Toxic Substances (7508C). June 2005.