Attachment #5

Assessment of the Screening Level Ecological Risk Assessment for Discharge of Effluent from the Treatment of Newport (Indiana) Caustic Hydrolysate (NCH)

By

United States Environmental Protection Agency, Region 2
at the request of the
Centers for Disease Control and Prevention

October 5, 2004

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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OCT - 5 2004

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Dear Dr. Sinks:

In response to a request from several New Jersey and Delaware Senators and Congressmen for a formal review of the Army's proposal for off-site treatment of the VX hydrolysate at the DuPont wastewater treatment facility and discharge to the Delaware River, the Centers for Disease Control and Prevention (CDC) agreed "to conduct a review of the off-site disposal plan within our areas of expertise." In turn, CDC requested that the United States Environmental Protection Agency's (EPA) Region 2 office review and comment on the Screening Level Ecological Risk Assessment for Discharge of Effluent From The Treatment of Newport (Indiana) Caustic Hydrolysate (NCH) prepared by DuPont dated March 3, 2004. This letter outlines EPA's comments on this document.

The basic question that EPA Region 2 was asked to respond to was "From an ecological standpoint, is the disposal of material as presented in the DuPont Chambers ecological risk assessment acceptable?" Based on our review of the information provided and the amount of outstanding issues that need to be addressed, EPA's position is that DuPont has not demonstrated that the disposal of material as presented in the ecological risk assessment is acceptable.

Enclosed is a detailed discussion of EPA's findings. In summary, the Screening Level Ecological Risk Assessment (SLERA) does not contain adequate information to conclude that there is no unacceptable risk from the discharge of treated VX hydrolysate to the Delaware River, and a number of constituents were left out of the analysis completely. In addition, there are several additional issues that need to be addressed before treatment and discharge of this treated hydrolysate to the Delaware River can occur including: whole effluent toxicity tests procedures, the potential for the presence of VX nerve agent and other toxic breakdown products in the hydrolysate, the addition of phosphorus to the estuary, and the NPDES permit with New Jersey.

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Therefore, EPA believes that the conclusions of the SLERA are not valid and that the ecological risk process on the Army's proposal to discharge treated VX hydrolysate to the Delaware River must continue.

If you have any questions regarding this letter, please contact me at (212) 637-3725 or have your staff contact Grace Musumeci, Acting Chief of the Strategic Planning and Multi-Media Programs Branch at (212) 637-3504.

Sincerely yours,

Walter Mugdan, Director
Division of Environmental Planning and Protection

Enclosure

cc: (w/ enclosure)
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ENCLOSURE A

General Comments

The Screening Level Ecological Risk Assessment (SLERA) lacks conservatism. SLERAs are meant to be "conservative assessments in that they provide a high level of confidence in determining a low probability of adverse risk, and they incorporate uncertainty in a precautionary manner" (USEPA, 2001). The goal of a screening assessment is to minimize the likelihood of underestimating potential or current risk to ecological receptors through the use of conservative assumptions ensuring that the results will most likely overestimate actual risk.

DuPont's lack of conservatism in the SLERA is illustrated by the following:

- The SLERA does not include and evaluate all detected constituents found in the VX hydrolysate. DuPont focused the assessment only on the "principal constituents"of ethyl methylphosphonic acid (EMPA) and methylphosphonic acid (MPA). The Waste Characterization Profile Sheet located in Appendix B of the March 2004 Treatability Study indicates that several metals including arsenic, chromium, and lead were found in low ppm concentrations in the hydrolysate. Metals were also found in the hydrolysate as indicated in a July 2002 Oak Ridge National Laboratory report prepared for the Army (Oak Ridge National Laboratory, 2002). EA2192 or (S-[2-diisopropylaminoethyl] methylphosphonothioic acid), another breakdown product of VX nerve agent, is not included in the SLERA (more on this constituent below).

- Because some compounds in the hydrolysate mixture are unidentified, a conservative screening assessment of the mixture toxicity should be performed by assuming that unidentified chemicals are as toxic as the most toxic identified chemical in the mixture and by applying a concentration addition model to all constituents. The results would not constitute a risk estimate but could be used to determine whether the issue of mixture toxicity can be eliminated or requires more study.

- Maximum concentrations of all detected hydrolysate constituents, not just the "principal components," must be used in the screening level risk quotients. Concentrations for both EMPA and MPA are estimated in the SLERA.

- Dilution factors should not be used for estimating the in-stream concentrations of MPA and EMPA or any other detected constituents. In order to be conservative, the maximum hydrolysate concentrations for all detected constituents must be used in the risk calculations without a dilution factor.

- The Risk Characterization section of the SLERA should contain a Hazard Index (HI) calculation for constituents that have the same ecological effect endpoint and/or the same mechanism of toxic effect. EMPA and MPA were assumed to have similar toxic mechanisms in the SLERA and their hazard quotients should have been added together to

calculate a hazard index. All detected nerve agent breakdown products found in the hydrolysate with similar toxic mechanisms as EMPA and MPA should be included in the Hazard Index calculations.

In order to have a high degree of confidence in the predictive value of the hazard quotient method, there must be great certainty in the constituent concentrations and NOAELs used in the SLERA. Based on the non-conservative assumptions used in this SLERA, USEPA has little certainty in both the concentrations and NOAELs used in the hazard quotient calculations and therefore, does not believe that a statement of "no unacceptable risk" can be made for hazard quotients less than 1. The use of more conservative assumptions in the SLERA as listed above will certainly increase the risk quotients and risk indices. These increases will ultimately produce higher risk quotients that may approach or exceed 1 indicating a potential for adverse ecological effects and that a more thorough risk assessment is warranted

Toxicity Test Issues

A full Summary of Findings and Technical Recommendations (Enclosure B) follows this and provides an overview of the toxicity tests, a data review, and recommendations. Only the recommendations are presented here as follows:

- The data from the Treatability Study and the pure chemical testing are acceptable as screening evaluations.

- The results from the data study are not acceptable due to the limited effluent concentrations used in testing. The acute toxicity testing done for the data study must be re-run with the following concentrations of effluent after treatment through the second bio-reactor: 12.5%, 25%, 50%, 75% and 100%. Testing must be conducted with the following three species that are currently listed in the NJPDES permit: *Pimephales promelas* (fathead minnow), *Cyprinodon variegatus* (sheepshead minnow) and *Ceriodaphnia dubia*. The sheepshead minnow is included because any tests conducted on effluent from the treatment of NCH through the first and second phase PACT must consider all scenarios under the current NJPDES permit. This includes a discharge into the Delaware estuary when the receiving water salinity is greater than 3.5 ppt. When salinity is greater than 3.5 ppt the NJPDES permit states that testing must be conducted with the sheepshead minnow, *C. variegatus*.

- In addition, because the NJPDES permit is under review it is likely that chronic endpoints (which were to be reviewed for inclusion in the current permit) will be required. Therefore, chronic testing should be conducted on the final NCH effluent using species to be determined by the NJDEP in the new NJPDES permit. At a minimum, chronic testing with the same three species used for acute testing, ie *P. promelas, C. variegatus* and *C. dubia,* should be conducted to provide more sensitive endpoints to the data study than acute testing alone.

- All testing must be conducted following all quality control procedures as outlined in the EPA acute and chronic testing manuals (EPA 2002, 2002a & 2002b) in order for the data to be acceptable.

Some of these required QA/QC procedures include:

- test with both freshwater and marine species
- use controls on all tests
- conduct/pass reference toxicant tests with organisms cultured in-house or supplied from an outside source
- use organisms of the same age at start of the test and ensure ages are within the proper age range
- use required number of replicates and number of organisms per replicate for all tests
- ensure sample holding times are less than 36 hours
- use concentrations of 12.5%, 25%, 50%, 75%, and 100% effluent.

VX nerve agent and other toxic breakdown products could be present in the hydrolysate.

The VX nerve agent method detection limit in the hydrolysate is 20 ppb. According to a May 15, 2004 US Army document prepared by Parsons titled VX hydrolysate analytical testing results Response to CEC Request for Information: Item No. 1, this limit evolved from a Department of the Army pamphlet that states "The thoroughness of the neutralization process will be verified by laboratory analyses to assure that an agent concentration above the emergency drinking water standards in TB Med 577 does not exist . . . " The drinking water standard for nerve agents is listed as 0.02mg/l (20 ppb) in the Army's Medical Technical Bulletin Sanitary Control and Surveillance of Field Water Supplies (TB Med 577). This detection limit is based solely on the protection of humans from a drinking water source and may not be protective of aquatic organisms through ingestion or dermal exposure.

Acute exposure studies of the VX nerve agent have been performed demonstrating that 7 out of 10 juvenile striped bass were killed after 14 to 20 hours of exposure to 20 ppb (method detection limit) of VX nerve agent. All of the white perch (10 of 10) exposed to 25 ppb (slightly above the detection limit) of VX nerve agent in aqueous medium died in approximately 9 hours (Weimer, et.al, 1970). This report stated that "the effects of chronic exposures to lower levels of VX have not been studied." These chronic exposure studies, using aquatic species included in the NPDES permit, should be performed prior to discharge of the hydrolysate effluent to the river. Discharge of even small amounts of VX nerve agent remaining in the hydrolysate effluent to the Delaware River could have potentially adverse effects on aquatic organisms since this effluent is planned to be discharged about two times per day for approximately two years.

EA2192 is another toxic breakdown product generated during the destruction of VX nerve agent. According to a November 2001 US Army Center for Health Promotion and Preventive Medicine report, "based on its persistence and toxicity it has been suggested in several reports that EA2192 be viewed as a serious consideration wherever VX is being destroyed." The report also states that EA2192 may "pose a greater potential for chronic toxicity" than VX and once in solution, it is extremely persistent in the environment. This constituent was not included or evaluated in the SLERA nor were any data on this constituent's toxicity presented in the document.

There is no information demonstrating that the SET is capable of treating VX nerve agent or EA2192 that may be present in the hydrolysate so that if they were present in the effluent, they

would go untreated and be directly discharged into the Delaware River. Important aquatic species that could be adversely affected by the presence of VX nerve agent, EA2192, and any other toxic breakdown products in the river include striped bass, shad, white perch as well as invertebrates such as crabs, clams, and lobsters.

The addition of phosphorus to the Delaware River could be detrimental.

Based upon the data presented in the risk assessment, we cannot accurately predict the availability of phosphorus in the receiving waters based on breakdown of the phosphonic acid compounds, which are proposed to be discharged. If they are easily broken down to biologically available phosphorus which is generally considered to be total phosphorus (portions of both the inorganic and organic phases of total phosphorus have been found to be biologically available), they will have more of an impact than if they do not break down easily in the environment.

As discussed in Chapter 2 of EPA's October 2001, "Nutrient Criteria Technical Guidance Manual: Estuarine and Coastal Waters," often both nitrogen (N) and phosphorus (P) "elicit greater phytoplankton biomass stimulation than the sum of both N and P added separately. There are reported cases where both N and P are required to elicit phytoplankton biomass production response in estuaries, suggesting that N and P supply rates are equally limiting." This Guidance goes on to state that, "a number of temperate estuaries exhibit seasonal shifts in nutrient limitation with winter-spring P limitation and summer-fall N limitation."

In addition, according to the Draft National Coastal Condition Report II (USEPA, 2004), the tributaries of the Delaware River near the outfall of the SET already have poor grades for water quality, dissolved inorganic phosphorus (DIP), and benthic index. Although the current conditions in the Delaware Estuary do not demonstrate that eutrophication is occurring, it is unclear of the effect of the addition of MPA and other phosphorus-containing compounds from the discharge of the VX hydrolysate effluent into the Delaware River. The concern is that the addition of these compounds could increase the amounts of DIP in the estuary to such a point that the system would create unwanted algal blooms. Given the fact that the proposed discharge is located in Zone 5 of the Delaware River, which is characterized as the transition zone, an increase in the concentration of P to the system may result in phytoplankton biomass production, as outlined above.

EPA recommends that hydrodynamic modeling considering the addition of MPA and other phosphorus-containing compounds from the discharge of the VX hydrolysate effluent into the Delaware River be conducted to demonstrate that the addition of these compounds will not have any adverse effects on the estuary and its tributaries.

NPDES Permit Issues

DuPont Chambers Work discharges wastewater into the Delaware River under the terms, conditions and provisions of a National Pollutant Discharge Elimination System (NPDES) permit that is administered by NJDEP. The NJDEP has been delegated as the permitting authority for the State of New Jersey. EPA's role in the NPDES program involves oversight of New Jersey

State's NPDES permitting program.

The current permit (NJ0005100) was issued by NJDEP on December 31, 1998 and expired on January 31, 2004. Although the permit has expired, the conditions of the permit are considered to be administratively extended and still in effect, and enforceable. Effluent limitations were included in the permit to address Chamber Work facility's discharge of process wastewater, stormwater, cooling water, groundwater remediation wastewater, leachate, and wastewater delivered from offsite facilities.

The following represent issues that USEPA has concerning the treatment and discharge of the VX hydrolysate at the DuPont SET facility that need to be addressed before the SET's treatment of VX hydrolysate effluent can be discharged to the Delaware River through the permitted outfall:

- DuPont needs to clarify whether their Chamber Works facility was authorized under the current NJPDES permit (NJ0005100) to treat the Army's Newport Caustic Hydrolysate (NCH).

- The current NJPDES permit issued for this facility (NJ0005100) that expired January 31, 2004 does not include a limit nor a requirement to monitor and report on MPA, thiolamine, and EA2192 if DuPont is allowed to accept the Army's NCH for treatment. USEPA is concerned that the Army's VX hydrolysate sent to DuPont's SET treatment facility for treatment will contain MPA, thiolamine, and EA2192, which are not limited, and will be discharged to the Delaware River and Estuary. In sufficient dosages, these pollutants may present serious hazards to aquatic organisms. Based on DuPont's study, SET WWTP has limited effects on the treatment of MPA. There is a concern about the environmental effects of MPA and other toxic breakdown products that may be associated with the Army's wastewater.

- Since the proposed Army project is expected to take several years to complete, we recommend the Army's application be addressed and evaluated by NJDEP in the upcoming renewal process. Additionally, the Army's proposal would be considered a major alteration per 40 CFR 122.62 (a) (1) since the addition of this wastestream will result in changes in the permittee's practice that are different in the DuPont's NJPDES renewal application.

- The Army and/or DuPont should provide effluent characterization studies so that a decision can be made on whether additional limitations and/or conditions on the identified pollutants are necessary in the renewal permit.

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ENCLOSURE B

SUMMARY OF FINDINGS AND TECHNICAL RECOMMENDATIONS - DUPONT TOXICITY EXPOSURE DATA FOR NEWPORT CAUSTIC HYSDROLYSATE

ACRONYMS:

ACH: Aberdeen Caustic Hydrolysate, waste currently being treated by DuPont from the Army Aberdeen Test Center, Aberdeen, MD

SET: DuPont Secure Environmental Treatment Center located at the DuPont Chambers Works site in Deepwater, NJ. Operates under NJPDES #0005100 for DSN662 (formerly DSN661).

EMPA: Ethyl Methylphosphonic acid

NCH: Newport Caustic Hydrolysate, or VX Hydrolysate, is the byproduct of the neutralization of VX nerve agent .

MPA: Methylphosphonic acid

PACT: Powdered Activated Carbon Treatment System (DuPont patented technology); multi-step process of aeration, biodegradation and clarification of wastes.

OVERVIEW

The DuPont Chambers Secure Environmental Treatment facility in Deepwater, NJ is seeking an Army contract to treat 4 million gallons of wastewater, Newport Caustic Hydrolysate (NCH), from the neutralization of a stockpile of VX nerve agent in Newport, IN. The Center for Disease Control is reviewing DuPont's Human Health Toxicity Assessment for the project whiled EPA Region 2 reviewed the Ecological Risk Assessment.

As part of the assessment, DuPont contracted with EA Engineering, Science and Technology, Inc, to conduct toxicity tests for three different phases of the project.

1. Treatability Study: Small scale studies designed to test different NCH treatments in order to remove odor, maintain efficient operation of the DuPont PACT biotreatment system and to meet NJPDES permit limits. Acute. 48 hour toxicity tests were conducted using Fathead Minnows, *Pimephales promelas*, on effluents from 10 potential treatments. This study simulated wastes from treatment through the PACT system.

2. Pure chemical testing: EMPA & MPA are major constituents of NCH. The treatability study demonstrated that only a small amount of EMPA will be converted to MPA during processing. Chronic toxicity tests were conducted on EMPA & MPA using a freshwater species, *Ceriodaphnia dubia* a water flea, and the opossum shrimp, *Americamysis bahia*, which is a marine species.

3. Basic Data Biotreatment Study: Designed to test treatment of NCH as processed along with outside wastes handled by SET on a routine basis. Acute, 96 hour toxicity tests were conducted using the Fathead Minnow, *Pimephales promelas,* a freshwater species. This

study simulated wastes from treatment through both first and second stage PACT systems.

DATA REVIEW

1. Treatability Study

The treatability studies were conducted by DuPont using a single stage Eckenfelder reactor which simulates the first of the two-stage PACT used in processing wastewater. Samples of NCH were treated and processed ten different ways through the Eckenfelder to simulate various feed rates and possible ways the facility could control NCH odors and pH with different stabilizers before safely discharging into the Delaware Estuary. EA Engineering conducted limited scale acute 48 hour toxicity tests using fathead minnows on the resulting wastewater. Tests were repeated approximately a month later on the same samples with a CO_2 headspace to control pH drift. LC50s were calculated for each treatment and both series of tests.

The data from the first series of tests conducted on January 8-12, 2004, are acceptable with qualifications. An LC50 cannot be calculated with certainty because the highest test concentration was only 50% effluent. This was based on the SET NJDPES permit limit of an LC50 of ≥50% effluent for acute fathead minnow testing. The 50% effluent concentration should have been bracketed with not only lower concentrations but at least one dilution higher, preferably two concentrations, i.e., 75% and 100%. The data, however, is acceptable to show trends in the various treatments to assist DuPont in determining the best way to process the NCH.

All data from the second series of tests conducted on February 9-13, 2004 are unacceptable for the following reasons:

- holding times for wastewater far exceeded standard 36 hours
- no controls were tested
- DuPont's NJPDES permit does not indicate the use of CO_2 headspace to control pH drift
- two samples were tested at 25% and 50% dilutions while the remaining eight samples were tested at only 50%
- an LC50 cannot be calculated from only one or two concentrations nor without valid control data
- Fatheads were different ages from those tested in first series
- these results may not be combined with the first test series results to estimate an LC50 for each treatment

2. Pure Chemical Testing

Ethylmethylphosphonic acid (EMPA) and methylphosphonic acid (MPA) are major constituents of NCH. After the treatability studies it appeared that the majority of MPA would be released untreated into the Delaware Estuary and that only a small amount of EMPA would be converted to MPA during biotreatment through the PACT. EA Engineering conducted pure chemical chronic toxicity tests using freshwater and marine species (the water flea, *Ceriodaphnia dubia*, and the opossum shrimp, *Americamysis bahia*, respectively) for both EMPA and MPA. The marine species sheepshead minnow, *Cyprinodon variegatus*, was also tested using MPA.

Data was provided for range finding tests and definitive tests. The toxicity data for the definitive tests only were reviewed with emphasis on control survival, test design, reference toxicant testing, water quality, statistical analysis, organism handling/acclimation and effluent holding/handling (See Table 1). There are four possible determinations for reviewed data:

A - Acceptable Q- Acceptable w/Qualifications U- Unacceptable N- Notdetermined

Table 1. QA/QC Checklist for Pure Chemical Testing

Chemical	EMPA	EMPA	MPA	MPA	MPA
Organism	Daphnid *C. dubia*	Mysid *A. bahia*	Daphnid *C. dubia*	Mysid *A. bahia*	Minnow *C. variegatus*
Control Survival	Q[1]	Q[1]	Q[1]	Q[1]	Q[1]
Reference Toxicant	A	Q[2]	A	Q[2]	A
Test Concentrations	A	A	A	A	A
Test Procedures	A	A	A	A	A
Temperature	A	A	A	A	A
Dissolved Oxygen	A	A	A	A	A
pH	A	A	A	A	A
Salinity	N/A	N/A	A	A	A
Acclimation Procedures	A	A	A	A	A
Sample Holding Time	A	A	A	A	A
Statistical Analyses	A	A	A	A	A
Loading Factors	A	A	A	A	A

1 - A sodium hydroxide control should have been run in conjunction with a normal control to test the effect of adjusting the pH of the test solutions prior to testing with sodium hydroxide

2 - Reference toxicant testing with *A. bahia* using KCl was out of acceptable range for IC25.

Results of the definitive testing with MPA and EMPA are acceptable except for those conducted with *A. bahia* due to the out-of-range reference toxicity testing. The reference toxicity test was conducted by the lab which provided the organisms. The out-of-range result may have been avoided if EA had conducted their lab with *A.abdita* after acclimating to test conditions.

3. Basic Data Biotreatment Study

This study built on the treatability study by testing both the first and second stages of the PACT system. It also mimics real life situations in which NCH pretreated with peroxide and then with one of two possible stabilizers would alternate being processed through the PACT with other wastes such as ACH.

There are inconsistancies between the numbering of the samples in Appendix K-1 of this draft report. The numbers in the first table of the appendix, page K-1, appear to match the sample numbers in Table 14 on page 42 of the report; however, the data sheets in Appendix K do not match up with these numbers.

Due to these inconsistencies, it is impossible to review the data for each individual test. The test results, however, are not acceptable because as in the treatability studies, an LC50 cannot be calculated with certainty because the highest test concentration was only 50% effluent. Even though this was acceptable with qualifications for the range finding tests, it is not acceptable for definitive testing.

RECOMMENDATIONS

- The data from the Treatability Study and the pure chemical testing are acceptable as screening evaluations.

- The results from the data study are not acceptable due to the limited effluent concentrations used in testing. The acute toxicity testing done for the data study must be re-run with the following concentrations of effluent after treatment through the second bio-reactor: 12.5%, 25%, 50%, 75% and 100%. Testing must be conducted with the following three species that are currently listed in the NJPDES permit: *Pimephales promelas* (fathead minnow), *Cyprinodon variegatus* (sheepshead minnow) and *Ceriodaphnia dubia*. The sheepshead minnow is included because any tests conducted on effluent from the treatment of NCH through the first and second phase PACT must consider all scenarios under the current NJPDES permit. This includes a discharge into the Delaware estuary when the receiving water salinity is greater than 3.5 ppt. When salinity is greater than 3.5 ppt the NJPDES permit states that testing must be conducted with the sheepshead minnow, *C. variegatus*.

- In addition, because the NJPDES permit is under review it is likely that chronic endpoints (which were to be reviewed for inclusion in the current permit) will be required. Therefore, chronic testing should be conducted on the final NCH effluent using species to be determined by the NJDEP in the new NJPDES permit. At a minimum, chronic testing with the same three species used for acute testing, ie *P. promelas, C. variegatus* and *C. dubia,* should be conducted to provide more sensitive endpoints to the data study than acute testing alone.

- All testing must be conducted following all quality control procedures as outlined in the EPA acute and chronic testing manuals (EPA 2002, 2002a & 2002b) in order for the data to be acceptable.

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