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**DUPONT TECHNICAL ASSESSMENT ON  
U.S. ARMY NEWPORT (INDIANA) PROJECT**

**EXECUTIVE SUMMARY**

E.I. du Pont de Nemours and Company  
Wilmington, Delaware 19898  
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## **TRANSPORTATION SAFETY ASSESSMENT AND RISK MANAGEMENT PLAN**

### **Statement of Purpose**

DuPont has performed a thorough transportation safety assessment, considering these critical transportation factors:

1. Hazards of the wastewater material
2. Design requirements of the transportation equipment
3. Features of various transportation route
4. Transportation risks

*There would be no transportation of VX nerve agent.* If the Army awards the contract to DuPont, wastewater (Newport Caustic Hydrolysate, or NCH) will be transported from Newport, Indiana, to the DuPont SET facility in Deepwater, New Jersey. The NCH wastewater will be certified as having no detectable levels of nerve agent present, using the state of the art analytical techniques.

### **Methodology**

This transportation safety assessment was consistent with existing methodologies developed or used by various government agencies, including the U.S. Department of Transportation's Risk Management Self-Evaluation Framework (RMSEF), and the Guidelines for Chemical Transportation Risk Analysis published by the Center for Chemical Process Safety.

VRiskMap, a commercially available Geographic Information System offered by Visual Risk Technologies (Nashville, TN), was used in the evaluation of various transportation route options.

## Key Findings

- The wastewater (NCH) does not pose any unique or new concerns in transportation. NCH is a medium-hazard material, defined as Corrosive, Packing Group II, by the U.S. Department of Transportation (DOT). Several household products, including drain and oven cleaners, are classified similarly (or at a higher hazard level).
- The transportation equipment to be used for this project meet or exceed DOT requirements.
  - Tank trucks are built to the American Society of Mechanical Engineers (ASME) standards and have a higher Maximum Allowable Working Pressure (MAWP) than required by DOT. This means that they are more robust than is required, having a thicker wall on the container, which would provide additional protection during an accident.
  - DOT specifies many important features of the tanks, including material of construction, thickness of material, pressure relief systems, emergency valve shut-off, and accident damage protection for valves and other fittings. The tanks to be used for transportation meet or exceed these requirements.
- All transportation options have equivalent and low chances of accident or release.
  - Less than one accident and significantly less than one release would be statistically predicted with loaded tank trucks over the *entire* project. There is roughly a 1 in 3,000 chance of a truck accident per trip or a 1 in 13,000 chance of a release of product per trip.
- The transportation of NCH poses only a moderate hazard to emergency responders and other persons in the immediate vicinity of the spill (range of 30-50 yards), and is very unlikely to have wide-reaching effects on population or the environment. Overall, the potential consequences from a spill are low and do not differ from other potential spills of other commercially transported, corrosive materials.

## Conclusions

- The wastewater being transported for this project does not pose any unique or new concerns in transportation. The risks along all of the identified routes are very low to populations, employees, emergency response personnel, and the environment due to transport of NCH. (see Figures 1 and 2)

- The routes, carriers, and transportation equipment were carefully selected to even further reduce that risk, and result in a very low chance of an accident or a release of material.
- In order to further assure safe shipment of the material, DuPont's risk management plan includes:
  - Thorough safety qualification of carriers and selection of the best in industry, qualifications which must be maintained over the entire shipping campaign
  - Dedicated fleet of drivers and equipment for transportation
  - Team drivers to reduce transit time and layover, and provide added security
  - Global Positioning Systems (GPS) in every truck for communication and security
  - Late-model, high-quality equipment
  - Speed governors to restrict maximum travel speed
  - Trailers built to ASME boiler code standards

### DuPont's Preferred Route

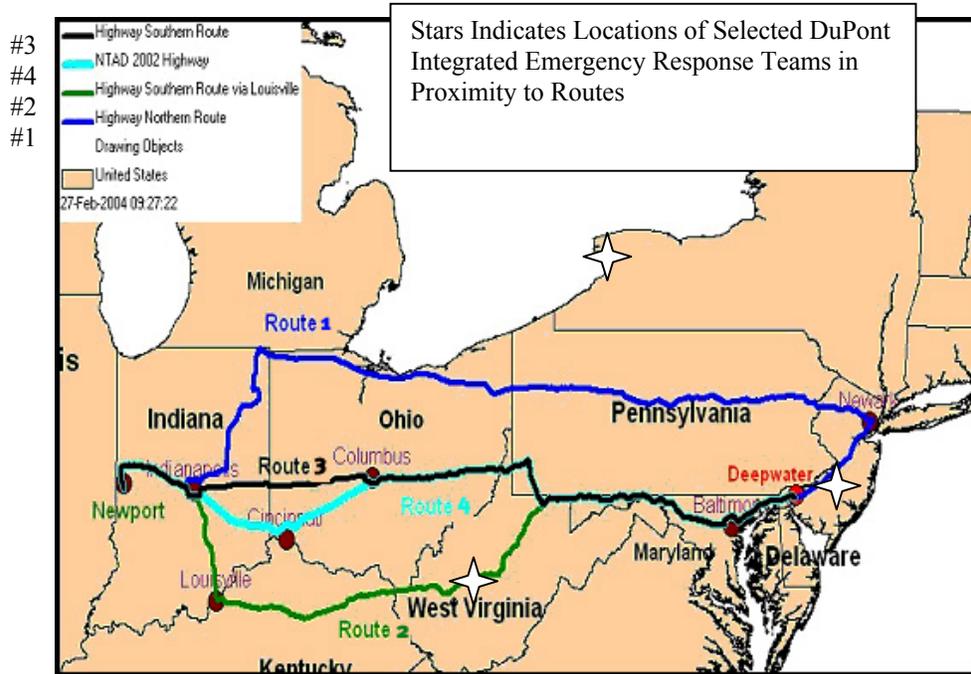
The identified preferred route, (No. 1 in the chart below):

- utilizes the most interstate highways – enhancing its statistical safety ratio
- minimizes travel over waterways – enhancing the water “exposure” metric
- is the most efficient in coordinating emergency response capabilities among DuPont responders and appropriate state and local responders

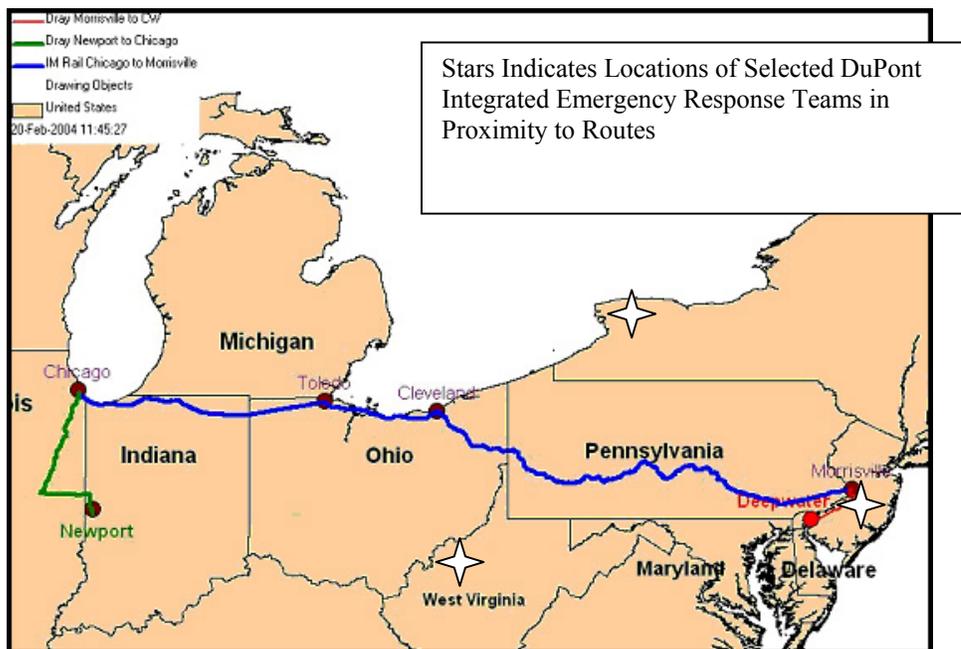
In the event of weather, traffic or other issues affecting the preferred route, an alternative route has been identified (No. 2 in the chart below) based on several comparable criteria.

Public comments and input on the transportation routes are available as part of the current public comment process and at the upcoming public information sessions.

**Figure 1: Map of Four Potential Highway Routes**



**Figure 2: Map of Potential Highway-Rail Intermodal Route (#5)**



## TREATABILITY STUDY

### Statement of Purpose

The objective of this study was to determine if the SET Wastewater Treatment Plant (WWTP) at the Chambers Works site (Deepwater, NJ) could effectively treat Newport (Indiana) Caustic Hydrolysate (NCH) at the U.S. Army's anticipated generation rate. Currently, the SET facility treats approximately 15 million gallons of wastewater per day. The approximate production rate of NCH is anticipated to be one to two truckloads (a total of 3,000 to 7,000 gallons) per day.

The study evaluated both pretreatment through chemical oxidation as well as biotreatment utilizing the patented PACT<sup>®</sup> process (Powdered Activated Carbon Treatment with activated sludge).

In the study, three general criteria for the effective treatment of NCH were used:

- Ability to meet SET WWTP operational requirements
- Ability to maintain control of wastewater and sludge odors
- Ability to assure permit compliance

### Methodology

Pretreatment by chemical oxidation was conducted to evaluate dosages and operating conditions. A biotreatability study was conducted using continuously fed Eckenfelder-type PACT<sup>®</sup> bioreactors.

Over the history of the SET WWTP, DuPont has demonstrated the suitability of this scale of testing to screen wastewaters for acceptance. Eckenfelder-type reactors have been used by DuPont to design several of its wastewater treatment systems currently in operation. The bioreactors were operated to simulate the conditions at the WWTP using actual wastewater and activated sludge under plant process conditions. Several wastewater parameters were monitored in the influent and effluent to each bioreactor including dissolved organic carbon (DOC), biochemical oxygen demand (BOD), chemical oxygen demand (COD), ethyl methyl-phosphonic acid (EMPA), methylphosphonic acid (MPA), and other parameters. Reactor conditions such as pH, temperature and mixed liquor suspended solids (MLSS) were monitored and controlled at levels similar to those maintained in the full-scale SET WWTP.

## Key Findings

Key findings of the treatability study include:

- The DuPont WWTP can effectively treat the stated volume (3,000 to 7,000 gallons per day) of NCH generated at the Newport (Indiana) site. In addition, the bioreactor system operated within normal SET WWTP operating conditions at a NCH production rate of up to 10,000 gallons per day.
- Pretreatment by chemical oxidation was effective in odor control. Odor intensity results were indistinguishable between the wastewater and sludge in the control and those from the test streams.
- Chemical oxidation pretreatment destroys the thiolamine, but has limited effect on EMPA and MPA. Biotreatment will convert a substantial portion of EMPA to MPA while overall treatment of MPA will be limited. EMPA and MPA at the estimated levels are not toxic to aquatic organisms in the Delaware River and Estuary.
- Following biotreatment at the WWTP, no other organic components or degradation products of the NCH were identified in the bioreactor effluent.
- Solid residues generated from the treatment of NCH will be placed in DuPont's on-site RCRA permitted subtitle "C" landfill, not in public landfills
- The study demonstrated that key permit parameters such as BOD<sub>5</sub>, percent BOD removal and Whole Effluent Toxicity for the WWTP would be met during the treatment of the NCH.
- Modeling of the physical parameters indicates that no atmospheric emissions of MPA, EMPA or thiolamine would result from the treatment of NCH.

## Conclusions

This treatability study conclusively demonstrates that all three major success criteria can be met and the SET WWTP can safely and effectively treat the NCH.

## SCREENING LEVEL ENVIRONMENTAL RISK ASSESSMENT

### Statement of Purpose

The objective of this review is a screening level environmental risk assessment for the effluent discharge to the Delaware River and Estuary resulting from the waste treatment of Newport (Indiana) Caustic Hydrolysate (NCH) by the DuPont Secure Environmental Treatment (SET) wastewater treatment plant (WWTP) located at Deepwater, New Jersey. This assessment evaluated the environmental exposure pathways and screening level risk to ecological receptor species in the Delaware River and Estuary.

### Methodology

U.S. EPA risk assessment guidance was used in the development of this assessment (U.S. EPA 1997). Screening level exposure and hazard characterizations were developed for EMPA and MPA, the principal constituents of the SET WWTP effluent that result from the treatment of NCH. These exposure and hazard characterization data were then used to develop risk quotients that were evaluated to assess risk to the receptor species.

The following information was considered in this process:

- Physical/chemical properties of EMPA and MPA
- Estimated effluent concentrations for EMPA and MPA from the study of NCH treatability (Reich et al. 2004)
- Physical mixing properties for the SET WWTP effluent discharge in the Delaware River
- Experimental and modeled aquatic toxicity data for EMPA and MPA using representative, sensitive aquatic species

### Findings

- The primary environmental exposure pathway for MPA and EMPA is surface water. Based on their physical-chemical properties, EMPA and MPA are not volatile (no airborne exposure) and do not bioaccumulate (do not build up in organisms or the food chain).
- Phosphonic acids are present in the environment from naturally occurring and industrial sources.

- EMPA and MPA at anticipated discharge concentrations are not toxic to aquatic organisms in the Delaware River and Estuary.
- In surface water, EMPA will naturally biodegrade into MPA and ethanol. The low levels of ethanol released will be used as a food source by microorganisms and will not pose a hazard to the environment.
- Biological processes will eventually biodegrade MPA to inorganic phosphate and methane.
- Based on the low concentrations of MPA and the limited bioavailability of its phosphorus content, no significant addition of phosphorus will occur in the estuary. Any utilization of the phosphorus in MPA as a nutrient for plant growth is likely to occur in phosphorus-limited areas of the open ocean.

## **Conclusion**

The screening level risk assessment indicates that discharge of effluent from the treatment of NCH by the SET WWTP will have no adverse effect on the environment.

## TOXICOLOGY ASSESSMENT OF HEALTH HAZARDS

### Statement of Purpose

A toxicology assessment was conducted to evaluate the potential human health hazards and risk relevant to transportation of NCH from Newport, Indiana to Deepwater, New Jersey and subsequent treatment at the DuPont Secure Environmental Treatment (SET) wastewater treatment plant (WWTP) located at Deepwater, New Jersey.

### Methodology

The wastewater (NCH) is a water-based mixture containing 80% water and the following compounds: diisopropylamino ethylthiolate (thiolamine), sodium ethyl methylphosphonate, sodium hydroxide, sodium methyl phosphonate, ethanol, diisopropylamino ethyl disulfide and diisopropylamine.

All currently available information on the NCH mixture physical properties, exposure scenarios, toxicity and regulatory standards were evaluated and used to assess the human health hazard/risk potential of NCH during transportation. The NCH toxicological assessment was conducted on the complete NCH mixture.

One of the NCH components, thiolamine, is in the mercaptan chemical family and has an odor, which can be detected at very low concentrations. However, thiolamine will be completely destroyed during treatment at the SET facility. A toxicological assessment was conducted for the residual methylphosphonic acid (MPA) and ethyl methylphosphonic acid (EMPA) expected to remain following NCH treatment at the SET facility.

Additional toxicity testing and modeling were conducted to complement the available information in the MPA and EMPA toxicity databases. The assessment included the following activities.

- Reviewed U.S. Army reports related to the composition, chemical and toxicological properties of NCH
- Comprehensively searched Toxline, Medline, Toxnet and Scifinder 2004 databases for toxicity information on NCH components, including MPA and EMPA and similar compounds

- Reviewed the American Industrial Hygiene Association (AIHA) Emergency Response Planning Guides (ERPGs) for sodium hydroxide, the component of NCH which drives the toxicity considerations
- Conducted dermal toxicity tests on NCH required for DOT corrosivity classification
- Conducted predictive toxicity and metabolism modeling of EMPA and MPA using METEOR, DEREK and TOPKAT programs
- Conducted acute oral toxicity tests on MPA and EMPA

### **Key Findings**

- NCH is a water-based liquid with very low vapor pressure. Using DOT definitions, NCH is not a poison or acutely toxic material, but it is considered to be a corrosive material due to the presence of sodium hydroxide (pH 12-14).
- NCH presents no unique physical or chemical hazards as compared to other corrosive sodium hydroxide (lye) waste materials.
- Dermal and eye exposure to NCH liquid and inhalation of NCH droplets are the most relevant exposure considerations for people in the immediate vicinity of a NCH release, such as those involved in emergency response or clean up activities.
- Predictive toxicity models were uninformative, but metabolism modeling indicated that MPA and EMPA are not metabolized in humans.
- Based on acute oral toxicity tests, MPA and EMPA had approximately the same order of acute toxicity as table salt.

### **Conclusion**

An assessment of NCH hazard information led to the conclusion that NCH, although a corrosive mixture, can be safely transported and treated at the DuPont SET facility. Additionally, the toxicity testing, exposure information, predictive modeling and literature searches support the conclusion that MPA and EMPA present a low risk of toxicity to humans.

## **OVERALL CONCLUSION OF DUPONT TECHNICAL ASSESSMENT ON U.S. ARMY NEWPORT (INDIANA) PROJECT**

The four assessments, which were reviewed by several independent scientists including the Virginia Institute of Marine Sciences, Virginia Polytechnic Institute and the U.S. Centers for Disease Control and Prevention – conclude that the wastewater from the U.S. Army’s Newport, Indiana site can be safely transported, managed as a corrosive material, effectively treated at the DuPont SET facility and disposed of under permits with both U.S. EPA and the New Jersey Department of Environmental Protection without adverse impact on the environment.



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**SCREENING LEVEL ECOLOGICAL RISK ASSESSMENT  
FOR DISCHARGE OF EFFLUENT  
FROM THE TREATMENT OF  
NEWPORT (INDIANA) CAUSTIC HYDROLYSATE (NCH)**

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## SUMMARY

The objective of this review is the development of a screening level environmental risk assessment (SLERA) for the discharge to the Delaware River and Estuary of the effluent resulting from the waste treatment of Newport (Indiana) Caustic Hydrolysate (NCH) by the DuPont Secure Environmental Treatment (SET) wastewater treatment plant (WWTP) located at Deepwater, New Jersey. The approach used for development of the SLERA was patterned after U.S. EPA Risk Assessment guidance (U.S. EPA 1997). The treatability study (Reich et al. 2004) conducted on the treatment of NCH by the SET WWTP was used to define the composition of the effluent from the treatment of NCH. The SLERA identifies the relevant exposure pathway(s) and exposure concentrations for the principal constituents in the effluent to develop a screening level exposure characterization. Ecological receptor species of interest in the Delaware River and Estuary were identified and toxicity data from laboratory studies and accepted models were used to develop a screening level hazard characterization. A screening level risk assessment for the receptor species of interest was developed using a risk quotient approach based on the exposure and hazard characterizations.

The NCH as received by SET WWTP is expected to contain water (80-85%) and sodium hydroxide (3-5%) as primary constituents with minor amounts of the sodium salts of ethyl methylphosphonic acid (EMPA) and methylphosphonic acid (MPA), diisopropylamino ethylthiolate (thiolamine) and diisopropylaminoethyl disulfide. Chemical oxidation of the NCH with hydrogen peroxide has been shown to reduce the odor of the caustic hydrolysate. This oxidation effectively destroys the main sulfide compound, thiolamine. Based on the treatability study results, (Reich et al. 2004), the SET WWTP treatment regime will effectively eliminate trace organic compounds in the NCH, with the exception of EMPA and MPA. The combined concentration of EMPA and MPA is estimated to be 21 mg/L in the plant effluent at the base-loading rate of NCH assuming a WWTP discharge of 10 million gallons per day at internal outfall 662 and plant site effluent of 26 million gallons per day at outfall 001, the outfall to the Delaware River (Reich et al. 2004). EMPA and MPA are both water soluble and ionized in aqueous solution at environmental pH values ranging from 4 - 9. Estimated Henry's law constants for both chemicals are less than  $10^{-8}$  atm-m<sup>3</sup>/mole, indicating they are unlikely to volatilize from water. Estimated log  $K_D$  values (adsorption coefficients) are less than -2.5, indicating little tendency to adsorb or bioaccumulate. These observations indicate that further environmental transport and transformation of EMPA and MPA released to the aqueous

environment will occur in surface water and that surface water will be the primary exposure pathway.

Phosphonic acids such as EMPA and MPA are a group of both synthetic and naturally occurring compounds that contain one or more C-PO(OH)<sub>2</sub> groups. Phosphonates are released to the environment during use as scale inhibitors for cooling waters, desalinization systems and oil fields. In pulp, paper and textile manufacturing phosphonates are used as peroxide bleach stabilizers and they are used as scale inhibitors, chelating agents, and bleach stabilizers in detergents. Methylphosphonic acid (MPA) is released to the environment during its production and in the manufacture of detergent additives, pharmaceuticals, lubricants, flame retardants and a wide variety of other industrial products. The utilization of phosphonates was 56,000 tons worldwide in 1998; 40,000 tons in the US and 15,000 tons in Europe; the demand for phosphonates has increased steadily at 3% annually.

In biologically active aquatic environments, biodegradation is likely to play an important role in transformation of EMPA released to aqueous environments. Ethanol and MPA are the primary degradation products of EMPA. Ethanol is rapidly consumed in aerobic systems while MPA transformation appears to be slower. Biodegradation is thought to control the rate of disappearance of MPA in environmental media. Biological transformation of MPA released to surface waters may be slower under anaerobic conditions or conditions where microbial activity is low.

Partitioning behavior of MPA may exhibit similarities to inorganic phosphate in environmental media. MPA can potentially adsorb to numerous mineral phases and equilibrium adsorption to metal oxide-hydroxide phases in sediments may influence the distribution of MPA released to aquatic environments. Salinity and oxic/anoxic boundaries will affect the distribution and formation of mineral phases that may be active in MPA adsorption. Adsorption to solids may affect the distribution of MPA released to the river, however, competition with bound inorganic phosphate will limit the availability of binding sites for MPA. Photodegradation reactions driven by iron complexation may also play a role in environmental transformation of MPA.

Potential nutrient (i.e., phosphorus) addition to the Delaware River was evaluated based on the proposed discharge concentrations of EMPA and MPA as a result of NCH treatment. The harmonic mean flow estimate at Trenton, NJ is 7208 cubic feet per second (cfs) plus 2305 cfs for Delaware River tributaries between Trenton and Deepwater, New Jersey yielding a total harmonic mean flow at Deepwater of 9513 cfs (DRBC 1998). Assuming a harmonic mean flow of 9513 cfs at Deepwater, NJ, a discharge volume of 26 mgd per day from outfall 001, and EMPA and MPA concentrations of 10 and 11 mg/L, respectively, in the discharge, the total

phosphorus concentrations in the river would increase from approximately 155 µg/L (5 µM/L, Santoro 1998) to approximately 180 µg/L. This calculation is extremely conservative, however, since physical-chemical characteristics of the two compounds make it unlikely that the phosphorus contained in EMPA and MPA will be readily available for utilization by algae or aquatic plants. In addition, reports in the literature suggest that the high turbidity of the transition zone and the bay play a major role in limiting the growth of both algae and aquatic macrophytes. This observation coupled with the relatively small potential phosphorus addition due to EMPA and MPA (both in terms of concentration and bioavailability) and the 100 day flushing time for the bay will result in limited potential for eutrophication of the river and bay due to the effluent discharge of EMPA and MPA. Any utilization of these compounds as a phosphorus source is likely to occur in phosphorus-limited regions of the open ocean.

Since surface water will be the principal exposure pathway for ecological receptors in the Delaware River and Estuary, marine and freshwater fish and invertebrates are the most appropriate receptor species for use in this screening level risk assessment. Typical species used for effluent and ambient aquatic toxicity testing are reasonable surrogates for the key species identified in studies of the river and estuary. The marine mysid shrimp, *Americamysis (Mysidopsis) bahia*, and the sheepshead minnow, *Cyprinodon variegatus*, are representative of important food resources in the Delaware River and Estuary. The freshwater invertebrate species, *Ceriodaphnia dubia* and *Daphnia magna*, are not representative fauna of Zones 4 and 5 of the Delaware River but are sensitive freshwater invertebrate species used in regulatory toxicity testing of chemicals; the fathead minnow, *Pimephales promelas*, and the bluegill sunfish, *Lepomis macrochirus*, are freshwater fish species also frequently used in regulatory testing of chemicals.

The estimated, in-stream concentrations of EMPA and MPA at a distance of 100 meters from the Chambers Works outfall 001 are used as the exposure concentrations for screening level calculations of the potential in-stream risk of EMPA and MPA to aquatic organisms. Based on an estimated effluent concentration of 10 mg/L – EMPA, 11 mg/L – MPA, the in-stream concentration 100 m from outfall 001 for each compound is estimated to be 0.7 mg/L (e.g. 10 or 11 mg/L divided by 15 X dilution factor at 100 meters). The acute risk characterization for EMPA and MPA is based on modeled or experimental acute EC/LC<sub>50</sub> values and the chronic risk characterization for MPA is based on chronic No-Observed-Effect-Concentration (NOEC) values from the laboratory toxicity studies with *Ceriodaphnia dubia*, *Americamysis bahia*, and *Cyprinodon variegatus*. NOEC values from these studies ranged from 87 mg/L for *Ceriodaphnia dubia* to 500 mg/L for the marine mysid shrimp, *Americamysis bahia*, and > 1000 mg/L for the marine sheepshead minnow, *Cyprinodon variegatus*.

The risk quotient approach developed by the USEPA (1997) uses the quotient of the exposure concentration value (0.7 mg/l) divided by the toxicity endpoint (NOEC, EC/LC<sub>50</sub>) for the receptor species. If the risk quotient is less than 1.0, particularly if the risk quotient is much less than 1.0, it can be concluded that the chemical does not pose an unacceptable risk for the receptor species. Acute risk quotients for all species were below 0.0007 indicating no unacceptable acute risk to aquatic organisms. Chronic hazard quotients ranged from 0.00004 for effects on green algae to 0.008 for effects on reproduction of *Ceriodaphnia dubia* and 0.0007 to 0.0014 for growth effects on the marine invertebrate and fish species. These chronic risk quotients indicate that the estimated in-stream concentrations of MPA and EMPA resulting from the treatment of NCH will not pose an unacceptable chronic risk to aquatic organisms.

In conclusion, the estimated SET WWTP effluent levels of 10 mg/l and 11 mg/l for EMPA and MPA pose no unacceptable risk to aquatic organisms in the Delaware River and Estuary.

## PROBLEM FORMULATION

The objective of this review is the development of a screening level environmental risk assessment (SLERA) for the discharge to the Delaware River and Estuary of the effluent resulting from the waste treatment of NCH by the SET WWTP located at Deepwater, New Jersey. The approach used for development of the SLERA was patterned after U.S. EPA guidance (U.S. EPA 1997). The treatability study (Reich et al. 2004) conducted on the treatment of NCH by the SET WWTP was used to define the composition of the effluent from the treatment of NCH. The SLERA identifies the relevant exposure pathway(s) and exposure concentrations for the principal constituents in the effluent to develop a screening level exposure characterization. Ecological receptor species of interest in the Delaware River and Estuary were identified and toxicity data from laboratory studies and accepted models were used to develop a screening level hazard characterization. A screening level risk assessment for the receptor species of interest was developed using a risk quotient approach based on the exposure and hazard characterizations.

## Site Description

The Delaware River estuary extends a total of 215 kilometers (134 miles) from the mouth of Delaware Bay near Liston Point, Delaware to the head of tide at Trenton, New Jersey (Figure 1). The total surface area of the estuary is approximately 1989 square kilometers with a mean depth of 7.4 meters and a total volume of approximately  $14.7 \times 10^9$  cubic meters (Frithsen et al. 1995). The estuary is composed of the Delaware Bay, the tidal portion of the river, and the transition zone between these areas. The hydrodynamics of the estuary are principally the result of the

tides with typical horizontal advection of approximately 10 kilometers over a tidal cycle. The bay has an average depth of approximately 9.7 meters but much of the bay is shallower. The Delaware Bay is well mixed with little long-term vertical stratification (Biggs 1978, Smullen et al. 1983). However, Sharp et al. (1986) noted that, while persistent stratification does not exist during most of the year, during periods of high freshwater discharge in the spring some limited stratification of the bay may exist both spatially and temporally. The transition zone is approximately 50 kilometers in length and exists between the head of the bay and the lower limit of the tidal portion of the river near Marcus Hook (Frithsen et al. 1995). The tidal portion of the river extends from approximately Marcus Hook south of Philadelphia to the rapids at Trenton, New Jersey. This portion of the river is typically freshwater but may experience some brackish water intrusion during periods of low flow.

The watershed surrounding the estuary has a surface area of approximately 34,836 square kilometers or approximately 17-18 times the area of the estuary. Land use within the estuary watershed is approximately 50% forested, 31% agricultural, and 14% urban with the remaining 5% comprised of wetlands, water, open and brush regions, and barren areas (Frithsen et al. 1995). The forested areas are primarily located in the northern portions of the watershed, the urban areas are located principally between Trenton, New Jersey and Wilmington, Delaware, and the agricultural areas exist mainly in the lower Delaware portion of the watershed. The Delaware and Schuylkill Rivers provide the majority (approximately 70-75%) of the freshwater flow in the Delaware River estuary. Flow is typically highest in March-April and lowest in August-September with seasonal changes driven primarily by precipitation (Frithsen et al. 1995). The average flushing time for the estuary has been estimated to be approximately 100 days (Sharp et al. 1986).

## **SET WWTP Operation**

The DuPont SET treatment facility is located at the DuPont Chambers Works site in Salem County near the community of Deepwater, New Jersey (Figure 1). The manufacturing site comprises approximately 600 acres bounded by a non-manufacturing area that includes a DuPont owned and maintained wildlife habitat to the north, the Delaware River to the west, Salem Canal to the south, and the Deepwater, New Jersey community to the east. The site is located within the transition zone of the Delaware River estuary at approximately River Mile 69 just north of the Delaware Memorial Bridge.

The SET WWTP effluent discharge location is identified as outfall DSN001 (NPDES Permit #NJ0005100). Outfall 001 discharges approximately 10-15 million gallons per day (mgd) of

treated process wastewater and approximately 15-25 mgd of non-contact cooling water and stormwater. The Chambers Works site has two water intakes; one intake is located on the non-tidal freshwater Salem Canal and one intake is on the tidal Delaware River in Delaware River Basin Commission (DRBC) Zone 5 downstream of outfall 001.

Depending on the level of freshwater discharges from the non-tidal Delaware River and the Schuylkill River, tidal flows in the Delaware River can reach 8-12 miles upstream of the Chambers Works facility. DuPont contracted with Lawler, Matusky and Skelly Engineers (LMS) to conduct a hydrographic study and dye dispersion studies under low and high flow regimes during the late 1980s (LMS 1989, 1990). These studies demonstrated that the Delaware River in the vicinity of Chambers Works is well mixed vertically (in agreement with other studies) with no significant vertical salinity gradient. In the immediate vicinity of the Chambers Works site, elevated dye concentrations near the eastern shore of the river compared to the western shore indicated potential incomplete horizontal mixing of the effluent. Based on an assessment of near-field effluent dilution conducted by LMS (1989), the average effluent dilution within approximately 30 meters of outfall 001 is approximately 6:1 river water:effluent. The dilution factor at a distance of 100 meters from outfall 001 is approximately 15:1 river water:effluent. Due to the salinity of the Delaware River in DRBC Zones 4 and 5, there are no drinking water intakes in these zones of the river.

In addition to various chemical-specific monitoring requirements that are part of the facility National Pollutant Discharge Elimination System (NPDES) permit, the facility is also required to meet a specific monthly acute effluent toxicity limit of an  $LC_{50}$  of 50% effluent based on testing with the freshwater fish species, *Pimephales promelas*, the fathead minnow. The facility must also “monitor and report” the results of quarterly acute effluent toxicity tests with the freshwater cladoceran, *Ceriodaphnia dubia*.

## **NCH Treatability Study**

The objectives of the NCH treatability study conducted by DuPont SET were: 1) to evaluate the effectiveness of the SET wastewater treatment process (chemical oxidation and biological treatment) in treating NCH, including evaluations of wastewater and sludge odor control and successful control of plant operations (e.g., dissolved organic carbon removal, pH control, solids management, etc.) and 2) to ensure the ability of the facility to meet all existing permit requirements during any treatment operations. The NCH as received is expected to contain primarily water and sodium hydroxide (CAS# 1310-75-2) with minor amounts of the sodium salts of ethyl methylphosphonic acid (EMPA, CAS# 1832-53-7) and methylphosphonic acid

(MPA, CAS# 993-13-5), diisopropylamino ethylthiolate (thiolamine, CAS# 5842-07-9), and diisopropylaminoethyl disulfide (CAS# 65332-44-7). Chemical oxidation of the NCH with hydrogen peroxide has been shown to substantially reduce the odor of the caustic hydrolysate (Reich et al. 2004). This oxidation effectively destroys the main sulfide compound, thiolamine.

The thiolamine degradation products have been identified as acetic acid, diisopropylamine, N,N'-Diisopropylamineurea, and mixed disulfide degradation products including N-[2-(ethyldithio)ethyl]-N-(1-methylethyl)-2-propanamine. Based on the results of the treatability study, the SET WWTP treatment process will effectively eliminate trace organic compounds in the NCH, with the exception of EMPA and MPA. The overall concentrations of EMPA and MPA are reduced to a combined total of approximately 55 mg/L through the WWTP and 21 mg/L at outfall 001 at the base-loading rate for NCH assuming a WWTP discharge of 10 million gallons per day (gpd) at internal outfall 662 and plant site effluent of 26 million gpd at outfall 001 (Reich et al. 2004).

### **Environmental Fate of NCH Components in SET Effluent**

EMPA and MPA are both water soluble and ionized in aqueous solution at environmental pH values of 4-9 (Table 2). Estimated Henry's law constants for both chemicals are less than  $10^{-8}$  atm-m<sup>3</sup>/mole, which means that they are unlikely to volatilize from water (Table 4).

Estimated log  $K_D$  (adsorption) values are less than -2.5 (Advanced Chemistry Development, Solaris V4.67), indicating little tendency to adsorb or bioaccumulate. These observations indicate that further environmental transport and transformation of EMPA and MPA released to the aqueous environment will occur in surface water and that surface water will be the primary exposure pathway.

Kingery and Allen (1994) reported that EMPA has degradation rate constants at 25°C of  $2.4 \times 10^{-10} \text{ h}^{-1}$  and  $3.6 \times 10^{-3} \text{ h}^{-1}$  in water and soil, respectively. Verweij and Boter (1976) report a half-life for EMPA of approximately 3 days in moist, humic sand. Observations in the presence of soil and sand and reviews of phosphonate behavior by Nowack (2003 a, b) suggest that interactions with mineral phases may accelerate EMPA hydrolysis. Davies and Newton (2001) report that the P-CH<sub>3</sub> bond is stable on clean and oxidized aluminum surfaces while the P-OCH<sub>3</sub> bond is unstable even at room temperature. Oxidized aluminum phases are common components of clay and mineral surfaces in soils and sediments. Transformation of EMPA by mineral phases in sediments may play an important role in accelerating degradation of EMPA released to aqueous environments. Observations from NCH treatability testing with PACT sludge from Chambers Works yielded half-life estimates for EMPA biotreatment of 35-77 hours

with a median time of 36 hours (Reich et al. 2004). Fry and DeFrank (1996) also reported biodegradation of EMPA in bacterial enrichment cultures. In biologically active aquatic environments, biodegradation is likely to play an important role in transformation of EMPA released to aqueous environments. Ethanol and MPA are the primary degradation products of EMPA (DeFrank et al 2000; Fry and DeFrank, 1996). Ethanol is rapidly consumed in aerobic systems while MPA transformation appears to be slower (DeFrank et al 2000; Fry and DeFrank, 1996, Reich et al., 2004).

Biodegradation is thought to control the rate of disappearance of MPA in environmental media (Kingery and Allen 1994), although transformation catalysed directly or indirectly by complexation may also be important (Nowack 2003a). The carbon-phosphorous (C-P) bond is less labile than the more common O-P, N-P or S-P bonds. Phosphonates are generally thought to be resistant to biodegradation under environmental conditions (NIH 2002) but, due to the presence of natural phosphonates in the environment, bacteria have evolved the ability to cleave the C-P bond (Imazu et al. 1998).

The biodegradation of alkyl phosphonic acids has been demonstrated in a variety of environmental bacterial isolates including, but not limited to, *Pseudomonas testosteroni*, *Bacillus cereus*, *Escherichia coli* and *Klebsiella pneumoniae* (Egli 1987). The specific utilization rates of MPA were determined to be  $0.26\text{h}^{-1}$  in pure cultures of *Agrobacterium radiobacter* and  $0.029\text{hr}^{-1}$  in a continuous culture of *Pseudomonas paucimobilis* strain MMM101a (Kingery and Allen 1994). Enzyme systems responsible for MPA biodegradation are activated when cell growth is phosphate limited, even in the presence of inorganic phosphate (Schowanek and Verstraete 1990a, 1990b, 1991). End products of MPA biotransformation are inorganic phosphate and methane (Schowanek and Verstraete 1991), which are both rapidly transformed biologically. Based on surveys of marine phosphatase activity, geographic regions and microenvironments experiencing phosphorus limitation are widespread in the oceans (Hoppe 2003). MPA biodegradation to methane gas also may be an important removal process in phosphorus-limited marine environments [NIH, 2002]. Biological transformation of MPA released to surface waters may be slower under anaerobic conditions or conditions where microbial activity is low.

Aqueous samples of MPA have been shown to degrade to inorganic phosphorous (Pi) in the presence of divalent cations ( $\text{Ca}^+$  812  $\mu\text{M}$ ,  $\text{Mg}^{2+}$  170  $\mu\text{M}$ ,  $\text{Fe}^{2+}$  71  $\mu\text{M}$ ) or in growth medium (Kingery and Allen 1994). The samples showed an average increase of Pi of 2.48 and 4.34  $\text{mg P L}^{-1}\text{d}^{-1}$  and degradation rate constants of  $8 \times 10^{-5}$  and  $1.4 \times 10^{-4}\text{d}^{-1}$ , respectively, when incubated at 25°C.

Partitioning behavior of MPA shows similarities to inorganic phosphate in environmental media. MPA can potentially adsorb to numerous mineral phases (Nowack and Stone, 1999, Kataoka et al, 2001). Barja et al (2001) report a stable MPA-Fe(III) complex,  $\text{Fe}_2(\text{CH}_3\text{PO}_3)_3 \cdot 3\text{H}_2\text{O}$ . Equilibrium adsorption to metal oxide-hydroxide phases in sediments may influence the distribution of MPA released to aquatic environments. Nowack (2003a) also reported that Fe(III)-phosphonate complexes show characteristic absorption bands in the 300-330 nm region. This wavelength range in the near UV is active in chemical transformation near the water surface. Photodegradation reactions driven by iron complexation may also play a role in environmental transformation of MPA. Salinity and oxic/anoxic boundaries will affect the distribution and formation of mineral phases that may be active in MPA adsorption (Gunnars et al. 2002). Adsorption to solids may affect the distribution of MPA released to the river. However, competition with bound inorganic phosphate will limit the availability of binding sites for MPA.

Potential nutrient (i.e., phosphorus) addition to the Delaware River was evaluated based on the proposed discharge concentrations of EMPA and MPA as a result of NCH treatment. The harmonic mean flow estimate at Trenton, NJ is 7208 cubic feet per second (cfs) plus 2305 cfs for Delaware River tributaries between Trenton and Deepwater, New Jersey yielding a total harmonic mean flow at Deepwater of 9513 cfs (DRBC 1998). Assuming a harmonic mean flow of 9513 cfs at Deepwater, NJ, a discharge volume of 26 mgd per day from outfall 001, and EMPA and MPA concentrations of 10 and 11 mg/L, respectively, in the discharge, the total phosphorus concentrations in the river would increase from 155  $\mu\text{g/L}$  (5  $\mu\text{M/L}$ , Santoro 1998) to approximately 180  $\mu\text{g/L}$ . This calculation is extremely conservative, however, since physical-chemical characteristics of the two compounds make it unlikely that the phosphorus contained in EMPA and MPA will be readily available for utilization by algae or aquatic plants. In addition, reports in the literature suggest that the high turbidity of the transition zone and the bay play a major role in limiting the growth of both algae and aquatic macrophytes. This observation coupled with the relatively small potential phosphorus addition due to EMPA and MPA (both in terms of concentration and bioavailability) and the 100 day flushing time for the bay will result in limited potential for eutrophication of the river and bay due to the effluent discharge of EMPA and MPA. Any utilization of these compounds as a phosphorus source is likely to occur in phosphorus-limited regions of the open ocean.

### **Alternative Sources of Phosphonates and Methyphosphonic Acid (MPA)**

Phosphonic acids are a group of both synthetic and naturally occurring compounds that contain one or more  $\text{C-PO}(\text{OH})_2$  groups. Phosphonates are released to the environment during use as

scale inhibitors for cooling waters, desalinization systems and oil fields. In pulp, paper and textile manufacturing phosphonates are used as peroxide bleach stabilizers and they are used as scale inhibitors, chelating agents, and bleach stabilizers in detergents (Nowack 2003a). Methylphosphonic acid is released to the environment during its production and in the manufacture of detergent additives, pharmaceuticals, lubricants, flame retardants and a wide variety of other industrial products (Imazu et al. 1998, Booser 1995, Nowack 2003a, NIH 2002, Hilderbrand 1983). The utilization of phosphonates was 56,000 tons worldwide in 1998; 40,000 tons in the US and 15,000 tons in Europe; the demand for phosphonates has increased steadily at 3% annually.

## **EXPOSURE CHARACTERIZATION**

### **Complete Exposure Pathways**

EMPA and MPA will be discharged in the SET WWTP effluent as a result of treatment of NCH. The physical-chemical properties of EMPA and MPA indicate that they are water soluble, non-volatile, and unlikely to undergo significant partitioning to solids or lipids. The latter characteristics suggest that accumulation in sediments, bioaccumulation in invertebrates and fish, and food chain biomagnification in invertebrates, fish, and fish-eating birds and wildlife will not be important exposure pathways. Therefore, the principal environmental route of exposure to EMPA and MPA for ecological receptors in the Delaware River and Estuary will be via the water column. The physical-chemical characteristics of EMPA and MPA also suggest that the principal measurement endpoints of concern relative to water column exposure will be acute and chronic aquatic toxicity (e.g., short-term survival; long term survival, growth, reproduction). Other environmental matrices including soil, groundwater and the atmosphere are not likely to be significant pathways for exposure to EMPA and MPA based on NCH treatment at the SET facility.

### **In-stream Concentrations**

The estimated, in-stream concentrations of EMPA and MPA at a distance of 100 meters from the Chambers Works outfall 001 are used as the exposure concentrations for screening level calculations of the potential in-stream risk of EMPA and MPA to aquatic organisms. Based on an estimated effluent concentration of 10 mg/L – EMPA, 11 mg/L – MPA, the in-stream concentration at 100 m is estimated to be 0.7 mg/L (e.g. 10 or 11 mg/L divided by 15X dilution factor at 100 meters). This value is used as the exposure concentration for screening level calculations of the potential in-stream risk of EMPA and MPA to aquatic organisms.

## EMPA AND MPA HAZARD CHARACTERIZATION

### Ecological Receptors

During the last 15 years several studies have been conducted to evaluate the status of various biological communities in the Delaware River and Estuary. Frithsen et al. (1991) reported on the key biological communities of the river and estuary, Environmental Consulting Services, Inc. (1993) reported on the benthos of the estuary from the Chesapeake and Delaware Canal upstream to Trenton, O'Herron et al. (1994) discussed the results of a survey of the fishes in the same region and, most recently, Horwitz, et al. (2003) presented the results of an evaluation of the feeding habits of the white perch, *Morone americana*, and the channel catfish, *Ictalurus punctatus*.

The evaluation by Frithsen et al. (1991) identified seven types of biological communities and 40 species as important biological resources in the Delaware River and Estuary. The seven biological communities identified as important were phytoplankton, zooplankton, ichthyoplankton, benthos, parabenthos, fish and birds. Their analysis specifically excluded marine reptiles (e.g., turtles) and mammals due to the lack of available information.

Aquatic macrophyte production in the estuary is generally limited due to high turbidity. Phytoplankton is assumed to be the major source of organic matter to consumers with the estuary. This was the principal reason that phytoplankton was identified as a key biological resource. Zooplankton was identified as a critical component of estuary food webs because zooplankters act as the primary consumers of phytoplankton and, in turn, serve as a food resource for other organisms.

The benthic community was identified as important because these organisms are generally less mobile and longer lived than phytoplankton or zooplankton and can be sensitive, long-term integrators of water quality changes. Important benthic invertebrates identified by Frithsen et al. (1991) because of their current or historical commercial importance included the American oyster, hard clams, blue crabs, the American lobster and the horseshoe crab. These species are primarily inhabitants of Delaware Bay. Species of importance in the parabenthos included mysid shrimp, sand shrimp, and amphipods. Mysids were identified as a key biological resource of the Delaware estuary because they are important consumers of both plankton and benthos and serve as an important food resource for a variety of fish species (PSE & G 1984).

The list of important fish species compiled by Frithsen et al. (1991) also was based on commercial or recreational importance and included the American shad, striped bass, white

perch, summer flounder, an additional eight species, plus two species subject to special regulation. The Atlantic sturgeon is the subject of a federal management plan and the shortnose sturgeon is recognized as an endangered species by the federal government and New Jersey, Pennsylvania and Delaware. Important bird species included several species of the least tern and the laughing gull, five species of wading birds, seven species of shorebirds, three waterfowl species, and the northern harrier, bald eagle, osprey, and the peregrine falcon.

The assessment by Frithsen et al. (1991) of key invertebrate and fish communities was largely corroborated by the later studies by Environmental Consulting Services, Inc. (1993), O'Herron et al. (1994), and Horwitz et al. (2003). During their study of the feeding habits of white perch and catfish, Horwitz et al. (2003) noted that grass, opossum, sand, and cumacean shrimp were important food items for both species in DRBC Zone 5 of the Delaware River in terms of frequency, abundance and stomach weight.

Since surface water will be the principal exposure pathway for ecological receptors in the Delaware River and Estuary, marine and freshwater fish and invertebrates are the most appropriate receptor species for use in this screening level risk assessment. Typical species used for effluent and ambient aquatic toxicity testing are reasonable surrogates for the key species identified in studies of the river and estuary. The marine mysid shrimp, *Americamysis (Mysidopsis) bahia*, and the sheepshead minnow, *Cyprinodon variegatus*, are representative of important food resources in the Delaware River and Estuary. The freshwater invertebrate species, *Ceriodaphnia dubia* and *Daphnia magna*, are not representative fauna of Zones 4 and 5 of the Delaware River but are sensitive freshwater invertebrate species used in regulatory toxicity testing of chemicals; the fathead minnow, *Pimephales promelas*, and the bluegill sunfish, *Lepomis macrochirus*, are freshwater fish species also frequently used in regulatory testing of chemicals.

### Acute Aquatic Toxicity

The *Daphnia magna* 48-hr LC<sub>50</sub> for MPA was reported to be 3,273 mg/L (Williams et al. 1987); the analogous value for sodium chloride (table salt) is 4135 mg/L (Bureau, E.C.-E.C., *IUCLID Datasheet Sodium Chloride*. 2002, European Commission). The 96-hr LC<sub>50</sub> values for MPA based on testing with fathead minnows and bluegill sunfish testing were reported to be 10,617 mg/L and 12,380 mg/L, respectively (Williams et al. 1987). The analogous value for sodium chloride when testing bluegill sunfish was 9,675 mg/L (Bureau, E.C.-E.C., *IUCLID Datasheet Sodium Chloride*. 2002, European Commission). The 14-day EC<sub>50</sub> for the green algae, *Selenastrum capricornutum*, when testing MPA and sodium chloride were similar with

reported values of 17,805 mg/L (Williams et al. 1987) and 23,565 mg/L, respectively (Bureau, E.C.-E.C., *IUCLID Datasheet Sodium Chloride*. 2002, European Commission).

Williams et al. (1987) also evaluated the effects of MPA on freshwater protozoan communities. In these studies the authors evaluated effects of MPA on protozoans using both pre-colonized substrates (epicenter communities) and sterile substrates (colonizing communities). The sterile substrates were exposed to both MPA and the epicenter communities as a source of colonizing organisms. The 7-day EC<sub>5</sub> (effective concentration of MPA causing a 5% effect) was 509 mg/L for effects on colonizing species and 2795 mg/L for effects on epicenter communities. The corresponding 7-day No-Observed-Effect-Concentration (NOEC) values were 1960 mg/L for colonizing communities and 3820 mg/L for epicenter communities (Williams et al. 1987).

DuPont SET also contracted for additional chronic aquatic toxicity testing of MPA using the freshwater invertebrate, *Ceriodaphnia dubia*, the marine invertebrate, *Americamysis bahia*, and the marine fish, *Cyprinodon variegatus* (EA Engineering 2004). During the chronic testing it was possible to make observations to provide acute toxicity data for these same species. The results of these studies indicate that the 48-hour *Ceriodaphnia* EC<sub>50</sub> value and the 96-hour LC<sub>50</sub> values for *Americamysis* and *Cyprinodon* were all greater than the nominal highest MPA test concentration of 1000 mg/L (Table 3). In addition to the laboratory data for MPA, results of toxicity testing of the NCH effluent from the DuPont treatability study test reactors (Reich et al. 2004) indicate the WWTP facility will be able to meet existing NPDES biomonitoring requirements.

No acute effects data were available for EMPA, therefore, the U.S. EPA aquatic toxicity estimation program ECOSAR (U. S. EPA 1998) was used to estimate the acute toxicity of EMPA to freshwater and marine invertebrates and fish (Table 3). These estimated values suggest that the acute toxicity of EMPA to fish and invertebrates is comparable to that of MPA

## Chronic Aquatic Toxicity

Short-term chronic aquatic toxicity tests of MPA were conducted using U.S. EPA test methods typically used for evaluating the chronic toxicity of municipal and industrial effluents (U.S. EPA 2002 a, b). The results of these studies (Table 3) indicate that the 6-8 day short-term chronic toxicity NOEC for effects on *Ceriodaphnia* reproduction was 87 mg/L based on nominal concentrations of MPA. The corresponding chronic NOEC values for effects on growth of *Americamysis* and *Cyprinodon* were 500 and > 1000 mg/L, respectively, based on nominal concentrations of MPA.

## RISK CHARACTERIZATION

The risk characterization used for this screening level risk assessment is consistent with the risk assessment approach presented in U.S. EPA (1997). The risk quotient for a particular chemical, endpoint, and receptor species is the quotient of the exposure concentration value for the chemical in the matrix of interest (e.g., in-stream concentration of MPA) divided by the aquatic toxicity endpoint value of interest (e.g., EC/LC<sub>50</sub>, NOEC) for the receptor species. The exposure concentrations and the endpoint values must be expressed in the same units (e.g., mg/L). If the risk quotient is less than 1.0, particularly if it is much less than 1.0, it can be concluded that the chemical does not pose an unacceptable risk to the receptor species for the endpoint of interest.

Using this approach, acute EMPA and MPA risk quotients for the various species for which acute aquatic toxicity data, modeled or experimental, are available all are less than 0.0009 (Table 3). The acute risk quotients for *Ceriodaphnia dubia*, *Americamysis bahia*, and *Cyprinodon variegatus* are likely lower than presented but the calculation of the risk quotient was bounded by the fact that the highest MPA concentration tested in these studies was 1000 mg/L. These acute risk quotients indicate that the estimated in-stream concentrations of MPA resulting from the treatment of NCH will not pose an unacceptable acute risk to aquatic organisms.

The chronic risk characterization for MPA is based on chronic NOEC values from the studies using *Ceriodaphnia dubia*, *Americamysis bahia*, and *Cyprinodon variegatus*. These NOEC values range from 87 mg/L for *Ceriodaphnia dubia* to 500 mg/L for the marine mysid shrimp, *Americamysis bahia*, and > 1000 mg/L for the marine sheepshead minnow, *Cyprinodon variegatus*. Chronic risk quotients range from 0.00004 for chronic effects on green algae, to 0.008 for effects on reproduction of *Ceriodaphnia dubia*, and to 0.0007 to 0.0014 for growth effects on the marine invertebrate and fish species (Table 3). These chronic risk quotients indicate that the estimated in-stream concentrations of MPA resulting from the treatment of NCH will not pose an unacceptable chronic risk to aquatic organisms. No modeled or experimental chronic hazard data were available for EMPA, therefore, it was not possible to calculate chronic risk quotients for EMPA.

## CONCLUSION

The treatability study for NCH treatment at SET WWTP identified two compounds at measurable concentrations in the reactor effluent, EMPA and MPA. The focus of the SLERA was to identify the principal exposure pathway(s) for these two compounds and to evaluate the potential effects on important, representative, receptor organisms. Because EMPA and MPA are

not volatile and will not be bioaccumulated, the primary environmental exposure pathway is through surface water. Once in the surface water, EMPA will biodegrade to ethanol and MPA. Ethanol is readily consumed as an energy source for microorganisms and the MPA degrades over a longer timeframe. Biological processes will slowly break the MPA down into inorganic phosphate and methane that are readily used as nutrient sources by microorganisms. Other processes, such as photodegradation, may also work to break down MPA in the environment. Exposure characterization for important receptor species indicated that in-stream concentrations of EMPA and MPA as a result of NCH treatment will be below 1 mg/L for each compound. Acute and chronic hazard characterization data were evaluated or generated for representative freshwater and marine species and used to calculate screening level risk quotients. The SLERA results indicate that EMPA and MPA at estimated SET WWTP effluent levels of 10 mg/L and 11 mg/L will not pose an unacceptable risk to the sensitive invertebrate and fish species in the Delaware River and Estuary.

**TABLE 1.**  
**ESTIMATED EFFLUENT CONCENTRATIONS BASED ON TREATABILITY STUDIES<sup>1</sup>**

Component	Effluent concentration at outfall 001, mg/L	In-stream Concentration @ 30 meters (6X dilution), mg/L	In-stream Concentration @ 100 meters (15X dilution), mg/L
ethyl methylphosphonic acid (EMPA)	10	1.7	0.7
Methylphosphonic acid, (MPA)	11	1.8	0.7
2-(diisopropylaminoethylthiolate (thiolamine)	Non detect	--	--
2-(diisopropylamino)ethyl disulfide	Non detect	--	--
Ethanol	Non detect	--	--
Diisopropylamine	Non detect	--	--

1 – Reich et al. 2004

**TABLE 2.**  
**PHYSICAL – CHEMICAL CHARACTERISTICS OF EMPA AND MPA**

Compound	PKa	Estimated Water Solubility <sup>1</sup>	Estimated Vapor Pressure, mm Hg <sup>1</sup>	Estimated Henry's Law Constant, atm-m <sup>3</sup> /mole <sup>1</sup>
EMPA	2.75 <sup>2</sup>	soluble	1.09E-07	5.2E-09
MPA	pK <sub>1</sub> = 2.19 <sup>3</sup> pK <sub>2</sub> = 7.54 <sup>3</sup>	soluble	3.96E-10	1.22E-11

1 – U.S. EPA and Syracuse Research Corporation 2000

2 – Bossle et al. 1983

3 – Popov et al. 2001

**TABLE 3.**  
**ACUTE AND CHRONIC TOXICITY ENDPOINT VALUES**  
**AND RISK QUOTIENTS FOR EMPA AND MPA**

Species, Endpoint, mg/L (ppm)	EMPA Endpoint Value, mg/L <sup>1</sup>	EMPA Risk Quotient <sup>2</sup>	MPA Endpoint Value, mg/L	MPA Risk Quotient <sup>2</sup>
<b>Acute Toxicity</b>				
Daphnia magna, 48-hr EC <sub>50</sub>	8,196	0.00009	3,273 <sup>3</sup>	0.00021
Ceriodaphnia dubia, 48-hr EC <sub>50</sub>			>1000 <sup>4</sup>	0.0007
Pimephales promelas, 96-hr LC <sub>50</sub>	9,654	0.00007	10,617 <sup>3</sup>	0.00007
Lepomis macrochirus, 96-hr LC <sub>50</sub>			12,380 <sup>3</sup>	0.00007
Americamysis bahia, 96-hr LC <sub>50</sub>	12,917	0.00005	>1000 <sup>4</sup>	0.0007
Cyprinodon variegatus, 96-hr LC <sub>50</sub>	782	0.0009	>1000 <sup>4</sup>	0.0007
<b>Chronic Toxicity</b>				
Protozoans				
Colonization, 7-d EC <sub>5</sub> , Colonizing species			509 <sup>3</sup>	0.00138
Colonization, 7-d EC <sub>5</sub> , Epicenter species			2795 <sup>3</sup>	0.00025
Colonization, 7-d NOEC, Colonizing species			1960 <sup>3</sup>	0.00036
Colonization, 7-d NOEC, Epicenter species			3820 <sup>3</sup>	0.00018
<i>Selenastrum capricornutum</i> , 14-d EC <sub>50</sub>	4,925 (96-hr EC <sub>50</sub> )	0.00014	17,805 <sup>3</sup>	0.00004
<i>Ceriodaphnia dubia</i> , 6-8-d NOEC (reproduction)			87-125 <sup>4</sup>	0.008
<i>Americamysis bahia</i> , 7-d NOEC (growth)			500-1000 <sup>4</sup>	0.0014
<i>Cyprinodon variegatus</i> , 7-d NOEC, (growth)			>1000 <sup>4</sup>	0.0007

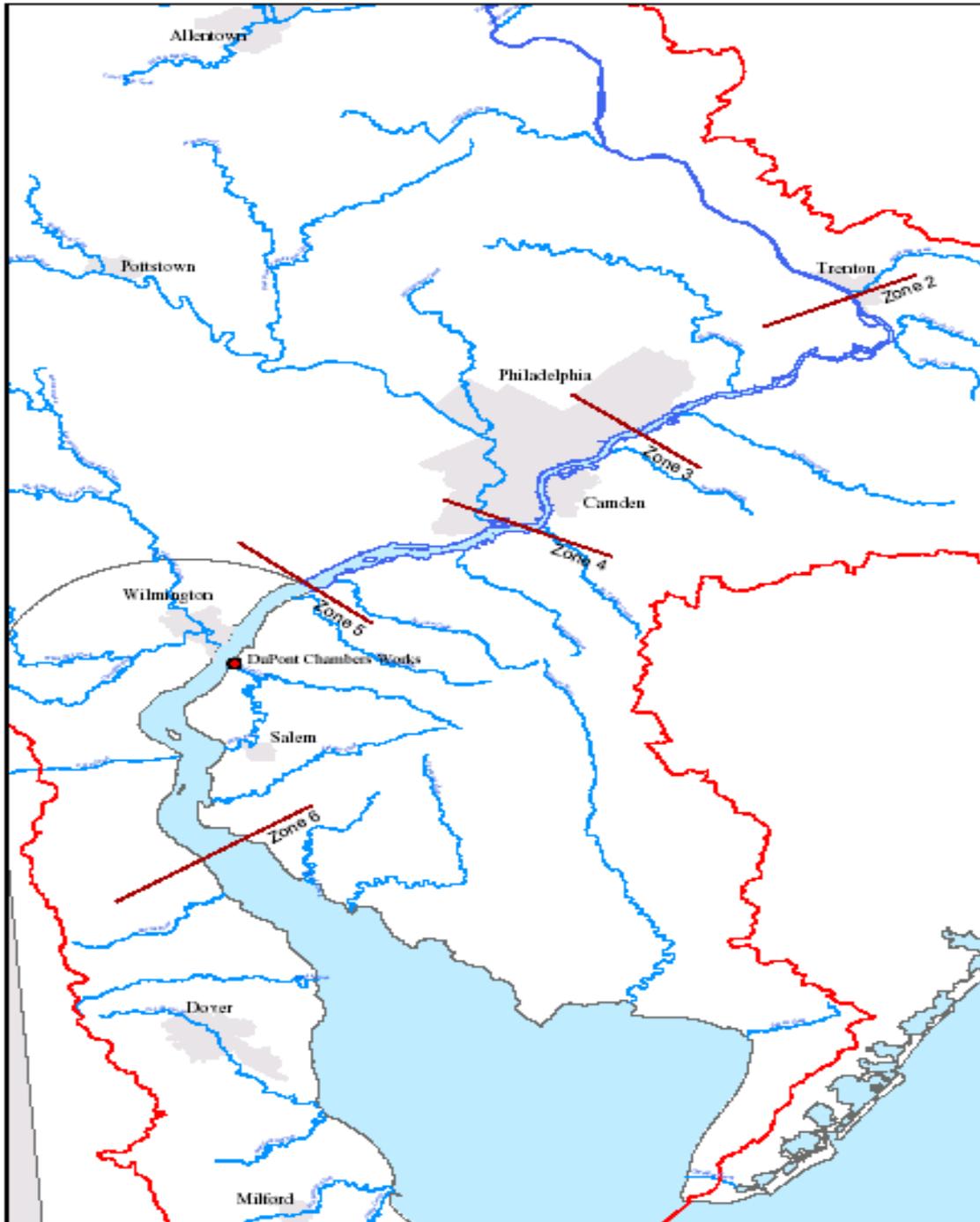
1 – U.S. EPA 1998.

2 – based on an in-stream concentration of 0.7 mg/L, i.e., 15X dilution @ 100 meters

2 – Williams et al. 1987

3 – EA Engineering 2004 – lowest value from rangefinding and definitive studies

## THE DELAWARE RIVER AND ESTUARY



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