
**U.S. Army
Chemical Materials Agency
Program Manager for the Elimination
of Chemical Weapons**

**FY03 Newport Chemical Agent Disposal
Facility Field Office Program Integration
Support**

**Evaluation of Issues Resulting from the
Independent Assessment of Hydrolysate
Treatment and Disposal in Dayton, Ohio**

Contract Number: DAAD13-01-D-0013

Task Number: I-03-AT-002

Final

Science Applications International Corporation

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EVALUATION OF ISSUES RESULTING FROM THE INDEPENDENT ASSESSMENT OF HYDROLYSATE TREATMENT AND DISPOSAL IN DAYTON, OHIO

1. INTRODUCTION

Dr. Bruce Rittmann was contracted by Montgomery County (MC) to evaluate the Perma-Fix of Dayton, Inc. (PFD) demonstration study and treatment plan for hydrolysate from the Newport Chemical Depot (NECD), Newport, Indiana. Hydrolysate is produced from the caustic neutralization of nerve agent, O-ethyl S-(2-diisopropylaminoethyl) methylphosphonothioate (VX). On 7 October 2003, Dr. Rittmann presented his findings to the Montgomery Commissioners, documented in a report entitled "Treatment of VX Hydrolysate by PermaFix of Dayton," dated 6 October 2003. Dr. Rittmann's report "...analyzes the scientific basis of the proposed treatment plan, evaluates the status of waste treatment at PFD, interprets the results of a demonstration study conducted at PFD, addresses specific issues, and provides a set of recommendations."

This document is intended to provide further clarification on programmatic issues related to hydrolysate production at the Newport Chemical Agent Disposal Facility (NECDF) and hydrolysate treatment and disposal at a commercial treatment, storage, and disposal facility (TSDF) that were not adequately addressed in Dr. Rittmann's assessment.

Section 2 provides background information on the planned process for treatment of the VX stockpile at NECDF. Section 3 provides a summary of the responses to the key issues and recommendations in Dr. Rittmann's report. Detailed responses to the report are provided in the table in appendix A. Acronym definitions and a list of references are provided in appendices B and C, respectively.

2. BACKGROUND

Following the terrorist attacks of 11 September 2001, the Army sought to accelerate the destruction of the VX stockpile in Newport, Indiana, to eliminate the risk of continued storage of the stockpile. Acceleration of the schedule could be achieved by taking advantage of existing capabilities in the commercial sector instead of duplicating or developing these capabilities on Army property. The U.S. Government's/Army's accelerated neutralization program is based on a partnership with private commercial enterprise. The Army and its NECDF Systems Contractor, Parsons Infrastructure and Technology (Parsons), are the experts responsible for the destruction of the chemical agent VX through well-tested technology. The method selected for agent destruction at Newport is caustic hydrolysis. The resulting product, hydrolysate, is a hazardous waste due to its highly corrosive nature and the presence of a flammable upper organic layer. Each shipment of hydrolysate from the NECDF will be analyzed to confirm that it is non-detect for VX with a Method Detection Limit (MDL) of less than or equal to 20 parts per billion (ppb) and contains no more than 20 parts per million (ppm) of S-(2-diisopropylaminoethyl)methylphosphonothioic acid (EA2192). Hydrolysate will not be shipped from the NECDF unless these criteria are met.

3. SUMMARY OF RESPONSES TO UNANSWERED QUESTIONS, SPECIFIC ISSUES, AND RECOMMENDATIONS

Dr. Rittmann's report raises many issues regarding the treatment of VX caustic hydrolysate (hydrolysate) by PFD. Some of these are scientific or technical and others are regulatory or policy related. Line-by-line responses to 96 comments are provided in the table in appendix A, where Dr. Rittmann's report is reproduced in the left-hand column, and where appropriate, detailed responses to each issue generally related to hydrolysate treatment at a TSDF are provided in the right-hand column. Those issues that are specific to treatment of hydrolysate by PFD have not been addressed in this response document. The following section provides a summary of the responses to key issues identified by Dr. Rittmann as unanswered questions, specific issues, or recommendations.

3.1 Demonstration Study: Unanswered Questions

In his final report, Dr. Rittmann states that, "The Demonstration Study, completed in July 2003 and reported in an August 29, 2003 Final Report from PFD, provides a preliminary validation that the proposed multi-step process can meet certification requirements. However, the study does not answer important questions." Dr. Rittmann identified five questions that were not answered by the Demonstration Study. In this section, the key questions that apply to any TSDF receiving hydrolysate are reproduced in italics and appropriate responses are provided.

- a. *Were the Schedule 2 compounds (and EA2192, if present) removed in the expected steps and to the expected degrees?*

Treatability studies are commonly done in the waste management industry to determine whether a waste type can be handled. Any TSDF receiving the hydrolysate for treatment would conduct a study to determine the fate of EMPA, MPA, and thiolamine.

The compound EA2192 must be confirmed to be less than 20 ppm before release from the NECDF. At such low initial levels, and without a means of production, it is unnecessary to monitor EA2192 in the PFD treatment process.

- b. *Can the concentrations of the Schedule 2 compounds be reduced to far below the certification level by improved chemical treatment, biodegradation, or a combination?*

Analysis of Schedule 2 compounds to below the certification level is not considered warranted. Each batch would be analyzed to confirm that the release criteria were met prior to discharge. Additionally, MPA, the only compound with any measurable concentration at discharge to the Miami River, has very low toxicity (oral [rat] toxicity less than table salt, and a

reported ecotoxicity of 3273 [48-hour LC₅₀ *Daphnia magna*] to 12,380 mg/L [96 hour LC₅₀ *bluegill sunfish*] (Williams et al., 1987; Verweij et al., 1976; Munro et al., 1999; Demonstration Study Results). Both Parsons and PFD had been open with the Ohio Environmental Protection Agency (EPA) in discussions on conducting ecotoxicity tests on plant effluent.

- c. *Can post-biological adsorption and filtration be operated reliably?*

Post-biological adsorption and filtration is run reliably at wastewater treatment facilities around the world (Cheremisinoff and Cheremisinoff, 1994; Metcalf and Eddy, Inc., 1991).

- d. *Will the treated VXH cause receiving-stream ecotoxicity when diluted into the municipal wastewater?*

As previously indicated in responses to whether the level of Schedule 2 compounds could be decreased far below the required limit, there is no indication that treated hydrolysate effluent could cause ecotoxicity in the receiving stream (that is, the Miami River) (Munro et al., 1999; Dr. Rittmann's calculations based on demonstration study results). As calculated by Dr. Rittmann, of the trace constituents in the discharge to the Montgomery County sanitary sewer system, only MPA is significant. MPA has been shown to have toxicity similar to table salt. Munroe et al. (1999) states that, "no toxicity data were found for EMPA...and it may be expected to have the same low to moderate toxicity as IMPA and MPA." Therefore, the only compound with a potentially measurable concentration at discharge to the Miami River, MPA, has very low toxicity. (The expected worst-case concentration for this compound is orders of magnitude lower than observable exotoxicity effects.) Both Parsons and PFD, however, had been open with the Ohio EPA in discussions on

conducting ecotoxicity tests on plant effluent in order to ensure that this was in fact the case.

3.2 Specific Issues

Dr. Rittmann identified 12 issues associated with hydrolysate treatment at PFD that were raised by MC staff or that he considered to be important. Those issues that Dr. Rittmann indicated were problematic and relate to hydrolysate treatment at any TSDF are provided below in italics with responses following.

- a. *What are the risks of VXH itself? First, the very high pH of VXH makes it caustic and harmful to humans and materials. Second, it has a strong odor, particularly from thiolamine. Third, it is possible, at least in principle, that VX could be reformed if the pH were decreased below the 13 to 14 range used in hydrolysis. Most likely, reforming would require a deliberate act and would not be the result of a spill. Fourth, it is possible that VXH contains EA2192. Fifth, the organic layer in VXH is flammable. Therefore, the VXH must be kept sealed from the environment at all times.*

A detailed explanation of all the risks associated with hydrolysate is provided in the Project Manager for Alternative Technologies and Approaches (PMATA) information paper, entitled "What are the Hazards of Hydrolysate." (PMATA, 2003)

Hydrolysate is primarily classified as a hazardous waste due to its corrosive nature, that is, the high pH. The Material Safety Data Sheet (MSDS) for caustic (NaOH) solutions ranging in concentration from 0.8 to 8 percent by weight classify these as a hazard with a "Health Rating" of 2 (that is, Moderate), a "Reactivity Rating" of 1 (that is, Slight) and a "Contact Rating" of 3 (that is, Severe). NaOH is present at approximately 4 percent by weight in hydrolysate. Although not the most significant component in hydrolysate, it is the second-most toxic constituent with a

toxicity of approximately 140 milligrams per kilogram (mg/kg) (oral rat). Because of its relatively high concentration and toxicity, caustic corresponds to the second-most significant hazard associated with hydrolysate for oral exposure (that is, by swallowing hydrolysate). With respect to contact hazards (that is, damage caused by touching hydrolysate) it corresponds to the greatest risk of hydrolysate.

Comments regarding odor and hydrolysate handling are discussed in paragraph c.

There is no direct evidence that stabilizers cause VX formation in the hydrolysate or that VX forms in caustic hydrolysate over time (PMATA, 2003a). The hydrolysate is maintained at a pH above 14 to eliminate the possibility of formation.

The NECDF reactor system is designed to destroy EA2192. It is expected that EA2192 concentration in hydrolysate will be less than 1 ppm; however, hydrolysate will not be shipped from the NECDF unless it is first verified that EA2192 is not present above 20 ppm.

The flammability hazard associated with hydrolysate produced at a 33 percent loading relates to the presence of an organic upper layer with a flashpoint of 127°F (53°C) (as determined by Pensky-Martens Closed-Cup Test Method). The flashpoint is the temperature to which the liquid must be heated before the vapors from the liquid will ignite in the presence of an ignition source (for example, flame, spark, etc.). The flashpoint for 33 percent loading hydrolysate is similar to that of diesel fuel. The upper layer corresponds to approximately 3 to 5 percent (by volume) of the total hydrolysate. Under the current expected operation conditions in which less VX will be neutralized per hydrolysate batch, it is expected that the amount of upper layer will be decreased/eliminated. By decreasing the presence of the upper organic layer, it is expected that the flammability of

hydrolysate will be greatly reduced. The overall affect will be determined with further testing.

- b. *Is the multi-step treatment process ready to be implemented at full scale? No. While the scientific principles underlying the multi-step process are logical, it is new and unique. The demonstration testing did not answer key questions (previously listed), and continuous operation under realistic operating conditions has not yet been addressed. Therefore, the multi-step process still should be considered an “experimental method.”*

Treatment of the hydrolysate at any TSDF would first involve a comprehensive treatability study to determine the optimum operating conditions for this waste type, which is common commercial practice. Extrapolation of bench-scale testing is a pertinent issue in the establishment of a new treatment process. The overall intention of the project would be to integrate controlled startup of hydrolysate treatment at the TSDF with the scheduled slow ramp-up of agent destruction at NECDF. The Army and Parsons believe treatment of hydrolysate at a TSDF is amenable to full-scale implementation, although a closely monitored phased startup of the TSDF treatment of hydrolysate is warranted.

- c. *Will treatment of VXH increase the potential of odors from the PFD site? Yes. VXH has a strong odor, mainly the “skunky” odor from thiolamine. Therefore, the greatest odor risk comes from handling the original VXH and from the first oxidation step. To ensure that “skunky” odors are not released, PFD must capture all gases and treat those gases successfully in the thermal oxidizer. Achieving this will require site improvements that are part of the plan for treating VXH, and the performance must be verified and monitored.*

The primary odor-causing compounds in the hydrolysate are thiolamines, which are routinely handled by commercial TSDFs. A common method of odor control is the use of a regenerative thermal oxidizer (RTO), which oxidizes the odor-causing compounds in the biological reactors and the pretreatment areas. (Catalytic Products International, 2003; MEGTEC, 2003) PFD intended to expand the ventilation control system, but this had not been accomplished at the time that the plan to process hydrolysate at this TSDF was halted.

At the time of the report, PFD had been actively working with both the Regional Air Pollution Control Agency (RAPCA) and the Ohio EPA to resolve issues associated with plant odor.

- d. *Will the solids generated by the proposed treatment of VXH create risks? Yes. EMPA and MPA accumulate in the solids generated by chemical oxidation, and they could be leached under conditions related to a sanitary landfill. The risks associated with this situation are not well defined, but this issue deserves further investigation if significant amount of EMPA and MPA accumulate in the solids.*

With respect to solids disposal and potential leaching of EMPA and MPA, it is important to note that: (1) Over 90 percent of the overall MPA plus EMPA was destroyed during chemical treatment (Perma-Fix of Dayton, Inc., 2003), (2) MPA and EMPA occur in the precipitated solids in polymeric form (Perma-Fix of Dayton, Inc. personal communication, 2003), (3) Solids will be disposed of in a certified and regulated landfill where leachate is contained, and (4) EMPA/MPA do not meet the requirements to be considered an environmental risk in that they are not toxicants and would not have access to the environment (at levels that could pose a risk).

The low toxicity of the EMPA and MPA is discussed in detail in paragraph 3.1.

3.3 Recommendations

Dr. Rittmann made five recommendations for treatment of hydrolysate by PFD. His key recommendation is reproduced in the following paragraph with a response.

- a. *Parsons should carry out the first oxidation step in Newport, Indiana.*

Commercial facilities are capable of safely transporting and treating wastes with characteristics similar to the characteristics of hydrolysate. Parsons, the Army, and its subcontractor evaluated the implementation of peroxide and acid addition on site, both through laboratory testing (Parsons/Alion, 2003) and implementation requirements (Parsons, 2003). The results of this investigation indicated that substantial testing would be required for implementation that was not justifiable by the schedule or by gains in general process safety. The advantages identified by Dr. Rittmann include decreased odor and elimination of the possibility of VX formation, which can both be effectively managed by a commercial TSDF.

4. SUMMARY

Although parts of Dr. Rittmann's assessment are accurate, he has made a number of statements that require clarification. These have been addressed in this response document. Many of Dr. Rittmann's concerns are associated with specific PFD operations, and would not be applicable to treatment of the hydrolysate at other TSDFs.

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APPENDIX A
EVALUATION OF DR. RITTMANN'S REPORT

**APPENDIX A
EVALUATION OF DR. RITTMANN'S REPORT**

Comment	Dr. Rittmann Report	Evaluation (Clarification/Corrections/Additional)
1.	<p>Executive Summary This report provides Montgomery County (MC) with advice on the proposal by Perma-Fix of Dayton (PFD) to treat VXH, the hydrolysate produced by chemical destruction of the nerve agent VX. The report analyzes the scientific basis of the proposed treatment plan, evaluates the status of waste treatment at PFD, interprets the results of a demonstration study conducted at PFD, addresses specific issues, and provides a set of recommendations.</p> <p>The proposed multi-step process has a sound scientific foundation. Properly implemented and monitored, the multi-step treatment process could eliminate hazardous components in the VXH without causing health risk or odors to neighbors and without disrupting the operation and performance of MC's Western Regional Wastewater Treatment Facility. On the other hand, the multi-step process is new and unique, and its successful full-scale operation has not been proven at PFD or anywhere else. Therefore, MC and PFD should view the treatment of VXH as an "experimental method." Furthermore, PFD has not documented complete success with odor control at its site and with operation of its existing biological treatment reactors.</p>	<p>This "evaluation section" is intended to provide clarification on programmatic issues related to production at the Newport Chemical Agent I (NECDF) and hydrolysate treatment and disposal, commercial treatment, storage, and disposal issues that were incompletely addressed in Dr. Rittmann's assessment.</p> <p>Treatment of the hydrolysate at any TSDF requires a comprehensive treatability study to determine optimal operating conditions for this waste type, which is not currently in commercial practice. Extrapolation of bench-scale data is a pertinent issue in the establishment of a new process. The overall intention of the project is to integrate controlled startup of hydrolysate treatment at the TSDF with the scheduled slow ramp-up of operations at the NECDF. The Army and Parsons believe that the treatment of hydrolysate at a TSDF is amenable to full-scale implementation, although a closely monitored pilot-scale study of the TSDF treatment of hydrolysate is warranted.</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additional)
		The primary odor-causing compounds in the thiolamines, which are routinely handled by TSDFs. A common method of odor control regenerative thermal oxidizer (RTO), which odor-causing compounds in the biological pretreatment areas (Catalytic Products International MEGTEC, 2003). PFD intended to expand control system, but this had not been accounted for in the plan to process hydrolysate at this
2.	<p>The Demonstration Study, completed in July 2003 and reported in an August 29, 2003 Final Report from PFD, provides a preliminary validation that the proposed multi-step process can meet certification requirements. However, the study does not answer important questions:</p> <ul style="list-style-type: none"> • Were the Schedule 2 compounds (and EA2192, if present) removed in the expected steps and to the expected degrees? 	<p>Treatability studies are commonly done in the management industry to determine whether they can be handled. Any TSDF receiving the hydrolysate would be required to conduct a study to determine the release of EMPA, MPA, and thiolamine. The compound was confirmed to be less than 20 parts per million release from NECDF.</p> <p>PFD collected information describing the extent of compounds destruction at each step of the process development phase of the demonstration (that is, prior to the certification period). However, the report reviewed by Dr. Rittmann only contained preliminary end results (that is, final effluent concentrations).</p>
3.	Can the concentrations of the Schedule 2 compounds be reduced to far below the certification level by improved chemical treatment, biodegradation, or a combination?	Analysis of Schedule 2 compounds to below the certification level is not considered warranted. Each batch was analyzed to confirm that the release criteria were not exceeded at discharge. Additionally, MPA, the only compound with a measurable concentration at discharge to the receiving water body, has a very low toxicity (oral [rat] toxicity less than that of the reported ecotoxicity of 3273 [48-hour LC ₅₀ of 12,380 mg/L [96 hour LC ₅₀ of <i>bluegill sunfish</i>]) (Verweij et al., 1976; Munro et al., 1998; Study Results) Both Parsons and PFD had discussions with Ohio EPA in discussions on conducting ecological risk assessments on plant effluent.
4.	Was biological treatment representative of what can be expected at full scale?	The biological treatment process utilized in the demonstration was specifically designed and implemented to represent full scale.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
		full-scale PFD system. The biological react more than three hydraulic residence times (the microorganisms to plant waste and to state operations during full-scale production
5.	Can post-biological adsorption and filtration be operated reliably?	Post-biological adsorption and filtration is in wastewater treatment facilities around the world (Cheremisinoff and Cheremisinoff, 1994; Mott Inc., 1991).
6.	Will the treated VXH cause receiving-stream ecotoxicity when diluted into the municipal wastewater?	As previously stated (Comment 3), there is treated hydrolysate effluent could cause in receiving stream (that is, the Miami River). compound with a potentially measurable concentration discharge to the Miami River, MPA, has verified is, expected worst-case concentration is or lower than observable ecotoxic effects) (W Verweij et al., 1976; Munro et al., 1999; Der Results).
7.	<p>More documentation of the fate of the Schedule 2 compounds – along with other key components – at each step of treatment is necessary to ensure that the underlying foundation of the multi-step process is demonstrated.</p> <p>The following are brief statements of my five recommendations; complete statements are in the Recommendations section of the report.</p> <ol style="list-style-type: none"> 1. Parsons should carry out the first oxidation step in Newport, IN. 2. PFD should solve its current odor problems before it accepts VXH for treatment. 3. PFD should upgrade the monitoring and, perhaps, the performance of its SBR biological treatment system before accepting any VXH for treatment. 4. PFD should conduct additional laboratory testing to supplement the Demonstration Study so that they can answer the important questions (above). 	<p>As previously stated (Comment 2), documentation of Schedule 2 compounds was gathered by process development.</p> <p>The following comments respond to Dr. Rittmann recommendations:</p> <ol style="list-style-type: none"> 1. Parsons, the Army, and its subcontractors are implementing the implementation of peroxide and onsite, both through laboratory testing (2003) and implementation requirements (2003). The results of this investigation and substantial testing would be required for implementation that was not justified or by gains in general process safety identified by Dr. Rittmann include the elimination of the possibility of VXH from the site can both be effectively managed by TSDF.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>5. PFD should implement VXH treatment through a phased start up that has extensive monitoring.</p>	<p>2. At the time of the report, PFD had been working with both RAPCA and the Corps to resolve issues associated with plan expected that PFD would have these described prior to the start of hydrolysate ship described in comment 1, effective on techniques would be employed for loading shipment and during treatment at a facility.</p> <p>3. No comment.</p> <p>4. Agree. Any necessary laboratory tests conducted by the TSDF prior to receiving.</p> <p>5. Agree. As stated in Comment 1, the interface startup operations at the facility controlled startup at the TSDF.</p>
<p>8.</p>	<p>Basics of VXH and Its Treatment</p> <p>VX is a highly potent nerve agent that falls into the general classification of alkylphosphonic acid esters. The Chemical name of VX is O-ethyl-S-[2-(diisopropylamino)ethyl]methylphosphonothionate, and its nerve-agent action is an anticholinesterase. Because it is an ester, VX can be broken into its component parts by a common reaction called hydrolysis. In hydrolysis, the water molecule (H₂O) or the hydroxyl ion (HO⁻) reacts with the ester, splitting it into two parts. In the case of VX, the main two parts are EMPA and thiolamine:</p> $\text{VX} + \text{HO}^- \rightarrow \text{EMPA} + \text{thiolamine}$ <p>EMPA stands for ethyl methyl phosphonic acid, and it contains the phosphonic acid part of VX. The full name for thiolamine is diisopropylaminoethanethiol, and it contains the amine and thionate parts of the original VX. EMPA can undergo another hydrolysis reaction to form MPA:</p> $\text{EMPA} + \text{HO}^- \rightarrow \text{MPA} + \text{ethanol}$ <p>MPA (methyl phosphonic acid) still contains the phosphonic-acid component of VX. A parallel set of hydrolysis</p>	<p>The reactions are best expressed as follows:</p> $\text{RXN1: VX} + 2 \text{Na}^+\text{OH}^- \rightarrow \text{Na}^+\text{EMPA}^- + \text{Na}^+\text{thiolamine}$ $\text{RXN2: VX} + \text{NaOH} \rightarrow \text{Na}^+\text{EA2192}^- + \text{ethanol}$ $\text{RXN3: Na}^+\text{EA2192}^- + 2 \text{Na}^+\text{OH}^- \rightarrow 2 (\text{Na}^+\text{thiolamine})$ <p>In caustic, the first reaction (RXN 1) and the (RXN 2) occur in parallel, with approximately 10 percent destroyed to EMPA and thiolamine and the 10 percent to EA2192 and ethanol.</p> <p>As shown in the third reaction (RXN 3), MPA, the caustic hydrolysis of EA2192. The reaction Dr. Rittmann, the hydrolysis of EMPA to form thiolamine has not been observed in the hydrolysate. Experimentation has shown that EMPA is stable in caustic even at high temperatures.</p> <p>The stoichiometric expression of VX neutral above (RXN 1 to 3) is more appropriate because it is in chemical balance and also indicates that MPA, thiolamine, and EA2192 are predominately</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	reactions converts VX to MPA and the ethanol through another intermediate called EA2192, which is described later in the report: $\begin{array}{l} \text{VX} + \text{HO}^- \xrightarrow{\quad} \text{EA2192} + \text{ethanol} \\ \text{EA2192} + \text{HO}^- \xrightarrow{\quad} \text{MPA} + \text{thiolamine} \end{array}$	caustic hydrolysate as their sodium salts. They are virtually non-existent in hydrolysate. For convenience and in accordance with Dr. Rittmann's report, salts are referred to as EMPA, MPA, EA2192 (as opposed to the salt derivatives of EMPA and thiolamine) throughout the remainder of the report (PMATA, 2003b).
9.	PFD's treatment plan exploits the hydrolysis reaction shown above to break VX mainly into EMPA, MPA, thiolamine, and ethanol. To accelerate the hydrolysis reaction, they will use highly caustic conditions (pH approaching 14) to increase the concentration of the HO ⁻ reactant. Highly caustic conditions will be achieved by adding sodium hydroxide (NaOH). They also will increase the temperature to greater than 90°C (194°F) to speed the reaction. High pH and high temperature are well-known and reliable strategies to accelerate hydrolysis reactions, and past research with VX shows that they work as expected. Thus, the hydrolysis reactions to be carried out at Newport are based on sound science and have the potential to destroy VX to below its detection level, which is about 20 parts per billion (ppb).	The hydrolysis reactions described will be carried out at NECDF; the TSDF will not participate in the destruction process. For clarification, the pH of VX destruction reactions will be above 14 and the reaction will be conducted at 90°C or higher. For clarification, the MDL must be demonstrated to be 20 ppb or less. Hydrolysate cannot be shipped to the TSDF if the MDL is above 20 ppb or VX is detected above the MDL.
10.	The hydrolysis approach planned for Newport creates VXH as its product, and VXH presents a number of hazards that must be understood and addressed. The hazards fall into the categories of problems with the main products, other products, and high pH.	A detailed discussion of the hazards associated with hydrolysate is provided in the PMATA document, "Hazards of Hydrolysate?" (PMATA, 2003). Hydrolysate is primarily classified as a hazard due to its corrosive nature, that is, the high pH. The hazards associated with the main products, MPA, EMPA, and thiolamine, is the odor of thiolamine and this is addressed in the first treatment step at the treatment plant odor-control system (PMATA, 2003).
11.	<u>The main reaction products are EMPA, MPA, thiolamine, and ethanol.</u> The Army classifies the first three as "Schedule 2" compounds according to the Chemical Weapons Convention (CWC). Schedule 2 compounds could recombine to form VX if the right conditions were present (NRC, 2000). The right conditions include the presence of the Schedule 2 compounds,	While it is possible to form VX from schedule 2 compounds, there is no direct evidence that VX formation occurs in hydrolysate or that schedule 2 compounds recombine in hydrolysate (PMATA, 2003a). The very high pH favors VX destruction, which is the primary goal of the treatment process.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>a pH lower than the 13-14 range used for hydrolysis, and the presence of a stabilizer (e.g., dicyclohexylcarbodiimide or diisopropylcarbodiimide). VXH often has the first and third conditions; therefore, the very high pH is what guarantees that VX does not form from its components. At least in principle, VX could be reformed from VXH if the pH decreased significantly (NRC, 2000). The most likely means by which a significant pH drop could occur is by addition of strong acid, which would be a deliberate action. Extensive uptake of CO₂ from the atmosphere also will lower the pH (perhaps to as low as 11). Dilution also would lower the pH, but it also would lower the concentration of all components.</p>	<p>hydrolysate is maintained at a pH above 14 treatment and transportation.</p>
12.	<p>Thiolamine has a very strong "skunk" odor, and the major odor problem of VXH is associated with thiolamine. Prolonged inhalation could present a health risk, and the Material Safety Data Sheet for VXH (MSDS, 2003) states that the maximum allowable air concentration for worker exposure to thiolamine is 40 ppb (parts per billion).</p>	<p>The 40 ppb exposure level cited in the Mate Sheets (MSDS) of hydrolysate for the thiol maximum allowable air concentration for th (Parsons, 2003). This level is a highly cons for the airborne concentration to which a wc exposed for 40 hours a week without any de effects.</p>
13.	<p>MPA has shown mammal toxicity with oral or intravenous exposure (Munroe et al., 1999). The LD₅₀ was ≥ 5,000 mg/kg. The toxicity of MPA is much less than VX, which is acutely toxic to humans by oral, inhalation, or dermal routes at less than 0.14 mg/kg (NRC, 1996). I did not find toxicity information on EMPA.</p>	<p>MPA toxicity (rat oral toxicity of 5,000 milligr [mg/kg]), is less than sodium chloride (table oral toxicity of 3,000 mg/kg. More details re and hazards associated with hydrolysate ar comment 25 and an information paper prep (PMATA, 2003b).</p> <p>The toxicity of VX is not pertinent to describ hazards for hydrolysate. Hydrolysate will not the NECDF unless VX is non-detect with an less. Similar considerations apply to EA219 reactor system is designed to destroy EA219 that EA2192 concentration in hydrolysate will 1 ppm; however, hydrolysate will not be shij NECDF unless it is first verified that EA2192 above 20 ppm.</p>
14.	<p>Some VXH components may have ecotoxicity to aquatic organisms (Munroe et al., 1999). I did not find ecotoxicity data</p>	<p>Parsons and the U.S. Army were not able to on Ames test for EMPA in the reference cite</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additiona
	for EMPA, but Ames tests for mutagenicity suggested a reference concentration of 30 µg/m ³ .	
15.	Hydrolysis of VX also can produce <u>other products</u> , at least one of which is of concern. The most important other product is called EA2192, which is an alkylphosphonic acid ester with anticholinesterase (nerve-agent) activity like that of VX. In fact, the designation of EA stands for "experimental agent." EA2192 is much less toxic than VX, having an LD ₅₀ toward mammals of 0.017-630 mg/kg for oral or intravenous exposure (Munroe et al., 1999). Apparently, EA2192 does not have a dermal exposure route. Ea2192 can be hydrolyzed to MPA, but some accumulation of EA2192 is possible. According to information provided to me by PFD, they understand that EA2192 is not present at a concentration above its detection limit of 20ppm. However, information on EA2192 in VXH is sketchy at this time.	<p>The EA2192 LD₅₀ values are not clearly stated. Intravenous levels are 630 mg/kg and 0.017 respectively.</p> <p>EA2192 must be less than 20 ppm before it can be shipped from the NECDF for treatment. The detection limit for EA2192 compound is 1 ppb. At these levels, EA2192 is not considered to be a hazard.</p> <p>There have been several studies related to EA2192 hydrolysate. These include but are not limited to:</p> <ol style="list-style-type: none"> 1. Parsons, <i>EA-2192 Monitoring at the Newport C Disposal Facility</i>, 2002. 2. PMCD, Memorandum SFAE-CD-S. Screening Levels for Experimental Agent Operations at the Newport C Disposal Facility (NECDF), 27 Sept 2002. 3. U.S. Army Center for Health Promotion and Preventive Medicine, Analysis of EA-2192 Monitoring and Sampling Issues at Newport Chemical Facility, Aberdeen, MD, November 1997. 4. Bartram, P.W., Szafraniec, L.I., Hovav, Y., Beaudry, W.T., and Henderson, V.I. <i>Hydrolysis of S-(2-diisopropylamino)ethylphosphonothioic acid (EA-2192) and its hydrolysate</i>, ERDEC-TI AD B235-772, 1997. <p>There is no evidence of bioaccumulation of EA2192 (Munroe et al., 1999).</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
16.	An organic layer that is part of VXH is flammable. The organic layer mixes into the water when the pH is reduced during VXH treatment, which should eliminate flammability concerns.	The upper layer of hydrolysate, which consists of 5 percent of the total hydrolysate, has a flammability. This upper layer flammability is similar to diethylamine. See comment 78.
17.	The high pH of VXH is itself a hazard. Any solution with a pH near 14 is caustic and corrosive. It can cause irritation to severe tissue burns in humans and other living organisms, and it corrodes or dissolves many materials.	Agree. Appropriate precautions are provided (Parsons 2003).
18.	Due to all the hazards of the main reaction products, the other products, and high pH, VXH must be totally sealed from the environment at all times.	The main hazard from hydrolysate is its high pH as discussed in the information paper entitled "Hazards of Hydrolysate" (PMATA, 2003b). Hazards associated with the main reaction products are also discussed in this document and in comments 16 and 78.
19.	Treatment of VXH Figure 1 is a schematic of the treatment steps and what they are designed to accomplish. The current plan is to transport VXH to PFD in special trucks. VXH will be transported only if its concentrations of VX and EA2192 are below the detection limits of 20 ppb for VX and 20 ppm for EA2192.	Correction: Hydrolysate will be transported only if the concentration of VX is nondetect with a method detection limit (MDL) no greater than 20 ppb and the concentration of EA2192 is less than 20 ppm.
20.	The first step will be oxidation with a strong industrial oxidant at a somewhat elevated temperature (c. 55°C, or 131°F). The primary goal of the first step is to remove thiolamine by converting it to a disulfide. Removing thiolamine will eliminate the most odorous compound and one of the components needed to reform VX. With thiolamine removed, the pH can be reduced safely. Reducing the pH reduces problems of causticity and flammability. When I met on July 9 with representatives of Parsons, PFD, and MC, the Parsons representative indicated that they were considering doing the first oxidation step in Newport.	Although it has been shown that oxidation of thiolamine and that acidification will reduce corrosivity, the hazards (that is, with respect to VX form flammability) have not been demonstrated.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
21.	The second step will be another oxidation process using a catalyst to accelerate the reactions brought about by the oxidant. This is an example of an "advanced oxidation process," and it will be carried out at an elevated temperature (c. 80°C, or 176°F). The goal of the second oxidation is to remove EMPA and MPA. Destruction of EMPA and MPA will release a significant amount of phosphate, much of which will precipitate with metal cations (mainly Fe ³⁺) in the mixture to form inorganic solids. Ammonia (NH ₃) also should be released in this step.	The document indicates (in the third paragraph in Figure 1) that ammonia is produced during oxidation of the thiolamine. Ammonia produced during the subsequent aggressive oxidation step.
22.	The third step will be filtration of the oxidation effluent to remove the solids, most of which should be inorganic phosphates, such as FePO ₄ (s). The solids are to be disposed of in a Sub-Title D Non-Hazardous Landfill. It is likely that some organic compounds, including MPA and EMPA, will accumulate in the solids. This is significant, because MPA and EMPA could leach from the solids while in the landfill, posing a potential environmental risk if the leachate were to escape the landfill.	Risks associated with MPA and EMPA leachate are minimal due to the following reasons: <ul style="list-style-type: none"> • Over 90 percent of the overall MPA destroyed during chemical treatment (Dayton, Inc., 2003). • MPA and EMPA occur in the precipitated polymeric form (Perma-Fix of Dayton, Inc., 2003). • TCLP tests have shown that the TCLP limit of 0.1 percent (Dayton, Inc., 2003). • Solids will be disposed of in a certified landfill where the leachate is contained. • EMPA/MPA do not meet the requirements for being considered an environmental risk in a landfill and would not have access to the environment.
23.	The liquid effluent after filtration will be sent to an equalization tank, where it will be air stripped to remove NH ₃ released during the oxidation of thiolamine. The liquid effluent will then be mixed with other liquid wastewater treated by PFD. The ratio of oxidized VXH to other wastewater will vary, depending on the different flow rates of each and the concentrations of organic material in each stream. The ratio should be around 4 to 8 L of wastewater per 1 L treated VXH.	No comment.
24.	According to recent communications I received from PFD, they intend to treat the NH ₃ -containing off-gas by condensation, in	No comment.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	which the NH ₃ gas is removed from the gas stream and collected in a separate water stream. PFD then intends to treat the NH ₃ -containing liquid stream with an as-yet unspecified technique.	
25.	The mixed wastewater will then be treated in PFD's existing biological-treatment reactors. At least some of the organic products formed during the oxidation steps are biodegradable: e.g., ethanol. The biodegradability of MPA and EMPA, on the other hand, is not yet well defined, although Munroe et al. (1999) report that EMPA is biodegradable. Biodegradation is a logical follow up step after advanced oxidation, but the extent to which the organic components will be biodegraded cannot be predicted in advance.	As discussed in comment 13, the toxicity of be 5,000 mg/kg (oral rat). This corresponds toxicity. For comparison, consider that table slightly more toxic with a toxicity of approx (rat oral). The toxicity of EMPA is not know to be comparable to that of MPA since EMP the addition of an ethyl group. The toxicity < less than that of MPA, with a toxicity of appi mg/kg (oral rat). Although EMPA may be at hydrolysate, it is presumed low toxicity indic minor hazard. With relatively low concentra low toxicities, MPA and ethanol correspond: hazardous constituents of hydrolysate (PM/
26.	PFD has two activated sludge processes that operate in parallel as sequencing batch reactors (SBRs). The goal of biological treatment is to decrease the biodegradable organic matter, usually measured as the carbonaceous biochemical oxygen demand (CBOD). Good CBOD removal requires good removal of suspended solids (SS) from the effluent. Possible secondary goals are to reduce odor and toxicity in the effluent. PFD does not claim that EMPA and MPA will be biodegraded in the SBRs.	No comment.
27.	PFD also may treat the biological effluent by activated-carbon adsorption and filtration. Adsorption removes soluble organic compounds, and filtration removes suspended solids. Activated-carbon filters also are biologically active, which means that additional biodegradation is possible.	No comment.
28.	The liquid effluent is sent to the MC sanitary sewer. It ultimately is treated at the Western Regional Wastewater Treatment Facility. The effluent discharged by PFD must not create harm in the sewer or at the treatment plant. Wasted solids from PFD's biological treatment will be dewatered and sent to the same Non-Hazardous Landfill.	No comment.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additiona
29.	Off gases will be generated during all steps of treatment and transfer. All of the off-gas streams have potential to be odorous, and the original VXH is highly odorous due to thiolamine. PFD indicated that it plans to upgrade gas-collection and odor control so that no gas in contact with VXH is released without first being treated by thermal oxidation.	No comment.
30.	In summary, PFD proposes multi-step treatment to convert VXH into a liquid effluent that can be discharged safely to the sanitary sewer. On the one hand, each step of the multi-step process is based on a sound scientific foundation. Thus, I find no scientific reason to judge <i>a priori</i> that the proposed plan cannot work. On the other hand, the multi-step treatment scheme is new and unique. It has only been tested at the bench scale (described later), and it has never been tested under realistic operating conditions. This situation means that the start up of VXH treatment at PFD will be the first test with realistic operating conditions. Thus, the start up should be phased in and very closely monitored.	Startup of the hydrolysate treatment system would ramp up slowly, similar to the agent c at NECDF. The hydrolysate treatment will t monitored. See comment 1.
31.	<u>Current Status of Treatment at PFD-Performance of Biological Treatment</u> Currently, PFD treats wastewater with two SBRs operated in parallel. I requested and received operating data from PFD for the last six months (mid-January to early August 2003). I also have the last two years' effluent monitoring data from MC, and I use the 2003 MC data for comparison. Here, I summarize the operation and performance of the SBRs, which will be treating the oxidized VXH. This analysis provides important context for interpreting the results from the VXH demonstration study.	No comment.
32.	Compared to typical operation and performance of activated sludge, SBR treatment at PFD is unusual in many ways, which I summarize below. Much of the unusual nature occurs because PFD treats high-strength industrial wastewater. 1. The influent organic concentration is high (typical chemical oxygen demand [COD] of 30,000 mg/L), and	Concur.

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	the organic matter is relatively reduced (COD:TOC ratio of 3 to 4 gCOD/gC, where TOC means total organic carbon). The influent CBOD ₅ is typically around 12,000 mg/L, which suggests that a significant fraction of the influent COD is readily biodegradable.	
33.	2. According to PFD results, the fractional removal of CBOD ₅ is high (> 95%), but the effluent CBOD ₅ still is relatively high (100 – 1000 mg/L). However, CBOD ₅ results obtained by the MC laboratory are systematically much higher, typically around 2,800 mg/L, but sometimes as high as 21,500 mg/L (in 2003). PFD does not take effluent COD values, but effluent soluble TOC is high, typically over 2,000 mg/L. Thus, CBOD ₅ data reported by PFD appear to be inconsistent with their own soluble TOC data and with MC's CBOD ₅ data, which suggest much poorer CBOD removal. MC also reports high total N concentrations (230 – 3,500 mg/L) that are consistent with higher CBOD ₅ and TOC.	No comment.
34.	3. Mixed liquor suspended solids (MLSS) are fairly stable around 8,000 mg/L, but mixed liquor volatile suspended solids (MLVSS) are much lower, only around 1,000 mg/L. These results imply that most of the MLSS are inorganic solids, and active biomass is present at a low concentration. This judgment is supported by the very low values of Sludge Volume Index (SVI), around 50 mL/g. A very low SVI, especially when coupled with relatively high effluent SS of 100 – 1,500 mg/L, suggests that most of the suspended solids in the SBR are inorganic, not bacteria.	No comment.
35.	4. I computed that the Solids Retention Time (SRT) is around 100 days, which is a very large value. On the other hand, I computed a Food-to-Microorganisms ration (F:M) based on apparent CBOD ₅ removal and actual MLVSS of around 0.8 gCBOD ₅ /gMLVSS-day. The F:M is a large value in general and is an	No comment.

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	<p>extraordinarily high value for a system with an SRT of 100 days (when F:M should be less than 0.05 in the same units) (Rittmann and McCarty, 2001). The most likely explanation for the inconsistency between the SRT and the F:M values is that biological CBOD₅ removal is much less than implied by the effluent concentrations reported by PFD. On the one hand, the actual effluent CBOD₅ concentration may be much higher than reported by PFD, more like the values reported by MC. On the other hand, it is possible that some CBOD is being removed by air stripping, not biodegradation. Organic gases (e.g., methane and ethane), solvents, fuel components (e.g., toluene and benzene), and perhaps alcohols and aldehydes could be stripped with strong aeration. Laboratory testing results (described later) show that solvents and fuel components are present in SBR-treated wastewater, although at low concentrations.</p>	
36.	<p>5. The dissolved-oxygen concentration in the SBRs is not far from saturation for the reported temperatures. This information indicates that the SBR systems are not oxygen limited, which may support that aeration is strong and could cause significant air stripping.</p>	No comment.
37.	<p>In summary, the level of biological activity in the existing SBRs is uncertain. It is clear that most of the suspended solids are not biomass. SRT, F:M, and MC results suggest that CBOD removal is poor across the SBRs, despite a long SRT and high dissolved oxygen. Since the existing SBRs are to treat the oxidized VXH, the actual biological performance of the SBRs needs to be documented more thoroughly. At a minimum, PFD needs to document the actual CBOD removal occurring today. If CBOD removal is poor, PFD should upgrade the SBR performance before it begins to treat VXH.</p>	No comment.
38.	<p><u>Odors from PFD</u> Much of the area surrounding PFD is residential, and local</p>	The primary odor causing compounds in the thiolamines, which are routinely handled by TSDFs. A common method of odor control

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additiona
	residents already are complaining about odors from the PFD site. John Paul, head of the Regional Air Pollution Control Agency (RAPCA), said (August 5, 2003) that he would oppose the treatment of VXH at PFD until company officials prove that they can control odor problems. According to Paul, RAPCA inspectors found detectable to strong odors on 70 of 97 random visits to the neighborhood from May 2002 to June 2003.	regenerative thermal oxidizer (RTO), which causing compounds in the biological reacto pretreatment areas (Catalytic Products Inter MEGTEC, 2003). PFD intended to expand control system, but this had not been accor that the plan to process hydrolysate was ter
39.	At the July 9 meeting, PFD officials said that current odor problems are attributable to poor capture of gases from buildings, not from the treatment of off-gas. PFD said that they are working to improve capture of fugitive gases by keeping doors closed and other similar measures. When asked about odors from the wastewater treatment and the wastewater itself, PFD personnel described it a musty. Several of us smelled the odor from the effluent at the sampling station. We characterized the odor as "sharp", more "chemical" than musty. When I interviewed MC personnel who operate the Western Regional Wastewater Treatment Facility, they claimed to be able to identify the PFD wastewater by its characteristic "chemical" smell.	No comment.
40.	PFD installed a thermal oxidizer to handle the off-gases from the wastewater treatment system. Such a system ought to be effective, but I have no data documenting its actual performance. Furthermore, it is not clear what PFD does or will do when the thermal oxidizer cannot be utilized due to normal maintenance or a breakdown.	No comment.
41.	All areas used in the handling and treatment of VXH must be under negative pressure, so that any gases are captured and sent to the thermal oxidizer. The loading bay and area housing the oxidation reactor must be partitioned to achieve off-gas capture. The SBRs already have gas collection.	No comment.
42.	In summary, odor already is a major issue for PFD, and PFD is taking steps to eliminate current odor problems. Fugitive	See comment 38.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	emissions are not controlled well enough, and the performance of the thermal oxidizer is not documented. Handling and treating VXH will heighten the risk of odor, particularly from thiolamine; detectable odor surely will lead to public outcry.	
43.	<p><u>Demonstration Study</u></p> <p><u>Methods</u></p> <p>PFD had a Demonstration Study performed on site and using VXH that had been shipped to PFD for testing. Employees of SBR Technologies, Inc., who worked as a sub-contractor to PFD, conducted the demonstration testing. The study leader was Dr. Randall Marx. PFD released the Final Report on August 29, 2003, and they sent me a redacted version on September 4, 2003. They also released to me a draft report on July 28, 2003, and a full set of laboratory reports (c. 300 pages) on August 13, 2003. Dr. Marx and PFD/Parsons personnel also gave me (and MC staff) a comprehensive briefing on the Demonstration Study on July 9, 2003.</p>	No comment.
44.	According to the Final Report (PFD, 2003), the goal of the laboratory demonstration study was to "select and demonstrate a treatment process that would allow Perma-Fix of Dayton Inc. to meet current POTW permit limits, and a limit of 0.1% for each of the Schedule 2 compounds found in Hydrolysate: thiolamine, MPA, and EMPA." The process was required to run for a certification period of at least 10 days, during which time the Schedule 2 and permit criteria were to be met. Table 1 (which is Table 2 of the Final Report) lists all the certification limits.	No comment.
45.	The Final Report notes that the VXH tested contained "no stabilizer or stabilizer breakdown products." According to recent communications from Parsons/PFD, technical problems prevented them from using VXH with stabilizer for the certification testing. They intend to use VXH with stabilizer for future testing. Having no stabilizer present may have allowed	The original intent of the demonstration test acclimation of the bench-scale system with unstabilized hydrolysate with final certification stabilized hydrolysate that would be representative material to be shipped from NECDF. During representative hydrolysate, analytical issue:

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	greater VX destruction during hydrolysis than would have occurred with stabilizer present.	analysis of VX in hydrolysate prevented the hydrolysate. For contractual reasons, the d that PFD would be certified on the basis of 1 hydrolysate, with the intention that process conducted on fresh hydrolysate when it was is no direct evidence that the stabilizer conti ability to hydrolyze VX. No hydrolysate would leave Newport that h: concentrations of VX with an MDL of no gre The amount of VX destruction will be provei regardless of the stabilizer. Hydrolysate the the agent destruction criteria will be treated be shipped until the hydrolysate does meet
46.	The Demonstration Study simulated the proposed multi-step process by a series of bench-scale tests, which I list below with <i>my comments in italics</i> .	No comment.
47.	1. Oxidize thiolamine by adding strong oxidant in a beaker. The temperature increases to around 55°C.	No comment.
48.	2. In the same beaker, reduce the pH by adding acid.	No comment.
49.	3. To the same beaker, add catalyst and more oxidant to oxidize EMPA and MPA. The pH is controlled, and the temperature increases further, to around 80°C. Solids are produced.	No comment.
50.	4. Remove the solids by filtration through a glass-fiber filter in a Büchner funnel. <i>This filtration step reasonably approximates solids removal for pressure filtration.</i>	No comment.
51.	5. Adjust the pH and aerate with a ceramic diffuser to strip ammonia. <i>This step was not included in the original multi-step process. It became necessary because the ammonia released from thiolamine was going to cause the ammonia concentration to exceed its Final level, 100 mg/L as N (Table 1). Details on ammonia stripping and ammonia concentrations were</i>	No comment.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additiona
	<i>redacted in the Final Report and not present in the draft report. However, ammonia stripping is a well-established process that involves aeration at elevated pH.</i>	
52.	6. Blend the oxidized and filtered VXH with other wastewater being treated at PFD. <i>According to the Final Report, the volume ratio was 4 L of other wastewater per 1 L treated VXH. The blended CBOD₅ should have been approximately 4,000 mg/L, but information to estimate the blended TOC or COD was not stated.</i>	No comment.
53.	7. Treat the mixture in two 5.8-L SBRs. <i>According to the Final Report, the average TOC load was 4g/L-day when the mixed volumetric flow rate was 0.5L/day. The Final Report also states that the design F:M was 0.2 gTOC/gMLSS-day. The hydraulic detention time was 11.6 days for the bench studies, but the Final Report indicates that the typical hydraulic detention time for the full-scale SRBs will be about 5.3 days. The SRT and the F:M in units of gCBOD₅/gMLVSS-day are not stated in the Final Report.</i>	No comment.
54.	8. Mix the biological effluent with activated carbon and filter it through a glass-fiber filter. <i>This step was added in order that the final effluent "meet certification requirements." Contacting the biological effluent with activated carbon and then filtering out all solids with a glass-fiber filter do not simulate how an activated-carbon adsorption/filtration system will perform.</i>	No comment.
55.	9. Discharge the effluent.	No comment.
56.	One technical issue that must be addressed before the demonstration results can be interpreted is the reliability of the analytical data. Sections 7, 8, and 9 of the Final Report address the methods used, laboratory qualifications, and the Quality Assurance and Quality Control plan. The laboratory	No comment.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	data show detailed results of spike-recovery tests. My judgment is that the analytical methods, qualifications, and plan were satisfactory. Therefore, but with one possible exception, the experimental results can be analyzed with confidence that the analytical data are accurate.	
57.	The possible exception is CBOD ₅ . No spike-recovery testing is presented in the Final Report. The laboratory data provide the "final results" of their CBOD ₅ tests, but primary data or calculations are not shown. Given the apparent discrepancies between CBOD ₅ data reported by PFD and MC for the existing SBRs, as well as apparent discrepancies between PFD's CBOD ₅ data and other measurements of SBR effluent quality, I lack confidence in PFD's CBOD ₅ data.	No comment.
58.	<u>Analysis and Interpretation of the Demonstration Results</u> The Final Report provides average and maximum concentrations for the Schedule 2 compounds and a range of other materials listed in the discharge permit. Table 2 repeats the average values, since they are representative of maximum and daily values.	No comment.
59.	Based on the results in Table 2, the overall treatment scheme reduced Schedule 2 compounds to below the Army goal of 0.1%. Thiolamine was below the detection level on all days of the Final period. EMPA averaged 0.034% (c. 340 mg/L), and its range was narrow between 0.03 and 0.04%. MPA averaged 0.080% (c. 800 mg/L), with all values between 0.07 and 0.09%. While all values were below the 0.1% goal, MPA and EMPA were not far below it, and effluent concentrations were significant, in the 100s of mg/L range. That the EMPA and MPA concentrations were not far below the 0.1% certification level is significant in two ways. First, full-scale treatment may not be able to achieve removals as good as those achieved in bench-scale testing. Thus, the bench-scale results do not indicate a "margin of safety." Second, the EMPA and MPA concentrations in the influent to the Western Regional Wastewater Treatment Facility will not be trivial, which could have an effect on facility personnel and	Ecotoxicity data provided for MPA (Munroe <i>comment 3</i>), the only constituent of hydrolysis experimental results (Perma-Fix of Dayton, appreciable concentrations at the point of discharge environment, is orders of magnitude lower than to be toxic. As discussed in comment 13, the toxicity of EMPA is 5,000 mg/kg (oral rat). This corresponds to a toxicity of approximately 100 mg/kg (oral rat). For comparison, consider that thiolamine is slightly more toxic with a toxicity of approximately 100 mg/kg (oral rat). The toxicity of EMPA is not known to be comparable to that of MPA since EMPA has the addition of an ethyl group. The toxicity of EMPA is less than that of MPA, with a toxicity of approximately 100 mg/kg (oral rat). Although EMPA may be at low toxicity, it is presumed low toxicity indicator.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	the performance of the facility. The second issue is discussed more in the section on Specific Issues.	minor hazard. With relatively low concentrations and low toxicities, MPA and ethanol correspond to the most hazardous constituents of hydrolysate (PM10).
60.	What the results do not show is how the Schedule 2 compounds were removed in the different treatment steps. According to the principles underlying the multi-step process, thiolamine should have been destroyed in the first oxidation, while MPA and EMPA should have been mostly destroyed in the second oxidation. PFD supplied me with testing results not reported in the Demonstration Study Final Report (PFD, 2003). These results show that EMPA and MPA were destroyed – as expected – during the second oxidation step. These auxiliary data are valuable, but having step-by-step concentrations for all key components during the certification period would have been much better. In addition, mass balances – not just concentrations – need to be reported in order to track how much of the EMPA and MPA are destroyed.	The data requested here was produced. See comments 2, 61, and 62.
61.	According to Figure 2 of the Final Report, EMPA was present at about 5.7% in the raw hydrolysate and about 0.15% after oxidation. Dilution with the other wastewater would bring the EMPA concentration to about 0.03% in the influent to the bioreactor. This suggests that EMPA was not biodegraded in the SBR. The analogous numbers for MPA are approximately 0.7%, 0.25%, and 0.05%, which also suggest no biodegradation. PFD did not claim that EMPA and MPA would be removed by biodegradation, and dilution with other wastewater is necessary to meet the certification goal (0.1%) with the EMPA and MPA concentrations achieved by chemical oxidation.	The premise of the treatability study was that EMPA and MPA are resistant to biodegradation under expected conditions and needed some chemical oxidation. The suggested levels of EMPA are at the limit of detection, making it difficult to quantify biological degradation.
62.	The average values for effluent CBOD ₅ and suspended solids were 154 and 48 mg/L. These values are far lower than typical for the full-scale SBRs, and the reason probably is the activated-carbon adsorption and filtration after biological treatment. MLSS and MLVSS were not reported, making it impossible to compute SRT and F:M values, which would be valuable for comparison to the operation of the full-scale processes. Also, the Final Report provides no concentrations	Data of the unpolished bioreactor effluent show that EMPA and MPA had not been degraded. The likelihood of this observation motivated the use of a chemical treatment process to oxidize 90 percent of EMPA and MPA.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	of MPA, EMPA, CBOD ₅ , or VSS in the biotreatment effluent, and this makes it impossible to differentiate the effects of biological treatment from those of adsorption and solids filtration.	
63.	<p>The Final Report provides information (its Table 3) on the leaching of MPA, EMPA, and thiolamine from the solids produced after chemical oxidation. The Toxicity Characteristic Leaching Procedure (TCLP), developed to assesses the potential to leach hazardous materials from solids in sanitary landfills, gave the following %w/v values in the leaching liquid from the TCLP: MPA, 0.07, EMPA, 0.05, and thiolamine, "not measured." The thiolamine result probably means below the detection limit, but the entry might also mean "not tested." Given the lack of thiolamine in the final effluent, I assume that thiolamine was assayed, but not detected. The MPA and EMPA results confirm that the solids formed during chemical oxidation contained MPA and EMPA in significant amounts. Furthermore, these two compounds were leached under conditions that might be found in a sanitary landfill. Because the mass of solids produced was not provided in the Final Report, I cannot use the results of Table 3 (or Figures 1 and 2 of the Final Report) to estimate what fraction of the total removals of EMPA and MPA occurred due to association with the solids, versus oxidation. Recent information from Parsons/PFD states that destruction was at least 90%.</p>	<p>As stated in comment 22, leaching of EMPA/ significant concern for the following reasons</p> <ul style="list-style-type: none"> • Over 90 percent of the overall MPA destroyed during chemical treatment (Dayton, Inc., 2003). • MPA and EMPA occur in the precip polymeric form (Perma-Fix of Dayton Communication). • TCLP tests have shown that the TC the Schedule 2 limit of 0.1 percent (Dayton, Inc., 2003). • Solids will be disposed of in a certified landfill where the leachate is contained. • EMPA and MPA do not meet the requirements considered an environmental risk in toxicants and would not have access to the environment. <p>The TCLP test was not required for assessing MPA leachability, in that they are not toxic. I performed this analysis to be able to provide information on whether solids disposal did not present a risk to the environment. If EMPA was somewhat leachable, it was not in quantities suggesting a risk (Perma-Fix of Dayton Communication PMATA 2003b). The presence of MPA in the effluent is deemed unimportant in that it was held insignificant in comment 1, which is not a condition expected in a sanitary landfill.</p>
64.	Other permit parameters were less than the permit limits.	No comment.
65.	The results of the bench-scale demonstration study provide a preliminary validation that the proposed multi-step process can achieve the treatment objectives. On the one hand, no permit	Both the sample size and the duration of the study were much more extensive than studies typically conducted for a new waste stream in a biological treatment system.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>parameter exceeded its limit for the 10-day period, although MPA and EMPA were not far below the 0.1% goal. On the other hand, the results are significantly limited in five ways.</p> <ul style="list-style-type: none"> • First, they are for a relatively short time, even considering that PFD collected similar results for another 18 days before and after the 10-day certification period. 	<p>(Metcalf and Eddy, Inc., 1991).</p>
66.	<ul style="list-style-type: none"> • Second, the relationship between what was achieved in the bench-scale tests and what can be expected in full-scale operation is uncertain. A Ph.D. environmental engineer supervised the bench-scale tests; this is a much higher level of supervision than occurs normally. How well the operation of the biological process compared to operation of the full-scale biological process was not established. And, whether mixing, temperature, and pH can be controlled as well in large-scale operation is unknown. 	<p>The Army and Parsons are committed to tal needed to ensure the hydrolysate is safely : treated. The full-scale process will be base bench-scale studies. Mixing, temperature, : be accomplished at full scale.</p>
67.	<ul style="list-style-type: none"> • Third, the results presented are almost exclusively for the effluent after the entire treatment process. Since the multi-step process is new and unique and was designed based on assumptions that certain types of reactions should occur at each stage, the experimental results need to document that each step of the process achieved its assumed goals. For example, EMPA should not change much in the first oxidation, but it should be mostly destroyed in the second oxidation. EMPA not destroyed is either in the liquid or the solids, and its distribution needs to be determined. The fate of EMPA entering the biological reactor needs to be determined, too. 	<p>Data addressing this comment have been p See comment 2.</p>
68.	<ul style="list-style-type: none"> • Fourth, it appears that a significant removal of Schedule 2 compounds, CBOD₅, and suspended solids occurred during post-biological adsorption and filtration. The Final Report says that an activated-carbon adsorber/filter may be needed. The bench-scale testing for adsorption/filtration was not a 	<p>The data does not indicate that there was s Schedule 2 removal during adsorption/filtrat Adsorption/filtration was only added to conti Schedule 2 compound limits were achieved adsorption/filtration. (See comment 2)</p>

Comment: In that Dr. Irvine is an SBR expert, his SBR related comments do not need referencing.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>good simulation for sustained operation of an activated carbon adsorber/filter. An activated carbon filter would be prone to clogging and creation of anaerobic conditions, due to the high COD and SS loads to it. Sorption capacity probably would be saturated quickly. While the testing results with carbon adsorption and filtration show that these steps can improve effluent quality substantially, significant engineering and testing will be necessary to implement these steps reliably at full scale.</p>	<p>The multimedia filter precedes carbon adsorption removing suspended solids that might clog activated carbon (GAC) column) and saturation occurs before either clogging from bio-growth or the development of anaerobic conditions of the short time expected between the placement/regeneration of the activated carbon.</p>
69.	<ul style="list-style-type: none"> Fifth, the Final Report provided no results for EA2192. Laboratory testing pages show that an analytical technique was developed, but no data appear in the Report or in data sheets. PFD believes that EA2192 was not present above its detection limit, but this needs to be verified. 	<p>EA2192 was demonstrated to be below 20 µg/L (0.002 percent) before the hydrolysate was treated.</p>
70.	<p>While generally positive, the demonstration study leaves important questions unanswered:</p> <ul style="list-style-type: none"> Were the Schedule 2 compounds (and EA2192, if present) removed in the expected steps and to the expected degrees? 	<p>PFD has the data to show that Schedule 2 compounds are destroyed when expected and to the extent expected (comment 2). EA2192 is confirmed to be less than 20 µg/L before it leaves Newport and is not a concern in the treatment process.</p> <p>Hazards associated with the Schedule 2 compounds remaining in the hydrolysate are discussed in PMATA information paper, entitled "What about hydrolysate?" (PMATA, 2003)</p>
71.	<ul style="list-style-type: none"> Can the concentrations of the Schedule 2 compounds be reduced to far below the certification level by improved chemical treatment, biodegradation, or a combination? 	<p>There is no need to reduce the concentrations of the Schedule 2 compounds to below the certification levels. A representative batch would be analyzed to confirm that the levels have been met. The only compound with a concentration at discharge to the Miami River less than table salt (Williams et al., 1987; VFA, PMATA, 2003). Therefore, ecotoxicity is not a concern with the dilution of the salt in the 20 day discharge of the Western Regional Water Treatment Facility. See comment 70.</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
72.	<ul style="list-style-type: none"> Was biological treatment representative of what can be expected at full scale? 	<p>The biological treatment process utilized in specifically designed and implemented to re</p> <p>The biological reactors were "run" for more specifically acclimate the bioorganisms and state operations during full-scale production</p>
73.	<ul style="list-style-type: none"> Can post-biological adsorption and filtration be operated reliably? 	<p>Post-biological adsorption and filtration is run at wastewater treatment facilities around the world (Cheremisinoff and Cheremisinoff, 1994; Mott MacDonald Inc., 1991).</p>
74.	<ul style="list-style-type: none"> Will the treated VXH cause receiving-stream ecotoxicity when diluted into the wastewater at the Western Regional Wastewater Treatment Facility? 	<p>Ecotoxicity is not expected (see comments 72-74). However, both Parsons and PFD had been reviewed by EPA in discussions on conducting ecotoxicity testing on effluent in order to ensure that this was the case.</p>
75.	<p>More documentation of the fate of the Schedule 2 compounds – along with other key components, such as EA2192, CBOD₅, COD, TOC, phosphate, and organic and NH₃ nitrogen – at each step of treatment is necessary to ensure that the underlying foundation of the multi-step process is demonstrated. Ecotoxicity testing with treated VXH diluted into Western Regional effluent is warranted if MPA and EMPA concentrations are not reduced well below the concentrations achieved in the Demonstration Study. The next section on Specific Issues elaborates on the ecotoxicity issue.</p>	<p>Data for the fate of Schedule 2 compounds was provided by The Army, Parsons, and PFD. Data on the publicly-owned treatment works was provided by the MPA. The toxicity of the MPA has been compared to table salt (Williams et al., 1976; PMATA, 2003).</p> <p>See comments 2, 6, and 70.</p>
76.	<p>Given that the proposed VXH treatment is new and unique and the fact that EMPA and MPA were not removed to far below the 0.1% goal, it is advisable to carry out additional demonstration studies that explicitly addresses the information I mention in the preceding paragraph.</p>	<p>Extrapolating bench-scale testing is always done. The intention is to integrate controlled startup of treatment at the TSD with the scheduled cNECDF.</p> <p>See comment 1 and 71.</p>
77.	<p>Specific Issues</p> <p>This section addresses specific issues raised by MC staff or that I see as being particularly important.</p>	
78.	<p><i>What are the risks of VXH itself?</i> First, the very high pH of VXH makes it caustic and harmful to humans and materials.</p>	<p>A detailed explanation of all the risks associated with VXH hydrolysate is provided in the PMATA information.</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>Second, it has a strong odor, particularly from thiolamine. Third, it is possible, at least in principle, that VX could be reformed if the pH were decreased below the 13 – 14 range used in hydrolysis. Most likely, reforming would require a deliberate act and would not be the result of a spill. Fourth, it is possible that VXH contains EA2192. Fifth, the organic layer in VXH is flammable. Therefore, the VXH must be kept sealed from the environment at all times.</p>	<p>entitled "What are the Hazards of Hydrolysis 2003b).</p> <p>Hydrolysate is primarily classified as a hazard due to its corrosive nature, that is, the high pH. The Data Sheet (MSDS) for caustic (NaOH) solution concentration from 0.8 to 8 percent by weight is classified as a hazard with a "Health Rating" of 2 (that is, "Reactivity Rating" of 1 (that is, Slight) and "Flammability Rating" of 3 (that is, Severe). Sodium Hydroxide (NaOH) is not the most significant component in hydrolysate; the second-most toxic constituent with a toxicity of 140 mg/kg (oral rat). Because of its relative concentration and toxicity, caustic corrosion is the most significant hazard associated with hydrolysate exposure (that is, by swallowing hydrolysate or contact hazards (that is, damage caused by hydrolysate) it corresponds to the greatest risk.</p> <p>The primary odor-causing compounds in hydrolysate are the thiolamines, which are routinely handled by TSDFs. A common method of odor control is a regenerative thermal oxidizer (RTO), which destroys odor-causing compounds in the biological pretreatment areas (Catalytic Products International, MEGTEC, 2003).</p> <p>There is no direct evidence that stabilizers are present in the hydrolysate or that VX forms in caustic solution (PMATA, 2003). The hydrolysate is maintained at a pH above 14 to eliminate the possibility of reforming.</p> <p>The NECDF reactor system is designed to control EA2192 concentration; it is expected that EA2192 concentration in hydrolysate will be less than 1 ppm; however, hydrolysate will be treated in the NECDF unless it is first verified that EA2192 concentration is above 20 ppm.</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
		The flammability hazard associated with hydrolysate at a 33 percent loading relates to the presence of an upper layer with a flashpoint of 127°F (53°C) by Pensky-Martens Closed-Cup Test Method. This is the temperature to which the liquid must be heated for the vapors from the liquid will ignite in the presence of an ignition source (for example, flame, spark, etc.). The flashpoint for 33 percent loading hydrolysate is 127°F. The upper layer corresponds to 3 to 5 percent (by volume) of the total hydrolysate. Under current expected operation conditions in which the hydrolysate is neutralized per hydrolysate batch, it is expected that the amount of upper layer will be decreased/eliminated, thereby decreasing the presence of the upper organic layer and the flammability of hydrolysate is expected to be reduced. The overall effect will be determined by testing.
79.	<i>Is the multi-step treatment process proposed by PFD scientifically sound?</i> Yes. The chemical, physical, and biological principles upon which the multi-step process is based are based on sound science, and the demonstration study provided a preliminary validation that they can work.	No comment.
80.	<i>Is the multi-step treatment process ready to be implemented at full scale?</i> No. While the scientific principles underlying the multi-step process are logical, it is new and unique. The demonstration testing did not answer key questions (listed above), and continuous operation under realistic operating conditions has not yet been addressed. Therefore, the multi-step process still should be considered an "experimental method."	Startup of the hydrolysate treatment system would ramp up slowly similar to the agent degradation at NECDF. The hydrolysate treatment will be monitored. See comment 1.
81.	<i>Will treatment of VXH increase the potential of odors from the PFD site?</i> Yes. VXH has a strong odor, mainly the "skunky" odor from thiolamine. Therefore, the greatest odor risk comes from handling the original VXH and from the first oxidation step. To ensure that "skunky" odors are not released, PFD must capture all gases and treat those gases successfully in the thermal oxidizer. Achieving this will require site	See comments 1 and 7 (#2).

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	improvements that are part of the plan for treating VXH, and the performance must be verified and monitored.	
82.	<i>Can the thiolamine odor be eliminated before VXH is shipped to PFD?</i> Yes, Parsons can perform the first oxidation step at Newport, IN. In addition to removing thiolamine odor, the first oxidation step makes it possible to lower the pH and decrease the flammability hazard.	The responders agree that this could result hazardous hydrolysate; however, the benefit of the pretreatment onsite has not been fully evaluated.
83.	<i>Can the Schedule 2 compounds be reformed when the oxidized VXH is mixed with other PFD wastewater or wastewater in the sewers?</i> No. Although the hydrolysis products of VX could, at least in principle, reform VX, the oxidation products from thiolamine, MPA, and EMPA should not combine with each other or other constituents to reform thiolamine, MPA, or EMPA. This is the case because oxidation reactions are <i>de facto</i> irreversible. The main risk is from unreacted EMPA and MPA that remains in the liquid effluent and in the produced solids.	No comment.
84.	<i>Will the solids generated by the proposed treatment of VXH create risks?</i> Yes. EMPA and MPA accumulate in the solids generated by chemical oxidation, and they could be leached under conditions related to a sanitary landfill. The risks associated with this situation are not well defined, but this issue deserved further investigation if significant amount of EMPA and MPA accumulate in the solids.	With respect to solid disposal and potential leachate, it is important to note that: (1) Over 90 percent of the overall MPA destroyed during chemical treatment (Dayton, 2003) (2) MPA and EMPA occur in the precipitated polymeric form, (Perma-Fix of Dayton communication) (3) Solids will be disposed of in a certified landfill where the leachate is contained (4) EMPA/MPA do not meet the requirements for landfill and are considered an environmental risk in terms of toxicants and would not have access to the environment (at levels that could pose a risk)
85.	<i>Is the thermal oxidizer reliable for control of odors and other volatile components?</i> Yes and No. In principle, the thermal oxidizer should be able to destroy odors and other volatile contaminants in the off-gases. The key steps are (1) that all	No comment See comments 1 and 7 (#2).

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>the off-gases are collected and sent to the thermal oxidizer, and (2) that the thermal oxidizer performs well at all times. Contemporary odor problems at PFD indicate that one or both of the steps is not being achieved now. This is an issue that requires attention and improvement before VXH treatment begins.</p>	
86.	<p><i>What concentrations of EMPA and MPA will be in the wastewater at the static screens and in the total wastewater flow at the Western Regional Wastewater Treatment Facility?</i> The demonstration results and typical flow rates can be used to make a preliminary estimate of the concentrations of EMPA and MPA in the different wastewater flows. I make the following assumptions about representative conditions.</p> <ul style="list-style-type: none"> • The EMPA and MPA concentrations in the effluent of the SBRs equal those achieved in the demonstration study: c. 340 and 800 mg/L of EMPA and MPA, respectively. • The flow rate of the SBR effluent is 35,000 gallons per day. • The flow rate at the Opossum Creek Pump Station and, hence, as the static screens, is 650,000 gallons per day (0.65 MGD). • The total wastewater flow rate at the treatment facility is 12 million gallons per day (MGD). 	No comment.
87.	<p><i>Will VXH treatment lead to odors at the Western Regional Wastewater Treatment Facility?</i> No. Except for thiolamine, the components of VXH and its treatment products are not highly volatile and should not have strong odors. The PFD-treated wastewater already has a characteristic odor at the treatment facility. The addition of oxidized VXH is not likely to have a major impact on odor.</p>	In addition, there will be no thiolamine in the demonstration results indicate that thiolamine non-detect in the oxidation step (Perma-Fix 2003).
88.	<p><i>Do aerosols formed at the head works of the Western Regional Wastewater Treatment Facility constitute a risk to</i></p>	MPA and EMPA do not create a risk to the personnel due to their low toxicity, as discussed.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p><i>operations personnel?</i> Yes. The demonstration study suggests that some MPA and EMPA will remain in the PDF effluent. While present at concentrations below the 0.1% certification level, the concentrations could be in the range of 100s of mg/L. The table shown above indicates that the EMPA and MPA concentrations at the static screens should be greater than 10 mg/L with the SBR-effluent concentrations produced in the demonstration study. Thus, aerosol exposure is possible. Because toxicological data suggest that intravenous or oral exposure is required for human health risk, aerosol exposure is not necessarily a significant risk. Nevertheless, this issue deserves further investigation if the actual EMPA and MPA concentrations are in the 100s of mg/L range achieved by the demonstration study.</p>	<p>information paper, entitled "What are the Hazards of Hydrolysate" (PMATA, 2003b).</p>
89.	<p><i>Will EMPA and MPA accumulate in the sludge at the Western Regional Wastewater Treatment Facility?</i> No. EMPA and MPA are not hydrophobic (Munroe et al., 1999), which suggests that they should not accumulate in the sludge. The results from biological treatment in the demonstration study are not conclusive, but the apparent lack of removal in biological treatment supports that sorption to sludge was not important. Biodegradation of MPA and EMPA is not well defined, but they could be biodegraded in activated sludge treatment, which would further minimize accumulation on sludge. In summary, MPA and EMPA should not accumulate in the sludge of the Western Regional Wastewater Treatment Facility.</p>	<p>No comment.</p>
90.	<p><i>Could EMPA and MPA pass through the Western Regional Wastewater Treatment Facility and create an ecotoxicity risk in the receiving water?</i> Yes. Biodegradation of MPA and EMPA is not well defined. The demonstration study showed no evidence of biodegradation during biotreatment at PFD, but this may or may not be relevant for the Western Regional Facility. If MPA and EMPA are not biodegraded, the effluent concentrations could be greater than or around 1 mg/L (see the table above). Little data are available on ecotoxicity of MPA and EMPA, but one study on EMPA (in Munro et al.,</p>	<p>This would pose a problem if the POTW could not control the salt content of the effluent. Shear dilution, and all other treatments control the salt content of the effluent. The document does not give Ames-test mutagenicity data for EMPA. The document indicates toxicity for EMPA is comparable to table salt (Williams et al., 1999).</p> <p>The ecotoxicity risk posed by EMPA and MPA in the receiving water is considered to be significant. PFD, Parsons and Company were willing to perform ecotoxicity studies if</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
	<p>1999) gave an Ames-test mutagenicity reference concentration of only 30 µg/m³, which equals 3x10⁻⁵ mg/L. Thus, the fate of EMPA and MPA at the Western Region Facility and ecotoxicity of the Western Regional Facility's effluent are issues that deserve further investigation if the actual EMPA and MPA concentrations from PFD are in the 100s of mg/L range. Ecotoxicity testing of treated VXH diluted with effluent from the Western Regional Wastewater Treatment Facility is warranted if EMPA and MPA concentrations are not reduced to well below the concentrations attained in the Demonstration Study.</p>	<p>Ohio Environmental Protection Agency. See comments 3 and 13.</p>
<p>91.</p>	<p><u>Recommendations</u></p> <p>Based on my review of the proposed VXH treatment plan, the treatment operation at PFD, and the demonstration study, I offer the following recommendations to MC.</p> <ol style="list-style-type: none"> 1. Parsons should carry out the first oxidation step in Newport, IN. The first step of oxidation removes thiolamine, which offers large benefits: (1) the odor potential is decreased greatly; (2) the potential to reform VX is eliminated, (3) the pH can be lowered, and (4) the flammability hazard is reduced. These benefits make the once-treated VXH much less obnoxious and dangerous during transport to and handling at PFD. The trade-off is that the volume of VXH to be transported will increase due to the addition of chemicals for oxidation and lowering the pH. In my judgment, the benefits far out-weight the costs. 	<p>Dr. Rittmann does not provide data to support that the first oxidation step should be carried out by Parsons, the Army, and its subcontractor via implementation of peroxide and acid addition through laboratory testing (Parsons/Alion, 2002) implementation requirements (Parsons, 2002). This investigation indicated that substantial time was required for implementation that was not just a schedule or by gains in general process safety advantages identified by Dr. Rittmann including and elimination of the possibility of VX form: both be effectively managed.</p> <p>Oxidation of the thiolamine will minimize hydrolysis; however, it will also tend to increase the volatility phase, which will increase difficulties in handling pretreatment to provide a material with easier handling (a single-phase, non-odorous, non-flammable, non-corrosive waste), would also require acid addition and therefore require more than twice the current number of trucks to be used in material transport. If the material is capable of safely handling and treating hydrolysis pretreatment, it is unclear if additional trucks are warranted.</p> <p>There is no direct evidence that formation of hydrolysate (PMATA, 2003a).</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additiona
92.	2. PFD should solve its current odor problems before it accepts any VXH for treatment. This includes working closely with RAPCA and providing documentation of the performance of the thermal-oxidation system.	See comments 1 and 7 (#2).
93.	<p>3. PFD should upgrade the monitoring and, perhaps, the performance of its SBR biological treatment system before accepting any VXH for treatment. In addition to the measurements taken now, upgraded monitoring should include the following measurements, which are not taken now:</p> <p><u>SBR Influent and Effluent</u> (grab samples at least 3 times per week) Total and soluble COD Total and soluble TOC Total and soluble TKN</p> <p><u>Effluent</u> (grab samples at least 3 times per week) NO₂-N VSS</p> <p><u>Computed Values</u> (three times at least three times per week; daily is preferable) Running $SRT = V \times MLSS / (Q^e \times VSS^e + Q^w \times VSS^w)$, where superscripts e and w refer to the effluent and the waste sludge</p> <p><u>Gas Phase</u> (grab samples three times per week) Volatile organics from the SBR off gas</p> <p><u>CBOD Testing</u> Evaluate PFD's CBOD₅ values against MC's values and other measures, such as COD and TOC. Carry out ultimate-CBOD evaluations of PFD wastewater to help diagnose whether or not a problem exists. Fix problems in CBOD₅ testing, if they are uncovered.</p>	No comment.

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additions)
94.	<p>4. PFD should conduct additional laboratory testing to supplement the recently completed Demonstration Study. Additional testing should answer these key questions:</p> <ul style="list-style-type: none"> • Were the Schedule 2 compounds (and EA2192, if present) removed in the expected steps and to the expected degrees? • Can the concentrations of the Schedule 2 compounds be reduced to far below the certification level by improved chemical treatment, biodegradation, or a combination? • Was biological treatment representative of what can be expected at full scale? • Can post-biological adsorption and filtration be operated reliably? • Will the treated VXH cause receiving-stream ecotoxicity when diluted into the wastewater of the Western Regional Wastewater Treatment Facility? 	<p>PFD intended to perform a secondary optim receipt of fresh stabilized hydrolysate from I this period, any questions that could not be analysis of all data collected during the first study would be addressed.</p> <p>Parsons and the Army would not ship, nor v receive, hydrolysate that was not demonstr non-detect for VX at an MMDL less than or</p> <p>See responses to comments 2 through 6.</p>
95.	<p>More documentation of the fate of the Schedule 2 compounds – along with other key components, such as EA2192, CBOD₅, ultimate CBOD, COD, TOC, phosphate, and organic and NH₃ nitrogen – at each step of treatment is necessary to ensure that the underlying foundation of the multi-step process is demonstrated. Ecotoxicity testing with treated VXH diluted into Western Regional effluent is warranted if MPA and EMPA concentrations are not reduced well below the concentrations achieved in the Demonstration Study.</p>	<p>Treatability studies are commonly done in tl management industry to determine whether be handled.</p> <p>PFD collected information describing the ex compounds destruction at each step of the process development phase of the demons^l is, prior to the certification period). The corr must be confirmed to be less than 20 parts before release from the NECDF. The PFD could only destroy residual EA2192. There^l need to monitor EA2192 at PFD.</p> <p>See comment 2.</p>

Comment	Dr. Rittmann Report	Evaluation (Continued) (Clarification/Corrections/Additiona
96.	<p>PFD should implement VXH treatment through a phased start up that has extensive monitoring and involves oversight by a team consisting of MC, RAPCA, and Ohio EPA. Monitoring should include waste solids and off-gases, as well as the liquid stream. The full-scale treatment system is roughly the size of a pilot plant used for testing new processes in normal water and wastewater treatment. Therefore, it may not be of great marginal value to conduct a pilot study at an intermediate size. Instead, the start up should be extensively monitored, and a contingency plan must be in place in case the system does not perform satisfactorily.</p>	<p>Agree. Controlled startup at PFD would be controlled startup at the NECDF.</p> <p>See comment 1.</p>

APPENDIX B
ACRONYMS/ABBREVIATIONS

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ACRONYMS/ABBREVIATIONS

BOD	biochemical oxygen demand
CBOD	carbonaceous biochemical oxygen demand
COD	chemical oxygen demand
DCC	dicyclohexylcarbodiimide
DIC	diisopropylcarbodiimide
EA	Edgewood Arsenal
EA2192	S-(2-diisopropylaminoethyl) methylphosphonothioic acid
EMPA	ethyl methylphosphonic acid
EPA	Environmental Protection Agency
HRT	hydraulic residence time
Hydrolysate	VX caustic hydrolysate
IMPA	isopropyl methyl phosphonic acid
MC	Montgomery County
MDL	Method Detection Limit
mg/kg	milligrams per kilogram
mg/L	milligrams per liter
MGD	million gallons per day
MLSS	mixed liquor suspended solids
MLVSS	mixed liquor volatile suspended solids
MPA	methylphosphonic acid
MSDS	Material Safety Data Sheet

NaOH	sodium hydroxide
NECD	Newport Chemical Depot
NECDF	Newport Chemical Agent Disposal Facility
PFD	Perma-Fix of Dayton, Inc.
PMATA	Project Manager for Alternative Technologies and Approaches
POTW	publicly-owned treatment works
ppb	parts per billion
ppm	parts per million
RAPCA	Regional Air Pollution Control Agency
RTO	regenerative thermal oxidizer
SBR	sequencing batch reactor
SCBA	self-contained breathing apparatus
SCWO	supercritical waer oxidation
SRT	solids retention time
SS	suspended solid
SVI	Sludge Volume Index
TOC	total organic carbon
TSDF	treatment, storage, and disposal facility
VCH	VX Caustic Hydrolysate
VX	nerve agent, O-ethyl S-(2-diisopropylaminoethyl)methylphosphonothioate
VXH	hydrolysate produced by chemical destruction of the nerve agent VX

APPENDIX C
REFERENCES

APPENDIX C REFERENCES

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