Degradation of Chemical Warfare Agents in Potable Waters

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Background

- **Study is being conducted in support of the Joint Chemical Biological Radiological Agent Water Monitor (JCBRAWM) Program.**
  - **Overall objective of JCBRAWM is to determine the best way to protect military against contaminated water supplies: new detectors, new procedures, etc.**
  - **Information on fate of CWA's in potable waters is very limited.**
  - **This effort was not intended to be a mechanistic study.**
- **Current focus is on three CW agents: GD, HD and VX.**
- **Preliminary experiments conducted with EA 2192, a toxic hydrolysis product of VX.**

Water Matrices

- **High purity water (HPW) meeting standard for ASTM Type II reagent water.**
- **Synthetic source water (SSW) prepared with HPW using an established recipe. Represents a potential source water for fielded troops.**
- **Chlorinated water (CLW) prepared with HPW representing a finished drinking water for fielded troops. Initial disinfection level is 1-3 mg/L free residual chlorine.**
- **Brominated water (BRW) prepared with HPW representing a finished drinking water for fielded troops. Initial disinfection level is 1-3 mg/L free residual bromine.**

Representative batches of each test matrix have been characterized.

Reaction Conditions

- **Reactions conducted in a 2-liter jacketed reactor with temperature maintained by use of a re-circulating heater/chiller.**
- **Reactions conducted at 5 to 45 ° C.**
- **Neat high purity agent added to 1.5 L of water matrix to achieve initial concentrations of 1 to 10 mg/L for GD, 5 to 50 mg/L for HD and 0.25 to 2 mg/L for VX.**

Analytical Protocols

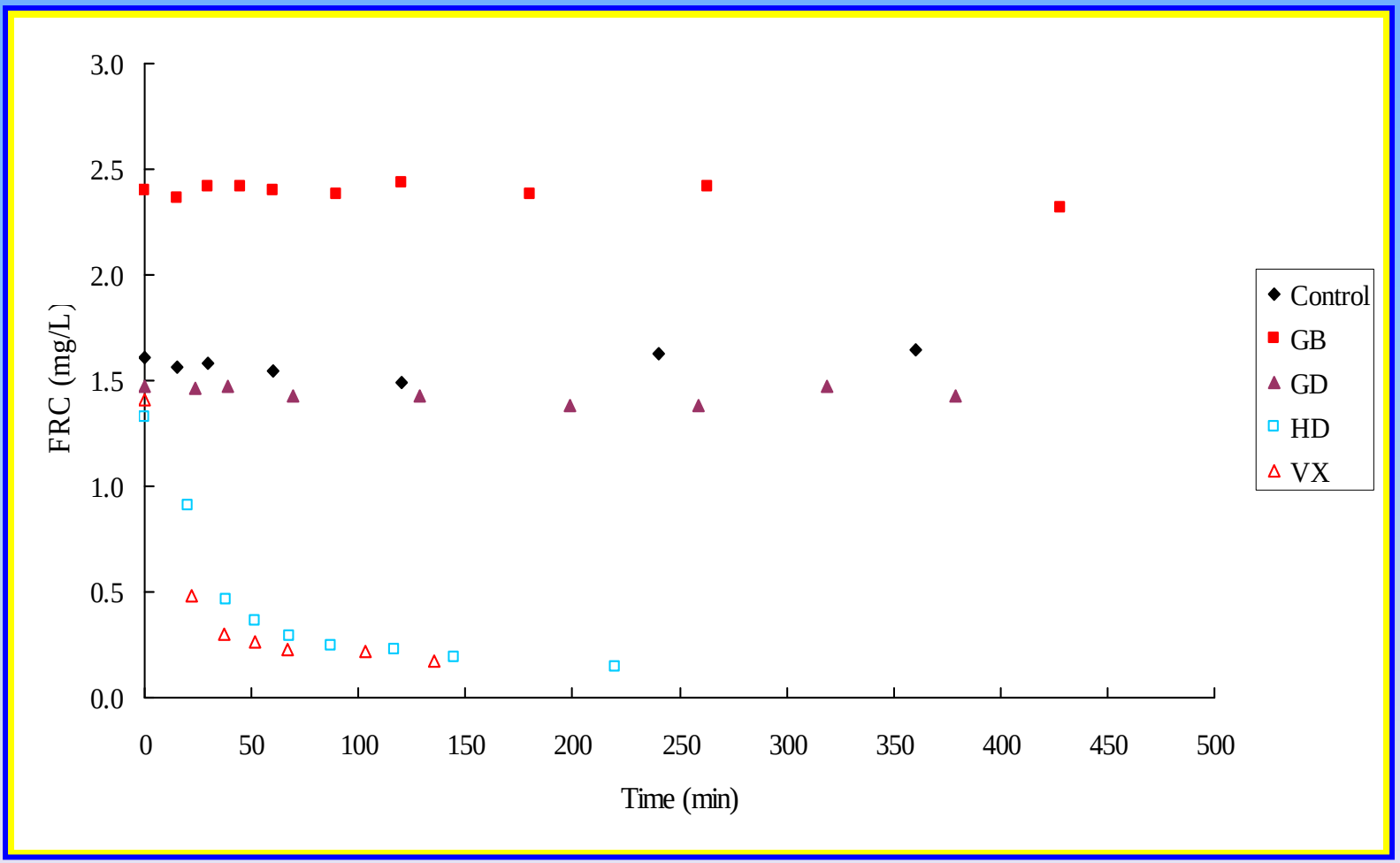
- **Time point samples removed from reactor starting 15 minutes after agent added. Samples for residual agent immediately quenched/extracted and analysis started within 2 hours.**
- **Time point samples also analyzed for pH, FRC, TRC, FRB and TRB. Minimal sample volume (10 mL) removed at each time point.**
- **Residual GD and HD determined by GC/MSD. Only residual agent determined.**
- **Samples from VX runs analyzed by LC/MS. Determining VX, EA2192, EMPA, MPA and diisopropylaminoethyl sulfonic acid.**

Isotopically-labelled GD, VX, EMPA and MPA used as internal standards.

GD Results

- **Results of reactions with HPW consistent with literature values.**
- **Results of reactions with CLW and BRW conflict with accepted field practice and previous literature.**
  - **Disinfection with chlorine and bromine not effective against GD.**
  - **Previous study conducted in 1950's with GB concluded chlorinated water was effective and hypochlorite ion acted as a catalyst. $t_{1/2}$ of GB = 0.5 hr.**
  - **Review of original 1950's lab notebook revealed phosphate buffer was used in the experiments.**
- **Loss of GD is approximately 20 times faster in SSW than in HPW.**
  - **Most likely due to interaction with phosphate, forming a mixed pyrophosphate/phosphonate intermediate.**
  - **In a 1986 study comparing HPW and 7 natural waters it was concluded the rate of GD hydrolysis was the same in all the waters. However, all waters were adjusted to pH 7.00. Currently tracking down notebooks to determine if phosphate buffer was used.**

Free Residual Chlorine



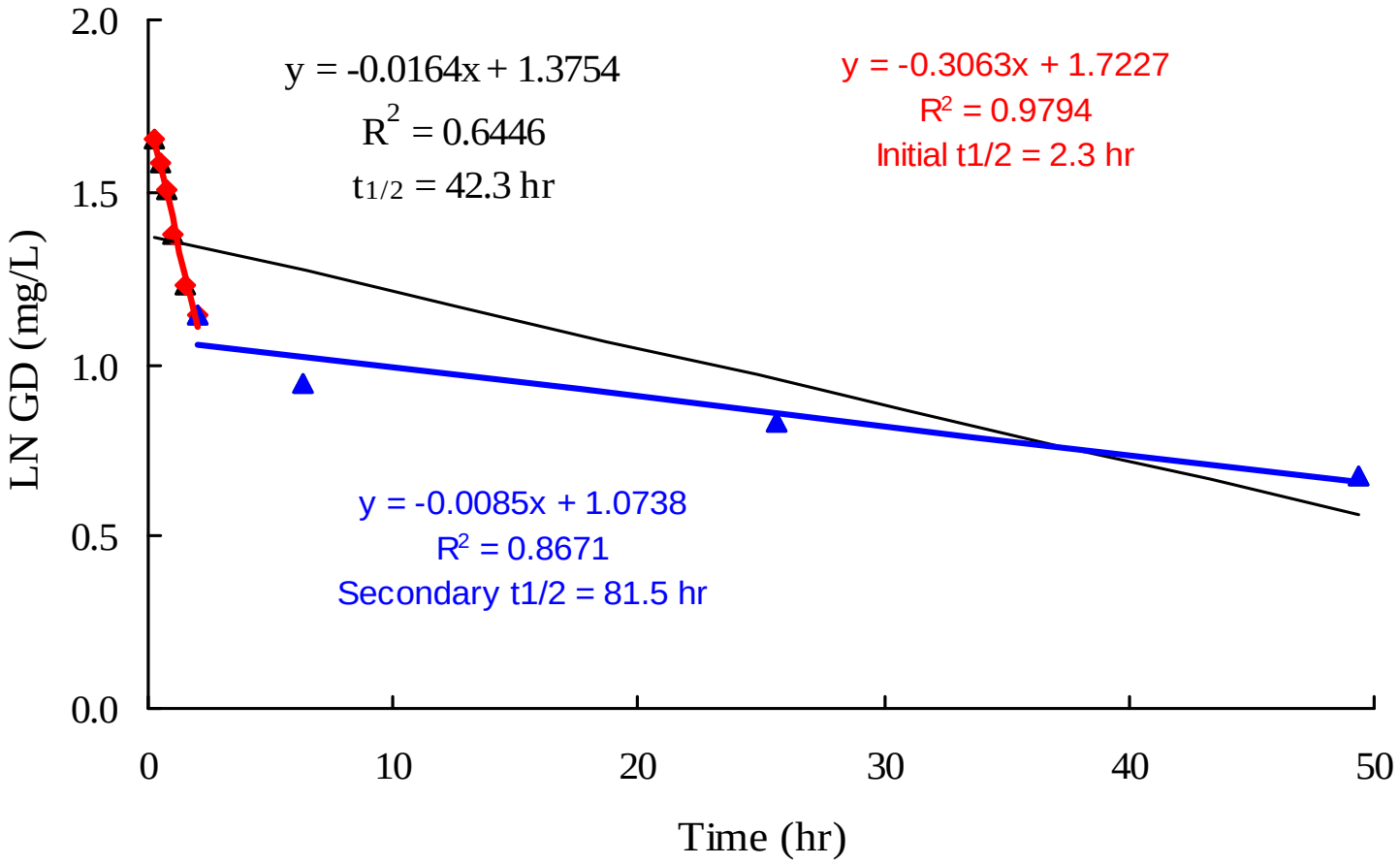
Stability of CLW exposed to various agents

Half-Life Summary for GD

Sample	Overall Average Half-Life (hr)		
Matrix	5 °C	25 °C	45 °C
HPW	Stable No change after 14 days	333	39.2
SSW	1,160	18.9	1.68
CLW	Stable No change after 14 days	314	Initial: 2.3 Secondary: 39.6
BRW	Stable No change after 14 days	292	Initial: 2.3 Secondary: 81.5

Half-lives calculated using a first order model.

Example of Bi-Phasic Behavior



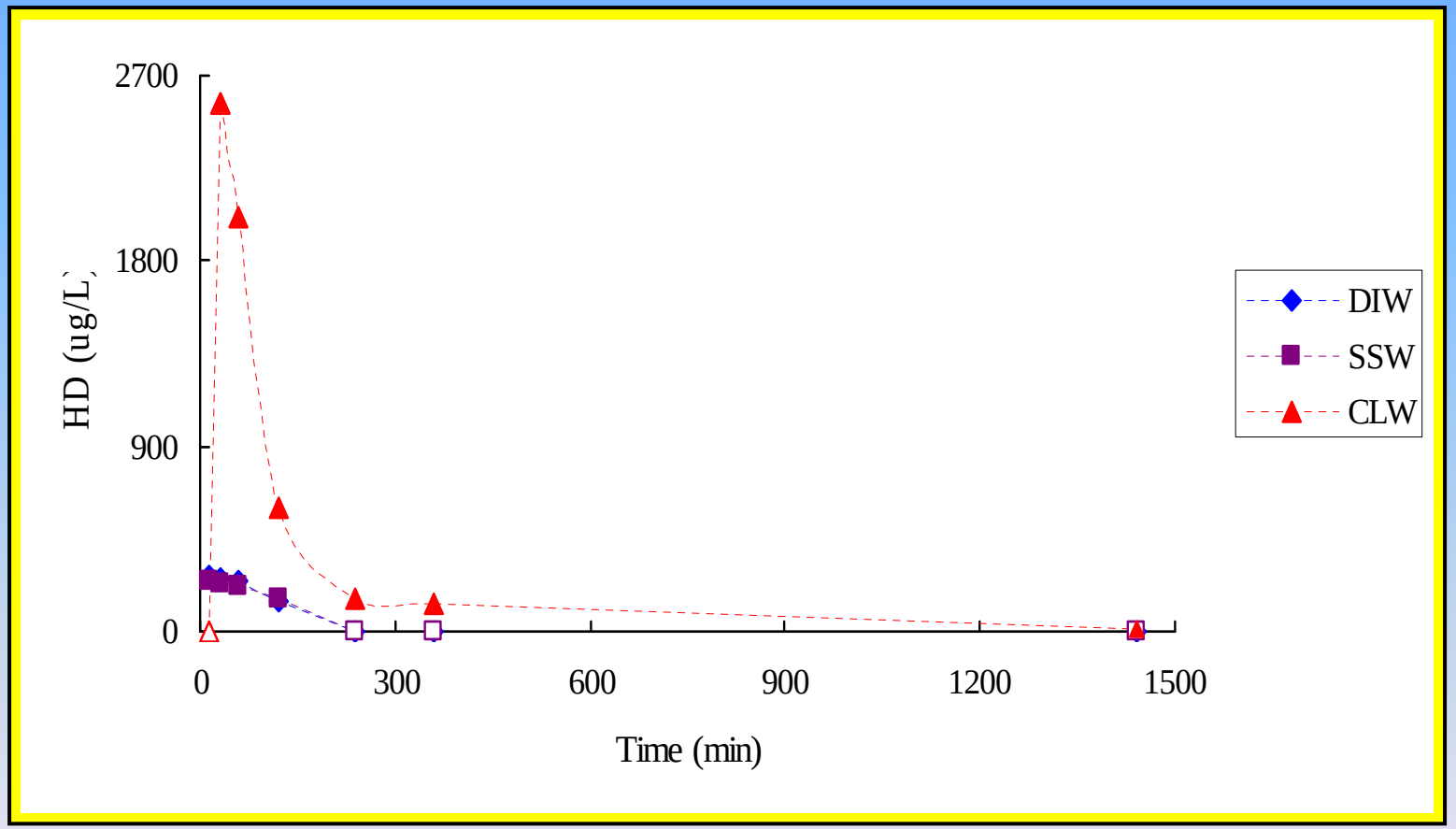
GD in BRW at 45 °C

HD Results

- **HD reactor experiments have been completed.**
  - **Data review and reduction is in progress.**
  - **Results obtained in HPW and SSW at 25 °C generally agrees with literature values when dissolution of HD is taken into account.**
- **Data obtained in SSW shows an increase of half-life with increasing temperature.**
  - **During these experiments the HD globules became increasingly opaque as the temperature increased.**
  - **It appears the elevated temperature accelerated the formation of a "crust", which protected the mustard from hydrolysis.**

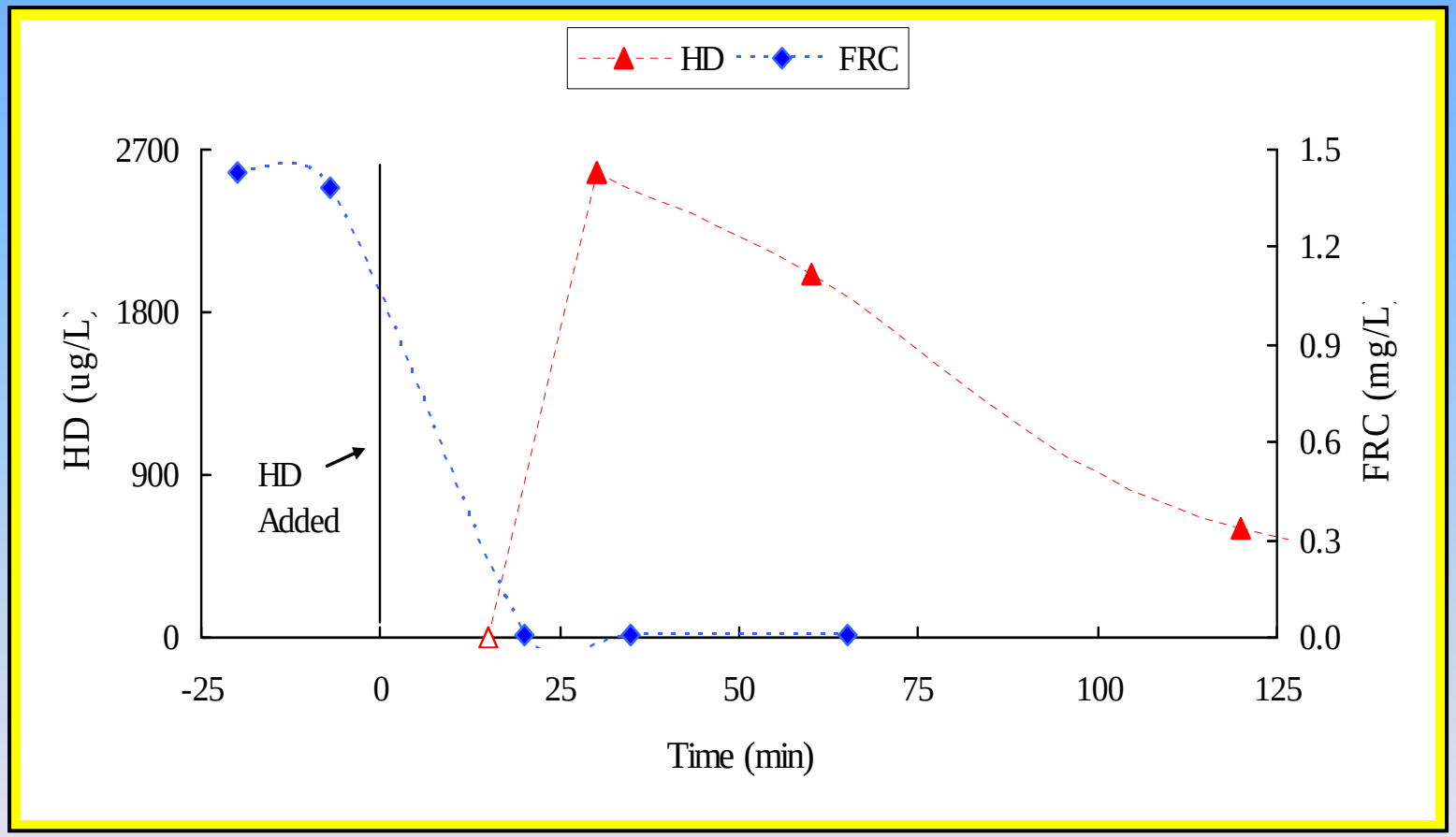
Low solubility of HD a complicating factor in the experiments.

Comparison of HD Degradation



All reactions @ 25 °C

Comparison of HD and FRC



Similar results obtained in BRW.

Half-Life Summary for HD

Sample	Overall Average Half-Life (min)		
Matrix	25 °C	35 °C	45 °C
HPW	119	NA	NA
SSW	154	243	800

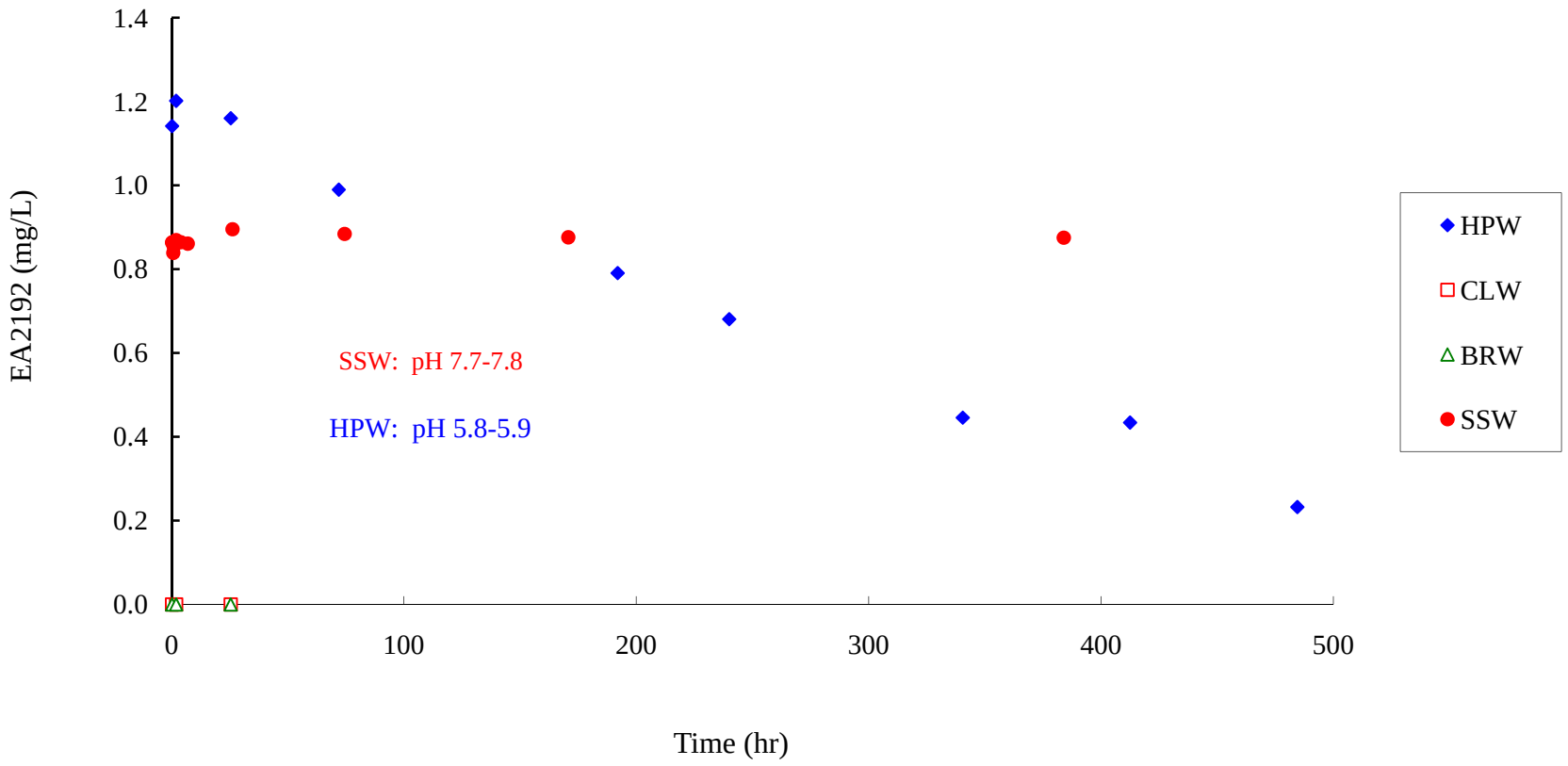
Data review and reduction is in progress for other sample matrices

Half-lives calculated using a first order model.

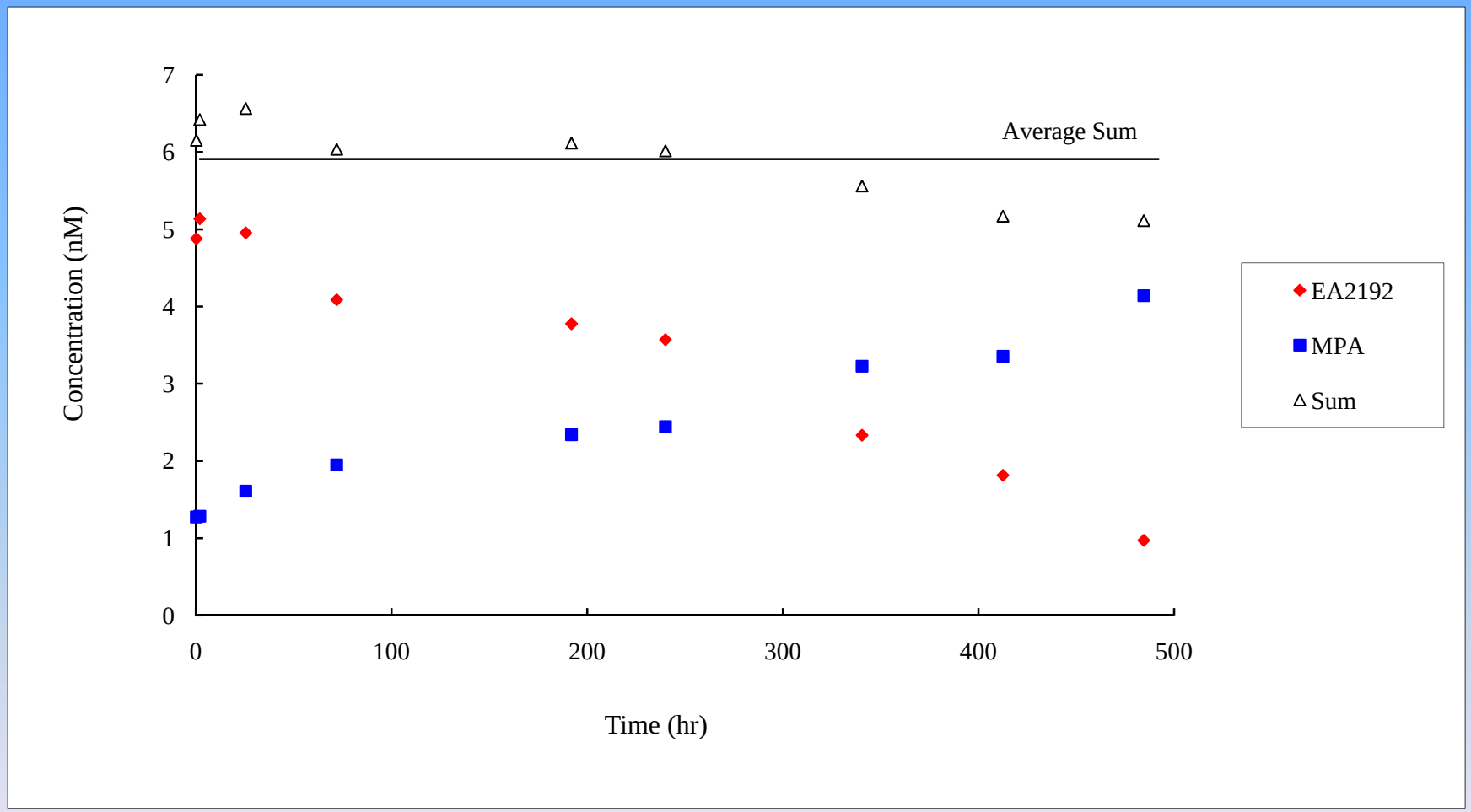
EA2192 and VX Results

- **Conducted a single reaction of EA2192 in each test matrix at 25 °C and 1 mg/L initial EA2192 concentration.**
  - **EA2192 stable in SSW.**
  - **EA2192 hydrolyzed in HPW.**
  - **EA2192 was rapidly removed in both CLW and BRW.**
- **VX runs are in progress.**
  - **VX stable in HPW**
  - **VX hydrolyzes in SSW; half-life consistent with literature values.**
  - **VX degrades in CLW and BRW, but at a slower rate than EA2192**

Stability of EA2192 at 25 °C

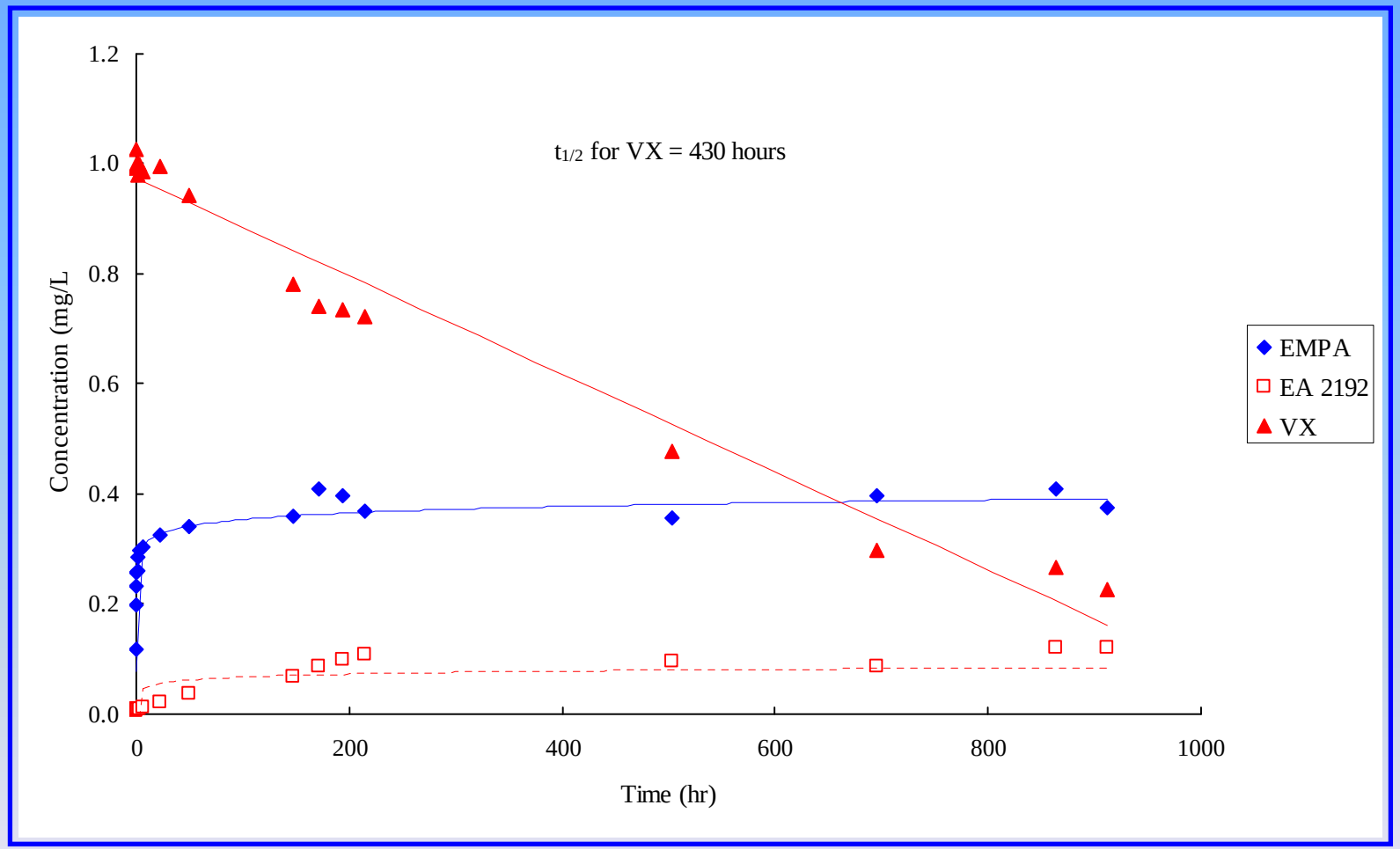


Reasonable Mass Balance



EA 2192 in HPW at 25 °C

VX in SSW@ 25 °C



Study went for 38 days before being terminated

Half-Life Data @ 25 ºC

Water Type	Overall Average Half-Life (hr)	
	VX	EA 2192
HPW	Stable No change after 22 days, pH = 5.8 - 5.9	282 20 day experiment; MPA produced
SSW	430 38 day experiment; EA2192 produced	Stable No change after 16 days; pH = 7.7-7.8
BRW	1.89 Sulfonic acid, EMPA and MPA produced	<<< 0.25 Sulfonic acid and MPA produced
CLW	32.9 Sulfonic acid, EMPA and MPA produced	<<< 0.25 Sulfonic acid and MPA produced

All experiments 1 mg/L initial concentration.

Potential Disinfection Byproducts

- **Reactions with higher concentrations of agent and disinfection agent conducted at 25 °C for 24 hours.**
  - **Molar ratio of agent and disinfection agent approximate those used in low level experiments.**
  - **Samples extracted and extracts analyzed by GC/AED and GC/MSD.**
  - **^{13}C-HD used to also conduct NMR experiments.**
- **GD Reactions:**
  - **No detectable disinfection by-products containing bromine.**
  - **Two unidentified disinfection by-products containing chlorine.**
  - **Emission spectra confirm presence of chlorine in each chemical.**
  - **Using dimensional analysis (1 chlorine/MW = 220), concentration of each chemical estimated to be 20 µg/L.**

Potential Disinfection Byproducts

- **HD Reactions:**
  - **10 trace level unidentified chlorine containing disinfection by-products.**
  - **6 trace level unidentified bromine containing disinfection by-products.**
  - **Significant by-product tentatively identified as monochlorinated mustard sulfoxide based on GC/MSD and NMR spectra.**
  - **Efforts continue to identify disinfection by-products.**
- **Bulk HD Reaction Products by NMR:**
  - **HPW and SSW – thiodiglycol**
  - **BRW – thiodiglycol and mustard sulfoxide**
  - **CLW – thiodiglycol, mustard sulfoxide and monochlorinated mustard sulfoxide (tentative ID).**

Experiments with VX will be conducted in the near future.

Issues

- **GD Reactions:**
  - **Efficacy of current disinfection protocols against GD and other G-class agents should be investigated.**
  - **Stability and toxicity of disinfection by-products should be evaluated.**
  - **How stable is the mixed pyro intermediate and what is the toxicity?**
  - **Taking a closer look at the GD data to determine if wall affects (sorption) are causing accelerated loss of GD from solution.**
- **HD Reactions:**
  - **Stability and toxicity of reaction products and disinfection by-products.**
- **General:**
  - **Influence of suspended solids and MOC of water distribution systems has not been evaluated.**
  - **Can agent sorbed to these materials be released?**
  - **Can sensors be developed which monitor hazard (i.e., sentinel monitor) instead of targeting a specific analyte?**

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Questions?