

**Title:** The Application of the Centers for Disease Control and Prevention (CDC) Recommended Airborne Exposure Limits (AELs) by the United States Army Chemical Materials Agency (CMA)

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**Background:**

The U.S. Department of Defense (DoD) is in the process of destroying the U.S. stockpile of chemical warfare agents (CWAs) in accordance with international treaty and Public Law 99-145 (50 U.S.C. 1521). The U.S. Department of Health and Human Services (DHHS) reviews DoD plans for disposing these munitions and makes recommendations to protect human health as mandated in Public Law 91-121 and Public Law 91-441. The DHHS/Centers for Disease Control and Prevention (CDC) originally recommended airborne exposure limit (AEL) criteria in 1988. CDC recommended revised airborne exposure limits using updated risk-assessment approaches for nerve agents tabun (GA or ethyl N, N-dimethylphosphoroamidocyanidate, CAS 77-81-6), sarin (GB or O-isopropylmethylphosphonofluoridate, CAS 107-44-8), and VX (O-ethyl-S-(2-diisopropylaminoethyl)-methylphosphonothiolate, CAS 50782-69-9) published in the United States Federal Register in October 2003 for implementation by January 1, 2005. DHHS/CDC then developed interim-AELs recommended for sulfur mustard (HD or bis (2-chloroethylsulfide, CAS 505-60-2)) published in the U.S. Federal Register in May 2004 for implementation by July 1, 2005. Table 1 lists the 2005 U.S. Federal Register values and the original 1998 values in italics.

**Table 1: CDC-Recommended Airborne Exposure Limits (AELs)**

| Agent                       |      | General Population Limit (GPL) | Worker Population Limit (WPL) | Short-Term Exposure Limit (STEL) | Immediately Dangerous to Life or Health (IDLH) |
|-----------------------------|------|--------------------------------|-------------------------------|----------------------------------|--|
| GA, GB (mg/m <sup>3</sup> ) | 2005 | 0.000001                       | 0.00003                       | 0.0001                           | 0.1  |
|                             | 1998 | <i>0.000003</i>                | <i>0.0001</i>                 | <i>none</i>                      | <i>0.2 - Army<sup>†</sup></i>                  |
| VX (mg/m <sup>3</sup> )     | 2005 | 0.0000006                      | 0.000001                      | 0.00001                          | 0.003  |
|                             | 1998 | <i>0.000003</i>                | <i>0.00001</i>                | <i>none</i>                      | <i>0.02 - Army<sup>†</sup></i>                 |
| H, HD (mg/m <sup>3</sup> )  | 2005 | 0.00002                        | 0.0004                        | 0.003                            | 0.7  |
|                             | 1998 | <i>0.0001</i>                  | <i>0.003</i>                  | <i>none</i>                      | <i>none</i>                                    |
| Averaging Time              | 2005 | 24-hours                       | 8-hours                       | 15-minutes                       | ≤ 30-min.                                      |
|                             | 1998 | <i>72-hours</i>                | <i>8-hours</i>                | <i>none</i>                      | <i>≤ 30-min.</i>                               |

<sup>†</sup>Value established by U.S. Army

**US Army Chemical Materials Agency (CMA) Implementation of AELs**

CMA incorporated the recommended AELs in programmatic plans in June 2004 for implementation by CDC's recommended dates. The new AELs were applied to CWA-stockpile disposal facilities.

Monitoring in process support areas, where unmasked workers will be present is performed at the STEL/WPL level. This assessment reviews the STEL and WPL levels due to their significance in protecting public health.

### **Monitoring Technology**

Monitors use gas chromatography (GC) to differentiate the agent of interest from other chemicals in the background environment. Due to the low volatility of VX, it typically cannot travel long distances through sample lines and has difficulty transporting through the monitors. For ease of analysis, VX is typically converted (derivatized) to the more-volatile G-analog (ethyl GB or O-ethylmethylphosphonofluoridate) using in-line silver fluoride pads. The G-analog conversion product is then analyzed and reported as VX. STEL and IDLH levels can be monitored using near-real-time (NRT) monitors capable of sampling, analysis, and reporting continuously in cycles of fifteen minutes or less. These monitors include the Automatic Continuous Air Monitoring System (ACAMS) using flame-photometric detection (FPD) and MINICAMS<sup>®</sup> capable of using one of several detectors including the FPD and halogen selective detector (XSD).

Due to the lower concentrations, monitoring at the WPL and GPL levels are generally performed using historical methods. This is accomplished by long-term collection of air samples on solid sorbent tubes which are analyzed in the facility laboratory using GC-FPD or GC-mass selective detection (MSD). Unlike NRT monitoring, results from historical monitoring are not known until the laboratory analyses are complete.

### **Quality Assurance**

CMA's quality assurance plan includes testing of the monitoring system using reference standards of CWA. Quantitative methods must pass an initial precision and accuracy validation using a range of concentrations bracketing the monitoring level. After passing initial validation, on-going validation is performed through testing at 100% of the monitoring level.

During quality control (QC) activities, such as validation testing, technicians must inject the same mass of CWA-standard as would be collected if the instrument were sampling air containing agent at 100% of the monitoring level. NRT monitors are tested through injection of the standard into the instrument. Historical monitors are tested by spiking CWA-standard onto the sampling media in the laboratory prior to sample aspiration. The spiked sample media is then placed at the sampling station for a full aspiration cycle to ensure representativeness, and then analyzed at the laboratory. It should be noted that air being sampled is drawn to the instruments through sampling tubes; sample line testing is generally performed as separate function from continuous validation and has not been considered in this analysis.

CDC's recommendations in the U.S. Federal Register stated that reduction factors in action/response level, due to statistical assurance, were not necessary if sampling and analysis methods are within +/-25% of the true concentration 95% of the time. CMA's monitoring plan has included these criteria as a goal. If a method can not achieve this goal, protective monitoring can be performed by reducing the action/response level; however, setting the threshold too low also makes the method subject to interfering chemicals resulting in false-positive readings. CMA typically set's the alarm level of their NRT monitors from seventy to fifty percent of the actual value.

### Methods and Procedures:

To compare instrument performance with CDC quality criteria recommendations described in the U.S. Federal Register, QC data from continuous method validation were analyzed to determine the percentages of QC results within the U.S. Federal Register quality control limits of +/-25% of the WPL. All quality control data was provided by through CMA. Note that this study represents analysis of quality control data and are not AEL excursions.

The scope of the study included the six CWA disposal facilities operating during or after AEL implementation: The Aberdeen Chemical Agent Disposal Facility (TOCDF), The Anniston Chemical Agent Disposal Facility (TOCDF), The Newport Chemical Agent Disposal Facility (TOCDF), The Pine Bluff Chemical Agent Disposal Facility (TOCDF), The Tooele Chemical Agent Disposal Facility (TOCDF), and The Umatilla Chemical Agent Disposal Facility (TOCDF).

CWA-disposal facilities typically operate in a series of CWA-disposal campaigns, where all munitions filled with one CWA are processed, the facility undergoes decontamination, and CWA-monitors are configured for the next CWA. For example, TOCDF destroyed all GB-filled munitions between August 1996 and March 2002, VX-filled munitions between March 2003 and June 2005, and began destroying HD-filled munitions in August 2006. For this study, the time frame for each facility and CWA-disposal campaign began with the implementation of nerve or mustard CWA AELs or beginning of a CWA-disposal campaign, continued during the campaign, and ended at the campaign completion or facility closure.

**Table 2: Percentage of QC Recoveries within +/-25% of AEL Target Value**  
**Bold values are at-or-above CDC-Recommended QC criteria of 95%**

| <b>Campaign and Facility</b> | <b>Start</b> | <b>End</b> | <b>Days</b> | <b>STEL</b> | <b>WPL</b> |
|------------------------------|--------------|------------|-------------|-------------|------------|
| GB ANCDF                     | 1-Jan-05     | 2-Mar-06   | 425         | <b>96%</b>  | 82%        |
| GB PBCDF                     | 4-Mar-05     | 31-Dec-06  | 667         | 93%         | <b>98%</b> |
| GB UMCDF                     | 1-Jan-05     | 31-Dec-06  | 729         | <b>96%</b>  | <b>98%</b> |
| HD ABCDF                     | 1-Jul-05     | 27-Jan-06  | 210         | 94%         | 79%        |
| HD TOCDF                     | 18-Aug-06    | 31-Dec-06  | 135         | <b>96%</b>  | <b>97%</b> |
| VX ANCDF                     | 23-Jul-06    | 31-Dec-06  | 161         | 84%         | 73%        |
| VX NECDF                     | 1-May-05     | 31-Dec-06  | 609         | <b>95%</b>  | 90%        |
| VX TOCDF                     | 1-Jan-05     | 3-Jun-05   | 153         | 92%         | 76%        |

### Results and Discussion

For each CWA-disposal campaign and facility, Table 2 summarizes the percentage of QC-test results meeting CDC-recommended QC criteria. The summary is intended to display overall performance; performance at individual stations may be better-or-worse than the overall value. Instances where 95% or more QC-test results are within +/-25% of the AEL target value are in bold. Instances where QC criteria are not met do not indicate that methods are ineffective, but do indicate that reduction of the action/response level is necessary. Since sampling is performed as a separate

procedure, the data can suggest meeting the CDC quality standards, but are not conclusive.

One might expect that facilities which have had CWA-disposal campaigns for longer durations to show greater performance than facilities with shorter durations, such as GB-WPL, but this does not correlate for all AELs. One explanation for site-to-site differences is that differences in environmental-background chemicals may cause chromatographic interference or degradation with the target CWA; therefore, methods that are effective for one site may not be transferable to others.

### **Conclusion and Implications for Further Research**

In 2005 CDC recommended revised AELs based on risk assessment approaches developed since the original 1988 AELs. CWA disposal facilities incorporated the new values in their monitoring plans. The revised AELs required revised air-monitoring methods due to the reduced concentrations and durations. The QC data collected since implementation of the new AELs suggest that performance goals are attainable for GB/HD/VX STEL and GB/HD WPL methods.

QC performance for the entire monitoring system must include transmission from the sample point to the instrument as well as instrument performance. Future research can incorporate sample line transmission test results with instrument performance.

### **References:**

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All data provided by U.S. Army Chemical Materials Agency, Aberdeen Proving Ground, Maryland.