Near-Real-Time Air Monitoring for Chemical Warfare Agents in the Destruction of Chemical Munitions

(at the Tooele Chemical Agent Destruction Facility, Deseret Chemical Depot, Utah)

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National Environmental Monitoring Conference

Seattle, Washington August 18, 2011

Outline

- Introduction
- Chemical operations conducted at TOCDF
- Means of protecting workers, the general public, and the environment
- Roles of chemical agent monitoring at TOCDF
- Regulatory controls and airborne exposure limits (AELs)
- Near real-time (NRT) monitoring system used at TOCDF (ACAMS)
- QA/QC requirements for NRT monitoring systems used at TOCDF
- Monitoring data summary (alarms, trending, continuous improvement)
- Summary

U.S. Stockpile of Chemical Weapons

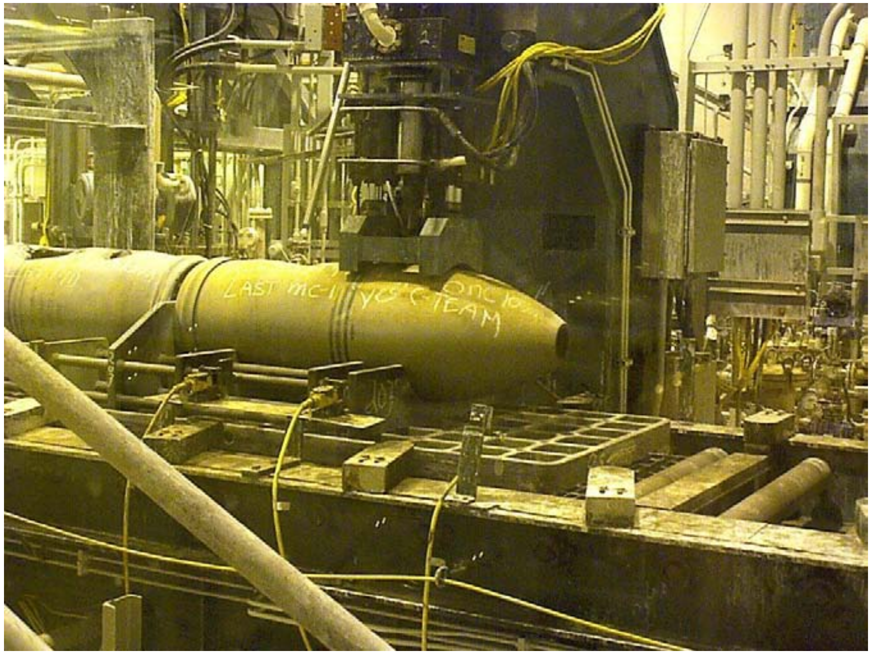
- In 1994, the US stockpile of chemical weapons was formally declared in response to the U.S. signing the Chemical Weapons Convention in 1993.
- The stockpile consisted of a total of 31,000 tons of sarin (GB), mustard (HD), and agent VX and small quantities of Lewisite (L) and tabun (GA).
- Agent destruction operations began at the Tooele Chemical Agent Destruction Facility (TOCDF, Deseret Chemical Depot, Utah) in 1996.
- More than 1.3 million munitions and more than 13,600 tons of chemical agent (GB, VX, and HD) have now been destroyed at TOCDF.

Examples of Operations Conducted at TOCDF

Storage Igloos and TOCDF

Transport of VX-Filled M55 Rockets

Examples of Operations Conducted at TOCDF



Accessing Agent in a Projectile

Incineration of Liquid Agent

Examples of Operations Conducted at TOCDF

Waste from the Deactivation Furnace Used to Destroy Energetics

Projectiles Removed from the Metal Parts Furnace

Examples of Operations Conducted at TOCDF

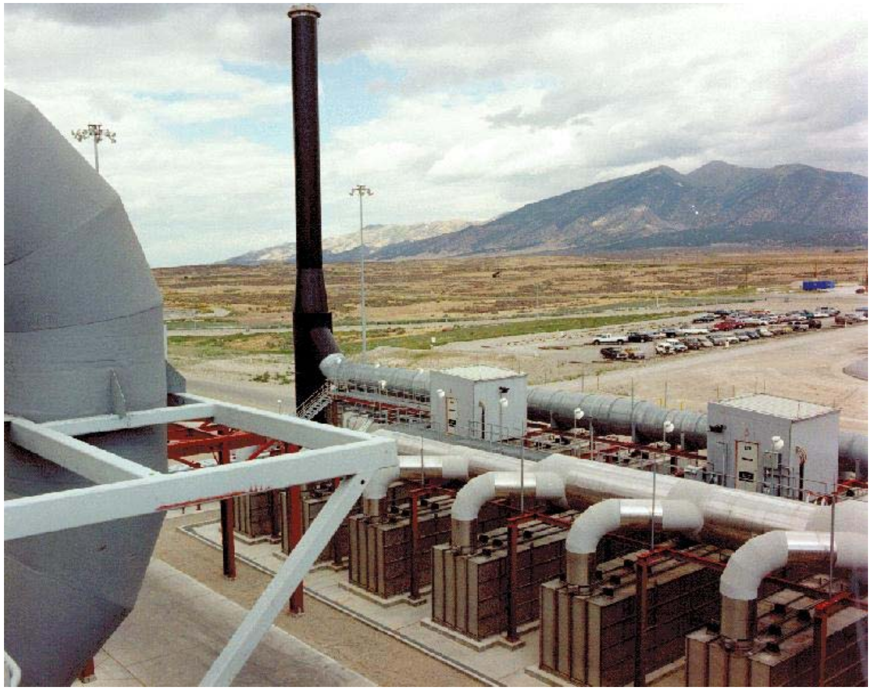
Ton Container on a Conveyer

Decontamination of Secondary Waste

Examples of Operations Conducted at TOCDF

Pollution Abatement System

Charcoal Filtration System

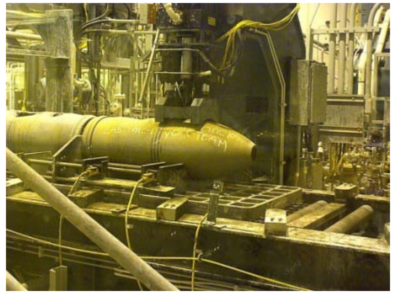


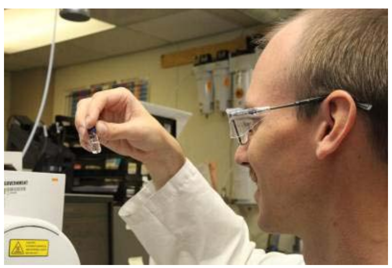
Examples of Operations Conducted at TOCDF

Entries for Maintenance/Repair

Monitoring Waste in a Drum

Activities requiring the protection of workers, the general public, and the environment.





Primary Means of Protecting Workers, the General Public, and the Environment at TOCDF

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- Agent containment within "engineering controls" (e.g., cascaded, negative-pressure ventilation systems)
- Charcoal filtration and other pollution abatement systems
- Fail-safe systems, interlocks, sensors, seals, etc.
- Hazardous risk assessments and effective quality controls
- Plans and SOPs to guide all plant operations or processes
- Active monitoring of systems and processes by well-trained, engaged, and empowered personnel—"corporate" culture
- Availability of suitable personal protective equipment (PPE)
- Well-exercised emergency response plans
- Effective corrective and preventive action programs
- Aggressive preventive maintenance
- Strong site supervision and management (URS and Battelle)
- Technical and management oversight by off-site "corporate" (Government, URS and Battelle)
- Local site management by the Chemical Materials Agency (CMA)
- Oversight by outside agencies (CMA in Maryland, CDC in Atlanta, Utah DEQ, etc.)

Primary Roles of Chemical Agent Monitoring at TOCDF*

- **<u>To detect chemical agent and sound an alarm</u> if concentrations greater than the applicable airborne exposure limit are reported as the result of the failure of a system, operation, or process**

- **<u>To provide an early warning of a problem</u> that may result in the detection of agent outside engineering controls before the applicable airborne exposure limit is exceeded (by the use of monitoring trends)**

- **<u>To ensure the use of appropriate PPE</u> (personal protective equipment) for the area in which workers will be located (based on monitoring conducted prior to entry)**

***Also ensures that site personnel will be able to take appropriate actions immediately, in the event of the detection of agent to ensure the protection of workers, the general public, and the environment.**

Other Roles of Chemical Agent Monitoring at TOCDF

- To ensure the immediate evacuation of an area in which workers are located in the event that the agent concentration increases to a level greater than appropriate for the PPE in use

- To verify the decontamination of personnel in PPE, equipment, and other items before removal from engineering controls (by monitoring in airlocks)

- To ensure the effectiveness of processes (e.g., by monitoring at the discharge airlock of the metal parts furnace, at the midbeds of charcoal filters, and at incinerator stacks)

- To verify the decontamination of waste intended for disposal off-site (through the use of headspace monitoring)

- **To provide a record that documents the absence of chemical agent outside engineering controls**

- **To confirm/refute the presence of agent reported by automated or manual monitoring systems**

Primary Guidance for Monitoring for Airborne Concentrations of Chemical Agents

Centers for Disease Control and Prevention

- Final recommendations for protecting human health from potential adverse effects of exposure to agents GA (tabun), GB (sarin), and VX. Federal Register, 2003, 68(196): 58348−58351.
- Interim recommendations for airborne exposure limits for chemical warfare agents H and HD (sulfur mustard). Federal Register, 2004, 69(85): 24164−24168.

US Army Chemical Materials Agency

- Programmatic Monitoring Concept Plan (MCP), 2004
- Programmatic Laboratory and Monitoring Quality Assurance Plan (LMQAP), 2008

Representative Airborne Exposure Limits

- **General Population Limit (GPL)**
  – a 24-hour time-weighted average

- **Worker Population Limit (WPL)**
  – an 8-hour time-weighted average

- **Short-Term Exposure Limit (STEL)**
  – a 15-min time-weighted average

Representative Airborne Exposure Limits

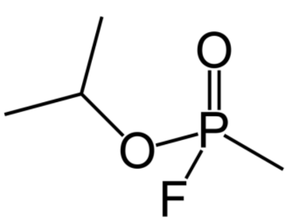
- **Source Emission Limit (SEL)**

- **Immediately Dangerous to Life and Health (IDLH)** – concentration above which supplied air (positive pressure) must be used

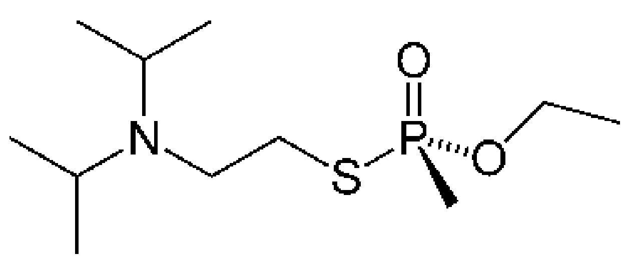
(Note: Some methods at TOCDF monitor at a site-specific Hazard Control Limit (HCL), which is much greater than the IDLH.)

Airborne Exposure Limits (AELs)
mg/m^3

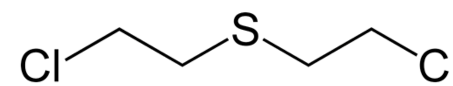
	GPL	WPL	STEL	SEL	IDLH
GB	0.000001	0.00003	0.0001	0.0003	0.1
VX	0.0000006	0.000001	0.00001	0.0003	0.003
HD	0.00002	0.0004	0.003	0.03	0.7



GB (Sarin)



VX



HD (Mustard)

Airborne Exposure Limits (AELs)

parts per trillion by volume*

	GPL	WPL	STEL**	SEL	IDLH
GB	0.17	5.2	17	52	17
VX	$\boxed{0.055}$	0.091	0.91	27	270
HD	3.1	61	460	4,600	$\boxed{110,000}$

*To meet quality requirements, air monitoring methods must be capable of monitoring concentrations as low as 0.2 AEL.

**Also, known as the Vapor Screening Limit (VSL), when used to clear decontaminated items.

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Systems Used at TOCDF to Monitor at the Airborne Exposure Limits (AELs) – parts per trillion by volume

	GPL	WPL	STEL	SEL	IDLH
GB	0.17	5.2	17	52	17
VX	0.055	0.091	0.91	27	270
HD	3.1	61	460	4,600	110,000

Monitored by DAAMS

manual samples collected at TOCDF

analyzed in a nearby laboratory at DCD

Monitored by ACAMS

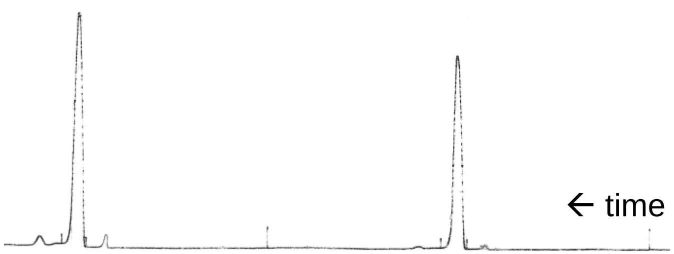
automated near real-time system

in-situ monitoring at TOCDF, 24/7

Agent detection by ACAMS is confirmed/denied by analysis of DAAMS samples.

Automatic Continuous Air Monitoring System (ACAMS) – near real-time monitor used at TOCDF

Courtesy of Meadoworks, Inc., Rupert, West Virginia



Automated monitoring system based on:

- Collection of the chemical agent of interest using an internal solid-sorbent tube
- Separation of the agent from other chemicals using, capillary gas chromatography
- Detection using a flame photometric detector (FPD)

The ACAMS reports the chemical agent concentration once every 5 min.

ACAMS at TOCDF

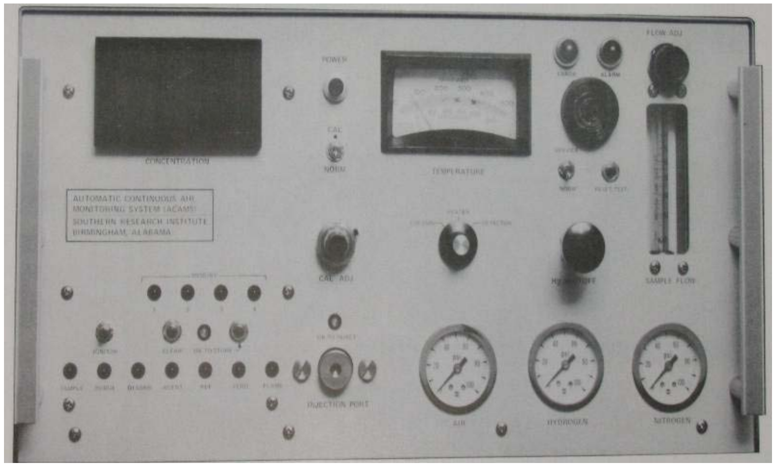
•**Typically, about 180 ACAMS units operate 24/7 at TOCDF.**

•**Each ACAMS includes local audible and visual alarms and a strip-chart recorder.**

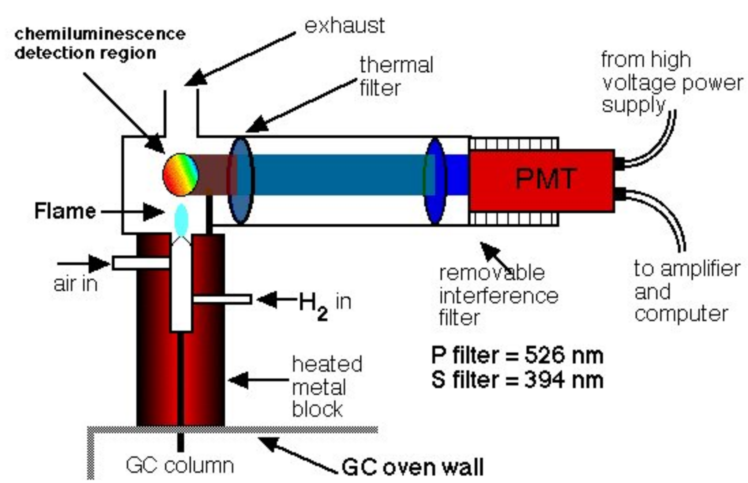
•**Each ACAMS necessary to protect workers, the general population, and the environment is interfaced to the Control Room.**

ACAMS Units (and DAAMS Tubes) Sample About 340 Different Plant Locations Through Heated Sample Lines

ACAMS – a well proven, mature technology



- First developed for use at the CAMDS disposal site, Deseret Chemical Depot (DCD), in 1980
- Used at the JACADS chemical agent disposal site, Johnston Atoll, 1990-1996
- In use at other agent disposal sites since 1994 (ANCDF, PBCDF, TOCDF, and UMCDF)



Quality Assurance/Quality Control at TOCDF*

- Air Monitoring Plan (AMP)—prepared by the site
- Laboratory Quality Control Plan (LQCP)—prepared by the site
- Laboratory Operating Procedures (LOPs)—prepared by the site
- Precision and Accuracy (P&A) studies for equipment and methods
- Initial baseline studies for equipment and methods (QP challenges)
- Continuing baseline studies for equipment and methods (QP challenges)
- Extensive, formal training of ACAMS operators and repair personnel
- Testing for positive and negative chemical interferences
- Continuous improvement, preventive actions, and corrective actions
- Strong support by management (Government, URS, and Battelle)
- Reachback support by corporate (URS and Battelle)
- Oversight by outside agencies (State of Utah, CDC, CMA, etc.)

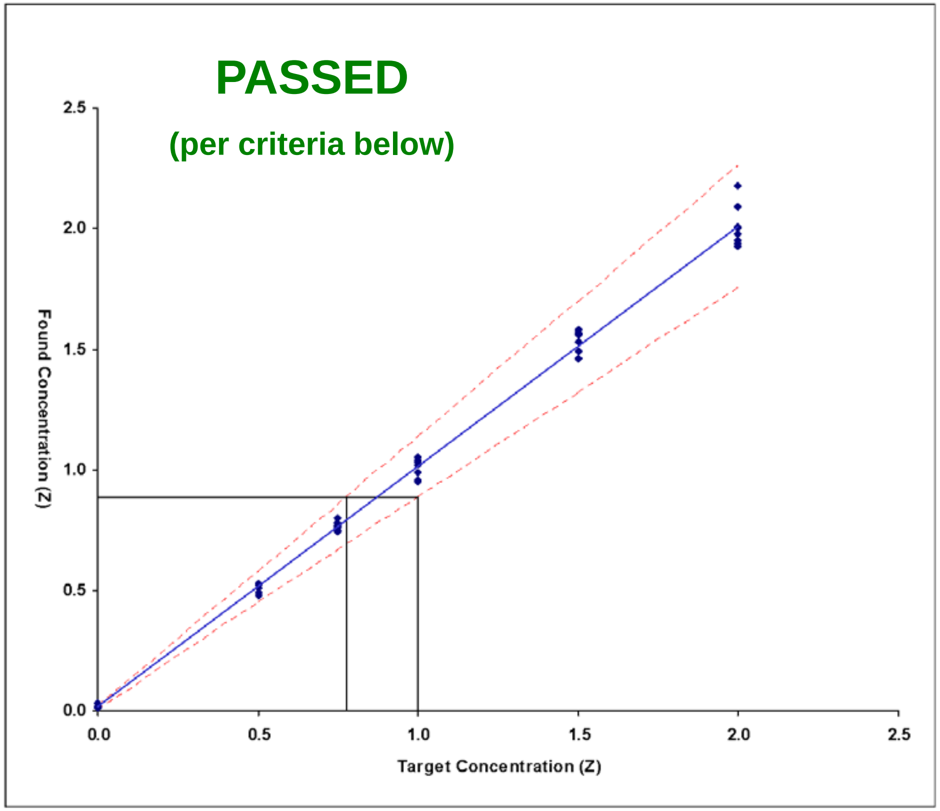
*NOTE: "Laboratory" operations include the analysis of manual DAAMS samples and NRT monitoring using ACAMS.

Class 1 Precision-and-Accuracy (P&A) Study

- An acceptance testing requirement specified in the LMQAP for quantitative NRT air monitoring equipment (ACAMS)
- Demonstrate the performance of a statistical sample of NRT monitors at TOCDF for a given method
- Method parameters include agent, AEL, GC column phase, solid sorbent, key NRT parameters and configuration, etc.
- Typically, 48 agent challenges at 6 different concentrations (0 to 2.0 AEL) conducted over a 4-day period (using agent standard solutions)
- ACAMS alarm levels at TOCDF are typically set at 0.5 AEL; for a few methods, the alarm level is 0.2 AEL

Target vs. Found

Study Name: ACAMS/GB/VSL/DB1/HAYESEP-D/V-G PAD



TAL (>LOQ): 0.7758 **LOQ:** 0.0144 **UIFM (≤ 25%):** 12.43%

Slope: 0.9963 **Y-intercept:** 0.0162 **Percent recovery (75-125%):** 101.25%

Typical CERTIFY Program Output for a Class 1 P&A Study

Certify - [Add / View P&A Study Results]

File Setup Study Description Reports Help

Study Results:

Dates of the P & A Study: Start Date: 5/25/2011 Finish Date: 5/28/2011

Study Name: ACAMS/GB/VSL/DB1/HAYESEP-D/

Description: ACAMS monitoring GB at the VSL using DB-1 analytical column and HAYESEP D PCT with V/G conversion pad

Method Name: ACAMS/GB/VSL

Description: ACAMS monitoring GB at the VSL

Z: 0	0.5	0.75	1	1.5	2
0.01	0.49	0.74	0.99	1.49	1.95
0.01	0.48	0.74	0.95	1.46	2
0.02	0.53	0.75	1.02	1.57	2.18
0.03	0.51	0.77	1.03	1.53	1.93
0.01	0.51	0.77	1.04	1.49	1.94
0.02	0.53	0.76	1.02	1.53	1.98
0.01	0.52	0.78	0.96	1.58	2.09
0.02	0.52	0.8	1.05	1.56	2.01

Number of Data Points: 48

Y-Intercept: 0.0162
Slope: 0.9963
CC: 0.9978
UIFM: +- 12.43 %
UIAS: +- 11.21 %

FAL: 0.8867
TAL: 0.7758
LOQ: 0.0144
DETL: 0.0072
DECL: 0.0234
Recovery: 101.25 %

TAL > LOQ? ☑
UIFM<= +/- 25%? ☑
75%=< Recovery <= 125%? ☑
Method Approved for Use? ☑

PASS

Calculate Results
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Initial Baseline Study

CMA LMQAP

13.4 Initial Baseline Study for Air Method Certification

The initial baseline study demonstrates the readiness of each monitoring system to support site operations.

- **Consists of at least one agent challenge per day for 28 days at 1.0 AEL (e.g., at 1.0 STEL)**
- **Each challenge (injection) made using 5.0-µL aliquot of a liquid standard solution**
- **Must meet statistical requirements specified in the LMQAP published by CMA**

Continuing Baseline Study (QP Challenges)

- <u>**Validates the performance of each ACAMS unit (station) by statistical evaluation**</u> of QP (Quality Plant) challenges conducted over each 28-day period during agent destruction operations—one challenge per ACAMS per day (per the LMQAP)

Method/Application[a,b]	Challenge Frequency[c]	Baseline Performance Standard
NRT – Permanent Station	One challenge event[d] per station per day	If the alarm setpoint is 1.0Z, the first challenge pass rate (PR1) shall be ≥ 95% each station. At a lower alarm setpoint, the statistical response rate (SRR_{AL}) shall be ≥ 95% and PR1 shall be ≥ 75% each station.

- <u>**Consists of challenges made using 5-μL aliquots of a standard solution**</u> **containing** agent at a concentration that results in the injection of the mass that would normally be pulled into the ACAMS with the airborne concentration at 1.0 AEL

- <u>**At TOCDF, more than 70,000 ACAMS QP challenges are typically conducted during a 12-month period**</u> with each ACAMS sampling the atmosphere normally sampled (e.g., stack gas, ambient air, etc.)

Typical Continuing Baseline Study Results

- Summary for the 4-week period ending 6/23/2011 (results for only 9 of 175 stations shown below)—**175 stations in service passed LMQAP requirements**
- Uploaded biweekly to the CMA Quality Control Data Reporting System (QCDRS)
- Reviewed continuously by CMA and the CDC with feedback to TOCDF

1	**Facility:**	INACCMO-PS REPORT
2	**Facility:**	TOCDF
3	**System:**	ACAMS
4	**Date Range:**	27/May/2011-23/Jun/2011
5	**Action Performed:**	See the attached document.
6	**Actions If Problem Persist:**	See the attached document.
7	**Actions To Prevent Reoccurence:**	See the attached document.
8	**Comments:**	See the attached document.

9	STATION	AGENT	MONITORING LEVEL	NALL	FIRST	LO	HI	FNEG	FNEG2	RESPONSE	S_RESP	ALARM LVL	INACC	MEAN	STDDEV	PR1	PR2	PRE	P1	F1	P2	F2	PCT	DUST PAD	CONVERSION PAD	CALIB	Z	NORMDIST	Statistical Performance	CF Performance
10	703A	H	SEL	41	41	0	0	0	0	100	100	0.2	0.12	1	0.12	100	-	100	41	0	0	0	3	0	0	1	-6.98	0	P	F
11	703B	H	SEL	41	41	0	0	0	0	100	100	0.2	0.11	0.98	0.08	100	-	100	41	0	0	0	3	0	0	1	-9.25	0	P	F
12	704A	H	SEL	45	45	0	0	0	0	100	100	0.2	0.15	1.06	0.09	100	-	100	45	0	0	0	1	0	0	0	-9.56	0	P	F
13	704B	H	SEL	54	45	4	5	0	0	100	100	0.2	0.2	1.01	0.19	80	33	87	36	9	3	6	5	0	0	8	-4.23	0	P	F
14	705A	H	SEL	46	46	0	0	0	0	100	100	0.2	0.18	1.12	0.06	100	-	100	46	0	0	0	0	0	0	0	-16.34	0	P	F
15	705B	H	SEL	46	46	0	0	0	0	100	100	0.2	0.1	0.96	0.07	100	-	100	46	0	0	0	2	0	0	0	-11.76	0	P	F
16	904C	L	VSL	49	43	2	4	2	2	95	99.12	0.4	0.28	1.02	0.26	86	67	95	37	6	4	2	0	0	0	1	-2.37	0.01	P	F
17	904D	L	VSL	48	43	2	3	0	0	100	99.98	0.4	0.19	1.02	0.17	88	100	100	38	5	5	0	2	0	0	7	-3.58	0	P	F
18	707A	H	SEL	168	168	0	0	0	0	100	100	0.2	0.1	1.04	0.07	100	-	100	168	0	0	0	1	0	0	0	-12.36	0	P	P

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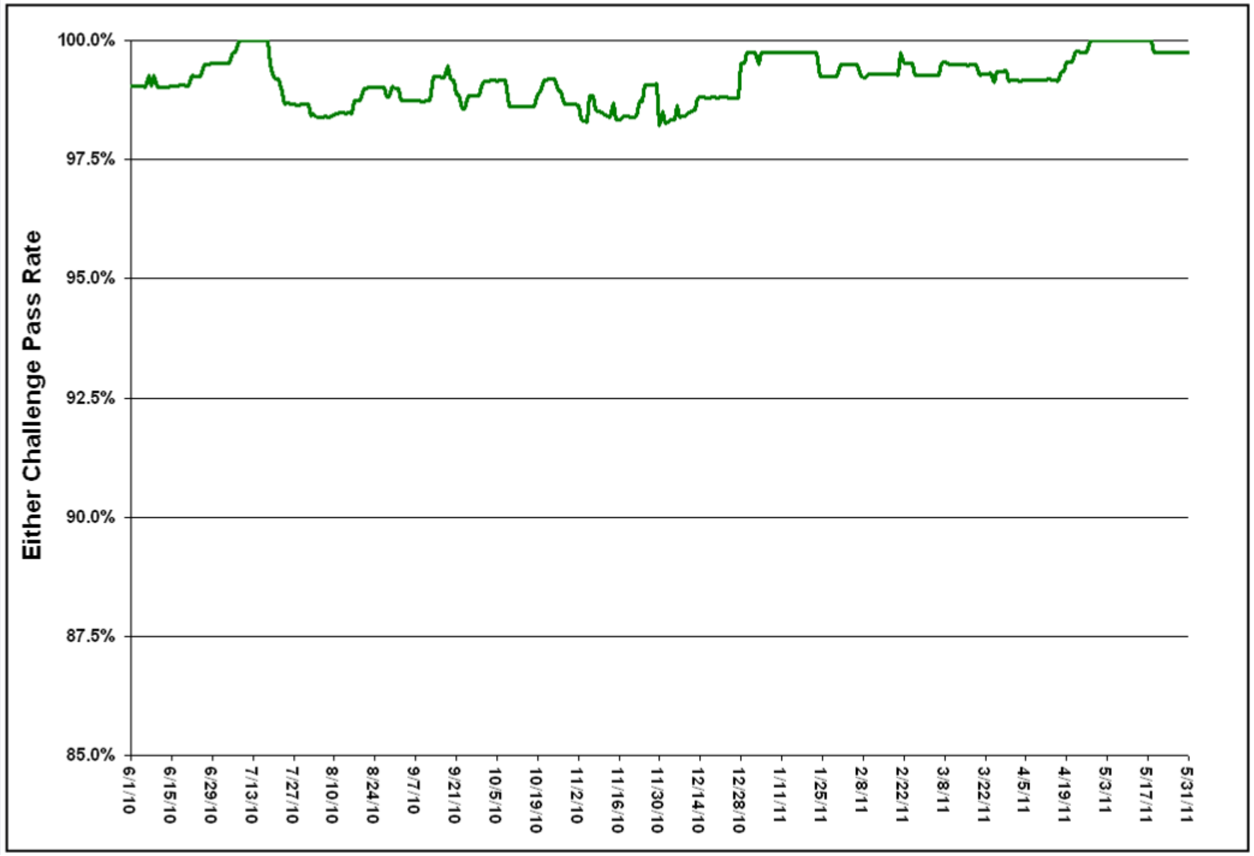
Pass Rates for HD Sample Line Challenges

- Over 5,000 QP challenges at the distal ends of about 340 ACAMS and DAAMS sample lines made during the year ending 5/31/2011 (total for HD, GB, and VX)
- Each QP challenge made while the air matrix from the sample location was flowing through the sample line



Summary of ACAMS Monitoring Data at TOCDF (year ending 5/31/2011)

- 177 ACAMS, operating 24/7 and each monitoring one location at a time
- Automated collection and analysis of more than **18,000,000 air samples**
- ACAMS alarms if the concentration reported exceeds 0.5 AEL*
- **ACAMS went into alarm 124 times** (a total of 419 instrument cycles)
- Non-agent ACAMS alarms may be caused by chemical interferences, ACAMS malfunctions, interruption of supplied gases, operator error, etc.
- Co-located DAAMS tube air samples collected at the same time were analyzed to determine whether alarms caused by chemical agent

*The alarm level for the exhaust stack of the pollution abatement system is set to 0.2 SEL.

Review of 124 ACAMS Alarms at TOCDF (year ending 5/31/2011)

- **DAAMS confirmed only 8 of the ACAMS alarms** as due to agent
- **7 alarms due to low levels of agent detected within the plant inside engineering controls** in areas where agent may sometimes be expected to be present and personnel are only present when wearing PPE
- **1 alarm due to low levels of agent detected in a room inside the plant Munitions Demilitarization Building** (where agent is destroyed)—maximum concentration of 1.28 STEL HD; 3 ACAMS alarm cycles; no people in area
- The MDB alarm was caused by a temporary upset in the ventilation system leading to the charcoal filtration system
- A root-cause-analysis was completed and corrective actions were taken to minimize the probability of such an adjustment again causing an agent release
- The causes of 93 alarms were known, non-agent events (e.g., equipment failure)
- The causes of 23 alarms could not be determined (but were non-agent related)

Review of Low-Level Trending Data

- All concentrations reported by ACAMS that are greater than 0.2 STEL but less than the alarm level (0.5 STEL) are reviewed
- The causes of such low-level concentration reports are eliminated, if possible
- Low-level concentration reports are almost always caused by chemical interferences
- At higher concentrations chemical interferences may result in agent concentration reports >0.5 STEL (i.e., result in false alarms)
- False alarms reduce confidence in the performance of the monitoring system and reduce operational effectiveness (i.e., personnel must don PPE)

Example of the Value of Low-Level Trending Data

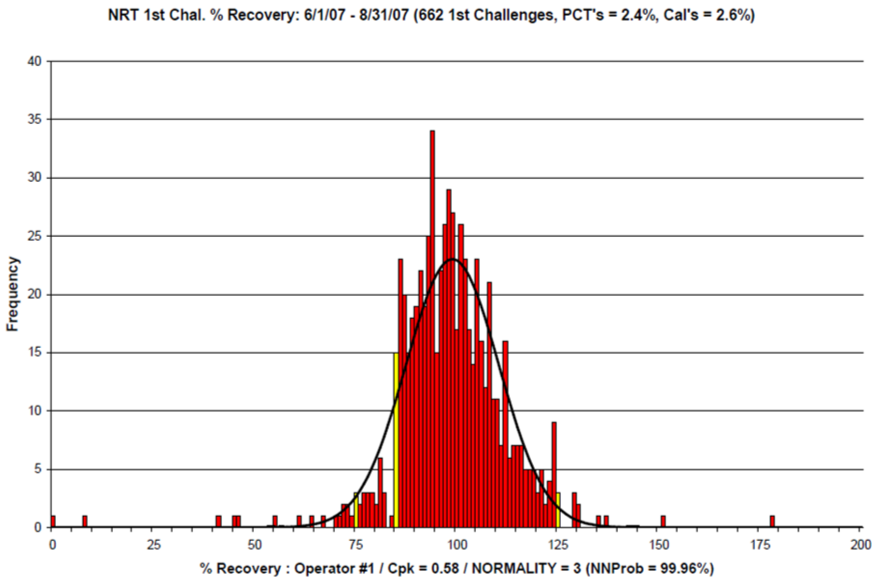
- Recently 5 different false alarms and low-level concentrations readings occurred for the GB and HD ACAMS units monitoring the Decontamination Vestibule and Decontamination Rooms at the TOCDF Medical Clinic

- These false positives were traced to the occasional presence of 1,2-ethanedithiol (EDT) vapor in these rooms, a reagent used in nearby systems monitoring for the agent Lewisite (L) in the same rooms

- On about 5/9/2011, modifications to the monitoring systems using EDT were made to reduce the concentration of the chemical in these rooms

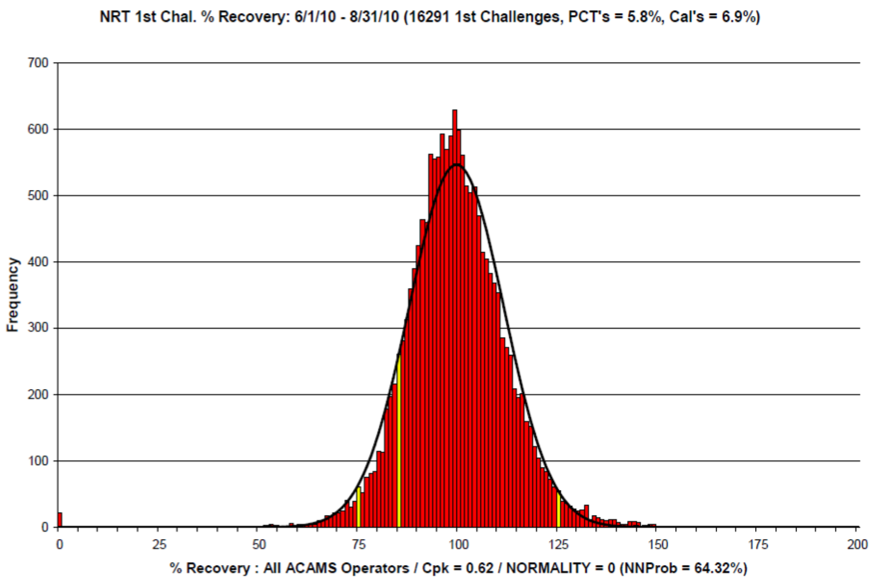
- As a result, no ACAMS false positives have been experienced at these locations since that date, resulting in improved operational effectiveness

Continuous Improvement—Example of Statistical Analysis to Improve NRT (ACAMS) Performance for QP Challenges



Typical ACAMS Response Distribution Before Additional ACAMS Operator Training – 2007

Typical ACAMS Response Distribution After Additional ACAMS Operator Training – 2010



Statistical evaluation of instrument-challenge data to identify poorly-performing instruments, analytical interferences, operator-specific problems, and other risks to the NRT monitoring of chemical agents.

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CONCLUSIONS
Regarding Monitoring and TOCDF Operations

- Many activities with the potential for releasing chemical agents take place
- Numerous non-monitoring measures are in place to prevent the release of agent and to protect workers, the general public, and the environment
- NRT monitoring systems (ACAMS) are used to detect agent vapors at low concentrations in near real time so that effective actions can be taken
- Strong management and regulatory oversight as well as robust QA/QC systems at TOCDF ensure the effectiveness of the monitoring program
- Monitoring and QC data for the year ending 5/31/2011 demonstrate the ability of the air monitoring systems to reliably detect agent and demonstrate the overall excellent performance and safety of agent disposal operations
- Reviews of low-level concentration reports, evaluations of statistical performance, and other measures demonstrate the site's continued commitment to improved performance