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Historical, Confirmation, and Certification Air Monitoring for Chemical Warfare Agents in the Destruction of Chemical Munitions

Presented by: George M. Lucier, Ph.D.

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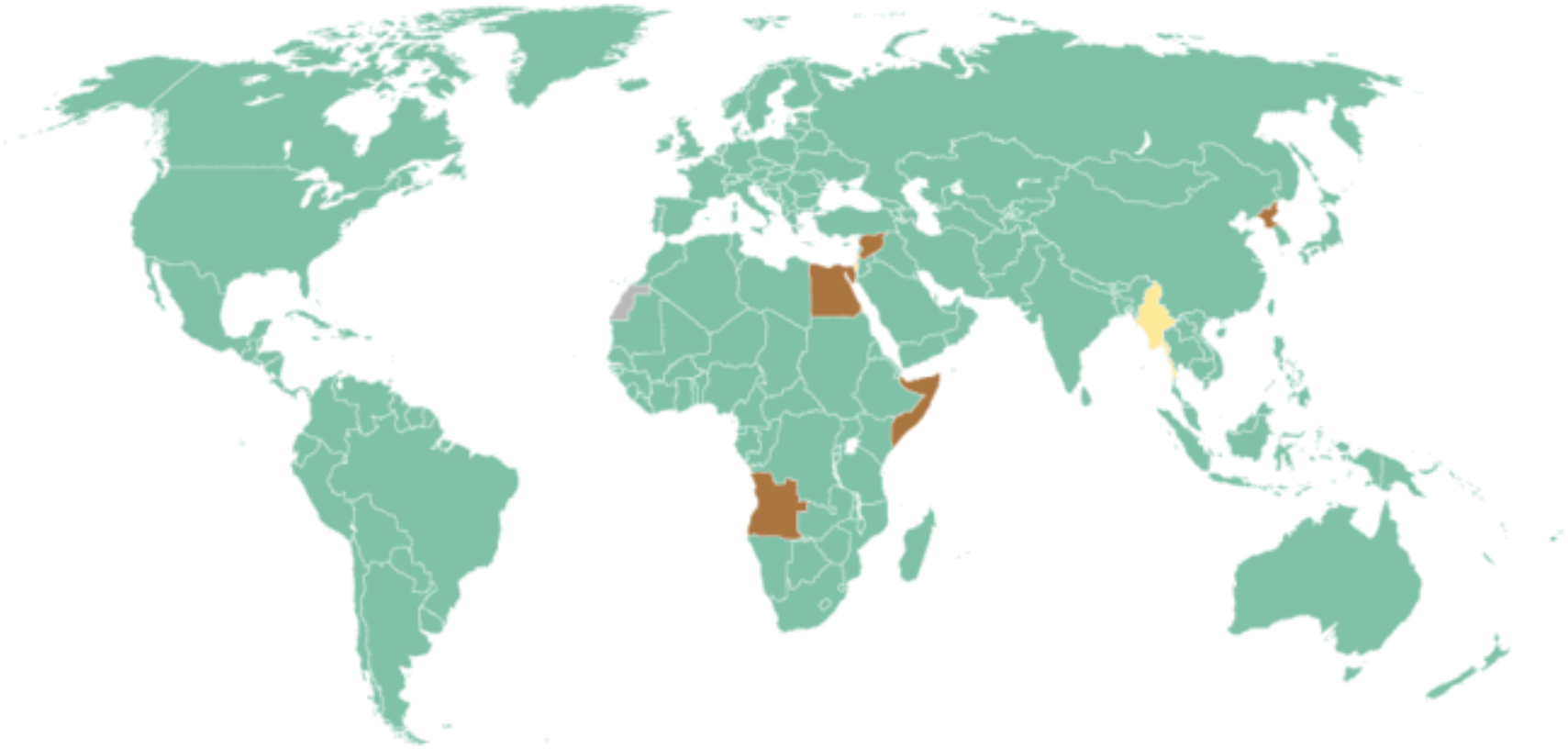
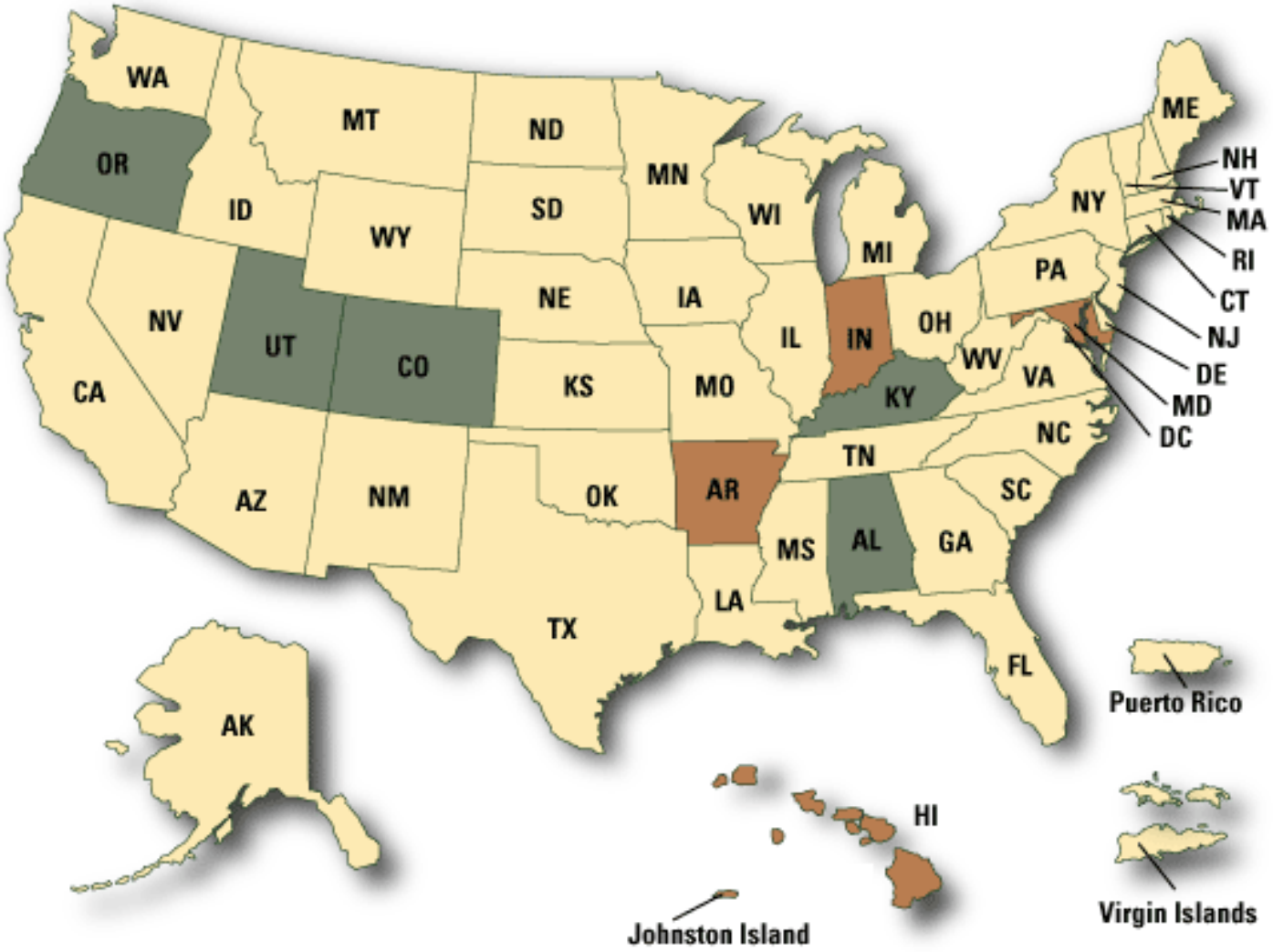
Co-authors: Greg Ball, Dawn Fifield, and Brad Garner

CWC Treaty Party States



Source: http://www.opcw.org/news-publications/publications/facts-and-figures

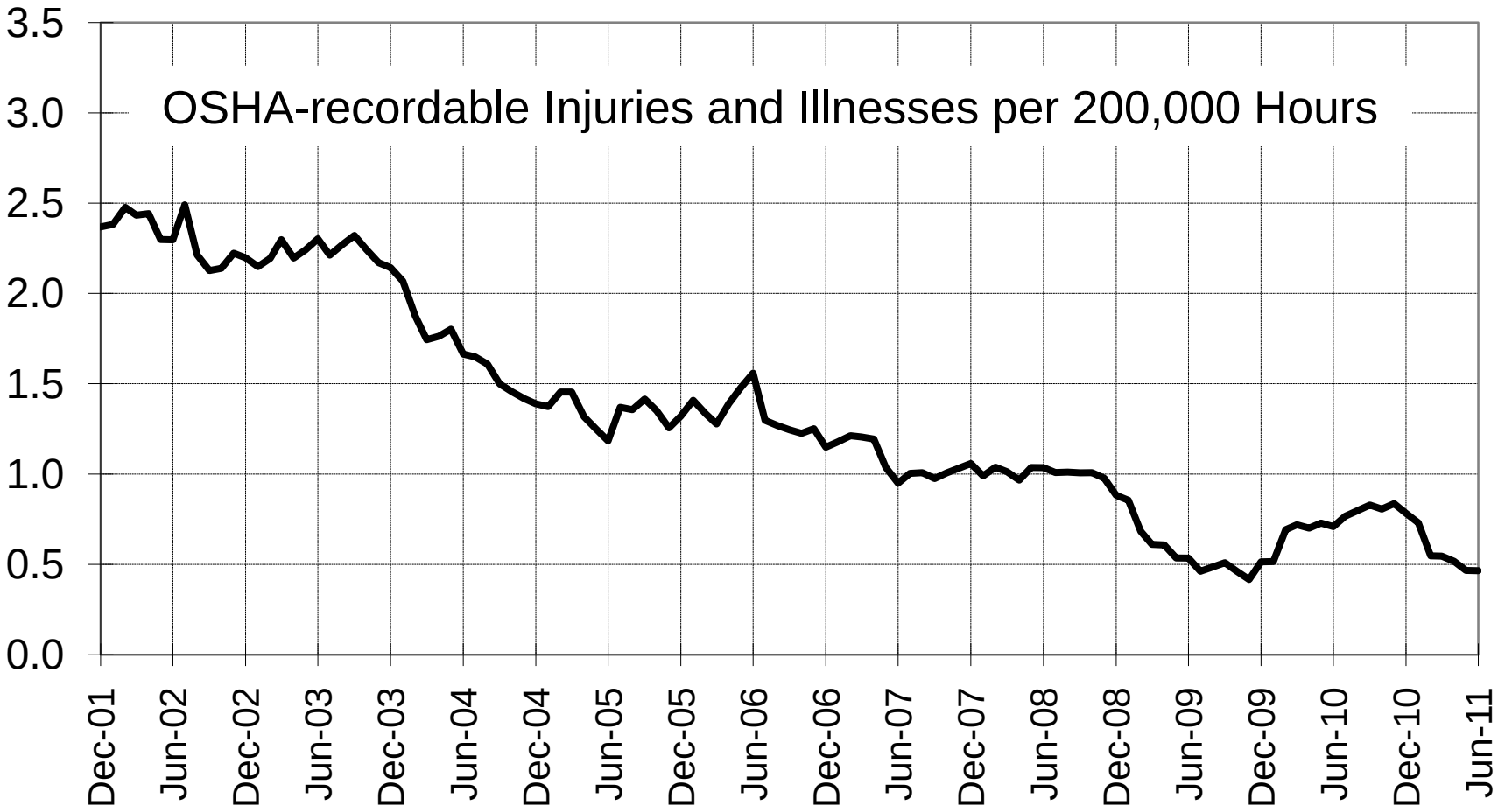
US Chemical Warfare Agent Stockpile



Source: http://www.cma.army.mil/map.aspx

Chemical Demilitarization Safety

- The injury trend spanning all nine sites has shown significant improvement over the last 10 years



Air Monitoring for CWA

- Near-Real-Time (NRT) monitoring of airborne CWA (described in the previous presentation) provides warning signals for safety and process control
- Other needs for monitoring of airborne CWA:
  - Historical
    - Typically 4-hr or 12-hr time-weighted average (TWA) samples that create a continuous record of agent concentrations (or lack thereof)
  - Confirmation
    - Used to confirm or refute NRT readings or initial historical readings (e.g., to refute false-positive readings)
  - Certification (aka “non-baseline”)
    - Verifies waste, equipment, or work areas to be below hazardous levels of CWA so that they may be dispositioned or otherwise used by non-agent workers

DAAMS Monitoring

- DAAMS = Depot Area Air Monitoring System
- Utilizes standard air-sampling practices for CWA historical, confirmation, or certification monitoring
  - Field samples are collected on a solid sorbent tube
  - Sample tubes are desorbed thermally into a GC or extracted for LC analysis (L only)
  - Priority sample results can be obtained in ~90 minutes
- DAAMS monitoring complements NRT monitoring, offering higher precision and selectivity than NRT methods – together, they comprise the air monitoring that permits safe detection and destruction of CWA

The TOCDF Mission

- TOCDF is the largest and most complex of the facilities in terms of stockpile
  - Originally held 44% of the US stockpile of chemical weapons
    - Three nerve agents: VX, GB (sarin), and GA (tabun)
    - Two blister agents: HD (mustard gas) and Lewisite (L, an arsenical)
    - Weapons configurations included rockets, mines, projectiles, mortars, bombs, spray tanks, cartridges, and ton containers
  - Current TOCDF mission includes closure of CAMDS, the experimental prototype facility for destruction of the US stockpile of chemical weapons
  - Three separate laboratories exist to support the mission
- To date, 99% of TOCDF's agent has been destroyed

Magnitude of the Monitoring at TOCDF

- Spanning the five chemical warfare agents, more than 50 DAAMS "methods" are maintained on over 30 instruments for more than 200 sampling stations
  - Methods are defined by sampling parameters, analytical parameters, and general composition of the air matrix
  - All methods must meet Utah State regulator (RCRA) requirements, and each one must be individually evaluated and approved by the federal government (CMA)
- Over 1400 DAAMS field samples are collected daily, most of which are 12-hour collections
  - Almost half of those samples collected are analyzed
  - The remainder are collected for confirmation purposes and are simply desorbed within 72 hours if they aren't needed

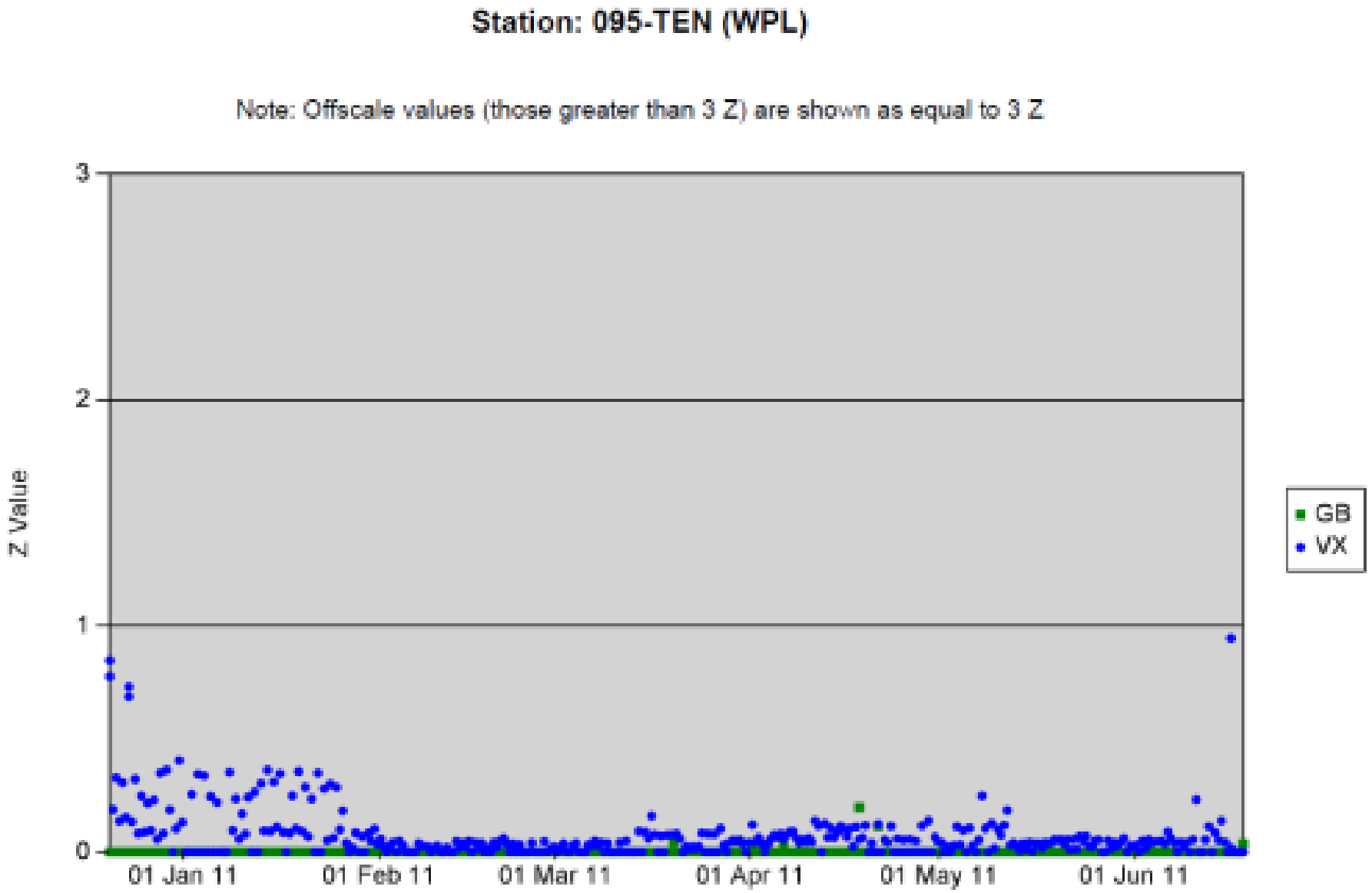
AELs and Detection Limits

- Airborne Exposure Limits (AELs) that define the monitoring levels (in terms of air concentrations) are established in the Federal Register
- Coupled with the DAAMS sampling and analytical parameters, the AELs define the detection-level masses for the methods
  - GB: 22 pg
  - GA: 60 pg [chromatographed as fluoro-tabun]
  - VX: 15 pg [chromatographed as G-analog]
  - HD: 1500 pg
  - L: 63 pg [chromatographed as the As(V) acid product]

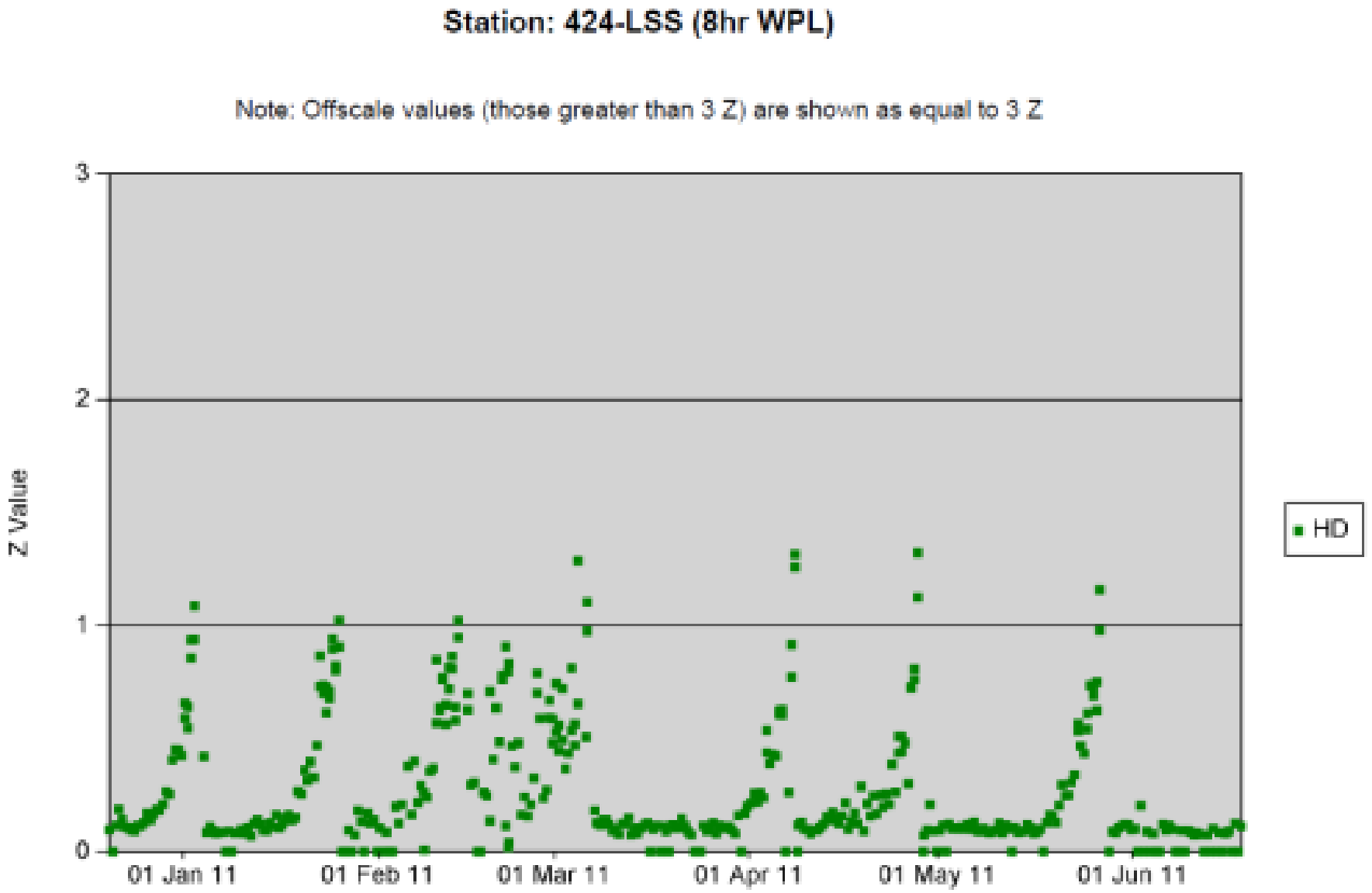
Statistical Evaluation and Trending

- The large magnitude of the DAAMS program at TOCDF provides us with a large population of quality data for statistical evaluation and trending
  - Low-level and quality analysis trending
    - Provides early warning to upset conditions
  - Peak-integration consistency monitoring
    - Guards against non-standard peak-integration practices
  - Calibration stability tracking
    - Provides feedback for instrument maintenance practices
  - Retention time window width optimizing
    - Strives for a balance between false-negatives due to narrow RT windows and false-positives due to wide RT windows

Field Sample Trending



Field Sample Trending

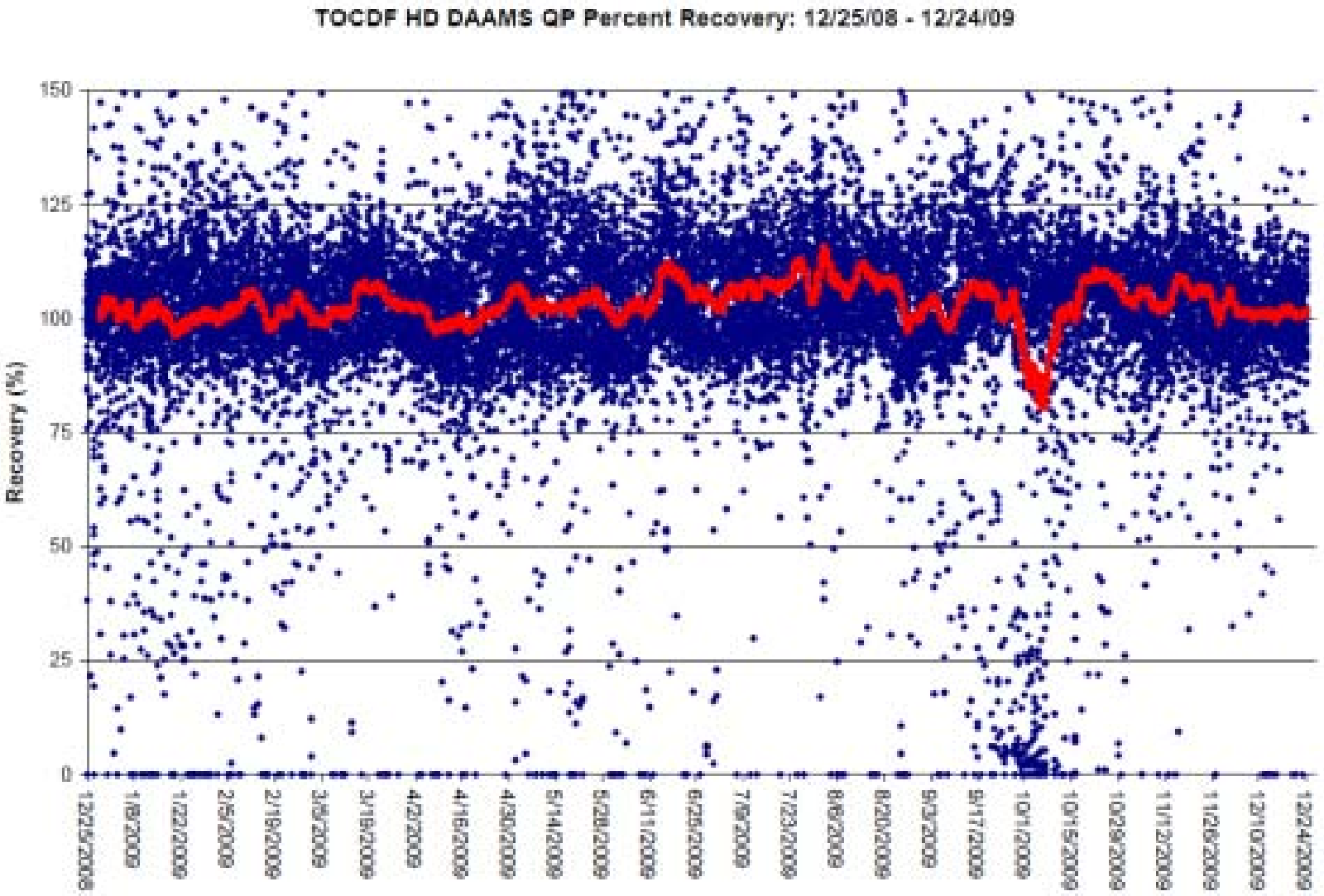


QC Samples

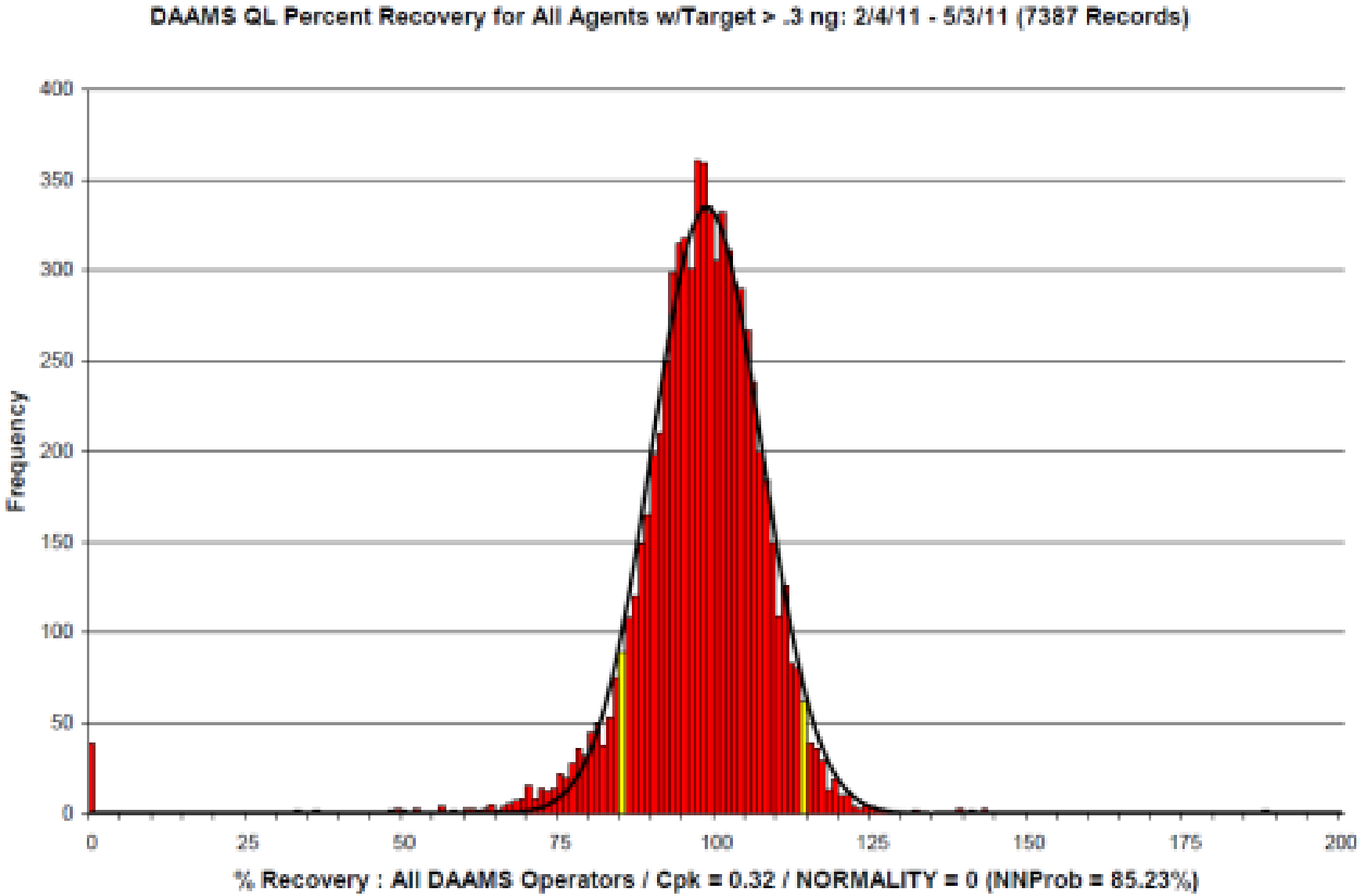
- QP Analysis – daily analysis of agent-fortified field samples (QPs) provides the data necessary for statistical evaluation of method performance; represents about 20% of the field samples analyzed
- QL Analysis – instrumental calibration verification samples (QLs) are analyzed at least one for every twenty field samples

- QP and QL DAAMS tubes are spiked with a mass that corresponds to the monitoring level of interest for the specific DAAMS method

QP Recovery Trending



Peak Integration Consistency



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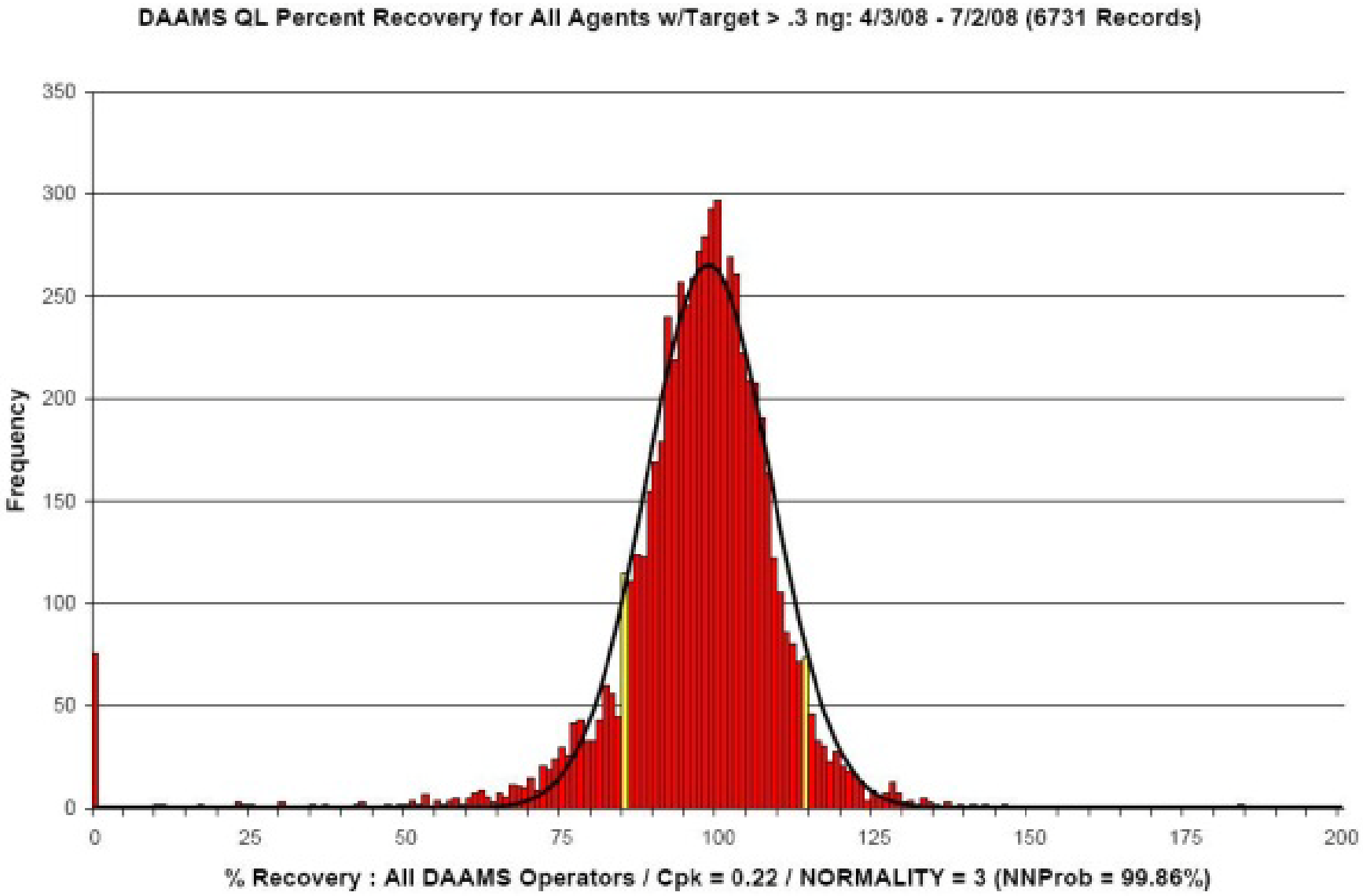
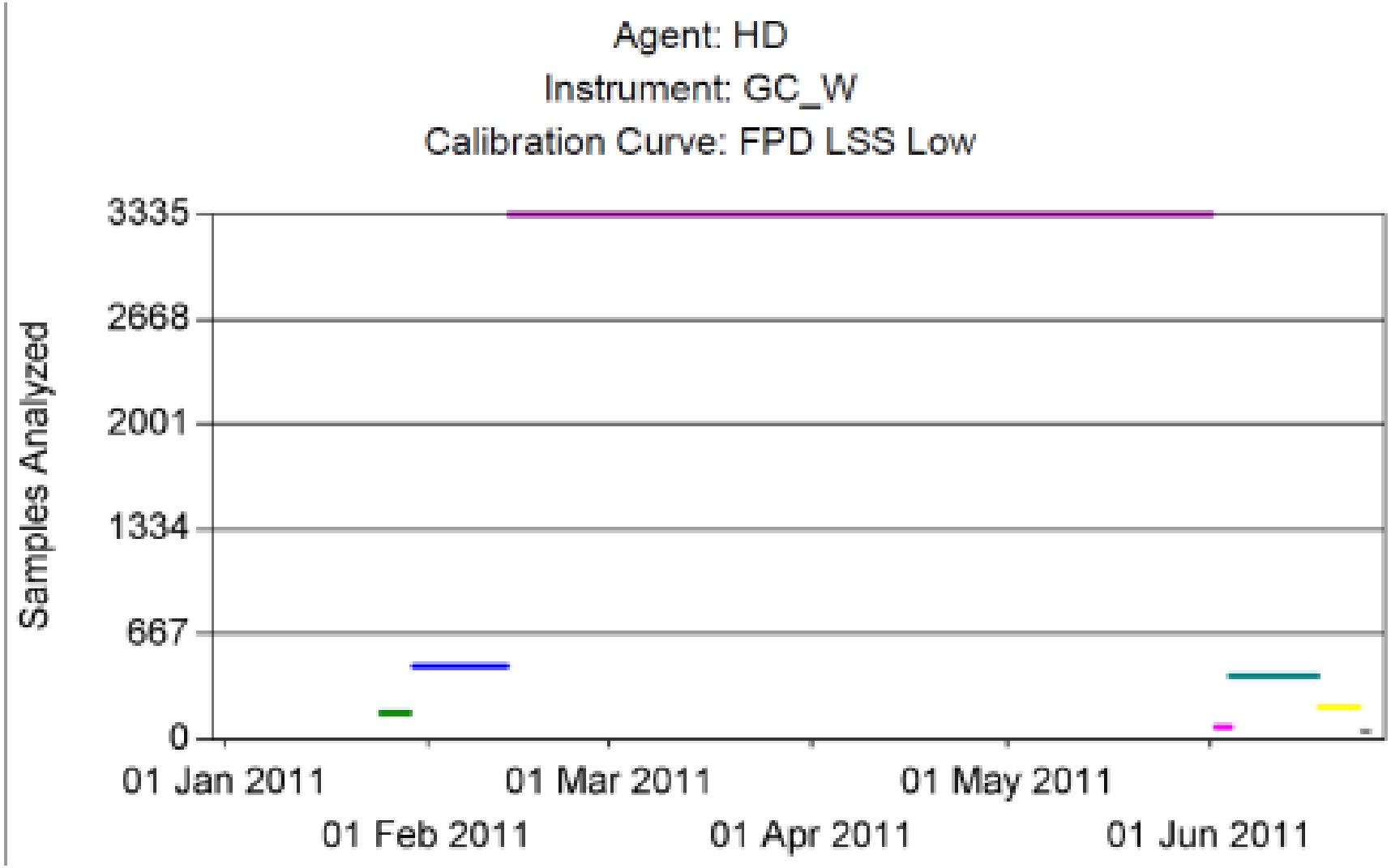


Calibration Stability Tracking



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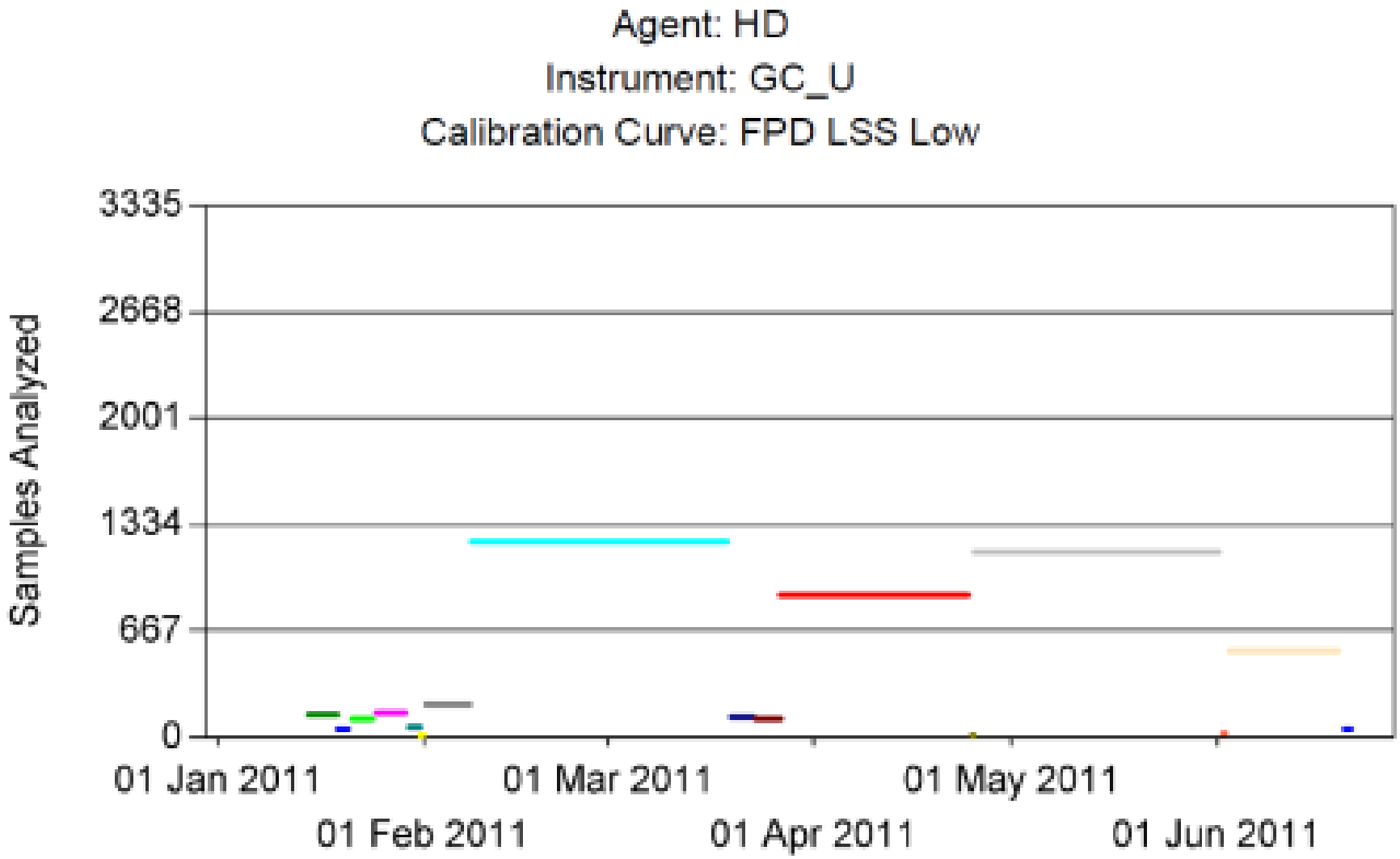
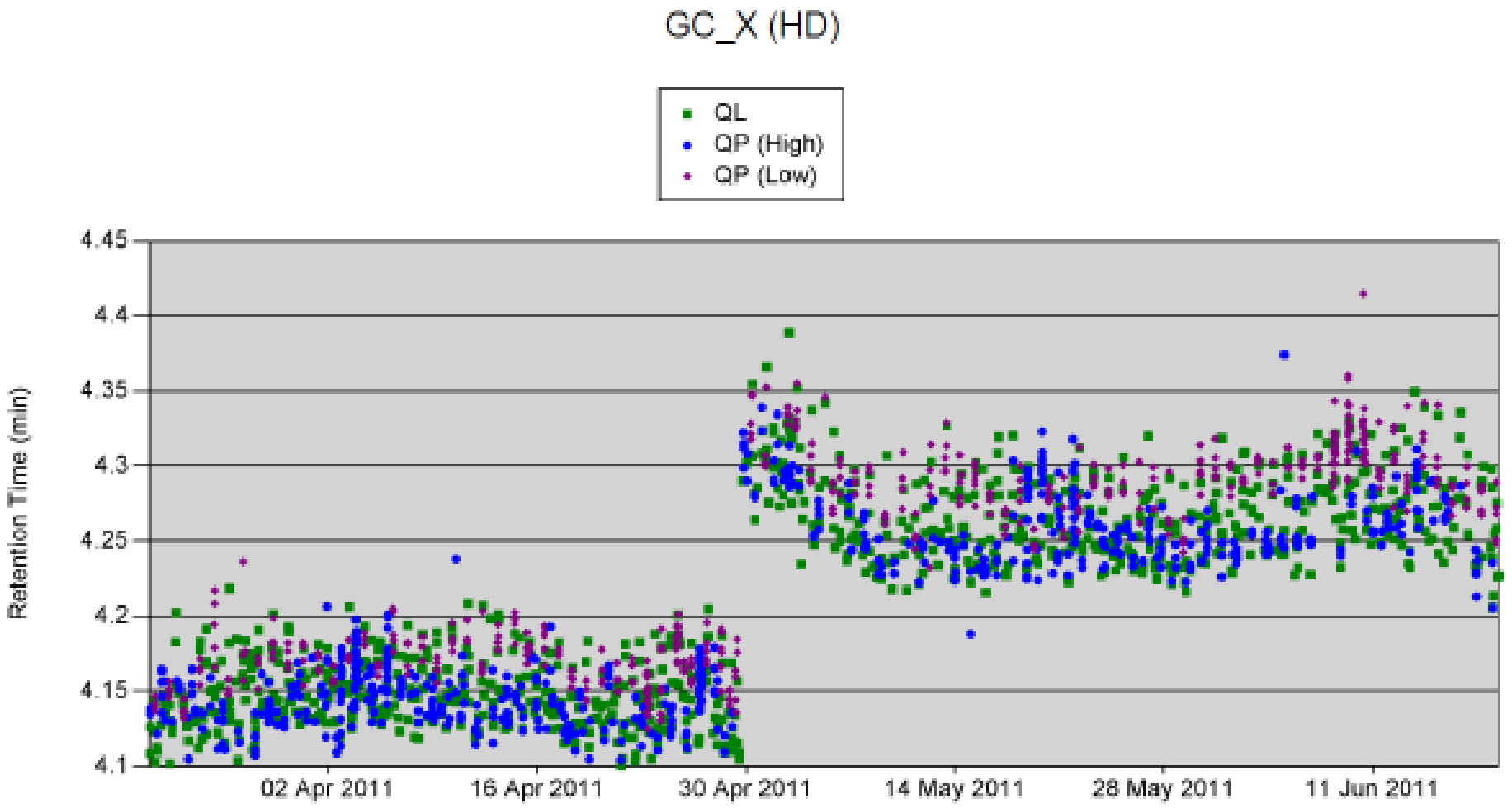
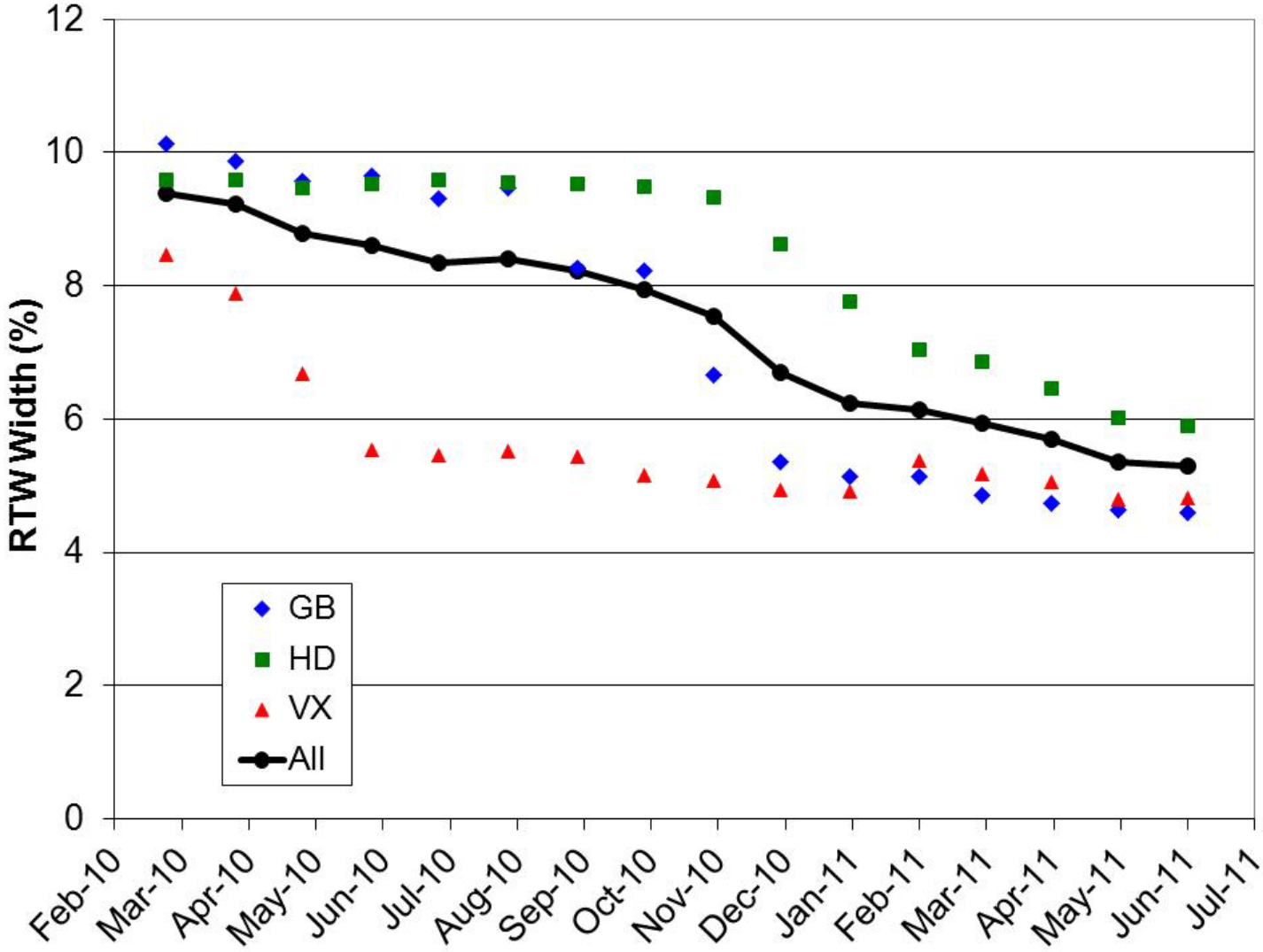


QP and QL Retention Time Data for Optimizing RT Window Widths



Sample-Load-Weighted Mean RTW Width Trend



The Future of DAAMS Monitoring

- The two remaining (pre-systemization) CWA stockpile sites in the US account for 11% of the original US stockpile
  - These two sites will likely need DAAMS monitoring through the end of this decade
- The direction of the non-stockpile program in the US regarding recovered chemical warfare material (RCWM) is not well-defined, but is likely to require DAAMS monitoring for decades to come
- National and international considerations for CWA terrorism are likely to rely more on NRT monitoring than DAAMS

Acknowledgements

- **John Archer** – TOCDF Laboratory Statistician
  - Provides ongoing statistical analysis and *ad hoc* reporting in support of TOCDF DAAMS method performance evaluation