MassDEP Field Assessment and Support Team (FAST)

After Incident Report

DEP RTN 4-22,656

New Bedford Clam Contamination Incident

June 2010

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BACKGROUND

On June 6, 2010, the 145 foot fishing vessel *ESS Pursuit*, while dredging for clams about 45 miles south of Long Island, netted 8 shell-sized munitions canisters believed to contain sulfur mustard. One shell reportedly broke open, exposing crew members to the suspected chemical warfare agent. All shells were jettisoned by the crew, some of whom experienced medical symptoms consistent with exposure to the agent (e.g., blistering). At least one crew member required hospitalization.

On June 7, 2010, the vessel subsequently unloaded the entire catch of clams (about 250 tons) at the Sea Watch International seafood processing facility at 15 Antonio Costa Avenue in New Bedford. Once authorities became aware of the medical emergency, the vessel was ordered to remain in New Bedford Harbor, and the clam catch was ordered to remain at the Sea Watch facility, which was shutdown and secured by the US Coast Guard (See Figure 1).

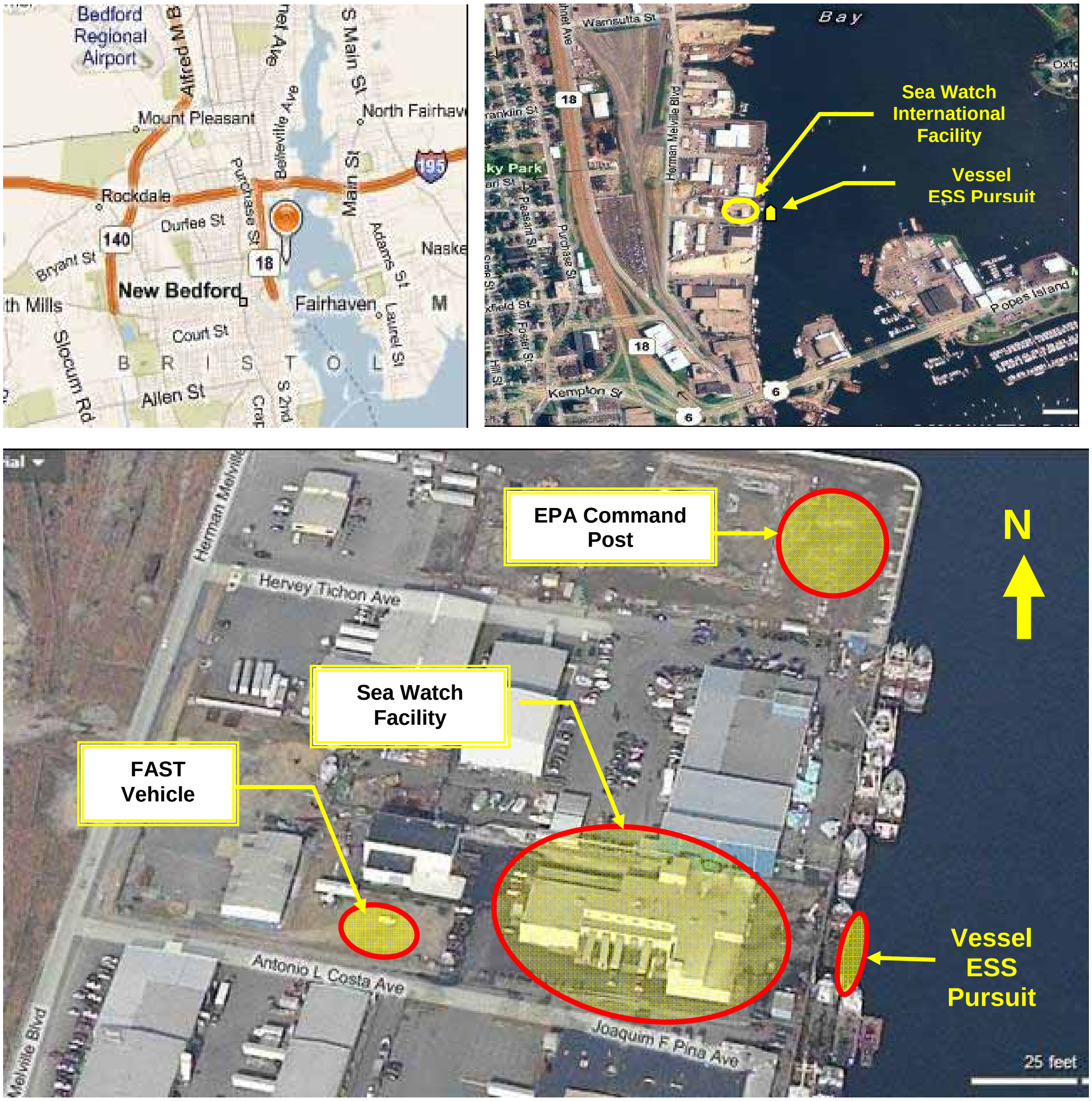


Figure 1 – Site Map

RESPONSE ACTIONS

A Unified Command was established by the Coast Guard, which included a State On-Scene Coordinator (Dan Crafton and Andy Jones of MassDEP/SERO). The *ESS Pursuit* was surveyed by the Massachusetts Civil Support Team (CST) using a HAPSITE GC/MS unit, and was subsequently decontaminated by a contractor (Clean Harbors).

Dealing with the embargoed clams was more problematic. The suspected chemical agent, "HD Sulfur Mustard", may have spilled on a small subset of the entire catch, which was contained in about 180 individual cages that each contained approximately 3000 pounds of clams. However, it was not possible to identify which (if any) of the cages may have contained the agent.

Initial considerations were given to sampling the catch. These proposals were subsequently dropped, given the difficulties in identifying representative samples and testing protocols. Eventually, Unified Command decided to transport the clams off-site as a hazardous waste, to permitted incinerators in Arkansas and/or Texas.

Prior to this operation, each cage was surveyed with specialized equipment to ascertain whether ordinance shells were present. No such materials were identified.

Plans were then made to transfer the clams from their cages into suitable storage and transport containers. This would be done by Clean Harbors' personnel in Level "B" protection, in an area just outside (easterly of) the Sea Watch facility building. It was anticipated that such operations would require about 72 hours of around-the-clock activities.

On Sunday, June 13th, Unified Command requested mobilization of MassDEP FAST assets to monitor ambient air during the duration of loading activities.

FAST ACTIVATION AND DEPLOYMENT

The FAST mobile laboratory vehicle and two team members arrived at the site at 6:00 AM on Monday, June 14th. The vehicle was stationed westerly of the Sea Watch Facility, as shown in Figure 1. The on-board weather station was deployed and activated. Large (D size) orthographic maps of the site were produced by the on-board printer and provided to Unified Command.

Although an air sampling plan had not yet been disseminated by the EPA (who were assisting the Coast Guard at the site), the overall plan and approach was verbally conveyed to the FAST team leader. The scope of the FAST monitoring effort was limited to analysis of Ammonia (NH_3) and Hydrogen Sulfide (H_2S) emissions. These contaminants were unrelated to the possible presence of mustard sulfur agent, but instead were of concern due to the state of decay of the clams, and historical problems experienced at this location with such decomposition products.

Instrumentation

AreaRAE Unit

The primary instruments used to accomplish the required air monitoring task were four AreaRAE air sampling units (RAE Systems, Inc.). Each 8.5 pound unit is equipped with a 400 cc/minute pump that continuously samples air, for analysis by 4 (changeable) sensors. Readings are transmitted real-time by radio frequency to a receiver located in the FAST vehicle. Data from the receiver is wired to a laptop PC that continuously displays concentration readings, which are updated every 2 seconds. Exceeding a (programmable) action level for each sensor produces a visible and audible (voice recording) alarm. Data readings for each sensor are recorded and logged independently on each AreaRAE unit as well as in the laptop PC program.

The FAST AreaRAE units each contain a 10.6 eV photoionization detector (for VOCs and other ionizable analytes), a combustible gas (Lower Explosive Limit) sensor, and two "toxic gas" sensors: Chlorine (Cl_2) and Hydrogen Sulfide (H_2S). For this incident, the US EPA provided FAST with 3 Ammonia (NH_3) sensors, which were installed in AreaRAE units 1, 2, and 3 on the morning of 6/14/10. Installation of these sensors required removal of the Chlorine sensors (which remained in unit 4). After installation, the NH_3 sensors required a "burn in" period of at least 60 minutes. Subsequently, the AreaRAE units were calibrated for NH_3, and "bump tested" with certified calibration gases for all other analytes (i.e., VOCs, H_2S, LEL, Cl_2). All sensors in all units performed satisfactorily.

By 11:00 AM, the 4 AreaRAE units were deployed; unit 1 in the "hot" (exclusion) zone, unit 2 south of the hot zone, unit 3 easterly of the hot zone, and unit 4 northerly of the hot zone, as depicted in Figure 2. AreaRAE Unit #3 was attached to the *ESS Pursuit*, as it was the only available location easterly of the hot zone. A photograph of this deployed unit is contained on the cover of this report; lower-right-hand corner.

Figure 2 – Deployment of FAST AreaRAE units

In addition to the AreaRAEs, two FAST hand-held V-RAE meters (RAE Systems, Inc.) were used throughout operations. These flashlight-sized units also contain a number of sensors, though are not currently equipped with radio transmission capabilities. V-RAE unit 1 contains 3 sensors: combustible gases, H_2S, and Cl_2. V-RAE unit 2 also contains 3 sensors: combustible gases, NH_3, and Hydrogen Cyanide (HCN). The V-RAE meters were used to provide spot-check verification of air quality at specific location. This was especially important for Ammonia, given the tendency of these sensors to "drift". Both V-RAE units performed satisfactorily in bump tests conducted for all sensors on the morning of 6/14/10.

The sensors in the AreaRAE units and V-RAE units had identical detection limits: about 1 ppmV for NH_3, and about 0.1 - 0.3 ppmV for H_2S.

Finally, an on-board gas chromatograph (SRI Systems) was used to conduct limited air quality testing. This unit was equipped with a photoionization detector (PID) and dry electrolytic conductivity detector (ELCD). In addition to VOCs, NH_3 and H_2S calibration gas standards were used to establish retention times and (approximate) response factors for both analytes.

<u>Baseline Monitoring</u>

From 11 AM to 1 PM on 6/14/10, before clam transfer operations began in the exclusion zone, “background” data was collected from the 4 AreaRAE units. In this context, background is a combination of ambient concentrations of Ammonia and Hydrogen Sulfide pervasive in the area combined with sensor drift:

☞ Ammonia is believed to be prevalent in the area because of the use of ammonia refrigerants; in fact, the Sea Watch facility itself stores a large amount of this material on site. Ammonia and Hydrogen Sulfide are also present due to the decomposition of seafood and seafood wastes (irrespective of the embargoed clams inside the Sea Watch building). A pungent odor was noted throughout the area, a condition apparently considered normal by on-site workers.

☞ The newly-installed NH_3 sensors in AreaRAE units 1, 2, and 3 appeared to drift as they continued to be burned-in. Ideally, these units would have been removed from service, re-zeroed, and re-calibrated. However, this was not desirable due to the need to initiate and continue clam loading operations, without any down time. As such, it was necessary to adjust readings to ascertain actual emissions during operational periods.

Over the 2 hour pre-operations baseline study period, the Ammonia reading in units 1, 2, and 3 steadily increased in concentration, consistent with a sensor drift condition. This drift started in the time following unit calibration (0900–1000 hrs), causing elevated readings at the start of the baseline study (1100 hrs). This is most evident in units 2 and 3, as displayed in Figure 3.

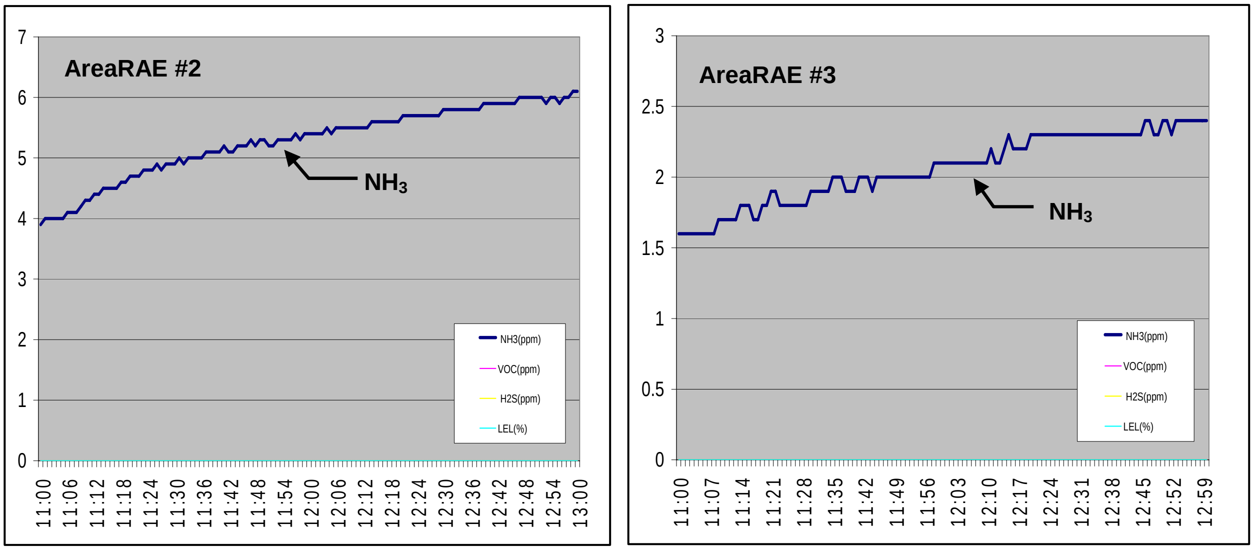


Figure 3 – Baseline Monitoring – AreaRAE Units 2 and 3

In addition to sensor drift, unit 1, located in the exclusion zone adjacent to the Sea Watch building, also displayed signs of (actual) increases in Ammonia and Hydrogen Sulfide levels, based on the pulsed increase in NH_3, with concomitant increases in H_2S. (see Figure 4).

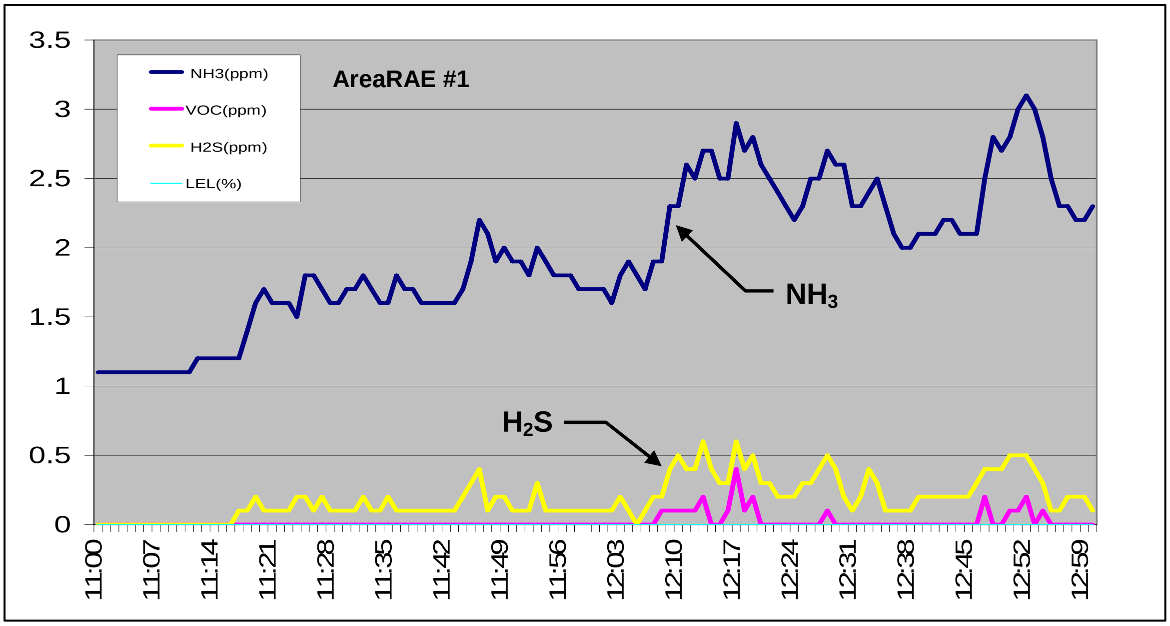


Figure 4 – Baseline Monitoring – AreaRAE Unit 1

ACTION LEVELS

An air sampling plan was written by EPA and approved by Unified Command. This plan set the following action levels for the contaminants of interest:

Exclusion (Hot) Zone – AreaRAE Unit #1

- 100 ppmV NH_3 or H_2S
- 10% LEL
- 100 ppmV VOCs

Perimeter – AreaRAE Units 2, 3, and 4

- 5 ppmV instantaneous reading of NH_3 or H_2S
- 1 ppmV average value of NH_3 or H_2S over 15 minutes

Various worker & public health metrics for the contaminants of concern are provided in Table 1.

Table 1 – Health Metrics

Health Metric	ppmV		Explanation	
	NH_3	H_2S		
IDLH	300	100	Worker	Immediately Dangerous to Life and Health
STEL	35	15		Short Term Exposure Limit – 10 to15 minutes
PEL	50	20		Permissible Exposure Limit (OSHA) – 8 hours
REL	25	10		Recommended Exposure Limit (NIOSH) – 8 hours
AEGL-1	30	0.33	Public	Acute Exposure Guidelines (EPA), mild/reversible effects, 8 hrs
AEGL-2	110	17		Acute Exposure Guidelines (EPA), serious effects, 8 hrs
Odor	0.7	0.8		Air concentration when an odor is first discernable

As can be seen, the perimeter action level for Ammonia was well below worker exposure limits and concentration deemed acceptable for the general public (i.e., AEGL-1). While well below worker exposure limits, the perimeter action level for Hydrogen Sulfide was above the AEGL-1 value of 0.33 ppmV. However, given the substantial distance to the nearest sensitive receptors (e.g., homes, schools, hospitals), perimeter concentrations of 1 ppmV would be substantially diluted in any air transport plume.

FAST was directed to immediately notified Unified Command and the Operations Unit if any of the established Actions Levels were exceeded.

METEROLOGICAL DATA

Wind direction and speed were continuously monitored on the Weatherpak weather station in the FAST mobile laboratory vehicle. These data were manually summarized and recorded every two hours by FAST personnel.

The nearest weather station with electronically downloadable data is in Fairhaven, approximately 1.25 miles northeast of the site, at Latitude N 41° 39’ 25”, Longitude W70° 54’ 03”. Pertinent data from this station is displayed in Figure 5. These data are consistent with observation recorded by FAST staff via the on-board Weatherpak station, except for wind direction Tuesday night/Wednesday morning, 6/14 – 6/15, which shifted at the site from NW to NE to E to S over the course of this time period (see Figure 5).

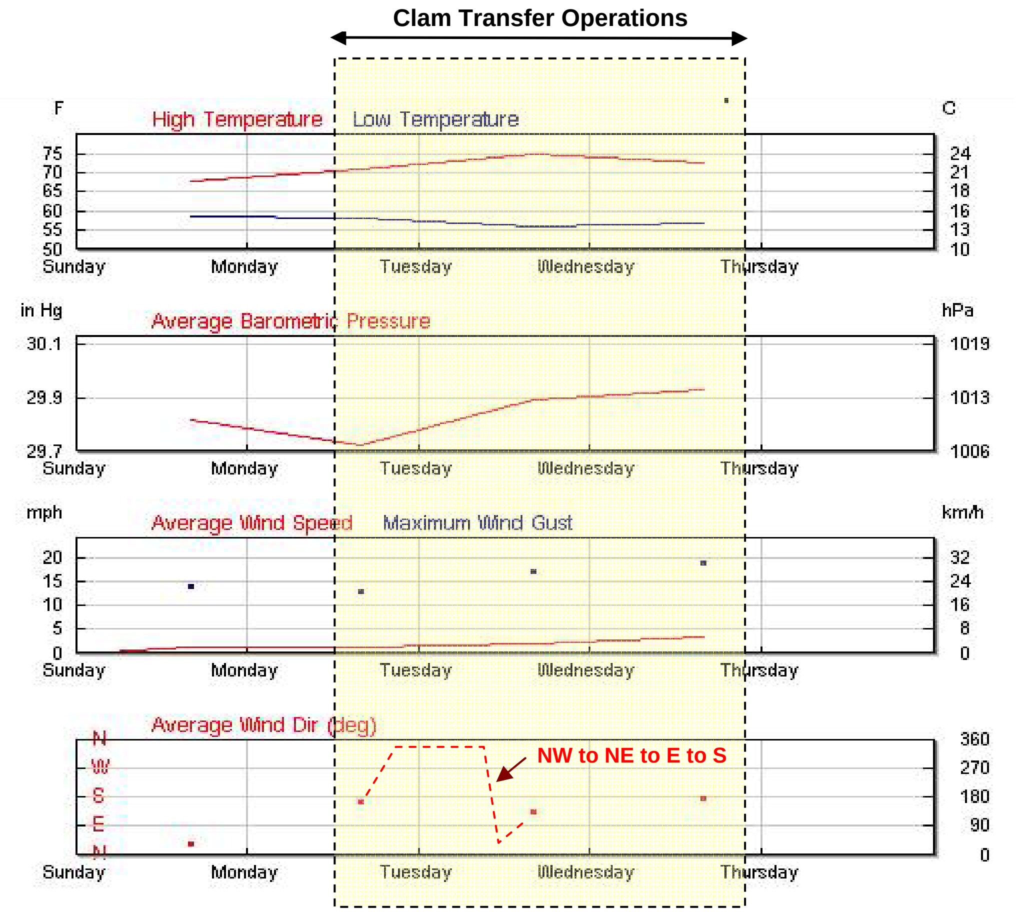


Figure 5 – Weather Conditions from 6/13/10 to 6/17/10

AIR MONITORING DATA

From 1300 hours on 6/14/10 to about 2300 hours on 6/16/10, readings for the 4 AreaRAE units were continuously viewed and logged by FAST personnel in the mobile lab vehicle. During this time period, each AreaRAE unit transmitted data for each sensor (NH_3, H_2S, LEL, and VOCs in units 1, 2, and 3, and Cl_2, H_2S, LEL, and VOCs in unit 4) every 2 seconds, a total of over 400,000 data points. Each unit was programmed to log data points over 60 second intervals (i.e., an average value over one minute).

In addition to electronic systems, FAST personnel recorded data summations every 2 hours on a “D” sized spreadsheet mounted on a wall in the mobile lab. This action facilitated communication of results to Unified Command, and observations of data trends on each individual unit. It was also necessary because it is not possible to download data from the AreaRAE units or laptop PC without suspending monitoring operations, which was not permissible.

At about 1500 hours on 6/15/10, because of the high drift, the unit 2 Ammonia sensor was “re-zeroed” using ambient air. During a scheduled shut-down in clam transfer operations around 1800 hours on 6/15/10, the battery in each AreaRAE unit was changed, which required instrument shutdown and re-start.

The collective data for all 4 AreaRAE units for the 3 days of operations are graphically presented in Figures 7 through 10.

In addition to the AreaRAEs, periodic measurements were made with the V-RAE meters at the exclusion zone perimeter. In all cases, ammonia levels did not exceed 1 ppmV, and Hydrogen Sulfide levels were not detectable.

An air sample was also taken near AreaRAE unit 2, at 5:30 PM on 6/14/10, for analysis on the FAST on-board Gas chromatograph (GC/PID/ECLD). The PID chromatogram from this effort is depicted in Figure 6.

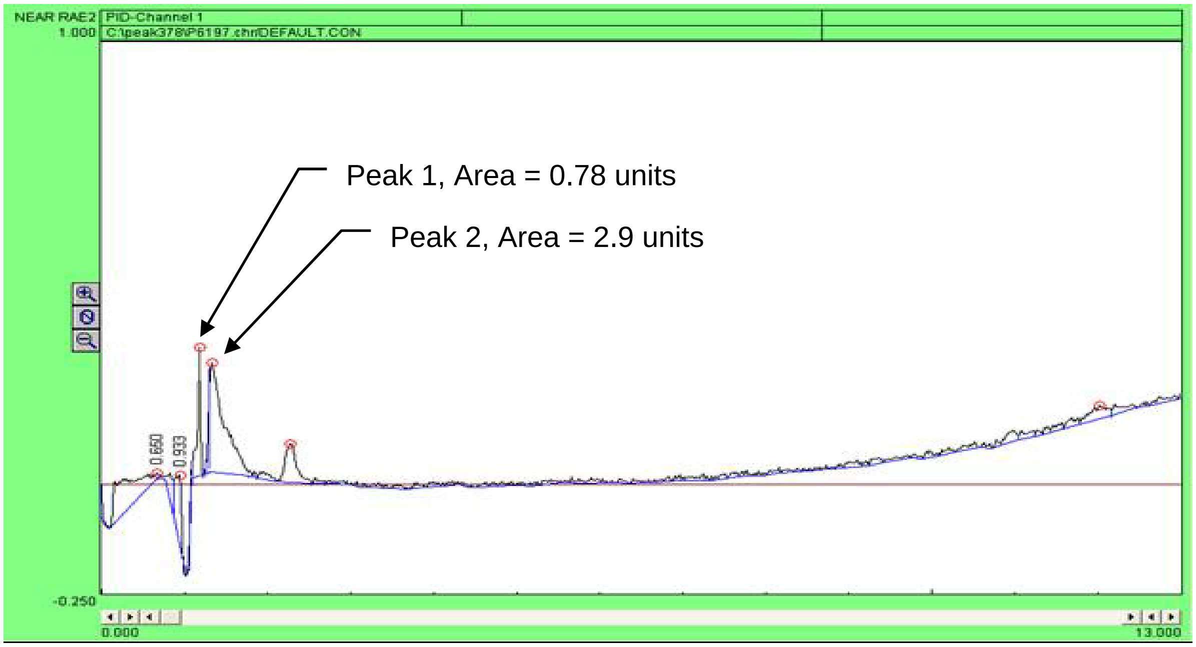
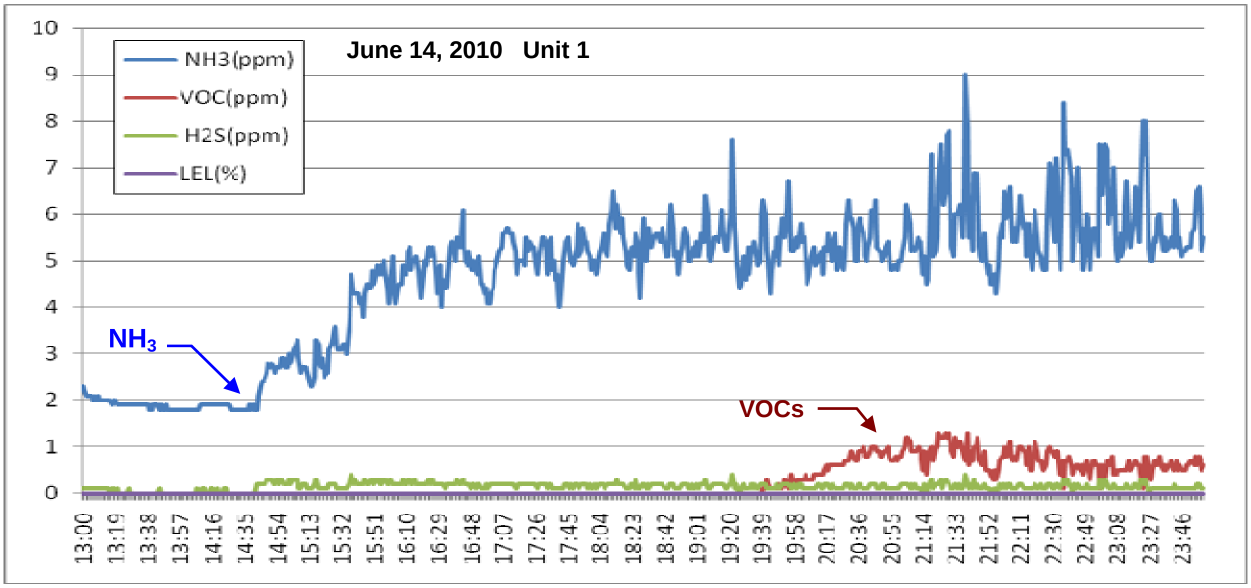
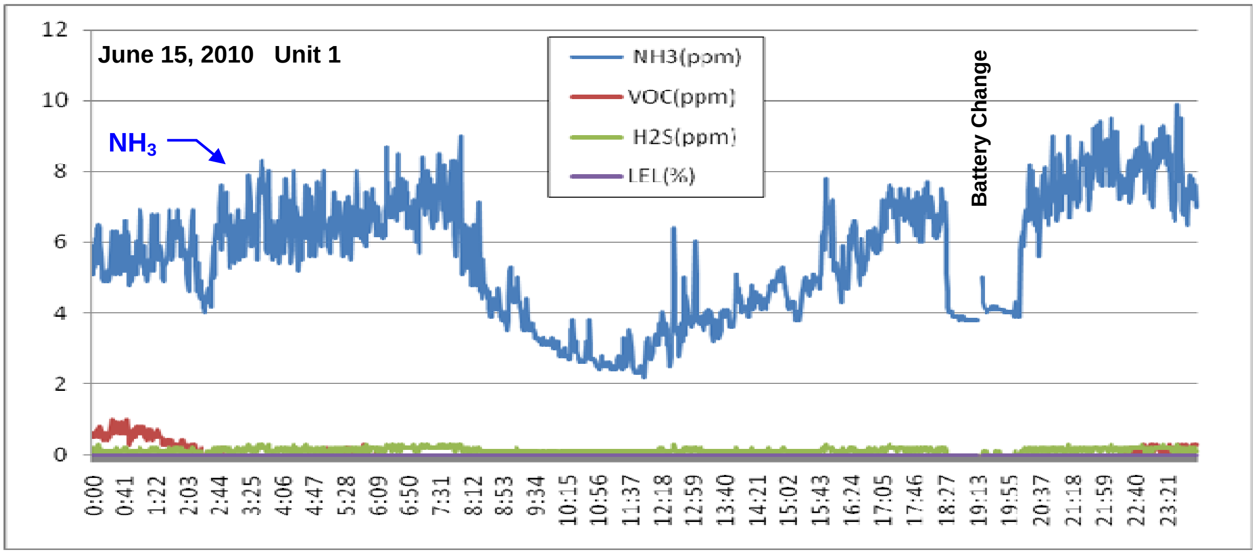


Figure 6: GC/PID Data for 6/14/10 near AreaRAE #2

Figure 7: AreaRAE Unit #1 (Hot Zone)





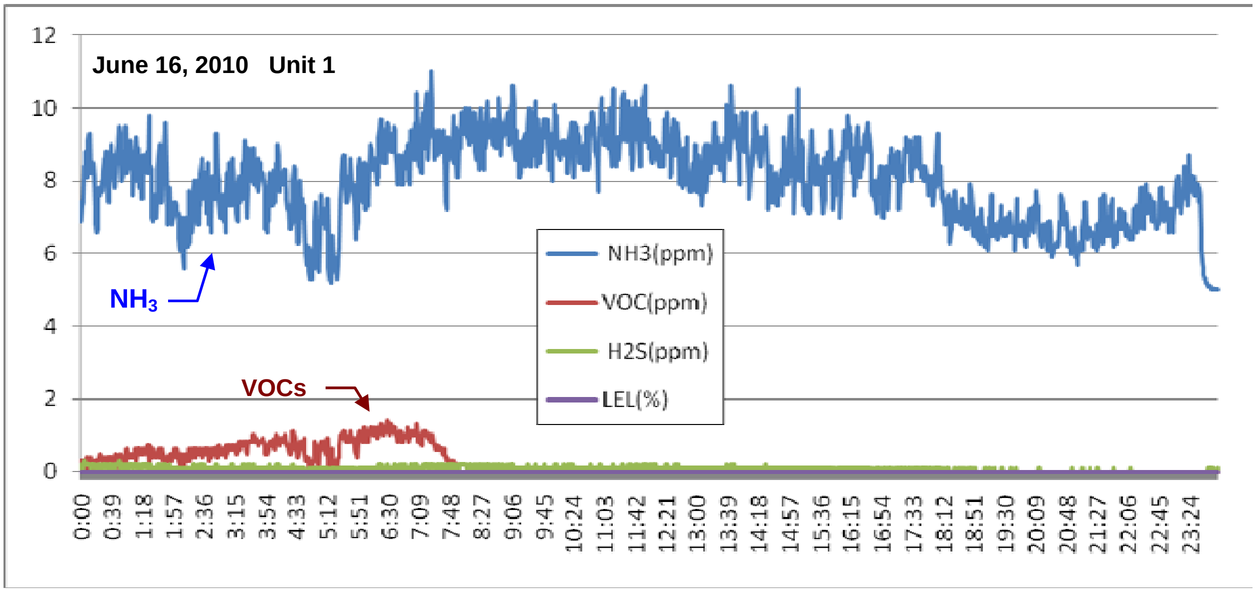


Figure 8: AreaRAE Unit #2 (Southerly)

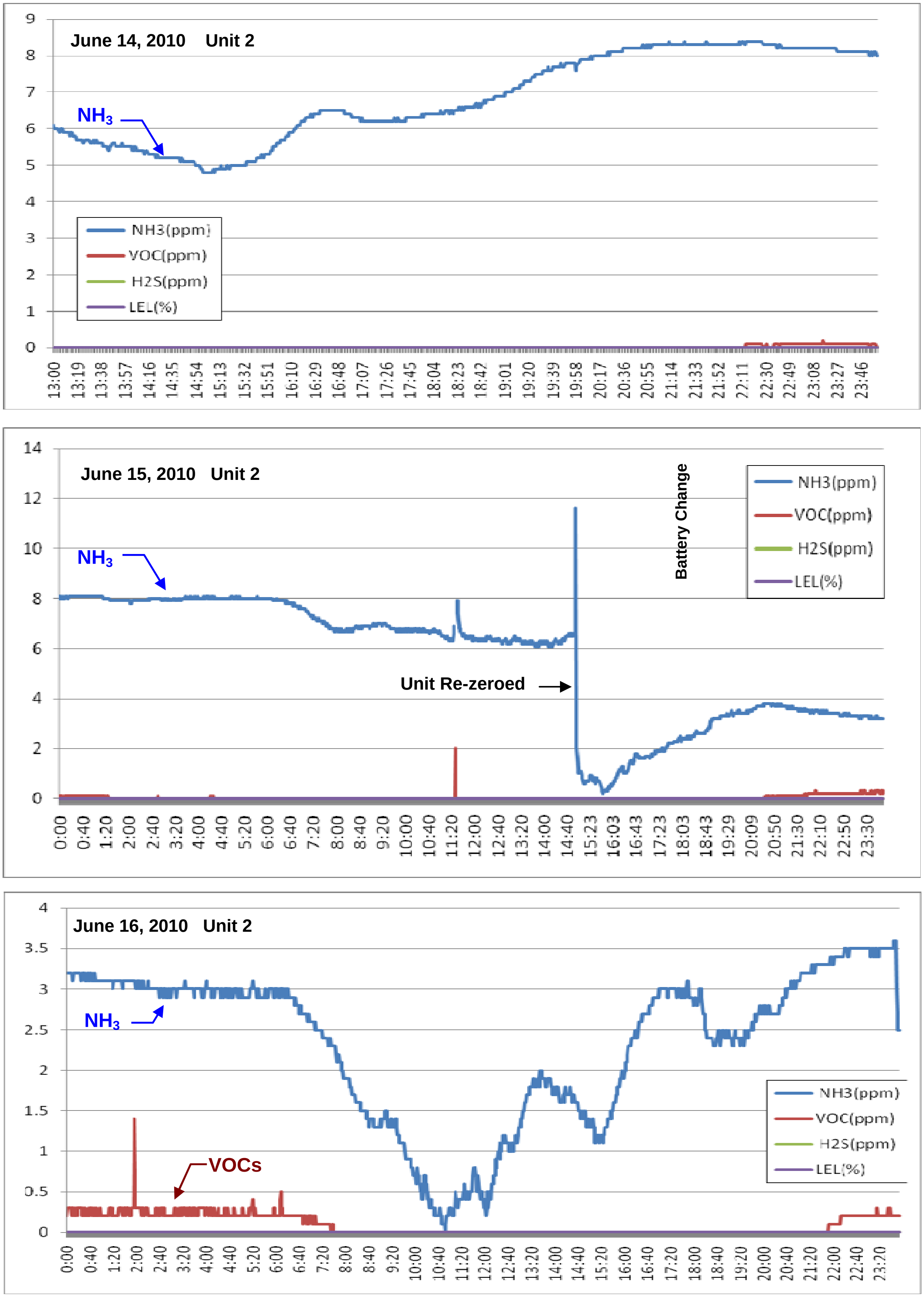


Figure 9: AreaRAE Unit #3 (Easterly)

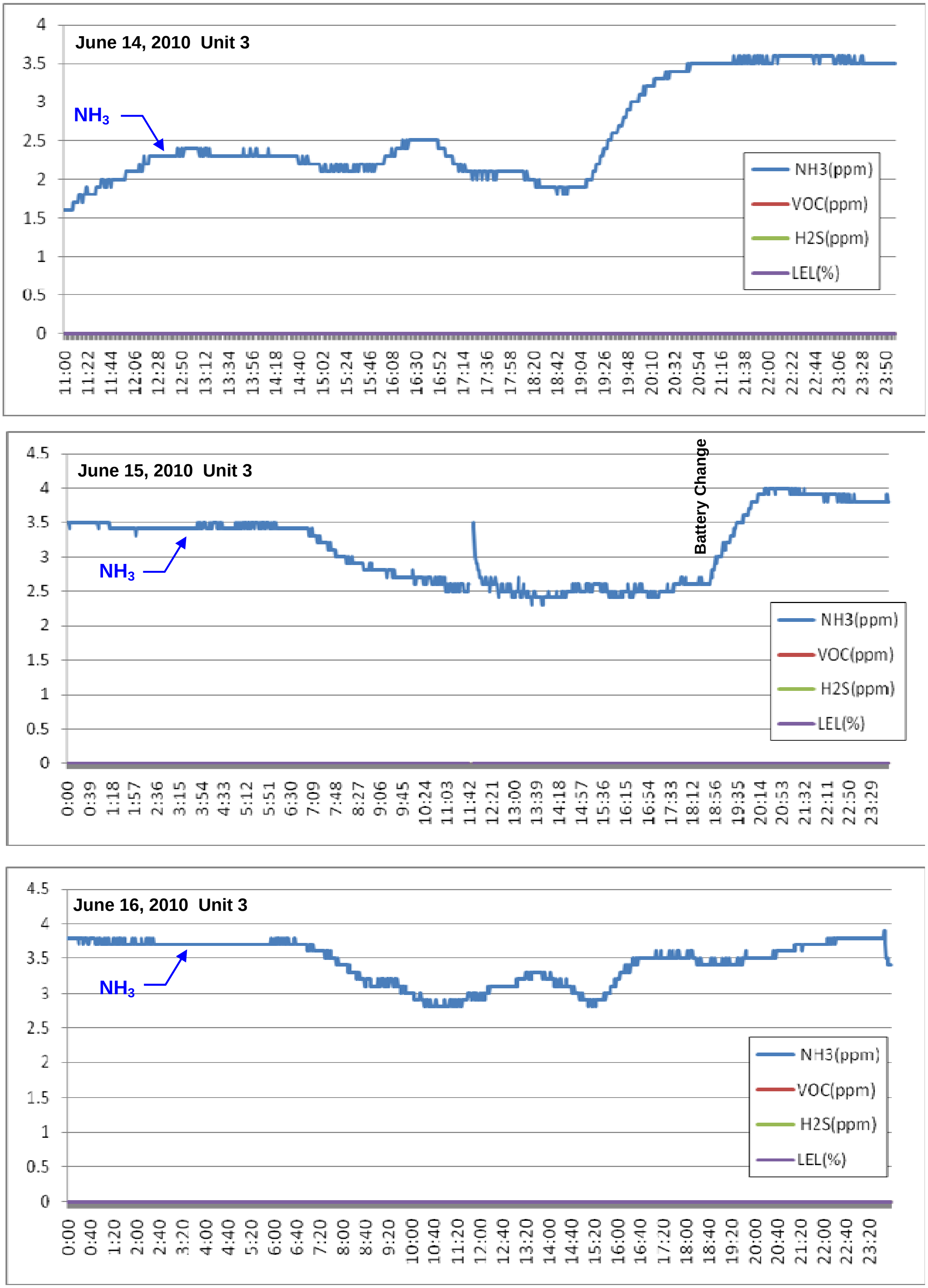
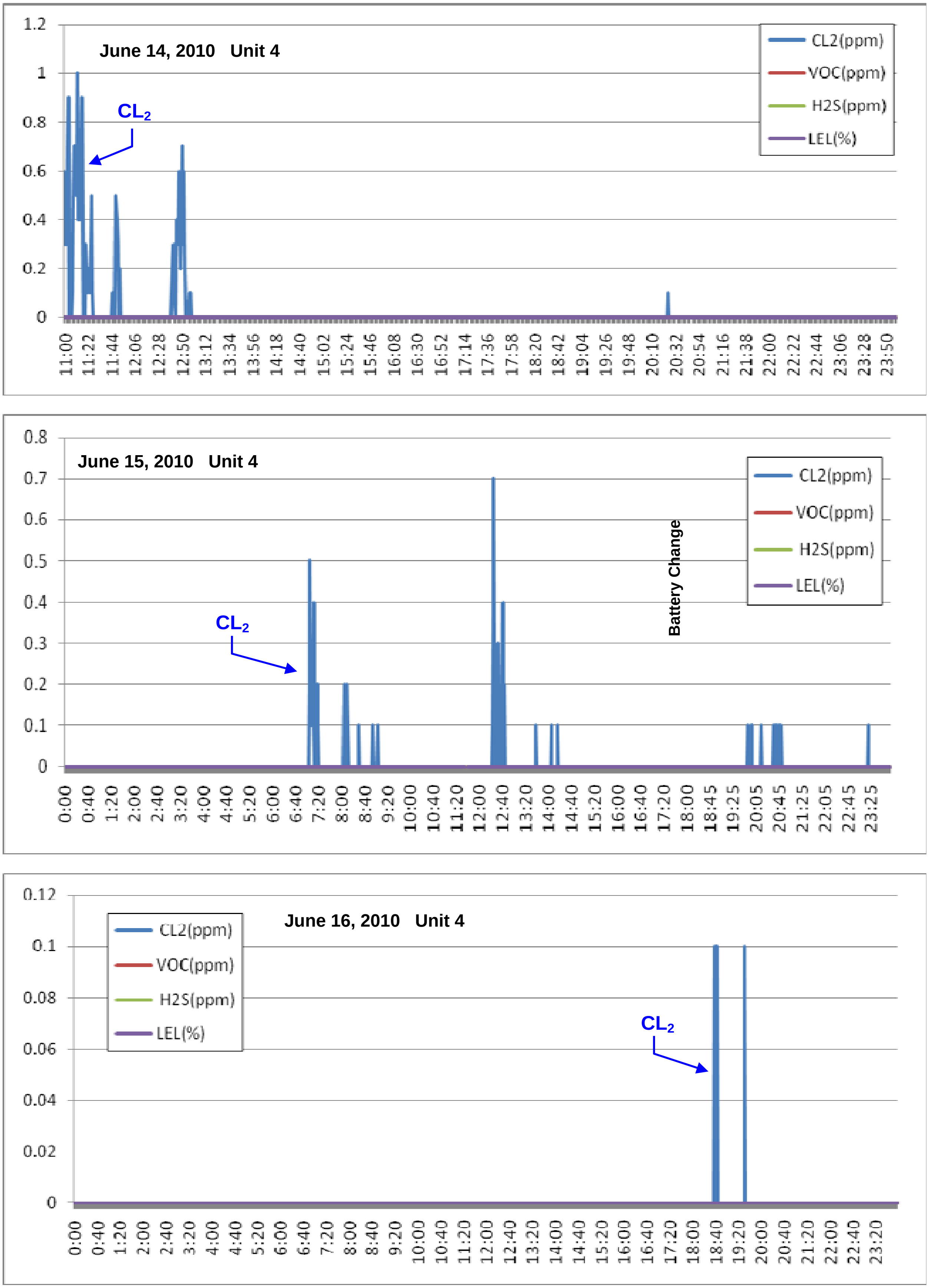


Figure 10: AreaRAE Unit 4 (Northerly)



Although the chromatography was not ideal, on the basis of repeated injections of NH_3 and H_2S standards from available calibration gas cylinders, both compounds were found to elute at about 1.1 minutes on the FAST GC/PID/ELCD VOC program, co-eluting with a peak found in blank samples (i.e., some compound in ambient air). The ambient air peak was about 2 Area Count units.

Approximate Calibration Factors (CF) were determined for NH_3 and H_2S, based upon chromatographic area counts/concentration of injected standard:

- CF for NH_3 = 2.5 ppmV/Area Count
- CF for H_2S = 0.25 ppmV/Area Count

It is not clear why Ammonia responded 10 times better on the PID than Hydrogen Sulfide, though it may be related to the lower ionization energy of Ammonia (10.16 eV, compared to 10.45 for Hydrogen Sulfide), and/or the “quenching effect” of methane which was contained in the H_2S calibration gas cylinders.

On the basis of the above, and with some degree of uncertainty, peak 1 or 2 could be NH_3 or H_2S (alone or in combination with other analytes or each other). Subtracting out 2 Area Count units for peak 2 (ambient air correction) put both peaks at around 1 Area Count. This suggests that values at this location could be no higher than about 0.25 ppmV H_2S or 2.5 ppmV NH_3.

DISCUSSION

The air monitoring task was complicated by the drift in the NH_3 sensors in AreaRAE units 1, 2, and 3. While this drift was not substantial, in the macro sense (i.e., up to about 7 ppmV in unit 2), it was of significance to this effort, given the established perimeter Action Level (i.e., sustained 1 ppmV increase over 15 minutes).

Ideally, the NH_3 sensor in each unit should have been burned-in for a longer period of time, replaced, and/or re-zeroed and re-calibrated in response to drift conditions. However, this would have required termination of air monitoring, which would have necessitated the termination of clam transfer operations, which was highly undesirable. As an intermediate step, because of the very high drift in unit 2, the NH_3 sensor was re-zeroed in-place at about 1500 hours on 6/15/10 (see Figure 8). This was done when the wind was from the SE to SW, i.e., when unit 2 was up-wind from the clam transfer operations.

Another complication arose when the batteries were changed in each AreaRAE unit (around 1800 hours on 6/15/10, after 34 hours of continuous use). This caused a baseline shift in some of the units, which, again, ideally should have been taken out of serviced and re-zeroed and re-calibrated.

Despite these limitations, based upon the totality of monitoring data and observations, it can be reasonably concluded that Action Levels were not exceeded in either the Hot Zone or site perimeter:

<u>Ammonia</u>

- ☞ In the Hot (Exclusion) Zone, even though there may have been some drift on the NH_3 sensor in AreaRAE 1, the displayed concentrations of NH_3, H_2S, and VOCs never came close to the designated limits. That being said, it is worthwhile to note the constant (1 ppmV or so) fluctuation in the NH3 readings, as well as periodic increases in H_2S and

VOC concentrations (Figure 7). This suggests that actual (low level) emissions of these analytes were likely occurring at this location.

- ☞ AreaRAE unit 2, located southerly of the work area/exclusion zone, had the most pronounced sensor drift problem. After being zeroed and calibrated at about 9:00 AM on 6/14/10, the newly-installed NH_3 sensor read 4 ppmV at the start of baseline monitoring at 11:00 AM, and 6 ppmV at the conclusion of baseline monitoring 2 hours later at 1:00 PM. It then slowly increased and decreased between 6 ppmV and 8 ppmV until 6/15/10, when it was re-zeroed in place at about 3 PM, when it began to slowly increase (following the installation of new batteries) to about 3 ppmV. The following day, the sensor was quite erratic, between zero and 3.5 ppmV.

  Despite these data, there is ample evidence that suggests that these readings were anomalous, and that actual levels of NH_3 at this location were consistent with the area-wide background value of about 1 ppmV:

  - ➢ first and foremost, spot measurements made at this location by FAST V-RAE unit 2, which contained a long-installed, steady, and calibrated NH3 sensor, always read between zero and 1 ppmV;

  - ➢ given the coastal wind gusts and the dynamic nature of clam transfer operations, one would expect that emissions from the work area would produce discrete spikes, as was seen for AreaRAE unit 1 (Figure 7). To the contrary, the NH_3 sensor readings from this unit slowly increased and decreased, with instantaneous changes generally only a fraction of a ppmV;

  - ➢ during the 3 days of monitoring, winds were from the south at all times except from about 9 PM on 6/14/10 to about 3 PM on 6/15/10, during which time the wind originated from a more northerly location. Therefore, AreaRAE unit 2 was up-wind of the work area/exclusion zone for most of the project. If there truly were elevated emissions of NH_3 from the clam transfer operations, readings should have increased during this time period, which was not the case; in fact readings slightly dropped;

  - ➢ as previously discussed, an air sample obtained from this location and analyzed on an on-board GC/PID unit suggests that the concentration of Ammonia could not be greater than about 2.5 ppmV. Note that this sample was taken at 5:30 PM on 6/14/10, when AreaRAE unit 2 was reading just over 6 ppmV;

  - ➢ finally, with an odor threshold of about 0.7 ppmV, and distinctive aroma, levels of Ammonia much above 1 ppmV should have been discernable. While a pungent odor was prevalent throughout the area, it was more consistent with a “rotting” condition (e.g., volatile organic acids), than an Ammonia smell.

- ☞ AreaRAE unit 3, located easterly of the work area and on the *ESS Pursuit,* also displayed signs of NH_3 sensor drift, in which readings ranged from about 2.5 ppmV to 4.0 ppmV. With two exceptions, these changes were gradual, as with AreaRAE unit 2. The two exceptions are on 6/15/10, when the battery was changed, and on 6/14/10, at about 7 PM, when concentrations increased from 2 ppmV to 3.5 ppmV NH_3 over about a 90 minute period. While the battery change-out effect has been noted, the rise on 6/14/10 cannot be explained by site conditions, as winds had been consistent throughout the day from the Southwest, as had levels of NH_3 in the hot zone (Figure 7). Given that spot checks with the V-RAE unit 2 indicated only about 1 ppmV concentrations of NH_3, and for other reasons discussed above for AreaRAE unit 2, it can be reasonably concluded that Action Levels were met at this location.

- AreaRAE unit 4, located northerly of the work area, did not have an NH_3 sensor. Periodic readings with V-RAE unit 2 did not indicate levels of Ammonia above 1 ppmV. Periodic (low-level) spikes were recorded on the Cl_2 sensor, though it was not clear if these were false positives and/or from the use of hypochlorite (bleach) solutions in the work area.

Hydrogen Sulfide

In contrast to the NH_3 sensor, no problems were noted with the H_2S sensors (which had long been installed and properly operating in the AreaRAE units). In general, AreaRAE readings were 0.3 ppmV or less, with occasional short-term spikes to 0.5 ppmV. This was corroborated by spot readings by V-RAE unit 1, as well as the GC/PID air sample.

Other Contaminants

There were no issues with explosive gases, given the absence of LEL readings. There were occasional “VOC” readings from the photoionization detector, with spikes up to 2 ppmV, though it is not clear whether these were truly VOCs or some other ionizable constituent. In either case, these levels were not of concern.

CONCLUSION

Continuous air monitoring was conducted by FAST during the clam repacking operation. Although problems were experienced with the Ammonia sensors that were newly-installed in the AreaRAE units, sufficient information and data existed to conclude that site concentrations of contaminants of concern were within established Action Levels.

Even under a worst-case scenario, in which the AreaRAE Ammonia sensor readings were correct, the maximum reported perimeter value of 9.5 ppmV was still well below concentrations deemed acceptable for the general population (i.e., the AEGL-1 limit of 30 ppmV).