MassDEP Field Assessment and Support Team (FAST)

After Incident Report	DEP RTN 4-22,102
NEW BEDFORD – New Bedford Waste Services	August 3, 2009

BACKGROUND

At around 10 AM on Monday, August 3, 2009, reports were received of workers being overcome by fumes at the New Bedford Waste Services transfer and processing facility on Shawmut Avenue in New Bedford. Eventually, over 100 people were reportedly treated at area hospitals, including two workers who had lost consciousness and were in critical condition.

The incident soon escalated to a Tier 4 Hazmat response category.

FAST ACTIVATION AND DEPLOYMENT

FAST was initially notified of the incident by SERO/ER at about 11 AM. By 11:30 AM, confirmation was received from SERO/ER that the incident appeared to be a significant event, and a request was made for FAST assistance.

Unfortunately, the FAST vehicle was being serviced at Liberty Chevrolet in Wakefield when the call was received. Liberty Chevrolet was immediately notified and directed to stop work. The vehicle was retrieved and brought back to NERO at 12:20 PM, and loaded with appropriate equipment and instruments, including both GCs. FAST members mobilized by the Team Leader (John Fitzgerald) consisted of Specialist (GC operator) Larry Immerman and Assistant Team Leader Albe Simenas.

The FAST vehicle left NERO at 12:45 PM and arrived at the site at 2:30 PM. Team members worked with SERO/ER, DFS, EPA, and the facility operators to evaluate available information, and plan appropriate assessment activities. A hot zone was set up around the impacted building, with Level A entry. By mid-afternoon, members of the National Guard Civil Support Team (CST) arrived with personnel and assets to assist in the (Level A) sampling and analysis

of the impacted area.

Two theories developed on what could have caused the fumes that apparently overcame the workers:

- Two 55 gallon drums of a 31% aqueous solution of sodium chlorite ($NaClO_2$) were reportedly on site, used to (a) sanitize/minimize odors in the sewer system, and (b) sanitize/treat water in a 10,000 gallon "Float Tank" used to clean and separate materials at the site. It was possible that this solution reacted with something in the incoming waste (float tank) or in the facility sewer to generate chlorine dioxide gas (ClO_2); or

- Something in the incoming trash was ruptured, resulting in fumes that overcame the workers.

FAST personnel produced large size aerial and "bird's eye view" maps of the site and facility, which were used by DFS responders to plan operations and memorialize findings. FAST also provided DFS with 3 AreaRAE units and 1 V-RAE meter (equipped with chlorine sensors) that were deployed and used in and near the building by DFS personnel in Level A protection. (In June, DEP AreaRAE units were re-programmed to share a common radio frequency with DFS units, to allow for interoperability).

The winds were from the south/southwest throughout the day, at between 1 and 2 MPH. Only industrial/commercial building were located downwind of the facility (reportedly evacuated), with the nearest residential neighborhood more than ½ mile away. AreaRAE and hand held meters indicated only low or none detect levels of contaminants in the ambient air in the vicinity of the impacted building.

Unfortunately, because of apparent miscommunications, air samples were not obtained from within the impacted structure. Throughout the day, FAST personnel were waiting for such samples for analysis on the on-board GCs. FAST had also requested that the CST analyze such a sample on their Hapsite GC/MS.

FAST personnel demobilized from the site just before midnight. Reportedly, DFS personnel continued response operations until about 3 AM Tuesday, sifting through a recently dumped load of wastes, looking for materials that might have precipitated the event. After resuming operations later on in the morning, response actions terminated at about 12:30 PM on Tuesday, 8/5/09, after which a declaration was made by Fire Services personnel that the facility no longer posed a risk to public safety. The exact cause of the incident or nature of the fumes was not determined.

DISCUSSION

Based upon the information and data available to FAST, it is not possible to determine the cause of the incident, or nature of the fumes that impacted facility workers. Based upon what is available as of August 6, 2009, the following analysis is offered.

Logically, it would appear that the fumes could have originated from:

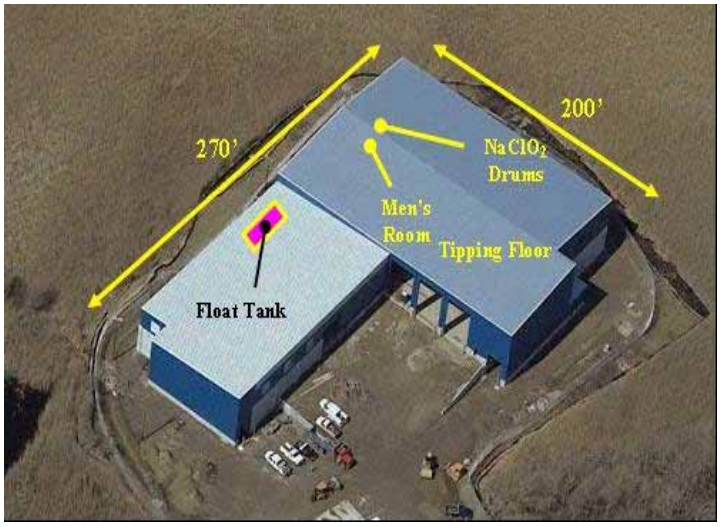
- the sodium chlorite solution stored within the facility in 55 gallon drums;
- a reaction between the sodium chlorite and waste materials in the Float Tank;
- a reaction between the sodium chlorite and waste or chemical materials in the building sewer;

- waste materials received and/or being processed at the facility, independent of any interaction with the sodium chlorite; or
- Hydrogen sulfide emitted from drains and/or sewer piping, or as a reaction byproduct with sodium chlorite and/or incoming wastes.

Additional steps may be taken to further evaluate waste materials that were brought into the facility. Such prospective steps are beyond the scope of this report.

Sodium Chlorite ($NaClO_2$)

The possible involvement of the sodium chlorite solution stored and used at the site warrants examination, given its properties and reaction/breakdown products, and given that both of the unconscious workers were reportedly overcome outside the first floor men's room, which is located immediately adjacent to the sodium chloride storage/dispensing area.



It was initially reported that two 55 gallon drums of sodium chlorite were contained in an (unused) lady's restroom on the first floor of the facility, immediately adjacent to the men's room. Subsequent reports indicate that there is only one drum containing product in this area, along with two other drums that are apparently empty.

Two metering pumps are situated on top of the partially filled drum. One pump directs solution to the 10,000 gallon Float Tank, located about 100 feet away. The other tank is pumped into an adjacent sink, where it is mixed with running water from a faucet, and discharged into the plant's sewer system. There is some question as to whether the pump to the sink was plugged in prior and during the incident.

Given that a solution of commercially available 31% sodium chlorite is relatively stable, and given reports that site entry teams noted that the storage drums appeared to be sound, a reaction between this solution and some other material appears to be the most promising scenario to further consider.

Chlorine Dioxide

Chlorine dioxide ($Cl0_2$) is used to bleach/sanitize. It is a gas but can be dissolved in water at low concentrations to be used as an aqueous solution. In this application, the sanitizing agent is chlorous acid ($HClO_2$).

To be cost effective, it is necessary to purchase a concentrated form of this material, to be diluted with water at the point of use. However, both $HClO_2$ and ClO_2 are unstable in concentrated solutions. Adding a sodium ion produces a much more stable concentrated product, sodium chlorite ($NaHClO_2$), which is distributed as a solid or as a liquid (aqueous) solution.

When placed in water, sodium chloride dissociates into the sodium ion (Na+) and a chlorine dioxide anion (ClO_2^-). It then combines with the hydrogen ions (H+) in water to produce chlorous acid:

$$Na^+ClO_2^- + H^+ \longrightarrow HClO_2^- + Na^+$$

Chlorous acid can react with various substances, including acids and organic materials, to produce chlorine dioxide (ClO_2) gas. The IDLH (Immediately Dangerous to Life and Health) value for ClO_2 is 5 ppmV. *The unanswered question in this incident is whether it is plausible to construct one or more scenarios where sufficient quantities of ClO_2 gas could have been produced from an uncontrolled reaction of the sodium chlorite/chlorous acid with some other reactant(s).*

Symptoms

If chlorine dioxide gas was produced in significant concentrations from the use of sodium chlorite at this site, could it explain the symptoms experienced by workers? According to various reports, the primary symptoms noted were **nausea, throat and eye irritation, and respiratory distress**.

OSHA (thttp://www.osha.gov/SLTC/healthguidelines/chlorinedioxide/recognition.html) reports that the acute symptoms for ClO_2 exposure are **irritation of the eyes, nose, and throat; cough; wheezing; shortness of breath**; bronchitis; pulmonary edema; headache; and **vomiting.**

This document goes on to indicate that ClO_2 is a "**severe respiratory and eye irritant in humans**. Inhalation can produce coughing, wheezing, **respiratory distress**, and congestion in the lungs [Patnaik 1992]. Irritating effects in humans was intense at concentration levels of **5 ppm**. Accidental exposure at 19 ppm of the gas inside a bleach tank resulted in the death of one worker (time of exposure is not specified) [ACGIH 1991]."

Thus, the reported symptoms appear to be consistent with an exposure to chlorine dioxide.

Possible Chlorine Dioxide Concentration Levels

Reportedly, relatively small amounts of the 31% sodium chlorite solution are used daily at the facility. On this basis, it could be possible to "rule out" impacts from this source, by looking at an upper limit/worst case scenario, where a reaction between the sodium chlorite solution and some unknown acid/organic/waste material liberated chlorine dioxide from either the Float Tank or (former lady's room) drain.

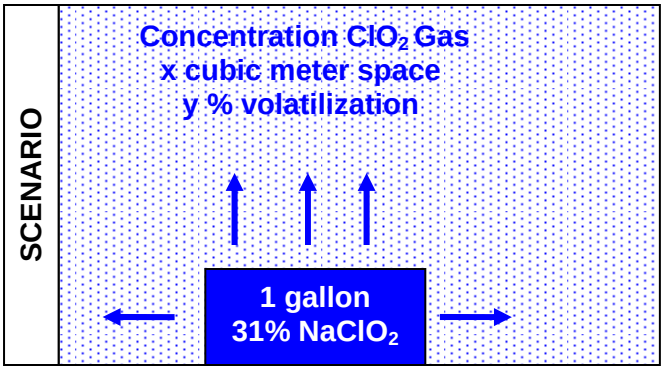
According to facility personnel, approximately 2 gallons/day are pumped into the 10,000 Float Tank, and approximately ½ gallon/day is discharged down the sink in the former lady's room. It is not clear what the pumping rate is, or the time period when pumping is accomplished.

There is obviously significant dilution of the sodium chlorite in the 10,000 gallon Float Tank (which is filled with water), as well as unknown dilution in the sink discharge (with the water being discharged from a faucet). In the Float Tank, it is unknown what percent of sodium chlorite/chlorous acid is consumed on a daily basis, but presumably that is dependent upon the nature of the waste and quality of water in the tank at any given time (i.e., some days, all of the sodium chlorite is presumably consumed; other days, there may be left-over residual

concentrations levels). It is also not clear how mixing and flow occurs in the discharge to the sink and facility sewer system.

The following analysis considers the maximum amount of chlorine dioxide gas that could exist in an enclosed space based upon the use of 1 gallon of a 31% sodium chloride solution, assuming 0.1%, 1%, and 10% of the available chlorine dioxide is released into an enclosed space of between 100 and 10,000 m^3.

Upper Limits of ClO_2 Concentration in Air
Via Off-Gassing from 1 Gallon of a 31% Sodium Chlorite Solution



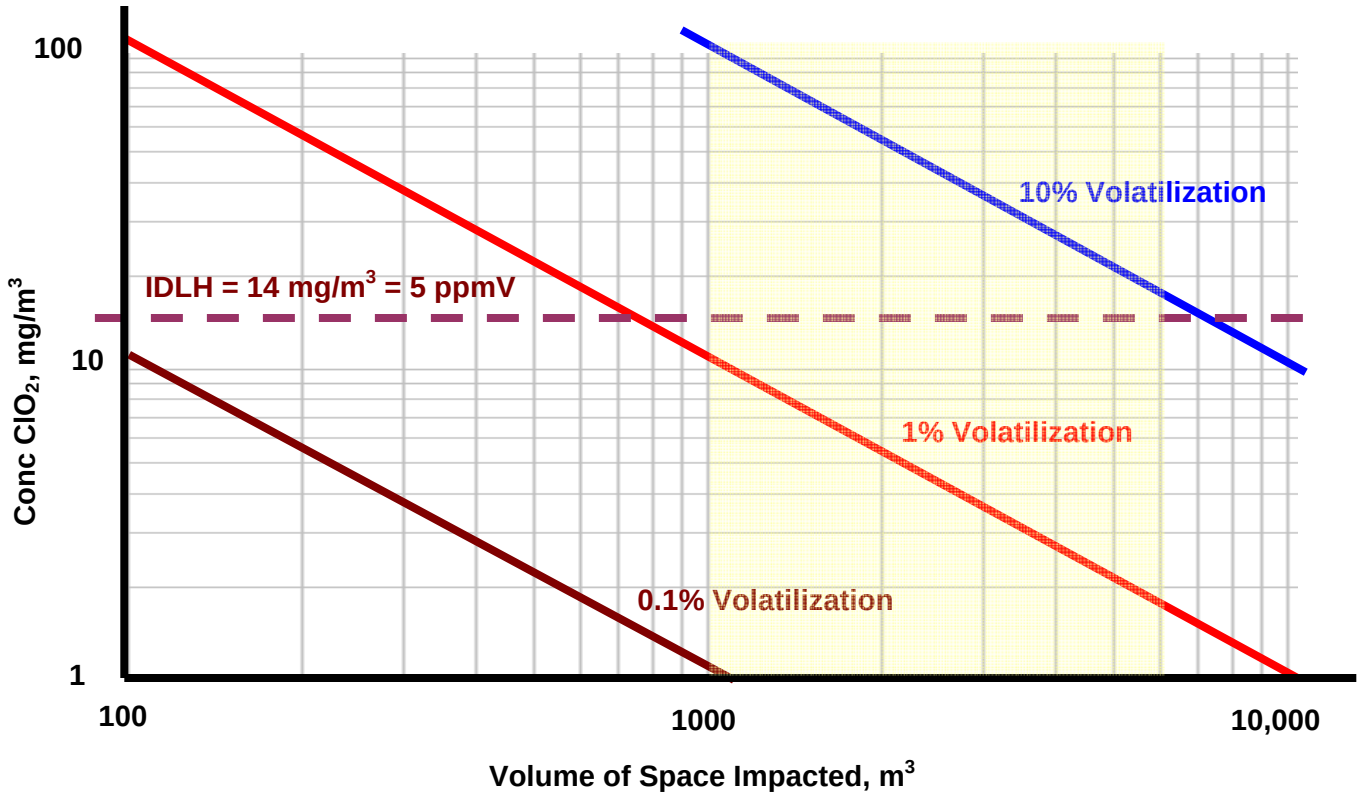
Density of 31% $NaClO_2$ solution = 1.27 g/mL

1 gal x 3785 mL/gal x 1.27 g/mL x 0.31 =
1500 g $NaClO_2$/gal of solution

$NaClO_2$ = 90 g/mole
ClO_2 = 67 g/mole
Thus, ClO_2 = 74% of $NaClO_2$ by weight
1500 x 0.74 = 1100 g ClO_2 per gal of solution

ClO_2 in Gaseous Form

1 mg/m^3 = 2.76 ppmV IDLH = 5 ppmV = 14 mg/m^3 Odor Threshold = 0.1 ppmV = 0.3 mg/m^3



On the basis of the above, it appears *possible* that the reported use of sodium chlorite *could produce levels of chlorine dioxide that could explain the symptoms noted during this incident*. For example, if 1% of the ClO_2 in a one gallon solution of sodium chlorite off-gassed into a 1000 m^3 space, the calculated air concentration in that space would be about 11 mg/m^3. If there were a total of 2 gallons of this solution in the Float Tank, and 1% of the possible ClO_2 emissions occurred into this 1000 m^3 space, the calculated value would be 22 mg/m^3 (8 ppmV), which is greater than the IDLH value of 5 ppmV. Off-gassing of 10% or more of the ClO_2 would likely exceed the IDLH virtually anywhere in the facility.

While the above indicates that sodium chlorite cannot be ruled out in this matter, it does not provide definitive evidence that such a reaction and emission occurred, given unknowns on what reactants may have existed, the extent and kinetics of that reaction and off-gassing, and the ventilation rate in the area of impact.

Hydrogen Sulfide

There is some evidence that Hydrogen Sulfide may have played a key role in this incident. This toxic gas could have been emitted as a by-product of a reaction between materials in the incoming waste, or could have been emitted from drains or sewer piping at the facility. The lines of evidence in support of this theory include:

- reports of sulfur/sulfide odors by plant workers during the incident; and
- the reported symptoms, including the two workers who had passed out, which are consistent with exposures to this toxicant.

While it appears likely that sulfides were present during the event, at least in localized areas, there are other lines of evidence that suggest that sulfides were not the primary factor or causative agent in this incident:

- Workers have provided conflicting reports on the odors associated with the fumes, including “propane gas mixed with ammonia”, “acetylene”, as well as sulfur-like. Given the distinctive and highly unpleasant “rotten egg” odor of sulfides, and an odor recognition threshold of only 0.5 ppbV, it is unclear why all workers would not have reported this very distinctive odor. By contrast, chlorine dioxide has a perhaps less distinctive “unpleasant chlorine-like” odor, with an odor threshold 200 times higher.

- The IDLH value for hydrogen sulfide is 100 ppmV, 20 times that of chlorine dioxide. That means that a relatively high concentration of hydrogen sulfide would have to have been produced at the facility (compared to chlorine dioxide) to produce the extreme respiratory distress noted. Moreover, given the large number of workers that experienced some symptoms, the amount and distribution of this gas would have to have been relatively significant.

- Data from real-time monitors (e.g., AreaRAEs) near and in the impacted structure did not indicate the presence of Hydrogen Sulfide above the detection limit of 1 ppmV. In contrast, an AreaRAE unit located just outside the Tipping Floor of the facility consistently identify “spikes” of chlorine up to 2 ppmV, over the course of the mid to late afternoon on 8/3/09, diminishing to mostly <0.1 after dark. Per RAE Systems Technical Note 114 (http://www.raesystems.com/~raedocs/App_Tech_Notes/), the response to the RAE chlorine sensor is essentially the same for chlorine dioxide as it is for chlorine. Moreover, H_2S will not produce a positive response on this sensor (in fact, it will create a slight negative reading).

Conclusions

Insufficient information and data is currently available to FAST personnel to make reasonable conclusions on the origin and nature of the fumes produced during this incident. However, the presence and use of sodium chlorite at this facility appears to be the most promising and/or most available avenue to pursue. This evaluation should consider not only the Float Tank, but also the sink discharge, and related feed/piping systems.

The above conclusions are subject to change as new information about the event and/or new investigative information is obtained.