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SUBJECT: FORENSIC REVIEW AND SAMPLING OF PPE/RESPIRATORY PROTECTIVE EQUIPMENT ASSOCIATED WITH PRIORITY INVESTIGATION 3-RIV-04

According to Robert Mulherin of the Riverside County Agricultural Commissioners (CAC) Office, on January 29, 2004, a 27 year-old male was handling a chlorpyrifos-containing pesticide. He was mixing/loading and applying the pesticide to a field of alfalfa. The next day, on January 30, in the early morning, he collapsed and subsequently expired. Since there was an association with pesticides involved in this fatality, the CAC collected the clothing and personal protective equipment (PPE) and sent it to the Worker Health and Safety (WHS) Branch of the Department of Pesticide Regulation. Personnel from the Industrial Hygiene Program would conduct the sampling of the items to establish if pesticides were present on the items.

On February 9, 2004 samples arrived at the California Department of Food Agriculture (CDFA) Chemistry Laboratory Services (CLS) in two 48-quart Coleman® coolers. Multiple angle photos of the coolers were taken before opening it by removing the strapping tape. For purposes of the WHS Branch tracking identification, the coolers were labeled respectively “A” and “B”. After opening the coolers the interiors were photographed before removal of contents. Within each of the coolers were two “blue ice” cooling packs. These cooling packs were approximately 7” square. On inspection, the packs were found to be fully melted. The coolers contained sample documentation generated by Robert Mulherin of the Riverside CAC. Riverside CAC had assigned these samples the identification sequence “33-RM-PV04-XXX”, “XXX” being the consecutive sequence sample number assigned by Riverside CAC. Samples were assigned WHS numbers parallel with their Riverside county sample number. The number is listed in Table One.

Table One: Original ID Codes and Sample Descriptors

Riverside CAC Sample number	Sample description	WHS ID	Comment
33-RM-PV04-001	Coverall	A.1	In plastic/paper bag
33-RM-PV04-002	Respirator, AO Safety®	B.2	In paper/Ziploc® bag
33-RM-PV04-003	1 pair of jeans	A.2	In plastic/paper bag
33-RM-PV04-004	Shirt, LS Jerzey®	B.2	In plastic/paper bag
33-RM-PV04-005	Inside swab of L rubber glove	B.3	Sealed in amber jar
33-RM-PV04-006	Inside swab of R rubber glove	B.4	Sealed in amber jar
33-RM-PV04-007	Inside swab of L rubber boot	B.5	Sealed in amber jar
33-RM-PV04-008	Inside swab of R rubber boot	B.6	Sealed in amber jar
33-RM-PV04-009	Swab sample	B.7	Sealed in amber jar

Samples 33-RM-PV04-005 through 33-RM-PV04-009 (WHS # B.3 – B.7) were left in their original containers for analysis by CLS. WHS did no further processing of these samples. The coveralls, work jeans, work shirt, and respirator were removed from their original bags and were processed for sub-sampling. All work was done within a chemical hood to prevent any contamination to either the laboratory or the investigators. The investigator handling the items wore vinyl gloves and these gloves were replaced each time the investigator moved onto a new item.

WHS Sample A.1 (worker's coverall) was removed from the bag and photographed. The coverall was dirty but showed no visible sign of spill or detectable odor of pesticide. The coverall was sectioned, using scissors, into six parts and each part labeled with a WHS sample number and placed in a pre-labeled large capacity glass jar. The sectioning and sample identification numbers of the coverall are in Table Two.

Table Two: Coverall Sectioning

WH&S ID Code	Section Description
A.1-001	Right arm
A.1-002	Left arm
A.1-003	Right leg
A.1-004	Left leg
A.1-005	Front of torso
A.1-006	Back of torso

Following completion of the sectioning of the coveralls, the jeans (Sample A.2) were removed from their plastic bag, photographed and noted to be clean and have no odor. The manufacturer label was intact and identified the brand as Route 66® size 34-32. The jeans were than sectioned

by cutting in half and placing each half in a pre-labeled large-capacity glass jar. The sectioning and sample identification numbers of the jeans are in Table Three

Table Three: Jeans (Pants) Sectioning

WH&S ID Code	Section Description
A.2-001	Right leg and pelvis
A.2-002	Left leg and pelvis

The work shirt (Sample B.2) was removed from the bag, photographed and placed in a pre-labeled large capacity glass jar for analysis. Work shirt was dark blue, "Jerzey®" brand size XL. Since this sample was not sectioned, there were no sub-sample identification numbers. As noted before, this was labeled as Sample B.2.

The respirator (Sample B.1) was the final item unpacked. It was shipped fully equipped with two chemical cartridges. The respirator was photographed, removed from the paper bag while still within a ZIPLOC® bag, photographed a second time, removed from the ZIPLOC® plastic bag and finally photographed again from multiple angles.

The AO Safety® brand respirator, Model 5700, size medium, and the attached cartridges appeared to be in very good condition: straps were intact and still had their elasticity, no visible cracks or undo wear was noted in the in the face piece, the yoke and cradle assemblies appeared undamaged, and the exhaust port cover was present, properly seated and undamaged. The filtering cartridges were intact with a slight discoloration on the metal of outside right cartridge (approximately 1" by ¼" wide, grey colored). The cartridges were labeled AO Safety®, R53- HE P100, NIOSH 11562, manufactured 06/20/03. According to the manufacturer, these cartridges are approved to provide respiratory protection against organic vapors, chlorine, hydrogen chloride, sulfur dioxide, chlorine dioxide, and hydrogen fluoride and are equipped with a P100 particulate filter that is effective against solid and liquid aerosols (99.97% filter efficiency level).

The cartridges were removed from the respirator and returned to the ZIPLOC® bag from whence they were removed. These are to be stored frozen for possible analysis of cartridge loading and remaining service life at a later time. CLS is presently not equipped to conduct those measurements.

The respirator was subject to further physical inspection. The gasket rings for the cartridge mountings were present and in good condition. As noted earlier, the exhalation port cover was present and in good condition with the exhalation valve present and in good condition. The exhalation valve was removed and showed no tears, discolorations, deformities or distortion. The exhalation valve was placed in a pre-labeled (WHS # B.1-001) 4-ounce glass jar for

analysis. The exhalation valve seating port was inspected and found intact with no cracks, pits or broken valve supports.

The exterior of the respirator was swabbed using cotton swabs dampened with ethyl acetate supplied by the laboratory. The wipe sample was placed in a pre-labeled (WHS # B.1-002) 4-ounce glass jar for analysis. The interior of the exhalation cover was swabbed in a similar manner and the wipe placed in a pre-labeled (WHS # B.1-003) 4-ounce glass jar for analysis. The inside of the mask was inspected further, with the right and left inhalation valves observed to be present and in good condition (no discolorations, distortions, punctures or tears) along with their seatings. The inhalation valves were removed and placed in a pre-labeled (WHS # B.1-004) 4-ounce glass jar for analysis. The interior of the respirator was then swabbed in the manner previous mentioned, and the swab was placed in a pre-labeled (WHS # B.1-005) 4-ounce glass jar for analysis.

The collected and processed samples were released to the custody of A. Scott Fredrickson, Agricultural Chemist with CLS. Mr. Fredrickson had been instructed by Riverside CAC to perform the following chemical analysis: organophosphate screen; carbamate screen; chlorinated hydrocarbon screen; and chlorpyrifos. Appropriate chains of custody have been recorded.

Digital photographs were taken of all the major processing activities. These photographs will be archived with the investigation results. Table Four summarizes the samples collected and processed by WHS.

Table Four: WHS Sampling Summary

WH&S ID Code Number	Sample Description
A.1-001	Coverall/Right Arm
A.1-002	Coverall/Left Arm
A.1-003	Coverall/Right Leg
A.1-004	Coverall/Left Leg
A.1-005	Coverall/Torso Front
A.1-006	Coverall/Torso Back
A.2-001	Jeans Pants/Right Leg
A.2-002	Jeans Pants/Left Leg
B.1-001	Respirator Exhalation Valve
B.1-002	Respirator Exterior Swab
B.1-003	Respirator Exhalation Cover/Interior
B.1-004	Respirator Inhalation Valves
B.1-005	Respirator Interior Swab
B.2-001	Blue Work Shirt

In addition, WHS sample numbers B.3, B.4, B.5, B.6, and B.7 were assigned to swab samples submitted by Riverside CAC that were not collected or processed by WHS.

The primary results were made available on February 19th. Not only were there detected residues of chlorpyrifos, but the initial screens also revealed malathion and DEF (tribufos, another organophosphate). Additionally, CLS reported preliminary indications that the herbicides pendamethalin (PROWL®) and norflurazon (SOLICAM®) may also be present on some of the items. CLS asked if further analysis, beyond that requested by Riverside CAC, was desired. After consultation with the WHS Agricultural Program Supervisor, the Senior Industrial Hygienist authorized the analysis for pendamethalin and norflurazon. These results were received on March 5th. The complete results are shown in Table Five. In the cases of the organophosphates, laboratory spike recovery was >90%; for the herbicides it was >80%. The carbamate screen yielded no detectable residues (limit of quantification for carbamates: 20 µg/sample). The chlorinated hydrocarbon screen was not performed.

Table Five: Results*of Investigative Samples Collected for 3-RIV-04

ID Code	Item Name	DEF	Chlorpyrifos	Malathion	Pendimethalin	Norflurazon
A.1-001	Right Arm Coverall	724	267	52	317	813
A.1-002	Left Arm Coverall	674	218	54	299	830
A.1-003	Right Leg Coverall	611	444	76	542	3,043
A.1-004	Left Leg Coverall	394	302	46	592	2,135
A.1-005	Front Torso Coverall	3,115	1,107	203	826	2,413
A.1-006	Back Torso Coverall	2,219	967	173	715	1,755
A.2-001	Right Leg Pants	893	1,181	722	88	1,092
A.2-002	Left Leg Pants	750	880	829	79	1,102
B.1-001	Respirator Exhaust Valve	0.22	ND	ND	ND	ND
B.1-002	Respirator Exterior	0.83	0.04	0.04	ND	0.89
B.1-003	Respirator Exhaust Valve Cover/Interior	0.11	0.01	0.01	ND	0.19
B.1-004	Respirator Inhalation Valves	0.32	ND	ND	ND	ND
B.1-005	Respirator Interior	1.18	0.01	0.01	ND	ND
B.2-001	Work Shirt	195	342	117	21	372
PV-04-005	Left Rubber Glove/Interior Swab	29.5	0.09	0.09	ND	3.93
PV-04-006	Right Rubber Glove/Interior Swab	35.8	0.45	0.45	ND	5.06
PV-04-007	Left Boot/Interior Swab	1.39	0.07	0.07	ND	0.18
PV-04-008	Right Boot/Interior Swab	1.5	0.18	0.18	ND	0.07
PV-04-009	Blank	ND	ND	ND	ND	0.06

***All values in µg/sample**

A breakdown of residue levels by location is shown in Table Six.

Table Six: Results*of Investigative Samples for 3-Riv-04 by Location

	DEF	Chlorpyrifos	Malathion	Pendimethalin	Norflurazon
Coveralls	7,737	3,305	604	3,291	10,989
Pants	1,643	2,061	1,551	167	2,194
Shirt	195	342	114	21	372
Gloves	65.3	0.54	0.54	ND	8.99
Boots	2.89	0.25	0.25	ND	0.25
Resp. Exterior**	1.16	0.04	0.04	ND	1.08
Resp. Interior***	1.5	0.01	0.01	ND	ND

*** All values in µg/sample**
**** Includes exhaust valve, exhaust cover, exterior wipe**
*****Includes interior valves, interior wipe**

In itself, it is not extraordinary that pesticide residue can be found on the protective coveralls of the worker; especially of the material the worker is purportedly applying the day he expired (chlorpyrifos). However, certain aspects of residues found are not clear. For chlorpyrifos alone, there appears to be a greater penetration of material through the legs of the coveralls onto the pants than through the upper-body portion of the coveralls onto the shirt. How much of the residues on the shirt and pants that was available for absorption (i.e. in direct contact with skin) is unknown.

Of greater concern are the other pesticide residues, found at much higher levels than the chlorpyrifos. Levels of DEF found on the glove swabs are 120 times the chlorpyrifos levels, while the amount of DEF from within the respirator is 150 times the chlorpyrifos levels. Glove swab levels for norflurazon are also much higher (16 times) than the chlorpyrifos levels.

From the residue levels reported in Table Five, it would appear that either the worker was applying (or being otherwise exposed to) other materials or that the cleaning of the PPE was inadequate to remove materials from previous exposures. Information supplied by Enforcement's Southern Regional Office suggests that between December 2, 2003 and January 29, 2004, the decedent may have handled chlorpyrifos and malathion, but may only have handled DEF in early November, if at all. The exact dates of the applications were not made available. The residues found in both the interior of the respirator and the interior of the gloves may be of special concern, since these devices are either in direct contact with the skin (glove and respirator) or are in intimate and confined contact with the worker's breathing zone (respirator). The Industrial Hygiene Program cannot ascertain the clinical and toxicological implications of these potential exposures. On the other hand, the presence of DEF and the other herbicides suggests that cleaning of the PPE was inadequate, that residues of these materials are much more

resistant to cleaning than otherwise suspected, or that other exposures to these materials were occurring but have not been discovered/disclosed.

According to Title 3, CCR Section 6738(a), the employer shall:

> "(1) Provide all required personal protective equipment, provide for its daily inspection and cleaning (according to pesticide labeling instructions or, absent any instructions, washed in detergent and hot water), and repair or replace any worn, damaged, or heavily contaminated personal protective equipment."

Given that the PPE was contaminated with multiple pesticides, some of which the last record of application was several months previous, it might be advisable for the investigating agency to conduct an examination of the PPE cleaning procedures and protocols used by the employer.