December 9, 2002

United States Environmental Protection Agency **Office of Pesticide Programs**

MEMORANDUM

SUBJECT: **Measurement and Assessment of Dermal and Inhalation Exposures to Didecyl Dimethyl Ammonium Chloride (DDAC) Used in the Protection of Cut Lumber (Phase III).**

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1.0 INTRODUCTION

The purpose of this report is to review the worker exposure study submitted to the U.S. Environmental Protection Agency (EPA) in support of the re-registration requirements for the antisapstain formulation containing Didecyl Dimethyl Ammonium Chloride (DDAC) as the active ingredient. This worker exposure study was submitted to fulfill Agency guideline requirements under Series 875.1100 Dermal Exposure- Outdoor; Series 875.1300 Inhalation Exposure- Outdoor ; and Series 875-Occupational and Residential Exposure Test Guidelines, Group B-Post-application Exposure Monitoring Test Guidelines. The study was reviewed for compliance with respect to these guidelines.

The following information can be used to identify this chemical review:

Title:	Measurement and Assessment of Dermal and Inhalation Exposures to Didecyl Dimethylammonium Chloride (DDAC) Used in the Protection of Cut Lumber (Phase III)
Formulation:	(1) NP-1, Kop Coat Inc. (2) F2, Walker Brothers
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Study Date:	October 25, 1999

2.0 EXECUTIVE SUMMARY

This study was conducted to estimate exposure to DDAC, an active ingredient commonly used in many antisapstain products. The study was used to examine individuals working with antisapstains while performing routine tasks at 11 sawmills/planer mills found in the Vancouver area of Canada, per the requirements of U.S. Health Canada's Pesticide Management Regulatory Authority regulations. Dermal and inhalation exposure monitoring data were gathered for each job function of interest. This study review is based

on Series 875 guidelines and provides a summary of the procedures used in the study, results obtained in the study, and a conclusion indicating identified gaps.

This study was designed to quantify dermal and inhalation worker exposures to DDAC, an active ingredient used in antisapstain formulations under field conditions. DDAC was used as a surrogate chemical because of its presence in many antisapstain products. Workers can be exposed to DDAC when in contact with treated wood or when exposed to diluted DDAC sprays or mists originating from sprayboxes and diptanks that are used to treat wood at sawmills. Two end use formulations (NP-1 and F2) containing DDAC were used in this study. Eighty- six workers and 18 job functions (tasks) were monitored for up to 8 hours. Many of the job functions may have been performed by one or more worker(s). When a single worker performed the duties of more than one job function, the title of the job function which represented the majority of their work efforts was used to identify the worker.

Dermal and inhalation exposure were estimated using inner passive whole body dosimeters (WBDs), gloves, and personal air samplers in the workers breathing zone, respectively. The WBDs and cloth dosimeter gloves were worn under the workers' clothing and gloves. Dermal exposure to DDAC was estimated by determining the DDAC residue found on each WBD and cloth dosimeter glove sample. Inhalation exposure was estimated by measuring the DDAC residue found on quartz filters and PUF adsorbent cartridge.

Known quantities of a characterized DDAC formulation could not be measured because the study was conducted in a continuously operating commercial setting. The DDAC was applied to the wood in closed systems where excess treatment solution from the wood and treatment vessels were recovered, retained, and recycled. Therefore, the amount of product or active ingredient handled by each worker is not known. The major source of worker exposure for DDAC in this type of facility is due to preservative remaining on or escaping from treated wood or equipment used for the antisapstain treatment. The concentration of the DDAC in the sawmills was measured in the Study Report, however, the correlation of the concentration to the exposure was not evaluated.

According to the Study Report, each dermal exposure level was normalized to µg/day, while the inhalation exposure was reported as an air concentration ($\mu g/m^3$). The "total" dermal exposure for each replicate for each worker was calculated by summing the normalized residue levels in the WBD (arms, top, and bottom), and all glove dosimeters worn during that replicate. For convenience, worker activity was divided into four separate strata: Dry, Wet, Maintenance, and Diptank. Dry activities involved exposure to dry treated wood; "wet" activities involved handling wood that is still wet with antisapstain. Maintenance activities included maintaining supply tanks, conveyer belts, and performing

cleanup operations for sprayboxes and diptanks. Diptank activities included treating wood using a diptank. Arithmetic mean exposures for the 4 strata of workers were in the following order (from lowest to highest): Dry (0.92 mg), Diptank (4.32 mg), Wet (6.53 mg), Maintenance (23.90 mg). Geometric mean dermal exposures across the 4 strata of workers were considerably lower, but were in the same order : Dry (0.62 mg), Diptank (1.66 mg), Wet (1.70 mg), and Maintenance (4.10 mg). The highest exposures were usually found on the gloves and the arms. The highest exposure (166 mg) for the maintenance strata was for the worker on the cleanup crew at sawmill 7. Highest exposure (95.26 mg) for the wet strata was for the piler worker on the cleanup crew at sawmill 4. Highest exposure (13.67 mg) for the diptank strata was the worker at sawmill 11. (Note that a duplicate sample was considerably lower (5.42 mg)). The highest exposure (2.33 mg) for the dry strata was for the tallyman at sawmill 2.

It should be noted that for inhalation samples, only 4 out of 20 samples were detected for DDAC for the maintenance strata, 2 out of 30 samples for the wet strata, 1 out of 20 samples for the dry strata, and no samples were detected for the diptank strata. Detected mean air concentrations were in the following order (lowest to highest): Diptank (not detected), Dry (0.0123 mg/m^3), Wet (0.068 mg/m^3), and Maintenance (0.117 mg/m^3). Versar normalized the detected inhalation concentrations to a workers breathing rate (16.7 L/min) to compare dermal and inhalation exposures. Normalized detected arithmetic mean exposures for the 4 strata of workers were the following: Diptank (not detected), Dry (0.0123 mg), Wet (0.10 mg),and Maintenance (0.12 mg). The normalized detected inhalation exposures were considerably lower than for the dermal exposures.

Concerns related to requirements under the Series 875 guidelines are as follows:1) the amount of product applied and the amount of active ingredient handled by each worker were not calculated; 2) dosimeters, and PUF/filters were not fortified at the same levels as those in the field; 3) the limit of quantification (LOQ) was not reported; 4) sites were all located in the same geographical area; (5) the registrant did not make corrections to the raw data, and 6) some information was omitted from the Study Report which includes: laboratory fortification recovery results, sample tracking history sheets, GLP compliance information and product labels. U.S. EPA guidelines state that corrections are not needed when field fortification recoveries are above 90 percent. Most but not all of the field fortifications were greater than 90 percent.

3.0 BACKGROUND

There were 11 participating sawmills/planer mills involved in the Phase III Worker Exposure Study, conducted in the Vancouver and Vancouver Island areas of British Columbia. Six sawmills/planer mills were sampled in stage 1 and five in stage 2. Stage 1

was completed between the months of September-October, 1998 and stage 2 was completed between the months of April-May, 1999. Several different types of chemical applications were applied at the different sawmills/planer mills. Application systems used were automated elevator diptank (5 mills), 2 linear spray system (2 mills), 4 linear spray system (1 mill), 1 linear spray system (1 mill), linear spray and automated elevator diptank (1 mill), and transverse system (1 mill). It could not be determined from the Study Report if the facilities and end use products used in this study were representative of a range of geographic locations, and formulations used, respectively. In addition, it could not be determined if species of wood products treated, and application parameters used for wood treatment were representative. It appears that the number of facilities, end use products and/or formulation used, and application parameters may be representative of most typical conditions found in sawmills/planer mills. However, there was no geographic variability (i.e., all facilities were located in the Vancouver area) for the selected locations.

There were only two variations of the antisapstain flow in the spray box systems in all of the eleven sawmills/planner mills. The spray box system was either a fully automated computerized delivery mechanism or a batch system. The computerized system regulated the delivery of antisapstain concentrate according to the level of formulation in the mix tank. In the batch system, the antisapstain concentrate was mixed with the equivalent amount of water in a large (2,500L) batch tank. The diluted formulation was then used to supply a day tank where the volume was maintained at approximately 300 liters.

The spray systems consisted of linear or transverse boxes where a diluted preservative was applied to the wood on a continuous moving conveyer belt. Wood logs were fed into a mill, debarked, and cut into varying lengths. After the wood entered the spray box, the preservative was applied to the surface of the wood for a period of 3-5 seconds. Splash guards surrounded the spray boxes to eliminate any droplets of spray from the rest of the mill area. Following treatment, the wood was stacked or sorted.

For the automated elevator dip tank, bundled wood was placed in a container that allowed the preservative to pass through freely. The bundled wood as transported to an elevator where it was slowly lowered into an automated elevator dip tank to prevent splashing. Elevator switches were located close enough to enable the motor operator to confirm that wood pieces had not dropped out of the container. The bundled wood was submerged for 30-120 seconds. As the bundled wood was lifted, the elevator was tilted slightly for 1-6 minutes allowing the excess treatment solution to flow back into the dip tank. The wood was then set out over drip areas for drying (45-60 minutes) before it was transported to the lumberyard.

Workers were divided into four strata: 30 wet workers, 20 dry workers, 20 maintenance workers, and 16 diptank operators. Wet workers handled wet treated lumber; dry workers

handled lumber after it is dry; and maintenance workers performed as operators or performed maintenance on the solution supply system. Diptank operators operated either forklift or automated elevators. The following is a job description of each of four strata; the number of volunteers are indicated in parenthesis:

Wet Workers

- *Grader (13)* - usually positioned first after the spray box; graded wet treated lumber by hand.
- *Piler (2)* - handled wet treated lumber when removing the lumber from the conveyor and piling it.
- *Sorter Operator (1)* - operated the automated sorting system, monitored the sorter system for problems, did not handle wood directly.
- *Bin Patrol (2)/Tray Attendant(1)* - ensured that the bin was not blocked or jammed, usually used a stick to move lumber.
- *End Stacker Operator (5)* - operated an automated stacking system, also known as dry stackers.
- *Bander Operator (1)* - attached bands around lumber and packaged the loads.
- *Stenciller (1)* - spray painted numbers and logos onto stacked lumber.
- *Tallyman (2)* - stapled information sheet onto the wood.
- *Trimmer (2)* - worked in trim line to size untreated lumber.

Dry Workers

- *Hula Trim Saw (2)* - operated hula saw to cut wood.
- *End Stacker(2*) - operated and automated stacking system at the end of a conveyer.
- *Stickman (1)* - placed sticks between stacks of wood manually.
- *Stenciller/Painter (2)* - spray painted numbers and logos onto stacked lumber.
- *Packager/Stappler Operator (4)* - operated the automated packaging machine (which moves lumber into place).
- *Tallyman (2)* - stapled information sheet onto wood.
- *Forklift Driver (6*) - drove forklift to carry dry treated limber to lumber yard.
- *Papercapper (1)* - stapled paper and caps onto stacked dry treated limber.

Maintenance Worker

- *Chemical Operator (11)* - maintained chemical supply balance and flushes and cleaned spray nozzle, if required.
- *Millwright (3)* - repaired all conveyer chains and kept operation of the mill running.

- *Cleanup Crew (6)* - performed general cleanup of the mill facilities.

Diptank Worker

- *Diptank Operator (16)* - spent an average of 2 to 6 hours in dipping activities that consisted of operating the control panel moving wood to and from the diptank, stenciling, sealing ends of dry treated lumber with wax. (Note: seven diptank operators were monitored twice).

4.0 PROCEDURE

4.1 Mixing/Loading/Application/Post-application Methods

The procedures used for mixing and loading the product were not discussed in detail in the Study Report. Most of the exposure appears to be during application (exposure to antisapstains while wood is being treated)and post-application (exposure to antisapstains after wood is treated). Mixing/loading operations appears to operate through metered pumps connected to storage tanks. However, a discussion of this operation was not provided in the Study Report. Spray systems consisted of linear or transverse boxes where a diluted preservative was applied to the wood on a continuously moving conveyer belt. Wood logs were fed into a mill, debarked, and cut into varying lengths. The wood entered the spray box where the preservative was applied to the surface of the wood for a period of 3-5 seconds. Splash guards surrounded the spray boxes to eliminate any droplets of spray from the rest of the mill area. Following treatment, the wood was stacked or sorted.

Known quantities of the DDAC formulations used at each site were not measurable, because the study was set up in continuously operating commercial settings. DDAC was applied in closed systems where excess treatment solution from the wood and treatment vessels were recovered and retained while sealed. Therefore, the amount of product or active ingredient handled by each worker is not known. The concentration of the sprayers were discussed by the registrant. However, the flow rates through the vessels were not specifically reported, so it was not possible to calculate the amount handled.

4.2. Exposure Monitoring

Dermal

Dermal exposures were determined using whole-body dosimetry (WBD), consisting of a 100 percent cotton thermal shirt and long pants. The workers at each site wore WBDs under a fresh work uniform consisting of a cotton short-sleeved t-shirt and

cotton work trousers and lightweight 100 percent cotton glove dosimeters under chemical-resistant or work gloves. At the end of the work shift, the dosimeters were removed and sectioned. The front sections (chest and stomach) and the upper and lower legs were extracted and each analyzed separately. The left and right arm sections were also analyzed separately. After removal, the dosimeter sections were placed over a hanger and covered with a garbage bags. Each section was then wrapped in aluminum foil, labeled and collectively placed in a zip-lock freezer bag and stored in a cooler packed with ice.

Hand exposures were estimated using cotton liners in gloves. At the beginning of each work cycle (or 8-hour shift), the worker washed his hands with soap and water and then put on gloves. At the end of 8 hour work shift, the liners were stored and analyzed to determine exposure to the hands. The workers were advised to wear the inner liner for the full monitoring period, even if they removed their protective gloves. Liners were removed only when the workers washed their hand or if the liners were wet. All liner samples were combined at the end of the work shift.

Inhalation

Inhalation exposures were monitored using active dosimetry. Air sampling was conducted using air sampling pumps (Gilian Model HFS 113A) connected to Polyurethane Foam (PUF) adsorbent cartridge with a quartz filter. This sampling unit allowed for the collection of vapours and airborne particles. Each pump was calibrated to a rate of 2 L/min before and after each sampling period. The air sampling intake was mounted in the breathing zone of the workers with the sampling tube pointing downward to prevent collection of droplets that normally might not be inhaled by the worker. The sampling pumps were shut off during lunch breaks. At one sawmill during breaks and lunches, workers spent time very close to work stations and the air sampling pump was allowed to run and was considered as part of the 8-hour sampling period. At the end of the sampling period, both adsorbent cartridges (PUF and quartz filters) were placed in an amber glass bottle, stored in a cooler packed with ice, transported to a laboratory in Guelph, and stored in a refrigerated storage room until analysis. The analysis was conducted on a combined sample of PUF and quartz filter cartridges.

4.3 Analytical Methods

Dermal

Each dosimeter was removed from the foil wrapping and cut into at least 8 pieces with scissors. The scissors were then rinsed with acetone (10 mL) into a flat bottom receiving flask. Using dressing forceps, the separate cotton pieces were placed into a Soxhlet chamber. The forceps and foil wrapping were rinsed with acetone and the rinse

collected in the receiving flask. Due to differences in the section sizes of the dosimeters, there was variation in the size of the Soxhlet apparatus, amount of aqueous tetramethylammonioum chloride (TMAC) added, amount of acetone added to the receiving flask and the dosimeter, and the size of the receiving flask (see Table 1). A mixture of TMAC and acetone was added to completely wet the fabric , which soaked for 30 minutes . DDAC was then extracted, in the presence of excess TMAC. The extraction efficiency of DDAC with TMAC was >95 percent Acetone (100ml) was placed in the receiving flask with a few boiling chips. After the Soxhlet extraction was run for a minimum of 16 hours, it was concentrated to a known volume. Quantification of DDAC was performed by injecting 10 µl of the sample into a High Performance Liquid Chromatograph (HPLC) equipped with an evaporative light scattering detector. (Note that hand liners were examined using a similar method. Both left and right glove liners were combined and extracted using the same Soxhlet extraction method).

Inhalation

Each PUF and quartz filter was placed in an amber bottle and transported to the laboratory. They were placed into a Soxhlet extraction chamber mixed with 4 mL of 10,000 µg/mL TMAC and then added 20 mL of acetone to completely soak the filter for 30 minutes. In the presence of excess TMAC, an extraction efficiency removal of 90 percent and higher was routinely obtained. One hundred mL of acetone was placed in the receiving flask with a few boiling chips. After the Soxhlet extraction was run for a minimum of 16 hours, the extraction solution was concentrated to a known volume. DDAC was analyzed by adding 0.2 mL of 1,000 µg/mL of didodecyldimethylammonium chloride (DoDAB as an internal standard) to 0.8 mL of extraction solution. Quantification of DDAC was the same as that for the dermal dosimeters.

5.0 RESULTS

5.1 Method Validation

Aqueous dilutions of two antisapstain formulations (28:1 dilution of NP-1, and a 3.5:1 dilution of F2), and standard aqueous DDAC stock solutions were used as spiking solutions for cotton material. A 28:1 dilution of NP-1 and standard aqueous DDAC stock solutions was used for the PUF and quartz filters. Each spiking solution level was analyzed in tiplicate.

For the cotton material, a known volume of the spiking solution (i.e., known amount of DDAC in µg) was deposited onto 8 pre-cut 10 x 10 cm (total area of 800 cm^2) sections of cotton fabric, and allowed to dry for 8 hours. Using dressing forceps, the separate cotton pieces were placed into a Soxhlet chamber. A mixture of 4 mL of 200,000

µg/mL TMAC and 50 to 70 mL of acetone were added to completely wet the fabric and allowed to soak for 30 minutes. DDAC was extracted in the presence of excess TMAC. The extraction efficiency was approximately 95 percent. Acetone (100 mL) was placed in the receiving flask with a few boiling chips. After the Soxhlet extraction was run for a minimum of 16 hours, the extraction solution was concentrated to a known volume. DDAC was analyzed by adding 0.2 mL of 1,000 µg/mL of DoDAB, as an internal standard, to 0.8 mL of extraction solution. Quantification of DDAC was performed by injecting 10 µl of the sample into a HPLC equipped with a evaporative light scattering detector.

For PUF and quartz filter, a known volume of solution was placed in an amber bottle and transported to the laboratory. Each spiking solution was analyzed in triplicate. The PUF and quartz filter were then placed into a Soxhlet extraction chamber which was mixed with 4 mL of 10,000 µg/mL TMAC and 20 mL of acetone was added to completely soak the filter for 30 minutes. In the presence of excess TMAC, an extraction efficiency removal of DDAC with TMAC of 90 percent and higher was routinely obtained. The same methodology (as for dermal dosimeters) for extraction and analysis was used for the PUF and quartz filters.

The limit of detection (LOD) was 5.6 µg or 0.007 µg/cm^2 for DDAC in cotton WBD fabric samples and in glove pairs. The LOD for DDAC in airborne residue was 5.6 µg. The limit of quantification was not reported. The total DDAC recoveries from these fortified samples, ranged from 90 to 102 percent for cotton fabric, 90 to 120 percent for PUF, and 94 to 107 percent for the quartz filter.

5.2 Breakthrough/Retention Testing

Breakthrough/retention testing was performed in order to insure that DDAC residues would not migrate from the Quartz filter to the PUF cartridge. When the quartz filter was spiked with 50 µg of DDAC stock solution and then pumped for 8 hours, no evidence of breakthrough was observed when the PUF was analyzed. The average recovery for the quartz filter was 96.9 percent. Recovery of DDAC was 94.6 percent using diluted NP-1 formulation spike (200 µl) on the quartz filter and PUF. The DDAC concentration was 21376.4 µg/ml. The quartz filter and PUF were combined for extraction. In the event that a breakthrough did occur on the filter, the study author maintains that the PUF adsorbent was likely to capture the DDAC.

5.3 Laboratory Spikes

Recoveries of concurrent laboratory fortified samples for each matrix were not presented in this Study Report. Analysis of laboratory fortified recoveries is necessary to

monitor the accuracy and precision of the laboratory operations and to assess daily method performance, and possible losses in the laboratory.

5.4 Field Spikes

Field fortification samples were prepared at each of the eleven sawmills. Unexposed WBD sections, paired glove dosimeters, PUFs, and quartz filters were fortified with the diluted DDAC solution used in the sprayboxes and the dip tanks. The field samples were used to assess potential degradation or loss of residues due to exposure to environmental conditions, handling, packaging, shipping, and frozen storage.

Dermal Field Fortification Samples

The WBD sections at sawmills 1-6 were fortified at a high fortification level (2,000 µl) and a low fortification level (500 µl) of the diluted DDAC solution. WBD sections were only fortified with 500 µl of the diluted DDAC solution used in sprayboxes and dip tank mechanisms and the glove liners were fortified at 250 µl of the diluted DDAC solution at sawmills 7-11. It should be noted that the concentrations of DDAC used at each mill to dose the PUF/Filters, glove liners, and WBD sections were markedly different (see Table 2). The actual daily volume of antisapstain and/or mass of DDAC pumped through each sawmill was not reported. This data would be needed to calculate the amount of active ingredient handled.

Results from WBD dosimeters (500 µl and 2,000 µl) and glove liner (250 µl) field fortification samples are presented in Tables 3 and 4, respectively. The overall field fortification average recoveries (average of the averages), for whole body dosimeters (WBD's) and gloves were 93.2 percent and 95.9 percent, respectively. Data were not corrected for field recoveries. However, since the overall recovery was >90 percent and the majority of the average recoveries for the individual mills were also >90 percent, correction of the data may not be necessary. Field recoveries <90 percent were reported for only a few sawmills (Nos. 3, 4, and 7). These appear to be the only sawmills where an adjustment may have been practical. The other sites had 90 percent and greater recoveries.

Inhalation Field Fortification Samples

The PUF/Filters were fortified with 200 µl formulation for sawmills 1-6 and 40 µl formulation for sawmills 7-11. Results from inhalation field fortification PUF/filters are presented in Table 5. The overall field fortification average of the sawmill recoveries (average of the averages) for PUF/filters was 99.2 percent. The field fortification recoveries ranged from 81 to 112 percent. Sawmills 5,7, and 8 were less than 90 percent. Data were not corrected for field recoveries. However, since the overall recoveries were

>90 percent and the majority of the individual mills were also over 90 percent, correction of the data may not be necessary.

Based on the data presented in this study, the field fortifications appear to have a high degree of efficiency and reproducibility. The limit of detection was 0.007 µg/cm^2 for the dosimeters and glove liners and 5.6 µg for PUF/filters. It should be noted that the majority of the reported samples had levels at or near the detection limit. According to the reported data, the WBD sections were fortified between 2.8 µg/cm^2 to 17.6 µg/cm^2 and glove liner sections were fortified between 1.5 µg/cm^2 to 9.5 µg/cm^2. On page C-10 of the Series 875 guidelines (Part C:QA/QC), it is stated that "The low- and high-level fortifications should be in the range of the anticipated range of the anticipated level of the chemical on the substrate." It appears from the range of DDAD per section (µg/cm^2) reported on pages 263-299 of the Study Report, that (1) the actual range of the detected concentrations were 2-3 orders of magnitude lower than the fortification levels set for the WBD sections and (2) the detected concentration of the glove liners were 1-2 orders of magnitude lower than the fortification levels set for the glove liners. For the PUF/filters, the limit of detection was set at 5.6 µg. The field fortifications levels ranged from 173 µg to 5,310.1 µg. The detected PUF/filter concentrations ranged from 10.1 µg to 414.9 µg, with many of the samples detected at or near the detection limit. It appears that the detected concentrations were 1 to 3 orders of magnitude lower than the PUF/filter fortifications. Since the fortifications were not performed at the Limit of Quantitation (LOQ) or within the range of the detectable concentrations presented in this study, it is unclear if the field fortifications are representative. This is especially true since it appears that the recoveries reported for low level fortifications were less than those reported for the high level fortifications for WBD sections (see Table 3) and lower fortifications may lead to even lower recovery levels.

5.5 Formulation Testing

The field phase of this study was performed using commercial antisapstain sprayboxes and diptanks. Workers monitored the output concentrations of DDAC in the final diluted formulation from each participating sawmill. The formulation analyzed was either taken directly from the spray nozzles of the sprayboxes or from the tanks holding the diptank solution. For DDAC analysis, each individual formulated sample was warmed to room temperature, and then shaken vigorously for at least 15 seconds before a subsample was taken. A subsample of exactly 0.5 mL of 1,000 µg/mL of the internal standard, DoDAB, was added to 0.8 mL of the diluted formulation. Quantification of DDAC was performed by injecting 10 µl of sample into a HPLC equipped with an evaporative light scattering detector. Either NP-1 or F2 formulation was used at the sawmills. DDAC concentrations appear to be less for elevator diptanks than for sprayboxes. Over an 8-hour sampling interval, the average DDAC concentrations ranged from 4,193 µg/µl to 12,458 µg/µl, 16,526 to 28,827 µg/µl, and 13,143 to 22,776 µg/µl for

elevator diptank, sprayer, and mixtank, respectively. Product labels were not provided, therefore, it could not be determined if the concentrations of the formulations were applied at label recommended rates.

5.6 Storage Stability

Dermal

The stability of DDAC was determined using cotton sections prepared in the field and following a protocol similar to that used to prepare the low level (0.5 mL/800cm^2) field fortification spikes. These samples were stored under similar conditions with the rest of the dosimeter samples. Triplicates of the cotton sections were stored frozen prior to extraction at the following storage intervals: 40, 64, 65, 70, 165, 192, 197, 210, and 215 days. These sample results are presented in Table 6. The mean DDAC recoveries for the cotton sections ranged from 82 to 113.8 percent through out the stability study period (40 to 215 days). It appears there was not measurable dissipation of the residue. Recovery for residues after 40 days (82 percent) was actually less than the samples recovered after 215 days (107 percent). According to the registrant, the results from the dermal media storage stability study demonstrated that the stability of DDAC residue is acceptable in frozen dermal exposure monitoring media.

Inhalation

The stability of DDAC components in PUF/filters was not determined.

5.7 Exposures

Known quantities of a characterized DDAC formulation were not reported in this study because it was conducted in a continuously operating commercial setting. The DDAC solution was applied in closed systems where excess treatment solution from the wood and treatment vessel was recovered and retained, while sealed. Therefore, the amount of product or active ingredient handled by each worker is not known. The major source of worker exposure to DDAC in closed system facilities is either from antisapstain that remains on the wood, escapes from the treated wood, or escapes from the sprayboxes or diptanks during treatment. It appears that different concentrations and/or formulations of DDAC were used; however, it was not clear if different amounts of DDAC were used. From supplementary information provided in the Study Report, it appears that all sawmills are either ventilated through fans indoors or are located outdoors. Monitoring periods appear to be identical.

Dermal Results

The DDAC levels for WBD segment and glove pair from all workers, were not corrected based on the mean recovery of the appropriate analytical standard(s). The overall recovery of the analytical standards was greater than 90 percent; however, potential limitations to this approach may exist because the analytical method used was not measured for levels at or near LOQ (see section 6.4). EPA guidelines state that corrections are not needed when field fortification recoveries are at or above 90 percent.

The levels of DDAC found in worker gloves and WBDs (combined) are shown in Table 6.16, page145 in the Study Report. The calculated geometric mean and arithmetic mean daily dermal exposure levels of monitored workers are summarized in Table 7 of this review. Arithmetic mean exposures for the 4 strata of workers were as follows: Dry (0.92 mg), Diptank (4.32 mg), Wet (6.53 mg), and Maintenance (23.90 mg). Geometric mean dermal exposures across the 4 strata of workers were considerably lower as follows: Dry (0.62 mg), Diptank (1.66 mg), Wet (1.70 mg) and Maintenance (4.10 mg). The highest exposures were usually found on gloves and the arms. Highest exposure (166 mg) for the maintenance strata was for the worker on the cleanup crew at sawmill 7. The highest exposure (95.26 mg) for the wet strata was the piler worker on the cleanup crew at sawmill 4. The highest exposure (13.67 mg) for the diptank strata was for the worker at sawmill 11. (It should be noted that a duplicate sample was considerably lower (5.42 mg)). The highest exposure (2.33 mg) for the dry strata was the tallyman at sawmill 2. Differences in exposures between sites were not directly analyzed in the Study Report.

Inhalation Results

Inhalation worker exposure was measured for each worker task. During each replicate of monitoring, particulate exposure was measured using PUFs and volatile exposure was measured using filters. Inhalation samples were not corrected based on field fortifications because average field fortification recoveries were >90 percent. The detected residue levels and air concentrations of DDAC found in PUF/filters were summarized in Table 8 of this review (pages 89 to 93 in the Study Report). The registrant determined the air concentration using the following formula.:

$$\textit{Concentration } (\mu g/m)^3 = \left(\frac{(\textit{DDAC Found } (\mu g)}{\textit{Avg. flow rate } (L/\text{min}) \textit{ x sampling time } (\text{min})} \right) x\ 1000\ L/m^3 \quad \text{Eqn. 1}$$

The registrant did not normalize the data to mg/day; therefore, Versar used the NAFTA recommended values for breathing rates to normalize the air concentration($\mu g/m^3$) to mg/day. The new NAFTA recommended inhalation rates are 8.3, 16.7 and 26.7 L/ min

for sedentary activities (e.g., driving a tractor), light activities (e.g., flaggers and mixer/loaders <50 lbs containers), and moderate activities (e.g., loading >50 lb containers, handheld equipment in hilly conditions), respectively. Versar assumed that the activities performed by the workers in this study were light activities. Therefore, 16.7 L/min was selected as the breathing rate (BR). The equation used to convert from an air concentration to mg/day is as follows:

$$\textit{Inhalation Exposure } (mg/day) = \left(\frac{(\textit{DDAC Found } (mg/m^3) \times \textit{BR } (L/\text{min}) \times 480 \text{ min}/day}{1000\ L/m^3} \right) \qquad \text{Eqn. 2}$$

Inhalation exposure for each target compound was calculated from material found in the entire sampling train (PUF + glass filter) and with using different air flow rates (pp. 77-85 of the Study Report). The flow rates of the pump were commonly set near 2 L/min. For the most part, the levels of DDAC found, were below the detection limit (5.6 µg). Only one sample was detected above the detection limit for the dry strata (Hula Saw Operator). The highest detected airborne DDAC residue (414,9 µg) was in the maintenance strata for a member of the cleanup crew at sawmill 7. The highest detected airborne concentration (118.9 µg) for the wet strata was a piler at sawmill 4. It should be noted that DDAC was detected in only 4 out of 20 samples for the maintenance strata; 2 out of 30 samples for the wet strata; and 1 out of 20 samples for the dry strata. DDAC was not detected in the diptank strata. Since DDAC was not detected in the majority of the samples, it appears that the samples accurately represent the true inhalation exposure. It is not clear whether the analytical method used in the study was the most sensitive method to use for detecting DDAC inhalation residues or if another method may have been better suited. In order to characterize the inhalation concentrations, they were normalized to a workers breathing rate. Normalized detected arithmetic mean exposures for the 4 strata of workers were in the following order: Diptank (not detected) Dry (0.0123 mg), Wet (0.10 mg), and Maintenance (0.12 mg) (summarized in Table 9).

6.0 REVIEW OF THE STUDIES COMPLIANCE WITH SERIES 875

This study was reviewed for compliance with Series 875- Occupational and Residential Exposure Test Guidelines of the Pesticide Assessment Guidelines (U.S. EPA, 1998). A summary of the study's compliance with Series 875 guidelines is provided in Table 10. Table 10 is based on the "Checklist for Applicator Monitoring Data" and Series 875.1100, 875.1300, 875.2400 and Series 875.2500 Guidelines used by the U.S. EPA/OPP/HED in reviewing studies based on these guidelines. Table 10 is designed to (1) summarize Series 875 guidelines, (2) identify whether the study addresses compliance

checklist, and (3) is compliant with the guidelines. In addition, it presents comments describing compliance or non-compliance for selected areas of the checklist.

7.0 SUMMARY OF DATA GAPS WITH RESPECT TO SERIES 875

Pertinent items with regard to scientific validity and Series 875 compliance, not addressed in Table 10, are discussed below. The following issues were noted:

- The amount of product applied and the amount of active ingredient handled by each worker were not calculated, because DDAC was applied in a closed system where excess treatment solution was recovered, retained, and recycled. Monitoring the amount of solution over 8 hours is necessary to normalize exposure.

- Dosimeters and PUF/filters were not fortified at the same levels as those in the field.

- Product labels were not available to verify whether the product was applied at label recommended rates.

- A limit of Quantification (LOQ) was not reported.

- Each study site was located in the same geographical area.

- Information omitted from the Study Report included the following:
  - laboratory fortification recovery results.
  - sample tracking history sheets (dates of analysis and extraction, specific lack of information on handling and storage).
  - GLP compliance information.

Table 1. Sample Preparation Specifications

Sample size (cm^2)	Soxhlet Size	Flask Size (mL)	Acetone Added to the Dosimeter (mL)	Acetone Added to Receiving Flask (mL)	Amt. of TMAC
< 1110	Medium	300	50-100	100	4 mL of 200,000 µg/mL
1110-1450	Large	300	50-100	100	5 mL of 200,000 µg/mL
< 1450	2 Medium	300	50-100	100	2 mL of 400,000 µg/mL each
1450-2340	Extra Large	500	50-100	175	4 mL of 400,000 µg/mL
2340-2700	Extra Large	500	50-100	175	5 mL of 400,000 µg/mL

Table 2. Average Concentration of DDAC Used to Spike Field Matrices at the Mills

Concentration of DDAC (µg/mL)						
	Sawmill 1	Sawmill 2	Sawmill 3	Sawmill 4	Sawmill 5	Sawmill 6
PUF/Filters	9323.6±393.6	12,847.1±611.3	26,550.7±2084.7	25,638.3±568.1	20,627.2±351.5	18,407.3±457.9
Glove Liners	17514.9±480.4	13518.3±444.5	28150.5±360.2	27,357.1±463.4	21,474.9±11.7	18,573.6±530.5
WBD Sections	17,514.9±480.4	13518.3±444.5	28150.5±360.2	27,357.1±463.4	21,474.9±11.7	18,573.6±530.5
	Sawmill 7	Sawmill 8	Sawmill 9	Sawmill 10	Sawmill 11	
PUF/Filters, Glove Liners, WBD Sections	7090.7±363.3	4,334.7±21.6	12,567±294.3	4,445.4±50.8	6,463.6±165.7	

Table 3. Field Fortifications and Recoveries for Whole Body Dosimeters

Location	Low Fortification Spike Amount DDAC (µg/cm^2)	Percent Recovery (±SD)	High Fortification Spike Amount DDAC (µg/cm^2)[a]	Percent Recovery(±SD)
Sawmill 1	10.9	93.6± 2.7	43.8	95.6±1.0
Sawmill 2	8.4	92.9±5.9	33.8	99.7±8.4
Sawmill 3	17.6	92.9±3.0	70.4	89.4±3.7
Sawmill 4	17.1	89.4±2.4	68.4	83.5±0.6
Sawmill 5	13.4	93.2±0.5	26.8	101.7±5.0
Sawmill 6	11.6	100.3±2.6	46.4	116.3±2.0
Sawmill 7	4.3	79.1±3.7	NA[b]	NA
Sawmill 8	2.7	91.8±0.3	NA	NA
Sawmill 9	7.9	105.8±3.3	NA	NA
Sawmill 10	2.8	99.6±0.3	NA	NA
Sawmill 11	4	86.8±5.2	NA	NA

a = N=3
b = Not applicable

Table 4. Field Fortifications and Recoveries for Glove Liners [a]

Location	Spike Amount DDAC (µg/cm ^{2})	Percent Recovery(±SD)
Sawmill 1	5.9	97.5±0.7
Sawmill 2	4.6	92.3±10.6
Sawmill 3	9.5	89.9±6.9
Sawmill 4	9.3	92.8±2.3
Sawmill 5	7.3	93.7±0.4
Sawmill 6	6.3	99.4±10.1
Sawmill 7	2.4	83.1±2.3
Sawmill 8	2.2	97.7±10.4
Sawmill 9	4.3	103.6±0.7
Sawmill 10	1.5	105.3±7.6
Sawmill 11	2.2	99.7±1.8

a = n = 3

Table 5. Field Fortifications and Recovery for PUF and Quartz Filters

Location	Spike Amount DDAC (µg)	Percent Recovery(±SD)
Sawmill 1	1864.7	101.0±5.0
Sawmill 2	2569.4	111.7±7.5
Sawmill 3	5310.1	110.4±2.9
Sawmill 4	5127.7	108.4±0.2
Sawmill 5	4125.4	89.1±10.3
Sawmill 6	3681.5	105.9±2.9
Sawmill 7	273.4	81.1±3.2
Sawmill 8	173.4	87.4±0.4
Sawmill 9	502.7	103.0±1.3
Sawmill 10	177.8	100.6±17.1
Sawmill 11	258.5	92.2±6.9

Table 6. Storage Spike Fortifications on Cotton Sections

Location	Spike Amount DDAC (µg)	Storage Time (Days)	Percent Recovery(±SD)
Sawmill 1	10.9	165	105.2±1.8
Sawmill 2	8.4	215	107.4±2.6
Sawmill 3	17.6	192	109.0±2.5
Sawmill 4	17.1	210	97.3±2.2
Sawmill 5	13.4	197	113.8±7.4
Sawmill 6	4.3	40	82.0±0.4
Sawmill 7	2.7	64	98.0±3.5
Sawmill 8	7.9	65	97.0±1.7
Sawmill 9	2.8	70	97.0±1.7
Sawmill 10	4	70	99.5±8.8
Sawmill 11	N/A		

N/A = not applicable

Table 7. Summary of Overall Distribution of Dermal (Body + Hands) Exposures to DDAC (mg) in 4 Strata: Wet, Dry, Maintenance, and Diptank

Volunteer	Amounts of DDAC Found on Dermal (Body+Hands) Dosimeter (mg)			
	Wet	Dry	Maintenance	Diptank
1	0.12	0.03	0.22	0.07
2	0.19	0.08	0.26	0.14
3	0.21	0.09	0.29	0.31
4	0.32	0.4	0.33	0.45
5	0.42	0.52	0.44	0.5
6	0.43	0.54	0.72	0.55
7	0.47	0.58	0.94	1.34
8	0.49	0.6	1.2	1.98
9	0.61	0.6	1.31	2.34
10	0.88	0.74	3.5	3.48
11	0.89	0.78	6.07	3.94
12	0.98	0.83	6.11	5.42
13	1.03	1.07	8.03	9.26
14	1.09	1.08	21.45	12.39
15	1.25	1.13	22.15	13.32
16	1.47	1.29	29.08	13.67
17	1.56	1.59	46.37	
18	1.88	1.98	68.26	
19	2.38	2.1	95.22	
20	2.63	2.33	165.99	
21	3.05			
22	4.09			
23	5.23			
24	5.52			
25	7.47			
26	9.4			
27	10.45			
28	10.51			
29	25.61			
30	95.26			
Mean	6.53±17.25	0.92±0.65	23.90±41.21	4.32±4.83
Geometric Mean	1.70±4.47	0.62±3.02	4.10±8.37	1.66±5.01

Table 8. Summary of Detected Inhalation Exposures to DDAC (mg) in 4 Strata: Wet, Dry, Maintenance, and Diptank Strata

Amounts of DDAC Found on Inhalation PUF/filters						
Wet (mg)	**Wet[a] (mg/m^3)**	**Dry (mg)**	**Dry[a] (mg/m^3)**	**Maintenance (mg)**	**Maintenance (mg/m^3)**	**Diptank**
0.0127	0.0132	0.012	0.0123	0.0101	0.0104	none
0.189	0.1227			0.0152	0.0156	
				0.0299	0.0303	
				0.4149	0.412	
Mean 0.10	Mean 0.068	Mean 0.012	Mean 0.0123	Mean 0.12	Mean 0.117	Mean none

[a] Converted to mg/m^3 using Equation 1. Average flow rates provided in the Study Report on Table 4.12-4.15, pages 81-85.

Table 9. Summary of Normalized Inhalation Exposures to DDAC (mg) in 4 Strata: Wet, Dry, Maintenance, and Diptank Strata

Amounts of DDAC Found on Inhalation PUF/filters						
Wet (mg)[a]	**Wet (mg/m^3)**	**Dry[a] (mg)**	**Dry (mg/m^3)**	**Maintenance (mg)**	**Maintenance (mg/m^3)**	**Diptank**
0.106	0.0132	0.099	0.0123	0.0833	0.0104	none
0.98	0.1227			0.125	0.0156	
				0.243	0.0303	
				3.3	0.412	
Mean 0.543	Mean 0.068	Mean 0.099	Mean 0.0123	Mean 0.938	Mean 0.117	Mean none

[a] Normalized to standard breathing rates using Equation 2.

Table 10. Compliance with Series 875 Guidelines

FIFRA Compliance Checklist	Does the Study Address This Compliance Issue?	Does the Study Comply With This Part of Series 875?	Comments
General Criteria			
Investigators should submit protocols for review purposes prior to the inception of the studies	Yes	Yes	Criteria is met
Data collection in accordance with 40 CFR 160, Good Laboratory Practice Standards.	No	No	No statement was presented in the Study Report as to compliance with 40 CFR 160 GLPs
Expected deviations from GLPs should be provided and should be presented concurrently with any protocol deviations and their potential study impacts.	No	No	No deviations were noted and no statement that the study was in compliance with 40 CFR 160 GLPs
Prior "informed consent" must be obtained in writing from all subjects who will be exposed in the study.	No	No	Informed consent was not mentioned in the Study Report.
Test subjects should be regular workers, volunteers trained in the work activities required, or typical homeowners	Yes	Yes	Regular workers were examined.
All conditions specified on the product label must be observed, including whatever protective clothing is specified for workers to wear.	No	No	Product labels were not provided.
Studies must be designed so that an exposure is measured separately for each activity associated with an application.	Yes	Yes	Job categories were identified and assessed adequately.
Selected sites and seasonal timing of monitoring should be appropriate to the activity	Partly	Partly	Sites were considered typical however seasonal timing was not considered.

Table 10. Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the Study Address This Compliance Issue?	Does the Study Comply With This Part of Series 875?	Comments
Studies should be conducted under different geographic/climatologic sites	No	No	Sites were conducted at only was geographical location which was the Vancouver area.
Typical end use product of the active ingredient used.	Yes	Partly	The study identifies 2 end use products used in this study. They are F2 and NP-1. Labels for these end use products were provided.
End use product handled and applied using recommend equipment, application rates, and typical work practices.	Yes	Yes	Typical antisapstain wood treatment process assessed.
For exposure monitoring at least five replicates (e.g, individuals) at each of at least three sites for each job function should be monitored.	Yes	Yes	There were 86 workers at 11 sawmills.
Monitoring period is sufficient to collect measurable residues but not excessive so that residue loss occurs.	Yes	Yes	Exposure periods seemed long enough for the tasks required.
Dermal and/or inhalation exposure must be monitored by validated methodologies. Biological monitoring is consistent with and supported by pharmacokinetic data accepted by the Agency.	Yes	Yes	Dermal and inhalation methods used were identified in Series 875 regulations.
Field data should be documented, including chemical information, area description, weather conditions, application data, equipment information on work activity monitored, sample numbers, exposure time, and any other observation.	Yes	Yes	Study complied with these criteria.

Table 10. Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the Study Address This Compliance Issue?	Does the Study Comply With This Part of Series 875?	Comments
A sample history sheet must be prepared by the laboratory upon receipt of samples.	No	No	A sample history sheet was not provided.
Quantity of active ingredient handled and duration of monitoring period reported for each replication	Partly	Partly	Quantity of active ingredient handled was not described. Duration of exposure was identified for both dermal and inhalation exposures.
Dermal Guidelines Series 875.1100 and 875.2400			
Clothing worn by each study participant and location of dosimeters reported.	Yes	Yes	Study used whole body dosimeters (cotton thermal shirts, pants, and gloves). Sections (gloves, arms, bottoms) were measured appropriately.
If the stability of the material is unknown, or if the material is subject to degradation, the investigators must undertake and document a study to ascertain loss of residues while the pads are worn. It is recommended that collection devices be fortified with the same levels expected to occur during the field samples. The dosimeters should be exposed to similar weather conditions and for the same time period as those expected during field studies	Yes	Partly	Dosimeters were not fortified with the same levels experienced in the field.
Storage of samples consistent with storage stability data.	Yes	Yes	Storage of samples and storage stability are addressed in the study and the field samples were stored concurrently with the storage samples.

Table 10. Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the Study Address This Compliance Issue?	Does the Study Comply With This Part of Series 875?	Comments
Efficiency of extraction in laboratory provided as mean plus or minus one standard deviation. Lower 95 percent confidence limit is not less than 70 percent based on a minimum of seven replications per fortification level or prior Agency approval of extraction methodology provided.	yes	yes	Method validation testing appeared to be in the acceptable range.
Information on recovery samples must included in the Study Report. A complete set of field recoveries should consist of at least one blank control and the or more each of a low-level and high-level fortification. These fortifications should be in the range of anticipated residue levels in the field study.	Yes	Partly	Blanks controls were not clearly identified. The fortifications were not in the range of the residue levels detected in the field study.
Data should be corrected if any appropriate field fortified or storage stability is less than 90 percent.	Partly	Partly	Data was not corrected; however recoveries for the most part were >90 percent. Laboratory recoveries were not reported.
Sufficient control samples should be collected	Partly	Partly	Explanation of control samples was not clear.
Validated analytical methods of sufficient sensitivity are needed. Information on method efficiency (residue recovery) and limit of quantification (LOQ) should be provided	Partly	Partly	LOQ was not provided.
Inhalation Guidelines Series 875.1100 and 875.2500			

Table 10. Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the Study Address This Compliance Issue?	Does the Study Comply With This Part of Series 875?	Comments
The analytical procedure must be capable of measuring exposure to 1 µg/hr (or less, if the toxicity of the material under the same subjects may be used).	Yes	Yes	
If trapping media from field samples are to be stored after exposure, a stability test of the compound of interest must be documented. Media must be stored under the same conditions as field samples. Storage stability samples should be extracted and analyzed immediately before and at appropriate periods during storage. The time periods for storage should be chosen so that the longest corresponds to the longest projected storage period for field samples	Yes	Partly	Storage stability was only examined using cotton fabric.
A trapping efficiency test for the monitoring media must be documented.	Yes	Yes	
Air samples should also be tested for breakthrough to ensure that collected material is not lost from the medium during sampling. It is recommended that at least one test be carried out where the initial trap contains 10X the highest residue expected in the field.	Yes	Yes	

Table 10. Compliance with Series 875 (Continued)

FIFRA Compliance Checklist	Does the Study Address This Compliance Issue?	Does the Study Comply With This Part of Series 875?	Comments
A personal monitoring pump capable of producing an airflow of at least 2 L/min. should be used and its batteries should be capable of sustaining maximum airflow for at least 4 hours without recharging . Airflow should be measured at the beginning and end of exposure period.	Yes	Yes	
Appropriate air sampling media should be selected. The medium should entrap a high percentage of the chemical passing through it, and should allow the elution of a high percentage of the entrapped chemical for analysis.	Yes	Yes	
Personal monitors should be arranged with the intake tube positioned downward, as near as possible to the nose level of the subject.	Yes	Yes	
Field calibration of personal monitors should be performed at the beginning and end of the exposure period.	No	No	Study did not address the procedures for field calibration.
Field fortification samples and blanks should be analyzed for correction of residue losses occurring during the exposure period. Fortified samples and blanks should be fortified at the expected residue level of the actual field samples. Fortified blanks should be exposed to the same weather conditions.	Yes	Partly	Fortified samples were not at the same level as the detected residues.

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