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Agent Orange Investigative Report Series, No. 2

Contract: VA-101-12-C-0006

**INVESTIGATIONS INTO THE
ALLEGATIONS OF AGENT
ORANGE/DIOXIN EXPOSURE
FROM FORMER
RANCH HAND AIRCRAFT**

Compensation Service

Department of Veterans Affairs

810 Vermont Ave., NW

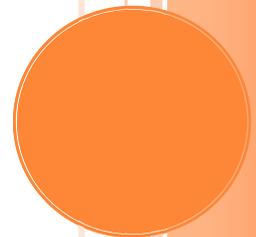
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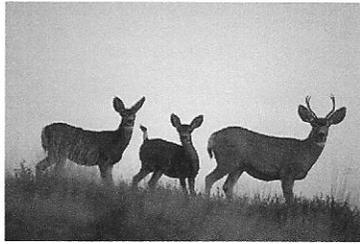
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November 2012





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30 November 2012

Mr. Michael D. Pharr
Contract Officer's Representative
Compensation Service
Department of Veterans Affairs
810 Vermont Ave., NW
Washington, DC 20420

Dear Mr. Pharr,

Please find attached to this letter the Final Report on : **Investigations into the Allegations of Agent Orange/Dioxin Exposure from Former RANCH HAND Aircraft.** This report is the second of many reports that will be prepared in fulfillment of Contract VA-101-12-C-0006, *Development of an Archival Directory of Agent Orange Documents*. The goal of developing this directory is to search and identify the thousands of documents, reports, and correspondence located within our National Archives and Records Administration and other document repositories that relate to the use of "Tactical Herbicides" including Agent Orange, *outside of Vietnam*.

As in the case of the UC-123K controversy, the Compensation Service did not have the records related to history of the aircraft, nor the detailed scientific studies conducted at Hill Air Force Base Utah on the quarantined UC-123K aircraft that were stored by the 309th Aerospace Maintenance and Regeneration Group at Davis-Monthan Air Force Base Arizona. Thus, the Department of Veterans Affairs has been dependent on limited documentation related to events involving possible exposure to Agent Orange.

This current report documents three factors critical for exposure assessment that were identified by former United States Air Force Reserve personnel who flew or maintained the UC-123K and the C-123K Post-Vietnam from 1972 to 1982. The 1st factor included a detailed history of the more than 200 C-123B aircraft that were modified to meet the needs of various military activities during the Vietnam War. The 2nd factor included a detailed examination of the various alleged "dry" Agent Orange residues that remained within the UC-123K aircraft assigned to Reserve units. The 3rd factor examined whether the residues were actually available through dermal or inhalation routes to the aircrews flying the UC-123Ks, and if the exposure was significant to cause disease. **The results could not prove that the Air Force Reserve personnel were not exposed to Agent Orange or its associated dioxin contaminant, but all the analytical and scientific studies suggested that if they were exposed, that exposure was negligible.**

Sincerely,

Alvin L. Young, PhD

Professor

DISCLAIMER FOR VA REPORTS

The conclusions reached in this report are based upon a comprehensive review of the historical records maintained in the publicly available files of the National Archives and Record Administration, and other archival repositories. However, the conclusions reached do not necessarily represent those of the Department of Veterans Affairs or any other Department or Agency of the United States Government.

This report is part of the Agent Orange Investigative Report Series, and should be considered as an amendable or living document. If additional authenticated documents or records are found that address the topic of this report, a re-evaluation of the conclusions may be necessary.

INVESTIGATIONS INTO THE ALLEGATIONS OF AGENT ORANGE/DIOXIN EXPOSURE FROM FORMER RANCH HAND AIRCRAFT

EXECUTIVE SUMMARY

Allegations made by former Air Force Reserve aircrews and maintenance personnel have raised health concerns about residual amounts of Agent Orange remaining in Post-Vietnam C-123K aircraft, that had been deployed by the Reserves between 1972 and 1982. Despite a recent exposure assessment by the Air Force Research Laboratory, Wright-Patterson AFB Ohio and a recent Advisory Opinion by the Department of Veteran Affairs, that “*it was unlikely that any dioxins from such residues would lead to adverse health effects*”, the controversy has continued. The present report on “*Investigations into the Allegations of Agent Orange/Dioxin Exposure from Former RANCH HAND Aircraft*” is intended to present factors not previously evaluated by the earlier assessment and Advisory Opinion.

There were three factors identified that were critical to the investigation. The first factor was a critical need to search the historical records on the history of the aircraft series C-123K and UC-123K. The “U” designation was for those aircraft used in defoliation and crop destruction missions in Operation RANCH HAND during the Vietnam War. The second factor was to understand the nature of the “dry” Agent Orange residues that were found in some of the aircraft, but especially those found in “Patches”, an aircraft “retired” to the Air Force Museum in 1980 and that underwent decontamination in 1994 prior to its display to the public. The third factor was to determine how the exposures could have occurred and their significance to the health of the Air Force Reserve personnel who comprised the aircrews and who serviced the aircraft after they were returned to the United States and used as cargo aircraft during the period of 1972-1982.

Results of the investigation into Factor Number 1. Twenty-three of 34 UC-123Ks were returned to the United States in 1970-1971, and after reconditioning were assigned to Air Force Reserve units. These aircraft had been assigned to RANCH HAND beginning in May 1968, but most of the UC-123Ks arrived in Vietnam between December 1968 and November 1969, a time when defoliation

operations were significantly reduced. Moreover, after November 1969, the Department of Defense directed that the use of Agent Orange be restricted and the tactical herbicides Agents Blue and White be substituted. Four of the UC-123K were reassigned to the Aerial Spray Flight at Rickenbacker AFB Ohio. Thus, Air Force Reserve crews were more likely to have flown in the 47 C-123Ks that were returned from Vietnam, rather than assigned to one of the 19 remaining aircraft that had been flown in Operation RANCH HAND, or if formerly assigned to RANCH HAND, an aircraft that very likely did not spray Agent Orange. Verification of the tail numbers provided in a veteran-prepared report confirmed that only 6 of 26 aircraft assigned to the 731st Tactical Airlift Squadron, Westover AFB Massachusetts were former RANCH HAND aircraft.

Results of the Investigations in Factor Number 2. The allegations put forth by former Air Force Reserve crew and maintenance personnel were that the residues within the 19 UC-123Ks reassigned post-Vietnam to their Reserve units were from Agent Orange, and that the magnitudes of these residues were exemplified by analytical studies conducted during the decontamination of “Patches”, a former RANCH HAND aircraft donated to the National Museum of the US Air Force, Wright-Patterson AFB Ohio. A search of the historical records provided a detailed history of “Patches” to include its assignments in international locust control programs, its use in tests and evaluations of spray equipment at Eglin AFB, Florida, to its use in Vietnam not only in Operation RANCH HAND, but frequently reconfigured for its use in hauling cargo or for insecticide missions in Operation FLYSWATTER. The extensive activities of “Patches” put in doubt the analytical results of the 4 (and only 4) samples analyzed for dioxin and furans in 1994. Indeed, the fingerprint of the analytical results suggested the potential contamination or cross contamination by PCBs, the insecticide Lindane, and other aromatic materials. Clearly “Patches” was not a representative aircraft for determining Agent Orange residues. Certainly the odors reported by veterans could be attributed to such pesticides as DDT or Carbaryl (Sevin®) rather than Agent Orange.

In 1996 and 2009, UC-123K aircraft in quarantine storage at the 309th Aerospace Maintenance and Regeneration Group (AMARG) at Davis-Monthan AFB were sampled for the residual Agent Orange constituents 2,4-D, 2,4,5-T and the associated dioxin, TCDD. One hundred forty samples (140) were collected from 4

aircraft with known histories of defoliation missions in Vietnam. The results indicated that no Agent Orange residues were found on the exterior of any aircraft or in air samples taken inside the tightly-closed aircraft. Two of the aircraft had trace levels of residues, near the lowest limit of analytical detection, on the fuselage floor, and were essentially considered “clean”. The other two aircraft had levels of Agent Orange residues on all interior fuselage surfaces that were tested. The average concentrations found in these two aircraft were statistically near the risk-based screening level for dioxins, based on a one-year industrial exposure scenario. The question remained, were these residues actually capable of providing a measureable exposure or dose to aircrew or maintenance personnel?

Results of the Investigation into Factor Number 3. The contaminant TCDD found in the dry residues within Post-Vietnam UC-123Ks was not water soluble. The only method for extracting and measuring TCDD within the aircraft interior surfaces was through the use of wipe samples “wetted” with the organic solvent hexane. Although there were measurable levels of TCDD within these dried residues, studies of dermal contact with TCDD have found that any exposures that occurred were “negligible” because the skin is a major barrier to TCDD uptake, contributing less than 1% over the long term to the body burden. Vapor exposures to TCDD at near ambient temperatures were extremely unlikely to result in any significant dose because TCDD is not volatile below 420° C (~ 780 °F).

Four epidemiological or analytical studies of Vietnam veterans or professional sprayers of 2,4,5-T herbicide provided supporting evidence that “primary” or “secondary” exposure to TCDD associated with the spraying of Agent Orange would not have resulted in diseases caused by the herbicides or its associated TCDD. However, it is important to note that all the analytical and scientific studies cannot prove that the Air Force Reserve aircrews and maintenance personnel assigned to the UC-123K were not exposed to Agent Orange and its associated dioxin contaminant. ***However, all the analytical and scientific studies suggested that if they were exposed, that exposure was negligible.***

INTRODUCTION

In the March/April 2008 issue of Orion Magazine, an article was published titled: “**Agent Orange: A Chapter from History That Just Won’t End**”- The author’s article focused on his visit to the Aerospace Maintenance and Regeneration Center (AMARC) on Davis-Monthan Air Force Base (AFB), Arizona where the remaining UC-123K RANCH HAND aircraft were stored for more than 22 years [1]. Why the visit? “*Because I’ve come to bear witness to American folly, to rest my eyes on the flying machines that flattened the forest of Southeast Asia, poisoned its people, and changed my life.*” The author, Ben Quick, described how his father had served in Vietnam and was the victim of a “*chemical rain (i.e., Agent Orange) that falls on American troops as they slink through the hinterlands of Vietnam in search of Viet Cong.*” Mr. Quick cited stories of Agent Orange and its associated dioxin, and thus concluded that the reason the UC-123K aircraft remained in an isolated location at AMARC was because the aircraft were contaminated by Agent Orange and its associated dioxin. This very sincere and emotional article triggered a cascade of concern by various Air Force Reserve aircrews that had flown some of those aircraft from 1972 – 1982, some 2 to 10 years after cessation of the RANCH HAND defoliation program during the Vietnam War [2].

In 2011, a retired Air Force officer who had served with an Air Force Reserve Unit filed a complaint with the Air Force Inspector General alleging that the Air Force knew that UC-123Ks were used for spraying Agent Orange in Vietnam and that the Air Force had failed to properly inform post-Vietnam aircrews of the risks [3]. The Air Force issued a “Consultative Letter” released on 27 April 2012 and prepared by the Air Force Research Laboratory, Wright-Patterson AFB, Ohio titled: ***UC-123 Agent Orange Exposure Assessment*** [4]. Subsequently, on 25 September 2012, the Veterans Benefits Administration, Department of Veterans Affairs issued an “Advisory Opinion” on “***Service-connection based on exposure to Agent Orange due to flying C-123 aircraft***” [5]. Both the Consultative Letter and the Advisory Opinion essentially agreed that it was unlikely that “*any dioxins from residual Agent Orange on aircraft surfaces, or that any exposure would lead to adverse health effects.*” The Compensation Service recommended that such claims associated with Agent Orange exposure be denied service-connection. Nevertheless, the Department of Veterans Affairs released a Public Health Notice on **Agent Orange Residue on Post-Vietnam War Airplanes** that concluded: “*Although the*

risk of long-term health problems from exposure to Agent Orange residue on post-Vietnam C-123 airplanes is minimal, Veterans who believe they have exposure-related health problems may file a claim for disability compensation. These claims will be decided on a “case-by-case basis” [6].

Despite the actions and conclusions by the Department of the Air Force and the Department of Veterans Affairs, the controversy has continued. Although the allegations were primarily related to the potential of remaining residues to provide a source for exposure and dose, there are other factors that need to be evaluated.

FACTORS CRITICAL TO THE EVALUATION OF THE ALLEGATIONS

In October 2012, a veteran-prepared report “*Request for Congressional Assistance with C-123 Veterans’ Claims: Establishing Agent Orange Exposure to Veterans*” was distributed to various Congressional delegations [7]. The essence of the report focused on the following three issues or factors critical to establishing that the United States Air Force Reserve crews and maintenance personnel were exposed to toxic chemical residues from post-Vietnam aircraft, and were thus entitled to service-connected compensation:

- That the aircraft alleged to be the sources of the exposure to residues of Agent Orange and its associated dioxin (2,3,7,8-tetrachlorodibenzo-*p*-dioxin, TCDD) were the former RANCH HAND UC-123Ks, and that these aircraft were generally the only aircraft that Air Force Reserve personnel at selected Air Reserve units flew or maintained;
- That the residues within these remaining UC-123Ks were from Agent Orange, and that the magnitudes of these residues were exemplified by analytical studies conducted during the decontamination of “Patches”, a RANCH HAND aircraft donated to the National Museum of the US Air Force, Wright-Patterson AFB Ohio; and,
- That the Agent Orange/ dioxin residue within the aircraft was a primary route of exposure and posed a far greater risk than those experienced by the RANCH HAND crews that flew the UC-123Ks in Vietnam because those crews were exposed for generally just one year, not multiple years as were the Air Force Reserve crews.

A BRIEF HISTORY OF THE C-123, UC-123B, AND THE UC-123K

In order to understand how many UC-123K aircraft were available to Air Force Reserve units after the termination of the RANCH HAND program in Vietnam, it was necessary to review the history of the C-123 aircraft. That history began in July 1955 when the Tactical Air Command's 309th Troop Carrier Group, Ardmore AFB Oklahoma took delivery of the first Fairchild C-123B "Provider", a twin-engine transport designed for assault operations into landing zones that had been only rudimentarily prepared. Fairchild Corporation of Hagerstown, Maryland produced 300 C-123B aircraft between the years 1954-1958 [8].

In November 1961, six Providers were sent to South Vietnam to start Operation RANCH HAND, the defoliation program. In December 1961, an additional squadron of C-123Bs (16 aircraft/squadron) were deployed to Vietnam from the 464th Troop Carrier Wing, Pope AFB, North Carolina. By the fall of 1964 there were four USAF C-123B squadrons flying airlift and airdrop missions. All of these squadrons, including RANCH HAND aircraft, were assigned to the 315th Air Commando Wing (later renamed the 315th Special Operations Wing) and which would remain the principal organization for all C-123B squadrons until 1970 [8].

By March 1965, RANCH HAND (now designated as the 12th Air Commando Squadron) was deploying seven UC-123Bs (the "U" designating spray aircraft) for defoliation and crop destruction missions [9]. In April 1968, the first UC-123Ks arrived at Bien Hoa Air Base, Vietnam. The 12th Air Commando Squadron was the last of the five units in the 315th Wing to get the improved aircraft [8]. The UC-123 "K" models were reworked "B" models with a powerful J-85-17 jet engine on each wing outboard of the conventional engines, improved engine armor plating, a strengthened windshield, a larger spray pump, and a flowmeter to assure a constant chemical flow rate of 3 gallons per acre [9].

Additional UC-123Ks continued to arrive in May 1968. By the end of June 1969, 29 UC-123Ks were assigned to the RANCH HAND squadron, and by November 1969, shortly after it reached a peak of 34 assigned aircraft, the squadron was suddenly reduced to 14 aircraft with the released aircraft reassigned to airlift units or returned to the Continental United States (CONUS) [8, 9]. On 1 January 1970,

the 315th Special Operations Wing was re-designated as the 315th Tactical Airlift Wing, while the RANCH HAND unit retained its Special Operations Squadron title. On 31 March 1970, USAF Headquarters again directed reduction of the spray squadron to eight aircraft – six for herbicide and two for insecticide – by the end of June 1970 [8]. In July 1970, the remaining aircraft were moved to Phan Rang, the Headquarters of the 315th Tactical Airlift Wing. On 28 January 1971, the Joint Chief of Staff officially cancelled all further USAF herbicide missions. RANCH HAND crewmen continued flying the two insecticide missions (Operation FLYSWATTER) until December 1971 [9].

A total of 46 aircraft were modified for spray operations in the ten years of herbicide and insecticide operations in Vietnam. This included 12 UC-123Bs that were never modified as “K” models, and 34 UC-123Ks. The last “B” model aircraft left Vietnam in January 1969. Nine RANCH HAND aircraft were lost to crashes, including 1 UC-123K in February 1971 [9]. As previously noted, beginning in November 1969 many of the UC-123Ks were either transferred to USAF airlift squadrons, or transferred to the South Vietnam Air Force, or assigned to Air America operations. These transfers required the removal of the spray systems including the 1,000-gallon tank, console, and spray boom. Never-the-less, the aircraft retained their designation as “UC-123Ks”. The tanks and spray booms were not returned to CONUS, but left at Da Nang, Bien Hoa, or Phan Rang.

A search of the historic records concluded that 183 C-123Bs were modified to “K” models, to include the 34 UC-123Ks assigned to RANCH HAND. Between 2 February 1962 and 27 December 1971, 62 of the various modified C-123s were lost to crashes/accidents in Vietnam. Like the UC-123Ks, the remaining C-123K aircraft were also widely distributed as the gradual withdrawal of US Forces from the Republic of Vietnam occurred. A large number of C-123Ks were transferred to the South Vietnam Air Force, with the first squadron transferred in 1970, and three additional USAF C-123K Squadrons by September 1971. Air America received 35 various C-123Bs, C-123Ks, or UC-123Ks; these were primarily assigned to airlift missions in Laos [10].

The records indicated that a total of 47 USAF C-123Ks and 23 UC-123Ks returned to CONUS throughout 1970 – 1971 with most of these aircraft being initially assigned to 309th Aerospace Maintenance and Regeneration Group (AMARG),

Davis-Monthan AFB Arizona. All of these aircraft underwent a reconditioning prior to reassignments to selected USAF Air Reserve units in 1971-1972. It should be noted that 4 of the UC-123Ks were assigned directly to the Air Force Reserves 907th Tactical Airlift Group, Rickenbacker Air National Guard Base Ohio. These 4 aircraft retained their special configuration for aerial spraying as part of USAF's aerial insecticide operations [11]. Eighteen of the 23 UC-123Ks returned to AMARG between 1980 and 1986.

CONCLUSIONS

Contrary to the allegation, both C-123K and UC-123Ks aircraft were assigned to USAF Reserve units during the period 1972 -1982. A few of the UC-123Ks had been assigned to RANCH HAND beginning in May 1968, but most of the UC-123Ks arrived in Vietnam between December 1968 and November 1969, a time when defoliation operations were significantly reduced. Moreover, after November 1969, the Department of Defense directed that the use of Agent Orange be restricted and the tactical herbicides Agents Blue and White be substituted. Thus, Air Force Reserve crews were more likely to have flown in C-123Ks, rather than assigned to an aircraft that had been formerly assigned to RANCH HAND, or if formerly assigned, an aircraft that very likely did not spray Agent Orange. Verification of the tail numbers provided in the veteran-prepared report confirmed that only 6 of 26 aircraft assigned to the 731st Tactical Airlift Squadron, Westover AFB Massachusetts were former RANCH HAND aircraft [7].

THE ALLEGATIONS ON THE RESIDUE REMAINING IN THE UC-123Ks

The October 2012 veteran-prepared report repeatedly emphasized that the residues remaining within the UC-123K aircraft assigned to Air Force Airlift Reserve units were those related to Agent Orange [7]. The basis for this conclusion came primarily from the analyses conducted in 1994 on one aircraft, namely "Patches" (tail number 56-4362) that had been donated to the National Museum of the United States Air Force, Wright-Patterson AFB Ohio in 1980 [12]. During its service in RANCH HAND, the aircraft had taken more than 600 hits from enemy ground fire, hence, the name "Patches" [13].

The history of "Patches" is informative as to the types of potential residues that could be present within its air frame. "Patches" was one of the original six C-

123Bs located at Pope AFB North Carolina that was modified for aerial spraying and was sent to South Vietnam, arriving in January 1962. However, before it was involved in defoliation missions, it was diverted at the request of the Department of State to the Middle East for locust control. It departed 2 May 1962 from Saigon to Tehran, Iran where it sprayed over 17,000 acres in Iran and Afghanistan with the insecticide Lindane [9, 14], returning to Langley AFB Virginia on 10 June 1962. On 14 June 1962, it was redeployed to Eglin AFB Florida to participate in a 30-day test of aerial spray equipment on Test Range C-52A of the Eglin Military Reservation [9]. While at Eglin, it sprayed the tactical herbicide “Purple” in the first tests of the modified aerial spray equipment [15]. Following its return to Vietnam, it was immediately dispatched to treat locust infestations with 57% Malathion [16]. From January through May 1963, it was temporarily converted to supporting logistical operations delivering ammunition, general cargo including maintenance supplies, and personnel [9].

From June 1963 through most of 1966, “Patches” supported RANCH HAND operations in both defoliation and crop destruction missions. However, on 14 October, “Patches” was reconfigured and dispatched again to treat locust infestations in Thailand with 95% Malathion [9, 16]. In April 1967, Patches was ordered permanently assigned to Malathion duty under the direction of the MACV (Military Assistance Command, Vietnam) Surgeon General’s Office and in support of Operation FLYSWATTER [17]. In June 1968, “Patches” left the insecticide flight to return to the United States for modification as a K model. In October 1968, “Patches”, now a UC-123K, returned to Vietnam and temporarily returned to flying defoliation missions, primarily involving- White (from a review of the Daily Air Activity Reports, 1 October – 1 December 1968). However, in late November 1968, it was returned to mosquito control duty. After termination of Operation FLYSWATTER in December 1971, “Patches” returned to CONUS in 1972 and served in the Air Force Reserves in an airlift capacity until it was retired to the USAF Museum in 1980 [13].

A 1994 – 1997 decontamination of “Patches” at the USAF Museum focused exclusively on the presence of dioxins and furans with the data converted to 2,3,7,8-TCDD equivalents (TEQs) and reported in nanograms per wipe sample. The assumption was that the 17 congeners identified of polychlorinated dibenzo-*p*-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) were congeners that

confirmed the residue was from Agent Orange [12]. There were only four wipe samples reported in the 1994 analyses, and the TEQ equivalents ranged from 4.1 ng/m² to 1,400 ng/m². An analytical study conducted by Dow Chemical Company of 82 samples of 2,4,5-T confirmed that the only quantifiable dioxin in 2,4,5-T was the 2,3,7,8-TCDD, although some samples showed traces of the penta (PnCDD), hexa (HxCDD), and hepta (HpCDD) PCDDs [18]. The wipe sample having the largest concentration of TCDD may have been a result of the aircraft spraying Agent Purple while at Eglin AFB in 1962, since Purple had much higher levels of TCDD than Agent Orange [15]. The other PCDDs and the PCDFs may have been present as a result of PCB-leaking electric transformers, and pentachlorophenol-treated ammunition boxes, both frequently transported as cargo in Vietnam [19]. The potential presence of PCBs and pentachlorophenol contributing to the residue also presented the possibility that the actual analytical methods may have had interferences from polychlorinated aromatics, and the values were not accurately determined [20]. This may have been especially true of the potential presence of 2,3,4,6-tetrachlorobenzene and 2,3,4,6-tetrachloro-phenylmethyl ether, both persistent products of the breakdown of Lindane, the insecticide sprayed by “Patches” in 1962 [14, 20]. Two subsequent wipe samples taken after decontamination in 1995 showed an average interior 2,3,7,8-TCDD concentration of 45 ng/m² [12].

The above assessment suggested that residues in “Patches” may not have been “representative” of the residues that may have persisted in other UC-123K aircraft deployed by Air Force Reserve units. From 1986 through 2010, there were 18 UC-123K aircraft being stored with AMARG at Davis-Monthan AFB. These aircraft were owned and managed by the 505th Aircraft Sustainment Squadron (ACSS), Hill AFB Utah. Four of the 18 aircraft were sampled for residual Agent Orange components, namely the herbicides 2,4-D and 2,4,5-T and the associated dioxin contaminant 2,3,7,8-TCDD [21]. The history of all 4 aircraft indicated they had been deployed in RANCH HAND missions in Vietnam (tail numbers 54-086, 54-4571, 55-4532, and 55-4544) [9, 10]. A total of 140 samples were collected from the 4 aircraft. The wipe samples consisted of gauze pads wetted with hexane for dioxin samples and with water for herbicide samples. Importantly, a comprehensive sampling protocol ensured that all key internal and external

surfaces were sampled in replicate for all four aircraft. Additionally, air samples were taken from within each aircraft [21].

The results of the sampling and analyses for the four aircraft are shown in Figures 1 and 2. The dioxin data were expressed in TEQs to be consistent with the data from “Patches”, although the primary dioxin was 2,3,7,8-TCDD with traces of the HpCDD and Octadibenzo-p-dioxin (OCDD) being detected in a few samples [21]. The fingerprint pattern of the 17 congeners identified in samples from “Patches” was not present in samples from the 4 aircraft sampled at AMARG. The analytical results for the 4 former RANCH HAND aircraft sampled at AMARG indicated:

There were no detectable levels of the phenoxy herbicides or associated TCDD on the exterior of the 4 aircraft that were sampled;

There were no detectable levels of the phenoxy herbicides or TCDD found in any of the air samples collected inside the 4 aircraft sampled;

Two of the 4 aircraft had trace levels of 2,4-D and 2,4,5-T at the detection level of $230 \mu\text{g}/\text{m}^2$ and $150 \mu\text{g}/\text{m}^2$, respectively (these were considered very low values); and

Two of the 4 aircraft had low levels of dioxin and phenoxy herbicides on all interior surfaces that were sampled (average concentrations of 14.6 and $18.2 \text{ ng}/\text{m}^2$ TEQ, 518 and $502 \mu\text{g}/\text{m}^2$ 2,4,5-T, and 587 and $453 \mu\text{g}/\text{m}^2$ 2,4-D for aircraft 55-4571 and 55-4532, respectively) [21].

Some additional observations: **1.** Interior floor areas were not found to be more heterogeneously contaminated than interior wall surfaces. In fact, interior floor concentrations were uniform in the two aircraft with measureable residual contamination; **2.** The results were consistent with previous sampling for phenoxy herbicides that was conducted in 1996. Both aircraft that were found to have trace concentrations (55-4544 and 54-0585) had non-detectable levels of herbicides on the fuselage floor in the 1996 samples. The two aircraft that had low levels of dioxins (TEQs) and herbicide concentrations in all interior surface samples (55-4532 and 55-4571) also had detectable herbicide levels in samples taken from the floor in 1996; and, **3.** Concentrations of dioxins found during the 2009 sampling

event were significantly lower than concentrations found in “Patches” in 1994, or composite samples collected in 1995 after decontamination, i.e., 45ng/m^2 [21].

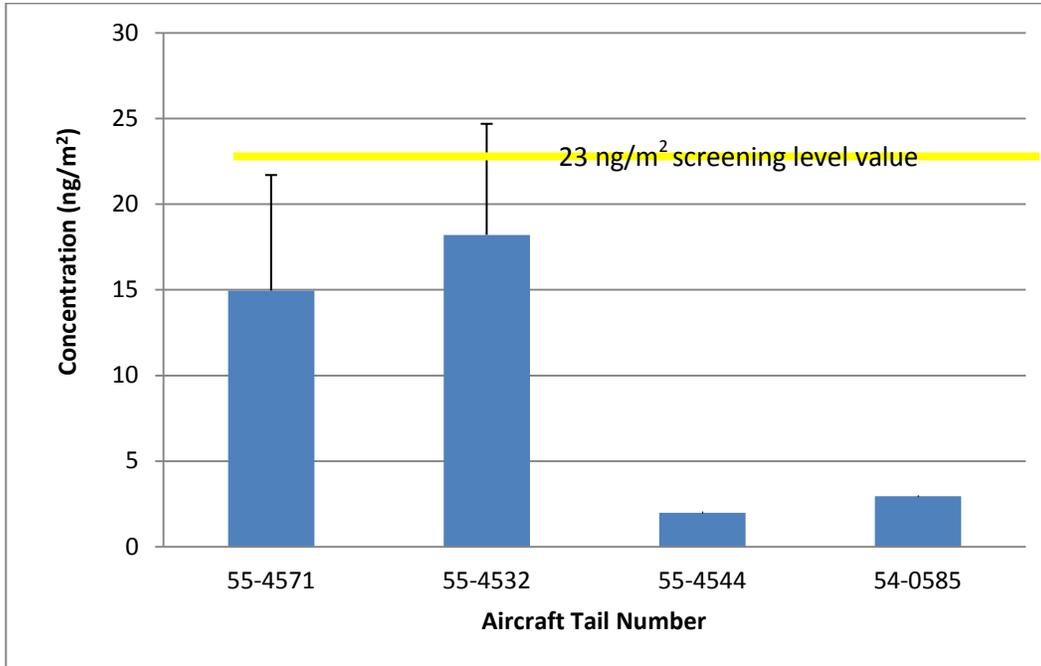


Figure 1. Average Interior Concentrations of Dioxins Reported as ng/m^2 TEQ, Compared to the Risk-Based Screening Level Value of 23ng/m^2 . Error bars indicate 95% upper confidence limits for average values approaching the risk-based standard [21].

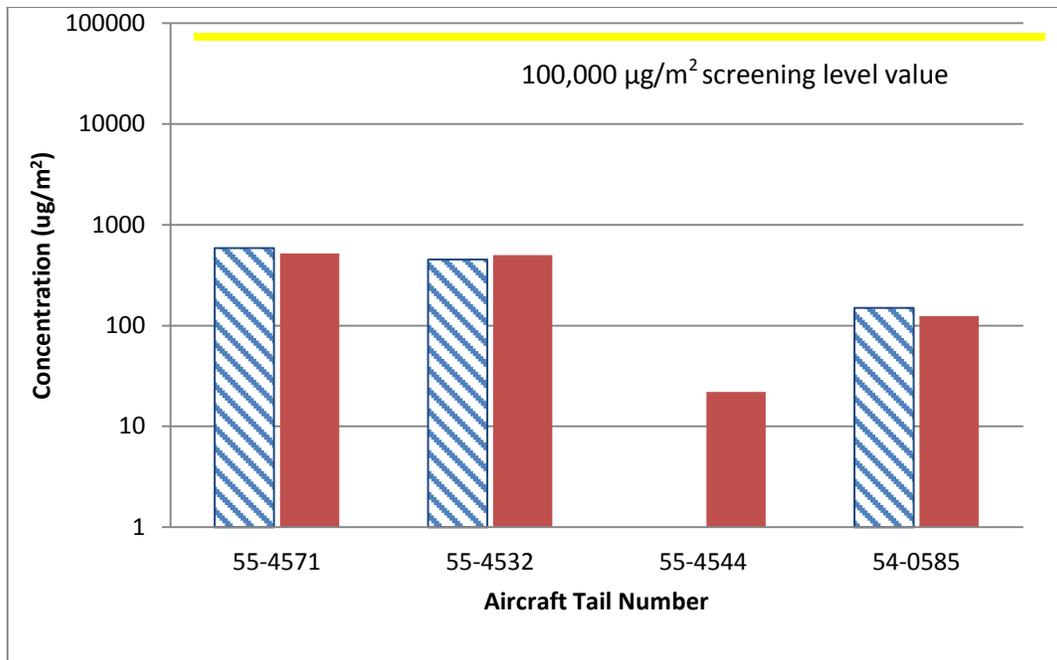


Figure 2. Average Interior Concentrations of 2,4-D (blue, diagonal fill) and 2,4,5-T (red, solid fill), Compared to the Risk-Based Screening Level Value of 100,000 µg/m². Note log scale of concentration axis [21].

In Figure 2, note that aircraft 55-4544 had no detectable levels of 2,4,5-T, suggesting that this UC-123K was a late arrival in 1969 to RANCH HAND and was very likely used primarily for spraying of Agent White, a formulation of picloram (Tordon) and 2,4-D.

Another issue related to the UC-123Ks controversy, was the issue of “smells/odors” in the aircraft. All three of the tactical herbicides had distinct odors. Although TCDD does not have an odor, Agent Orange had a “butanol-like” odor that was very persistent, i.e., years. Malathion and Lindane also had persistent odors, but there was another source not identified in the C-123Ks that returned from Vietnam, and that had to do with the odor associated with the quarantine procedures used for all returning aircraft and equipment from Vietnam [22].

During the gradual withdrawal of US Forces from the Republic of Vietnam, equipment and material which were not designated for turnover to the Vietnamese Air Force (VNAF) were returned to CONUS for further utilization. This “retrograde cargo” was required to undergo international quarantine procedures designed to eradicate disease vectors, insects and other pests, thus preventing their

introduction into the United States [22]. If a UC-123K or any of the C-123K models transported cargo in Vietnam and were reassigned to CONUS, they were frequently tasked to carry retrograde cargo, and hence were required to undergo quarantine procedures. The Military Quarantine Inspector was responsible for the inspection and certification of aircraft and retrograde cargo. The processing and quarantine procedures were conducted at major military installations in Vietnam. When the cargo was palletized and loaded onto the aircraft and ready for treatment, it was covered with plastic and tied down with cargo nets. The treatment consisted of a micronized DDT and Carbaryl (Sevin®) forcefully injected under the plastic covers. Even when the cargo was removed at destination, the odor of these insecticides persisted in the aircraft for many years [22]. It should be noted that EVERY C-123 aircraft, including the C-123K models, returning from Vietnam was subjected to quarantine procedures. The odors from these persistent pesticides were present in these aircraft for many years, and were likely those odors mistaken for Agent Orange, i.e., noting that 20 of the 26 aircraft identified in the October 2012 report “*Establishing Agent Orange Exposures to Veterans*” were not RANCH HAND aircraft but alleged to have been, based on odors presumably associated with residues [7].

CONCLUSIONS

The allegations put forth by former Air Force Reserve crew and maintenance personnel were that the residues within the 19 UC-123Ks reassigned post-Vietnam to their Reserve units were from Agent Orange, and that the magnitudes of these residues were exemplified by analytical studies conducted during the decontamination of “Patches”, a former RANCH HAND aircraft donated to the National Museum of the US Air Force, Wright-Patterson AFB Ohio. A search of the historical records provided a detailed history of “Patches” to include its assignments in international locust control programs, its use in tests and evaluations of spray equipment at Eglin AFB, Florida, to its use in Vietnam not only in Operation RANCH HAND, but frequently reconfigured for its use in hauling cargo or for insecticide missions in Operation FLYSWATTER. This extensive multiple activities of “Patches” put in doubt the analytical results of the 4 (and only 4) samples analyzed for dioxin and furans in 1994. Indeed, the fingerprint of the analytical results suggested the potential contamination by PCBs, the insecticides Lindane , and other aromatic materials. Clearly “Patches” was not

a representative aircraft for determining Agent Orange residues. Certainly the odors reported by veterans could be attributed to pesticides rather than Agent Orange, namely DDT and Carbanyl (Sevin®).

In 1996 and 2009, UC-123K aircraft in quarantine storage at the 309th Aerospace Maintenance and Regeneration Group (AMARG) at Davis-Monthan AFB were sampled for the residual Agent Orange constituents 2,4-D, 2,4,5-T and the associated dioxin, TCDD. One hundred forty samples (140) were collected from 4 aircraft with known histories of defoliation missions in Vietnam. The results indicated that no Agent Orange residues were found on the exterior of any aircraft or in air samples taken inside the tightly-closed aircraft. Two of the aircraft had trace levels of residues, near the lowest limit of analytical detection, on the fuselage floor, and were essentially considered “clean”. The other two aircraft had levels of Agent Orange residues on all interior fuselage surfaces that were tested. The average concentrations found in these two aircraft were statistically near the risk-based screening level for dioxins, based on a one-year industrial exposure scenario. The question remained, were these residues actually capable of providing a measureable exposure or dose to aircrew or maintenance personnel?

THE ALLEGATIONS THAT SIGNIFICANT EXPOSURE OCCURRED

The most important and relevant allegation was that the herbicide and dioxin (Agent Orange) “dry residues” within the UC-123K aircraft represented a primary route of exposure and, thus potentially posed a far greater risk than those experienced by the RANCH HAND crews that flew those same UC-123Ks in Vietnam. The supposition was that RANCH HAND aircrews and maintenance personnel were exposed to Agent Orange for generally just one year, not the multiple years as were contended by the post-Vietnam Air Force Reserve crews.

The assumption that analytical values of the “dry dioxin residues”, obtained through the use of “wipe” samples taken from within the interior surfaces of Post-Vietnam UC-123Ks, are determinants of the degree and level of individual exposures is simply not valid. The dioxin, 2,3,7,8-TCDD, tenaciously adheres to surfaces and is essentially inert because it is not susceptible to chlorination or dechlorination reactions, thus its long persistence time [23]. Extensive studies on the photodegradation of TCDD were conducted by Crosby et al., [24]. They found

that in sunlight and in the presence of Agent Orange, the TCDD molecule was readily dechlorinated (destroyed) because the n-butyl formulation of Agent Orange provided a hydrogen donor essential for the dechlorination of TCDD [24]. The acid forms of 2,4-D and 2,4,5-T (the forms found in the 2009 studies of residues in 4 UC-123Ks at AMARG, Figure 2) do not contribute the necessary organic hydrogen donor, and hence the continued persistence of TCDD [21]. The studies of TCDD persistence at Eglin AFB Florida confirmed that in the absence of the herbicide and sunlight, TCDD residues were still detected 25 years after massive levels of Agents Purple and Orange had been aerially sprayed on Test Area C-52A in the early and mid-1960s [15].

In their assessments of exposure to the TCDD within the UC-123K aircraft, Air Force Reserve personnel suggested that there were two major routes of exposure. The first was the residue that aircrews or maintenance personnel came in dermal contact with, and the time (duration and frequency) of that contact. The second route of exposure was through inhalation. It was logical for the aircrews to assume that if they could smell an odor, then through inhalation they were being exposed to what was in the odor [7, 25].

Dermal Exposure: Dioxin (TCDD) is essentially water insoluble. In both the studies conducted with “Patches” (1994) and the 4 aircraft at AMARG (2009), the TCDD residues on the interior surfaces of the aircraft were removed through the use of wipes “wetted” with the organic solvent hexane [12, 21]. Although there were measurable levels of TCDD in the residues, extensive studies have shown that actual dermal contact with TCDD contributes no more than 1% (and probably considerably less) over the long term to the body burden, and that 1% was considered by the Center for Disease Control and Prevention (CDC) to be a “negligible” exposure [26]. Thus, the skin is a major barrier to exposure from TCDD [26]. The risk assessments that have used the analytical data from the hexane wipe samples failed to recognize that those analytical values cannot be extrapolated to represent a human “dose”. This approach has been labeled the “big leap” in defining exposure in a population, e.g., aircrews, and the environmental matrix, e.g., the residues on the interior walls, and the storage of dioxin in the human body [27].

Inhalation Exposure: In considering inhalation of TCDD from the air contained within the UC-123K aircraft, the single most important property of TCDD is its “volatility”. To understand how the values of volatility for TCDD are derived, see **Appendix 1**. The data in **Figure 2 of the Appendix** clearly shows that the vapor pressure of 2,3,7,8-TCDD is extremely low, including at elevated temperatures. At ambient temperature (around 25° C, 77° F) TCDD is essentially in a solid state and its vapor pressure is about 9 to 11 orders of magnitude lower than that of liquid water. The 2,3,7,8-TCDD will only melt around 420° C (788° F). At 100° C (212° F), the boiling temperature of water, the vapor pressure of 2,3,7,8-TCDD is 7 to 8 orders of magnitude lower than that of water. As a consequence vapor exposures to TCDD vapors at or near ambient temperatures are extremely unlikely to result in a significant dose. To explain it in more practical terms, to have had TCDD volatilize within the crew compartment of the UC-123K, the air temperature would have had to be approximately 420° C or 788° F.

Supporting Epidemiologic Studies: The veteran-prepared report “*Request for Congressional Assistance with C-123 Veterans’ Claims: Establishing Agent Orange Exposures to Veterans*” claimed that that the exposures received by Air Force Reserve personnel were “primary exposures”, while RANCH HAND exposures were “secondary exposures”. In reality, a pathway that would have represented a primary exposure to Agent Orange and its associated TCDD would have been a direct exposure to the liquid herbicide. A “secondary exposure” would have been through secondary pathways such as the consumption of contaminated food, or the drinking of water with contaminated sediments. These are called “environmental exposures” and represent an indirect exposure [28].

There are two examples of veterans allegedly receiving environmental exposures. The first study compared the blood serum TCDD levels in 646 ground combat troops who served in heavily sprayed areas of Vietnam against 97 veterans who did not serve in Vietnam [29]. The 646 combat veterans had served one tour in III Corps, a heavily sprayed part of Vietnam near Saigon. Exposure estimates were based on military records and on self-reporting. For the Vietnam veterans, the fact that military records appeared to validate that they were exposed, coincided with their own perception of being exposed. However, the concentration of TCDD levels in Vietnam and non-Vietnam veterans were nearly identical, ~ 4 parts per trillion (ppt) [29]. To the Vietnam veterans in this study, the perception of

exposure and the reality of exposure were not the same, and the use of military records to determine locations of combat veterans in relation to RANCH HAND missions were also not good indicators for validating exposure to Agent Orange.

The second study was a 30-year postservice mortality study of a cohort of 9,324 male US Army veterans who had served in Vietnam, and whose presumption of exposure would have been consistent with the Department of Veterans Affairs policy [30]. The Vietnam veteran cohort was matched with a cohort of 8989 male non-Vietnam veterans [30]. The conclusion as reported in 2004:

Vietnam veterans continued to experience higher mortality than non-Vietnam veterans from unintentional poisonings and drug-related causes. Death rates from disease-related conditions, including cancers and circulatory diseases, did not differ between Vietnam veterans and their peers, despite the increasing age of the cohort (mean age, 53) and the longer follow-up (average, 30 years) [30].

There are two examples of long term populations studies where the cohorts were exposed to either Agent Orange in Vietnam or to the spraying of 2,4,5-T herbicide. The first study was the Air Force Health Study (AFHS). In 1982, the US Air Force initiated the Air Force Health Study, a study of the men of Operation RANCH HAND, the US-Vietnam allied program for the aerial application of herbicides during the Vietnam War [31]. For the 20-year study there were two cohorts; one cohort included 1,261 RANCH HAND veterans, and the other cohort represented the comparison group that consisted of 19,109 veterans who flew C-130s in Vietnam. The protocol used a matched retrospective cohort design intended to independently determine mortality, morbidity, and reproductive health [31].

The strength of AFHS was enhanced during the second physical examination in 1987 with the development of TCDD determination in blood serum at the parts per trillion level (ppt). Of the 995 RANCH HAND who were fully compliant in 1987 for the physical examination, 932 had serum specimens analyzed by CDC. The serum values for TCDD ranged from less than 10 ppt (considered “background”) to 618 ppt. The highest values were found in the maintenance personnel who came into direct contact with the liquid herbicide, and who were responsible for loading the herbicide into the planes, cleaning the spray equipment and repairing the aircraft [31]. During the six examinations conducted over the 20 years, the AFHS

investigated over 300 health endpoints on multiple occasions. ***The results of the AFHS did not provide evidence of disease in the RANCH HAND veterans caused by their elevated levels of exposure to Agent Orange and its associated TCDD contaminant*** [31].

The second study of a populations exposed to TCDD involved 2,4,5-T herbicide applicators in New Zealand [32]. Of 548 men employed as professional pesticide applicators in New Zealand from 1979 through 1982, nine were selected who had sprayed 2,4,5-T over a range of 7 to 30 years. Their blood serum levels ranged from 3 to 131 ppt (mean of 53 ppt TCDD), where the variation in TCDD was related to their duration of work exposure to 2,4,5-T. ***The authors concluded that increased risks from brief exposure to phenoxyherbicides are probably not attributable to the TCDD that contaminates 2,4,5-T herbicide*** [32].

CONCLUSIONS

The contaminant TCDD found in the dry residues within Post-Vietnam UC-123Ks was not water soluble. The only method for extracting and measuring TCDD within the aircraft interior surfaces was through the use of wipe samples “wetted” with the organic solvent hexane. Although there were measurable levels of TCDD within these dried residues, studies of dermal contact with TCDD have found that any exposures that occurred were “negligible” because the skin is a major barrier to TCDD uptake, contributing less than 1% over the long term to the body burden. Vapor exposures to TCDD at near ambient temperatures were extremely unlikely to result in any significant dose because TCDD is not volatile below 420° C (~ 780 °F).

Four epidemiological or analytical studies of Vietnam veterans or professional sprayers of 2,4,5-T herbicide provided supporting evidence that “primary” or “secondary” exposure to TCDD associated with the spraying of Agent Orange would not have resulted in diseases caused by the herbicides or its associated TCDD. However, it is important to note that all the analytical and scientific studies cannot prove that the Air Force Reserve aircrews and maintenance personnel assigned to the UC-123K were not exposed to Agent Orange and its associated dioxin contaminant. ***However, all the analytical and scientific studies suggested that if they were exposed, that exposure was negligible.***

REFERENCES

1. Quick B (2008): Agent Orange: A Chapter from History That Just Won't End. Orion Magazine, March/April 2008
2. Deforge J (2012): Veterans: Westover Planes Fouled with Agent Orange. The Republican, Massachusetts, April 01, 2012
3. Philpott T (2011): Ill Reservists Blame Post-War 'Spray Bird' Missions. Military Update, Centreville, VA, May 26, 2011 (www.militaryupdate.com)
4. Benjamin CR (2012): MEMORANDUM FOR AFMSA/SG3, SUBJECT: Consultative Letter, AFRL-SA-WP-CL-2012-0052, UC-123 Agent Orange Exposure Assessment, Post-Vietnam (1972-19812). Department of the Air Force, Air Force Research Laboratory, Wright-Patterson AFB Ohio. Approved for public release; distribution unlimited. Case Number: 888ABW-2012-2550, 27 April 2012
5. Murphy TJ (2012): SUBJECT: Advisory Opinion – Service-connection based on exposure to Agent Orange due to flying C-123 aircraft. Compensation Service, Veterans Benefit Administration, Department of Veterans Affairs, Washington DC, September 25, 2012
6. United States Department of Veterans Affairs (2012): Public Health Notice, Agent Orange Residues on Post-Vietnam War Airplanes. Released June 20, 2012
7. Carter, WT (2012): Request for Congressional Assistance with C-123 Veterans' Claims, Establishing Agent Orange Exposures to Veterans of the 74th Aeromedical Evacuation Squadron, the 731st TAS, the 901st Organizational Maintenance Squadron, and the 901s Aerial Port Squadron. Compiled October 2012, www.c123AgentOrange.com
8. Boyne WJ (2012): Mule Train: First Combat in Vietnam. Posted on June 10, 2012. <http://air-boyne.com/mule-train-first-combat-in-vietnam>
9. Cecil PF (1986): Herbicidal Warfare: The RANCH HAND Project in Vietnam. Praeger Special Studies, Praeger Scientific, Praeger Publishers, New York, NY
10. Baugher J (2010): USAF Serial Number Search Results. Criteria: UC-123K. <http://cgibin.rcn.com/jeremy.k/cgi-bin/gzUsafSearch>
11. Epifano T (1986): It's Up or Out After 30 for Aircraft, Too: Last Flight of the C-123 Provider. The Officer (the magazine of the Reserve Officers Association of the United States) 62: 15-18, October 1968
12. Stanek TR (1997): MEMORANDUM FOR USAFM/MUC, FROM: 74TH AMDS/SGPB. SUBJECT: Employee and Public Access to the C-123 (Patches). A collection of 25 pages of correspondence and reports dating

- from 22 September 1994 through 22 February 1986. Available from the 74th Medical Group, Wright-Patterson Air Force Base Ohio 45433
13. USAF File: UC-123K "Patches" in Vietnam 1971.jpg. Posted on Wikimedia Commons, on 12 May 2010
 14. MacCuaig RD (1973): The Occurrence of Insecticides in the Blood of Staff of a Locust Control Organization. WHO Pesticide Series, Report 269, Lindane (Available from the Armed Forces Pest Management Board Literature Retrieval System, Accession No. 90706)
 15. Young AL, Newton M (2004): Long Overlooked Historical Information on Agent Orange and TCDD Following Massive Applications of 2,4,5-T-Containing Herbicides, Eglin Air Force Base, Florida. *Env Sci Pollut Res* 11 (4):209-221 (Available from the Armed Forces Pest Management Board Literature Retrieval System, Accession No. 180535)
 16. Aerial Spray Operations (1963): Annual Report for 1963, Special Aerial Spray Flight, Tactical Air Command, Langley Air Force Base Virginia (Available from the Armed Forces Pest Management Board Literature Retrieval System, Accession No. 09831)
 17. Cecil PF Sr., Young AL (2008): Operation FLYSWATTER: A War Within a War. *Env Sci Pollut Res* 15 (1) 3-7 (Available from the Armed Forces Pest Management Board Literature Retrieval System, Accession No. 187736)
 18. Young AL, Van Houten WJ, Andrews WB (2008): State-of-Art: Agent Orange and Dioxin Remediation. 2nd Agent Orange and Dioxin Remediation Workshop, Hanoi Viet Nam, 18-20 June 2007. *Env Sci Pollut Res* 15 (2): 113-118
 19. Rappe C, Marklund S, Kjeller L-O, Bergqvist P-A, Hansson M (1985): Composition of Polychlorinated Dibenzofurans (PCDF) Formed in PCB Fires. Chapter 29, IN: Keith LH, Rappe C, Choudhary. Chlorinated Dioxins and Dibenzofurans in the Total Environment. Butterworth Publishers, Boston
 20. Smith LM, Johnson JL (1985): Evaluation of Interferences from Seven Series of Polychlorinated Aromatic Compounds in an Analytical Method for Polychlorinated Dibenzofurans and Dibenzo-*p*-dioxins in Environmental Samples. Chapter 18, IN: Keith LH, Rappe C, Choudhary. Chlorinated Dioxins and Dibenzofurans in the Total Environment. Butterworth Publishers, Boston
 21. Select Engineering Services (2009): Draft-Final, Dioxin and Herbicide Characterization of UC-123K Aircraft, Phase 1. Prepared for the 505 Aircraft Sustainment Squadron, Hill Air Force Base Utah, and the Hazardous Waste Program, 75th CEG/CEVC, Hill Air Force Base Utah.

Select Engineering Services, 1544 North Woodland Park Drive, Layton Utah, 84041

22. Porter KR (1971): Air Force Retrograde Program. Proceedings of the CINPAC Preventive Medicine Conference, Camp H.M Smith, Oahu, Hawaii, 18 – 22 January 1971 (Available from the Armed Forces Pest Management Board Literature Retrieval System, Accession No. 058174)
23. Eiceman GA, Rgheu HO: 1985. Adsorption, Chlorination, and Photolysis of Selected Chlorinated Dioxins on Flyash from Municipal Incinerators Using Laboratory Simulation of Emission Processes. Chapter 34, IN: Keith LH, Rappe C, Choudhary. Chlorinated Dioxins and Dibenzofurans in the Total Environment. Butterworth Publishers, Boston
24. Crosby DG, Moilanen KW, Wong AS (1973): Environmental Generation and Degradation of Dibenzodioxins and Dibenzofurans. Environ Health Perspect 5(3): 259-266 (Available from the Armed Forces Pest Management Board Literature Retrieval System, Accession No. 83739)
25. Brewer MP (2012): Update for VA Recognition for Agent Orange Exposure of C-123 Veterans. Veteran Veritas: Advocacy for our Veterans, March 12, 2012
26. Kimbrough RD, Krouskas CA, Carson ML, Long TF, Bevan C, Tardiff RG (2010): Human Uptake of Persistent Chemicals from Contaminated Soil: PCDD/Fs and PCBs. Regulatory Toxicology and Pharmacology 57: 43-54
27. Needham LL, Patterson DG, Turner WE (2002): Comparison of Assessing Levels of 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin in Selected Populations by Biomonitoring and Exposure Indices. Organohalogen Compounds 59:131-134
28. Jones KC, Bennett BG (1989): Human Exposure to Environmental Polychlorinated Dibenzo-*p*-dioxins and Dibenzofurans: An Exposure Commitment Assessment for 2,3,7,8-TCDD. The Science of the Total Environment 78: 99-116 (Available from the Armed Forces Pest Management Literature Retrieval System, Accession No. 145214)
29. CDC (1988): Serum 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin Levels in US Army Vietnam-Era Veterans. Journal of the American Medical Association 260 (9): 1249-1254 (Available from the Armed Forces Pest Management Literature Retrieval System, Accession No. 142755)
30. Catlin Boehmer TK, Flanders WD, McGeehin MA, Boyle C, Barrett DH (2004): Postservice Mortality in Vietnam Veterans: A 30-Year Follow-up. Archives of Internal Medicine 164: 1908-1916
31. Buffler PA, Ginevan ME, Mandel, JS, Watkins DK (2011): The Air Force Health Study: An Epidemiologic Retrospective. Annals of Epidemiology 9: 673-687

32. Smith AH, Patterson DG, Jr., Warner ML, MacKenzie R, Needham LL (1992): Serum 2,3,7,8-Tetrachlorodibenzo-*p*-dioxin Levels of New Zealand Pesticide Applicators and Their Implications for Cancer Hypothesis. *Journal of the National Cancer Institute* 84(2): 104-108

APPENDIX 1*

Evaluation of the Vapor Pressure of TCDD over a range of temperatures

Vapor pressure is an important physicochemical parameter for predicting the atmospheric concentrations of given compounds. Practically, it can be used to determine the transport and fate of contaminants in the environment and to characterize exposure in the context of a risk assessment. However, the precise measurement of the vapor pressure of low-volatility substances is an experimental challenge. This is the case of dioxins and more specifically 2,3,7,8-TCDD, for which a the range of values of vapor pressure found in the literature spread over several orders of magnitude.

Below is a summary of various values of vapor pressure reported in peer reviewed literature for 2,3,7,8-TCDD. In order to give these values a concrete meaning they were compared to the vapor pressure of water at different temperature. The data was synthesized in a graphic format and the numerical values are compiled in Table 1.

Vapor Pressure of TCDD at Different Temperatures

Generally, the reported vapor pressure of 2,3,7,8-TCDD ranges between 7.4×10^{-10} to 3.4×10^{-5} mm Hg (9.9×10^{-8} and 4.5×10^{-3} Pa) (ATSDR, 1998).

In 1984, Schroy and co-workers identified some data gaps in the physical and chemical properties of 2,3,7,8-TCDD. At the time, the vapor pressure of solids was seldom studied and no data was available for TCDD. Therefore, they undertook a research program to define the physical properties of 2, 3, 7, 8-tetrachlorodibenzo-p-dioxin (TCDD), including its vapor pressure. They provided estimates for a wide range of temperatures between 25 and 421°C. The vapor pressure spanned over about 11 orders of magnitude, between 1.5×10^{-9} and 7.6×10^2 Pa (Schroy et al., 1984). One should take caution with the reliability of these results since they differ from values published in later years by several orders of magnitude.

In a subsequent study, the same team reported all the physical and chemical data available for TCDD at the time, including the vapor pressure between 30 and 71°C

(Schroy et al., 1985). For some undetermined reasons, these results were about two orders of magnitude higher than those published in 1984.

In 1986, Podoll et al. studied the rates of volatilization and photolysis of TCDD. They measured the average vapor pressure in air at 25°C to be $7.4 \pm 0.4 \times 10^{-10}$ Torr which corresponds to about 0.987×10^{-7} Pa (Podoll et al. 1986). This value is comparable to those published by Schroy et al., Rordorf et al. as well as Delle Site¹ in the same temperature range (Delle Site; 1996, Rordorf 1989; Schroy et al., 1985). Shroy et al. also reported the boiling point of dioxin to be 421.2°C (Schroy et al., 1985).

More recently, Li et al. predicted the vapor pressure of 59 PCDDs and 131 PCDFs. Overall their results were higher than those published by Rordorf et al. even though the calculation methods were the same. In particular, the vapor pressure of 2,3,7,8-tetrachlorinated dibenzo-*p*-dioxin, at 25°C was estimated to be 6.2×10^{-6} Pa, which was 31-fold higher than the values provided by Rordorf (2.0×10^{-7} Pa). The results of these studies are plotted in Figure 1.

*From: Investigations into the Allegations of Agent Orange/Dioxin Exposure from Former RANCH HAND Aircraft. Agent Orange Investigative Report Series, No. 2, November 2012

¹ Delle Site reported vapor pressure values measured for different temperatures using 6 different methods.

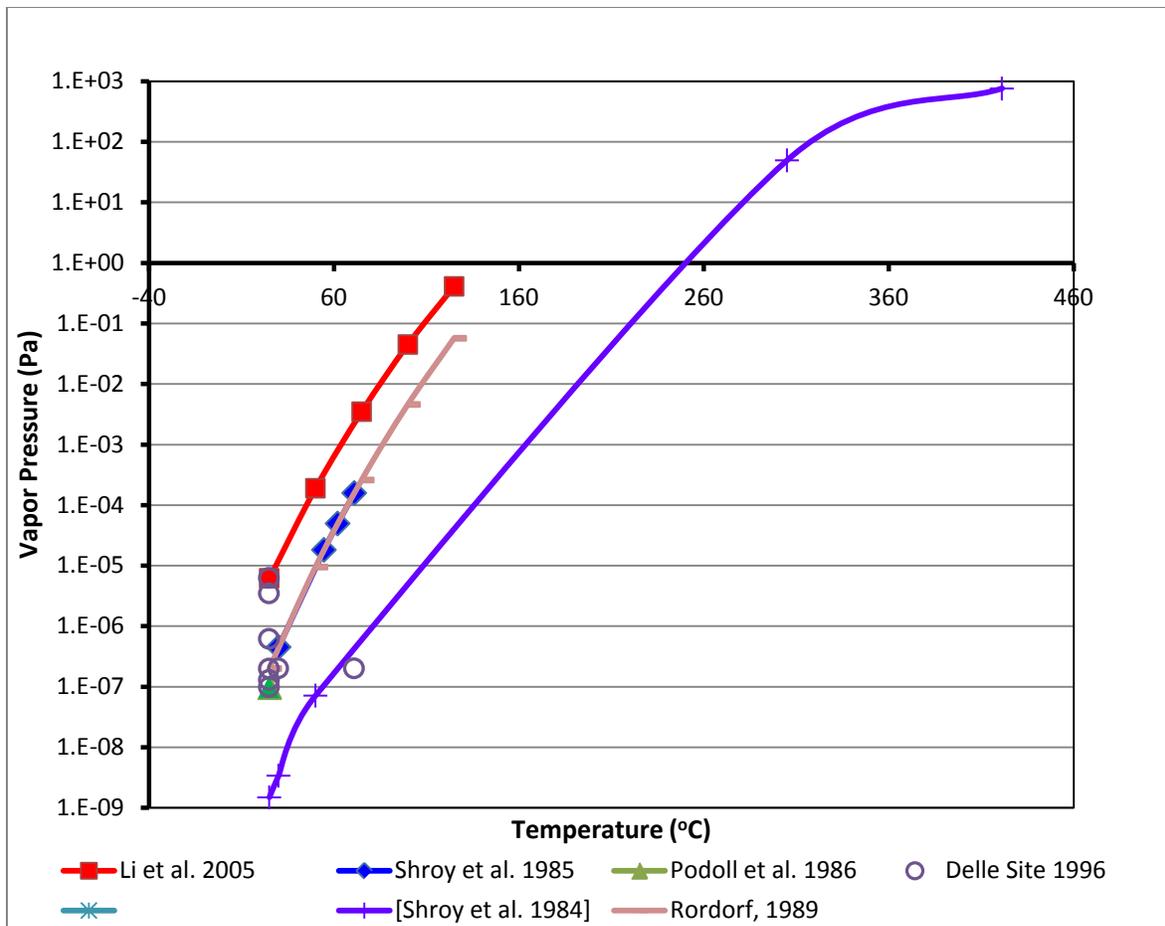


Figure 1. Reported values of vapor pressure for 2,3,7,8-TCDD at different temperatures.

Table 1. Published values of TCDD vapor pressure as a function of temperature.

Reference	Temperature (oC)	Pressure (Pa)
[Shroy et al. 1984]	25	1.49E-09
	30	3.40E-09
	50	7.15E-08
	305	4.95E+01
	421.2	7.60E+02
Shroy et al. 1985	30.1	4.53E-07
	54.6	1.83E-05
	62	4.97E-05
	71	1.59E-04
Podoll et al. 1986	25	9.87E-08
Rordorf 1989	25	2.00E-07
	50	9.50E-06
	75	2.60E-04
	100	4.60E-03
	125	5.70E-02
Delle Site 1996	24.85	9.90E-08
	29.85	2.02E-07 ^a
	70.85	2.02E-07 ^a
	24.85	1.30E-07
	24.85	3.50E-06 ^b
	24.85	6.30E-06 ^b
	24.85	2.00E-07
	24.85	6.20E-07
Li et al. 2005	25	6.20E-06
	50	1.90E-04
	75	3.50E-03
	100	4.50E-02
	125	4.10E-01

^a Reported as a pressure of 2.02×10^{-7} measured for a temperature ranging from 303 K to 344 K

^b Reported that a temperature of 298 K corresponding to a pressure measurement between 3.5×10^{-6} and 6.3×10^{-6} Pa

Comparison with the vapor pressure of water

The values of vapor pressure reported above were compared to the vapor pressure of water at different temperature. These values were calculated using the Antoine equation expressed as follows:

$$\log_{10}(P) = A - (B / (T + C))$$

where P is the vapor pressure (bar), T is the temperature (K) and A, B and C are parameters depending to the temperature and determined in various studies.. The values of these parameters were found on the website of the National Institute of Standards and Technology (NIST)² and are summarized in Table 2.

Table 2^a. Parameters used in the Antoine equation to determine the vapor pressure of water as a function of temperature.

Temperature (K)	A	B	C	Reference	Comment
379. - 573.	3.55959	643.748	- 198.043	<u>Liu and Lindsay, 1970</u>	Coefficients calculated by NIST from author's data.
273. - 303.	5.40221	1838.675	-31.737	<u>Bridgeman and Aldrich, 1964</u>	Coefficients calculated by NIST from author's data.
304. - 333.	5.20389	1733.926	-39.485	<u>Bridgeman and Aldrich, 1964</u>	Coefficients calculated by NIST from author's data.
334. - 363.	5.0768	1659.793	-45.854	<u>Bridgeman and Aldrich, 1964</u>	Coefficients calculated by NIST from author's data.
344. - 373.	5.08354	1663.125	-45.622	<u>Bridgeman and</u>	Coefficients

² NIST website. Physical properties of water available at:

<http://webbook.nist.gov/cgi/cbook.cgi?Name=water&Units=SI&cTG=on&cTP=on>

				<u>Aldrich, 1964</u>	calculated by NIST from author's data.
293. - 343.	6.20963	2354.731	7.559	<u>Gubkov, Fermor, et al., 1964</u>	Coefficients calculated by NIST from author's data.
255.9 - 373.	4.6543	1435.264	-64.848	<u>Stull, 1947</u>	Coefficients calculated by NIST from author's data.

^a Table available on the NIST website:

<http://webbook.nist.gov/cgi/cbook.cgi?Name=water&Units=SI&cTG=on&cTP=on>

Table 3. Vapor pressure of water as a function of temperature

Temperature (°C)	Pressure (Pa)
-17.25	1,386.354
-0.15	6,041.849
19.85	23,720.56
29.85	42,073.58
30.85	44,542.64
59.85	197,896.1
60.85	207,276.5
69.85	310,853.1
70.85	323,335.8
89.85	697,060.3
99.85	1,007,867
99.85	992,317.2
105.85	1,004,907
299.85	69,619,644

The calculated values of water vapor pressure are reported in Table 3. They are also compared with the values reported for 2,3,7,8-TCDD in Figure 2.

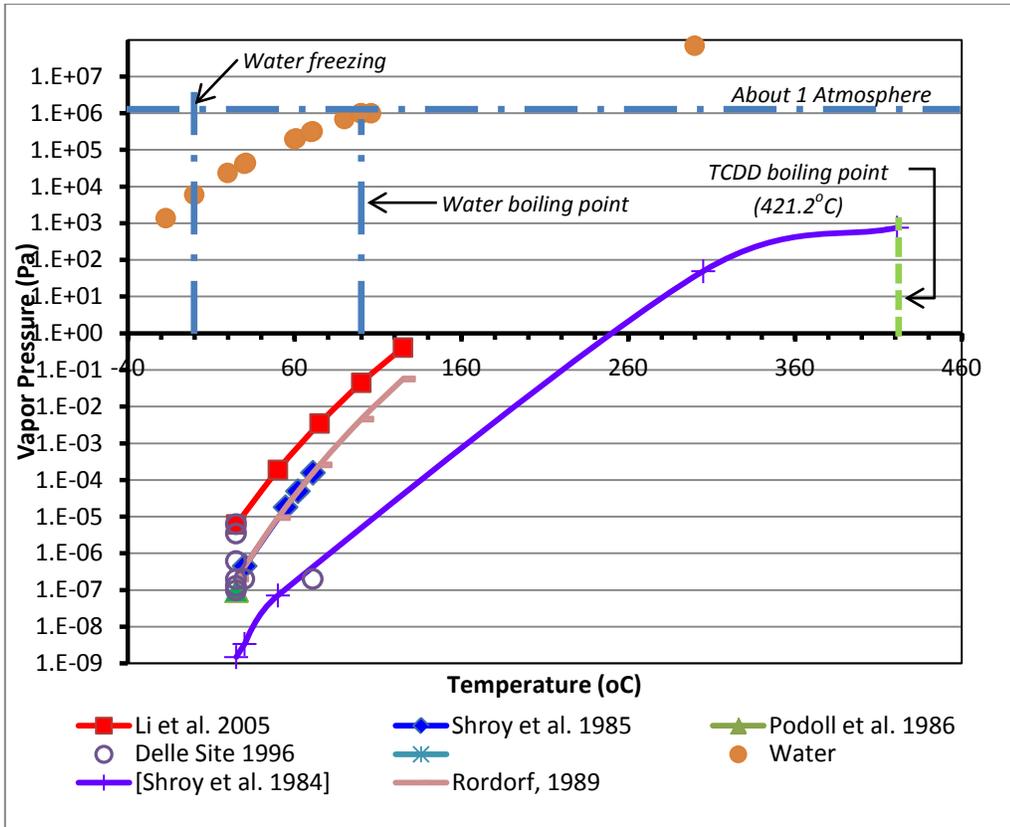


Figure 2. Comparison of the vapor pressure for 2,3,7,8-TCDD with that of water at different temperature

Conclusion

Figure 2 clearly shows that the vapor pressure of 2,3,7,8-TCDD is extremely low, including at elevated temperatures. At ambient temperature (around 25°C) TCDD is essentially in a solid state and its vapor pressure is about 9 to 11 orders of magnitude lower than that of liquid water. 2,3,7,8-TCDD will only melt around 420°C. At 100°C, the boiling temperature of water, the vapor pressure of 2,3,7,8-TCDD is 7 to 8 orders of magnitude lower than that of water. As a consequence, vapor exposures to TCDD vapors at or near ambient temperatures is extremely unlikely to result in a significant dose.

References

- ATSDR. 1998. Chlorinated Dibenzo-*p*-Dioxin. In: Services USDoHaH, editor. Toxicological profile. U.S. Department of Health and Human Services, Atlanta, GA, pp. 721.
- Delle Site A. The Vapor pressure of environmentally significant organic chemicals: A review of methods and data at ambient temperature J. Phys. Chem. Ref. Data, Vol. 26, No.1, 1997
- Li XW, Shibata, E and Nakamura, T. 2005. Thermodynamic prediction of vapor pressures for polychlorinated dibenzo-*p*-dioxins, polychlorinated dibenzofurans, and polybrominated dibenzo-*p*-dioxins, Environmental Toxicology and Chemistry, Vol. 24, No. 9, pp. 2167–2177
- Podoll RT, Jaber HM, Mill T. 1986. Tetrachlorodibenzodioxin: rates of volatilization and photolysis in the environment. Environ Sci Technol; 20: 490-492.
- Rordorf BF. 1989. Prediction of vapor pressures, boiling points and enthalpies of fusion for twenty-nine halogenated dibenzo-*p*-dioxins and fifty-five dibenzofurans by a vapor pressure correlation method. Chemosphere, Vol.18, Nos.1-6, pp 783-788
- Schroy JM, Hileman FD, Cheng SC. 1985. Physical/chemical properties of 2,3,7,8-TCDD. Chemosphere 1985; 14: 877-880.

Schroy JM, Hileman FE, Cheng SC. 1984. The uniqueness of dioxins? physical / chemical characteristics. For Presentation at the 8th ASTM Aquatic Toxicology Symposium to be held on April 15, 16, and 17, 1984 at the Draw Bridge Inn, Fort Mitchell, Kentucky.