Environmental Research 130 (2014) 34–42

Contents lists available at ScienceDirect

Environmental Research

journal homepage: www.elsevier.com/locate/envres

Post-Vietnam military herbicide exposures in UC-123 Agent Orange spray aircraft

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ARTICLE INFO

Article history:
Received 11 July 2013
Received in revised form
31 January 2014
Accepted 1 February 2014

Keywords:
Agent Orange
Phenoxyherbicides
Dioxin
Exposure modeling
Veterans
Vietnam War

ABSTRACT

Background: During the Vietnam War, approximately 20 million gallons of herbicides, including ~10.5 million gallons of dioxin-contaminated Agent Orange, were sprayed by about 34 UC-123 aircraft that were subsequently returned to the United States, without decontamination or testing, to three Air Force reserve units for transport operations (~1971–1982). In 1996, observed dioxin contamination led to withdrawal of these UC-123s from public auction and to their smelting in 2009. Current Air Force and Department of Veterans Affairs policies stipulate that “dried residues” of chemical herbicides and dioxin had not lead to meaningful exposures to flight crew and maintenance personnel, who are thus ineligible for Agent Orange-related benefits or medical examinations and treatment. Sparse monitoring data are available for analysis.
Methods: Three complementary approaches for modeling potential exposures to dioxin in the post-Vietnam war aircraft were employed: (1) using 1994 and 2009 Air Force surface wipe data to model personnel exposures and to estimate dioxin body burden for dermal–oral exposure for dried residues using modified generic US Environmental Protection Agency intake algorithms; (2) comparing 1979 Air Force 2,4- dichlorophenoxyacetic acid and 2,4-5-trichlorophenoxyacetic acid air samples to saturated vapor pressure concentrations to estimate potential dioxin exposure through inhalation, ingestion and skin contact with contaminated air and dust; and (3) applying emission models for semivolatile organic compounds from contaminated surfaces to estimate airborne contamination.
Results: Model (1): Body-burden estimates for dermal–oral exposure were 0.92 and 5.4 pg/kg body-weight-day for flight crew and maintainers. The surface wipe concentrations were nearly two orders of magnitude greater than the US Army guidance level. Model (2): measured airborne concentrations were at least five times greater than saturated vapor pressure, yielding dioxin estimates that ranged from 13.2–27.0 pg/m^3, thus supporting the likelihood of dioxin dust adsorption. Model (3): Theoretical models yielded consistent estimates to Model 2, 11–49 pg/m^3, where the range reflects differences in experimental value of dioxin vapor pressure and surface area used. Model (3) results also support airborne contamination and dioxin dust adsorption.
Conclusions: Inhalation, ingestion and skin absorption in aircrew and maintainers were likely to have occurred during post-Vietnam use of the aircraft based on the use of three complementary models. Measured and modeled values for dioxin exceeded several available guidelines. Deposition–aerosolization–redeposition homeostasis of semivolatile organic compound contaminants, particularly dioxin, is likely to have continually existed within the aircraft. Current Air Force and Department of Veterans Affairs policies are not consistent with the available industrial hygiene measurements or with the widely accepted models for semivolatile organic compounds.

Abbreviations: 2, 4-D, 2,4-dichlorophenoxyacetic acid; 2,4,5-T, 2,4,5-trichlorophenoxyacetic acid; A, aircraft interior surface; AT, Averaging time; BW, body weight; CF_a, area conversion factor; CF_{wt}, weight conversion factor; C_s, contaminant surface concentration; ED, Exposure duration; EF, exposure frequency; Fom_part, volume fraction organic matter in airborne particles; FT_{ga}, decimal fraction absorbed from gastrointestinal tract; FT_{re}, decimal fraction contaminant removed from skin-to-mouth; FT_{sm}, decimal fraction of contaminated skin touched to mouth; FT_{ss}, decimal fraction contaminant transferred surface to skin; FT_{we}, decimal fraction of contaminant collected onto wipe; h, convective mass-transfer coefficient; I, systematic intake; K_{oa}, octanol/air partition coefficient; K_p, airborne particle/air partition coefficient; NIOSH, National Institute of Occupational Safety and Health; OSHA, Occupational Safety and Health Administration; Q, ventilation rate; RH, probability of Ranch Hand aircraft; SA, exposed skin surface area; UC-123, Ranch Hand aircraft, known as the “Provider”; WD, type of worker; y_o, gas-phase concentration in contact with the emission surface; $\rho_{particle}$, density airborne particles

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http://dx.doi.org/10.1016/j.envres.2014.02.004
0013-9351

1. Introduction

1.1. Historical context

Between 1962 and 1971, the United States Air Force carried out Operation Ranch Hand in which approximately 20 million gallons of herbicides were sprayed by Fairchild UC-123 aircraft over a relatively small area (~16%) of the Republic of South Vietnam in order to defoliate vegetation used for concealment and to destroy crops used by enemy combatants. Approximately 10.5 million gallons were a 50:50 mixture of 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), popularly known as Agent Orange. The 2,4,5-T was contaminated with 2,3,7,8-tetrachlorodibenzodioxin, which will be referred to here as dioxin. The herbicides were shipped in color-coded drums, which accounts for their nicknames. Table 1 summarizes the known quantities of herbicides sprayed and number of aircraft (sorties) associated with each mission and Table 2 shows the distribution of missions by agent used and number of aircraft in the mission (Stellman et al., 2003). Some Operation Ranch Hand aircraft also sprayed the insecticide malathion. Table 2 provides data on the number of sorties (individual airplanes flown per mission) that were required to carry out this vast operation. The last Agent Orange Ranch Hand mission was on April 16, 1970 and missions using other herbicides ended January 7, 1971 (U.S. Department of Defense, 1970).

After service in Vietnam, the UC-123 spray planes were reassigned, from 1971 to 1982, to the Air Force Reserve for aeromedical evacuation missions. They were not decontaminated or tested for herbicides or dioxin contamination levels before their return to stateside service. No personal air samples or biological monitoring for herbicide exposure are known ever to have been collected from flight crew or aircraft maintenance personnel during post-war aircraft use. A complete list of all the Operation Ranch Hand aircraft and their fate has not been made public by the Air Force. Using unofficial lists, we estimate that about 34 aircraft carried out all the Ranch Hand operations shown in Tables 1 and 2.

Operation Ranch Hand aircraft were equipped with a 1000 gallons tank and pump to force liquid herbicide under pressure into lines connected to spray booms, one under each wing and a third beneath the centerline of the aircraft (Young, 2009). On average, each aircraft flew about 6000 herbicide missions and became heavily contaminated with chemical residues during loading, maintenance, fueling and while on missions. Few precautions were taken inasmuch as the herbicides were not thought to be harmful to humans (Military Assistance Command Vietnam (MACV), 1966). Planes were usually flown with pilot and co-pilot cockpit windows and aft rear cargo door open (Meek, 1981). A typical Ranch Hand mission employed more than one aircraft flying in formation, but, as shown in Table 2, missions could include from one to twelve aircraft. Spray legs were often repeated in a single mission such that planes would fly through previously sprayed airspace. Herbicide mist would enter the aircraft and deposit throughout their interiors. If pressurized spray lines were broken through malfunction, battle damage or maintenance mishap, they would release significant amounts of liquid herbicide into the aircraft interior.

1.2. Contamination arises as an issue

In 1979, air samples for 2,4,5-T, 2,4-D and malathion, but not dioxin, were taken from the interior of the aircraft known as “Patches” at Westover Air Force Base following complaints of persistent chemical odors (Conway, 1979). Patches had flown herbicide missions in Vietnam from 1961–1965. It is uncertain whether Patches was used for herbicide missions 1965–1967; however, in 1967 it was assigned to insecticide missions only. The bulk of herbicide spraying took place after Patches ceased to spray these chemicals. In 1980, Patches was retired to the National Aviation Museum of the United States Air Force (Fairchild C-123k Provider, n.d.), then to the USAF Museum at Wright-Patterson Air Force Base, OH. At the museum, staff concerns about dioxin exposure led to another round of testing. Based on a three-sample surface wipe survey of Patches, Weisman recommended restorers use Tyvek® coveralls and full-face respirators with high efficiency particulate filters and public entry and interior storage of materials or spare parts be prohibited (Weisman and Porter, 1994).

Other planes from the spray fleet were stored at the 309th Aerospace Maintenance and Regeneration Group facilities at Davis-Monthan Air Force Base, Arizona, and subsequently offered for public

Table 2
Distribution of identified Ranch Hand missions by herbicidal agent and numbers of aircraft (sorties) flown, 1961–1971[a].

	Number of Aircraft (Sorties) in Mission												
Agent	1	2	3	4	5	6	7	8	9	10	11	12	Total
Orange	119	907	1705	392	208	279	54	50	34		2	7	3757
White	53	191	574	190	116	229	22	27	18	1			1421
Blue	20	101	224	32	16	10	2		1				406
Purple	70	108	27	22	5	7	4	2					245
Pink	1	1	4										6
Unspecified	7	18	26	3	3	4	1	1					63
Total	270	1326	2560	639	348	529	83	80	53	1	2	7	5898

[a] Adapted from Stellman et al. (2003).

Table 1
Number of Ranch Hand missions, sorties and gallons sprayed by herbicide type and year.[a]

Agent		Years	Missions	Sorties	Gallons
Orange	50% n-Butyl ester 2,4,-D; 50% n-butyl ester 2,4,5-T	1961–1965	210	564	493,525
		1966–1969	3373	11412	10,709,737
		1970–1971	186	544	510,880
White	Acid weight basis: 21.2% tri-isopropanolamine salts of 2,4-D and 5.7% Picloram	1966–1969	1362	5212	4,976,885
		1970–1971	60	201	192,250
Blue	21% sodium cacodylate + cacodylic acid to yield ≥ 26% total acid equivalent by weight	1966–1969	349	1008	897,850
		1970–1971	60	177	151,035
Purple	50% n-Butyl ester 2,4,-D; 30% n-butyl ester 2,4,5-T; 20% isobutyl ester 2,4,5-T	1961–1965	267	566	471,043
Pink	60–40% n-Butyl: isobutyl ester of 2,4,5-T	1961–1965	6	15	13,291
Unspecified	Specific agent not stated in mission records	1961–1965	4	5	5000
		1966–1969	72	161	159,680
		1970–1971	7	22	22,000

[a] Adapted from Stellman et al. (2003).

sale; however, surface contamination tests revealed 2,4-D and 2,4,5-T above an unstated detection level (Porter, 1997). Extensive and costly follow-up tests for dioxin were recommended, but to our knowledge no further testing was undertaken. Instead, given public health concerns over dioxin, the Air Force Materiel Command Law Office withdrew the aircraft from sale in December 1996 (U.S. Department of Air Force, 1996). This withdrawal led to unsuccessful litigation by purchasers for damages from investments made based on sales contracts. The Court denied claims for damages because “the C-123 s evidenced the presence of hazardous chemical contamination and under applicable regulations, the aircraft could not be sold until they were decontaminated” (Board of Contract Appeals, General Services Administration, 2000).

In 2009, some of the aircraft stored by the Aerospace Maintenance and Regeneration Group were tested for dioxin residues. Of 138 samples, only 16 samples were taken from interior surfaces in two Ranch Hand aircraft. Each interior sample was positive for dioxins (US Department of the Air Force (USAF), 2009). As expected, all exterior samples were below detection limits given that dioxins rapidly decompose in sunlight (Choudhry and Webster, 1989). The available dioxin surface wipe data from both testing rounds are summarized in Table 3. All but two aircraft were smelted at an off-base contractor-operated smelting unit for conversion to aluminum ingots. The aircraft remain on display, but, unlike many other displayed aircraft, the public is not permitted entry into any of these aircraft.

1.3. Health and policy considerations

Dioxin exposure is a major health consideration for herbicide-exposed veterans, and 2,4,7,8-tetrachlorodibenzodioxin is the most potent dioxin congener. Dioxin is an impurity created during the manufacture of 2,4,5-T. Limited post-war testing of unused military herbicides revealed dioxin contamination levels as high as 45 ppm in Agent Purple and 13 ppm in Agent Orange (Stellman et al., 2003). Dioxins are highly persistent in the environment. Their high lipophilicity leads them to be stored for long periods in body fat. The biological half-life in humans has been estimated at between 5 and 10 years (Milbrath et al., 2009). Acute adverse health effects from dioxin exposure include chloracne, a severe acne-like condition (Suskind, 1985). Epidemiological studies have shown an association between dioxin and non-Hodgkin lymphoma (Bertazzi et al., 2001), soft tissue sarcoma (Zambon et al., 2007), chronic lymphocytic leukemia (Blair and White, 1985), and cancers of the larynx, lung, and prostate (IOM, 2006). The International Agency for Research on Cancer has classified dioxin as a human carcinogen (Group 1) (IARC Working Group on the Evaluation of Carcinogenic Risks to Humans, 1997). In animals, dioxin is a developmental toxicant causing skeletal deformities, kidney defects, and weakened immune responses in the offspring of animals exposed to dioxin during pregnancy (Abbott et al., 1992; Holladay et al., 1991). Indeed, it was data on possible birth defects in laboratory animals associated with 2,4,5-T that set off a string of administrative actions to restrict both domestic use and military use of the chemical in Vietnam (Hay, 1982). Long simmering controversies over the health effects of Agent Orange led Congress to pass the Agent Orange Act of 1991 (Martini, 2012). A provision of the Act instructs the Department of Veteran Affairs to contract with the Institute of Medicine to conduct scientific reviews of military herbicides used in Vietnam and of Vietnam-veteran health. The Institute of Medicine publishes biennial reviews of all available scientific evidence on health effects of the herbicides (Institute of Medicine (U.S.). Committee to Review the Health Effects in Vietnam Veterans of Exposure to Herbicides, 2009). The Secretary of the Department of Veteran Affairs takes Institute of Medicine recommendations on the likely relationship between military herbicide exposure and specific diseases into consideration in developing benefit policies for Vietnam veterans. Sixteen diseases in veterans or their offspring were eligible for compensation in 2013.

Table 3
Dioxin interior Ranch Hand aircraft surface wipe samples in three aircraft, 1994 and 2009.

Sample Location	Concentration, ng/m^2
Patches, 1994[a]	1400
Patches, 1994	250
Patches, 1994	200
A/C 4571, 2009[b]	18.42
A/C 4571, 2009	27.58
A/C 4571, 2009	21.66
A/C 4571, 2009	4.65
A/C 4571, 2009	7.72
A/C 4571, 2009	1.3
A/C 4571, 2009	9.28
A/C 4571, 2009	32.22
A/C 4571, 2009	10.3
A/C 4532, 2009	25.72
A/C 4532, 2009	26.35
A/C 4532, 2009	29.37
A/C 4532, 2009	12.96
A/C 4532, 2009	6.4
A/C 4532, 2009	11.66
A/C 4532, 2009	14.96

[a] US Air Force – Weisman samples on “Patches” (Weisman and Porter, 1994).
[b] US Air Force samples on aircraft stored outdoors in Davis-Monthan Air Force Base, Arizona (US Department of the Air Force (USAF), 2009).

Current Department of Veterans Affairs policy limits automatic awarding of military herbicide benefits to veterans with service in Vietnam or its interior waterways. Other veterans, those who did not have “boots on the ground” but may have come into contact with the *same* military herbicides, specifically produced for use in Vietnam, such as during disposal and testing operations, are not granted presumption of exposure but must establish, individually, the fact of his or her exposure. However, crew and maintenance personnel who operated the spray planes 1971–1982 in the United States are specifically denied benefits because the risk for exposure is “extremely low and therefore, the risk of long-term health effects is **minimal**” (emphasis in original) (U.S. Dept. of Veterans Affairs, 2012). Similarly, the Air Force has concluded that potential Agent Orange exposures to post-Vietnam UC-123 flight crews and passengers were unlikely to have exceeded acceptable regulatory standards or to have predisposed persons in either group to experience future adverse outcomes (Smallwood, 2012).

1.4. Approach

Here we apply three different and complementary accepted modeling methodologies to the previously described historical Air Force sampling data in order to estimate potential exposure in people who may have worked on or in proximity to the contaminated spray aircraft during post-Vietnam War assignments. We compare our estimates to available guidelines and standards and discuss implications of our findings with respect to current Veterans Administration and Air Force policies.

2. Methods

2.1. Dioxin dermal–oral exposure from direct contact

We used the surface wipe data obtained by two Air Force studies (US Department of the Air Force (USAF), 2009; Weisman and Porter, 1994) shown in Table 3 to estimate potential intake from dermal-to-oral ingestion associated with hand-to-mouth transmission. May et al. (2002) and later the US Army Center for

Health Promotion and Preventive Medicine (2009) adapted the generic intake model (Eq. 1), developed by the US Environmental Protection Agency (1989), to derive risk-based wipe surface screening levels for industrial scenarios.

$$I = C \times \frac{CR \times EFD}{BW} \times \frac{1}{AT} \quad (1)$$

where I is the intake (milligram/kilogram (mg/kg) body weight-day), C the chemical concentration, CR the contact rate (inhalation rate, ingestion rate, absorption rate), EFD the exposure frequency and duration, BW the body weight and AT the averaging time.

In the surface-screening level model, the contact rate (CR in Eq. 1) is the product of estimates for the following factors:

- exposed skin surface area (SA),
- decimal fraction of contaminant transferred from surface to skin (FT),
- decimal fraction of contaminated skin touched to mouth (FT_{sm}),
- decimal fraction of contamination removed from skin to mouth (FT_{re}),
- weight conversion factor (CF_{wt}),
- decimal fraction absorbed from gastrointestinal tract (FT_{ga}).

Exposure frequency and duration (EFD in Eq. 1) are estimated by four factors:

- exposure frequency, hand to mouth events per day (EF),
- work days per year (WD),
- exposure duration (ED),
- probability of being on a Ranch Hand aircraft (RH).

Exposure frequency factors were derived as follows. Pilot and crew flight time is based on interview data obtained by one of us (PAL) from a Westover Air Force Base, Air Force Reserve pilot assigned to a UC-123 between 1973 and 1981 (Lurker, 2013). We also used that author's (PAL) experience (1984–1986) as an industrial hygienist for Aerospace Maintenance and Regeneration Group and his personal observations of the four museum volunteers to modify parameters. Because the Air Force has not made public the identifying numbers of the aircraft used in Operation Ranch Hand, we relied on experienced personnel involved in the Westover Air Force Base operations who reported that eleven of the 24 UC-123 aircraft assigned at Westover Air Force Base were previously Ranch Hand aircraft (Lurker, 2013). For purposes of our model we assumed that the remaining twenty-two Ranch Hand aircraft were evenly divided between the two other twenty-four plane squadrons (Pittsburgh International Airport Air Reserve Station and Rickenbacker Air Force Base). Therefore, we hypothesized there to be an 11/24 or 0.46 probability that any single mission in the post-Vietnam period for these three Air Force Reserve squadrons would have been on a Ranch Hand aircraft (RH=0.46).

To be conservative in our estimate for the concentration C, we used the upper confidence limit of the combined 1994 and 2009 aircraft sampling data. While we believe the 1994 measures on Patches are much more likely to replicate 1971–1982 exposure levels, because they are closer in time to the events, and the aircraft sampled in 2009 had been stored outdoors in the Arizona desert where ultraviolet radiation and intense internal cabin heat would have degraded most of the dioxin present, we decided to err on the side of caution.

Substitution of the parameters shown in Table 4 leads to Eq. (2) for estimating systemic intake (I):

$$I = \frac{(RH)(C_s)(CF_a)(SA)(FT_{ss})(FT_{re})(CF_{wt})(FT_{ga})(EF)(WD)(ED)}{(FT_{we})(BW)(AT)} \quad (2)$$

The values we used for these factors, their units and sources are given in Table 4.

2.2. TCDD airborne contamination estimates using maximum saturation vapor pressure

In the second model, we applied the saturated vapor pressure method to determine whether the airborne concentrations of herbicides measured by Conway (1979) exceed predicted levels expected to arise from vapor pressure alone. This method is widely used in industrial hygiene and inhalation toxicology, where Henry's Law is used to estimate the maximum concentration of a solid or liquid substance that will become a gas in a closed space (Reinke, 2009). At standard temperature and pressure, the saturated vapor pressure is simply the product of the vapor pressure and the molecular weight of the substance in question. If the measured concentration exceeds the saturated vapor pressure, then an additional source of contamination, such as adsorption onto dust particles, must also be present.

We used the following vapor pressures: 1.4×10^{-7} mm Hg (Chemical Buyers, 2013) and 2×10^{-6} mm Hg (Walters, 2013) to calculate the saturated vapor pressures for 2,4-D and 2,4,5-T, respectively, shown in Table 5. Conversion factors are given in the footnote.

We then compared the saturated vapor pressure for 2,4-D and 2,4,5-T to the airborne concentrations in the air samples drawn by Conway (1979). Each measured value exceeded the saturated vapor pressure. The ratios between the measured air concentrations and the saturated vapor pressures are also shown in Table 5. Because each substance in a mixture of substances will exert its own independent vapor pressure, we can assume that dioxin will also be present at a concentration that exceeds its saturated vapor pressure, just as the measured chemicals here. In order to be conservative, we chose the lowest ratio of observed to saturated vapor pressure, which is five, and used this value to extrapolate the likely range of airborne concentrations that would have been found had Conway's analysis included dioxin. Because the vapor pressure of dioxin is difficult to measure, a range of values has been reported in the literature. We used three different published vapor pressures of dioxin, converted to mm Hg, in our model: 1.5×10^{-9} mm Hg (National Toxicology Program (NTP), 2011), 7.4×10^{-10} mm Hg (Podoll et al., 1986) and 3×10^{-9} mm Hg (Weschler and Nazaroff, 2008). We used a published range of likely contamination levels of dioxin in 2,4,5-T: 45 ppm and 13 ppm (Stellman et al., 2003).

Table 4
Definitions of the intake factor parameters for post Vietnam UC-123 exposure.

Parameter definition		Value	Comments
I	Systemic intake	calculated (pg/kg BW-day)	Picogram/kilogram body weight–day
C_s	Contaminant surface concentration	μg/100 cm^2	95% Upper confidence limit value: 285 ng/m^2
RH	Probability of being on a Ranch Hand aircraft	0.46 (unitless)	Based on 11 Ranch Hand aircraft among 24 C-123 aircraft at Westover Air Force Base Lurker (2013)
CF_a	Area conversion factor	0.0001 m^2/cm^2	
SA	Exposed skin surface area	326 cm^2	Surface area of both palm sides of the hand (US Army Center for Health Promotion and Preventive Medicine, 2009)
FT_{ss}	Decimal fraction contaminant transferred surface-to-skin	0.063 (unitless)	US Army Center for Health Promotion and Preventive Medicine, (2009)
FT_{re}	Decimal fraction contaminant removed from skin-to-mouth	1.0	Assumed to be 1 for conservative model
FT_{we}	Decimal fraction of contaminant collected onto wipe	0.50 (unitless)	Organic compound (US Army Center for Health Promotion and Preventive Medicine, 2009)
FT_{ga}	Decimal fraction absorbed from gastrointestinal tract	0.87	ATSDR (1998)
EF	Exposure frequency hand-to-mouth events per day	3/day	May et al. (2002)
ED	Exposure duration	12 years	1971–1982
CF_{wt}	Weight conversion factor	1000 pg/ng	
AT	Averaging time	4380 days	365 days/years × 12 years
WD	Work days for various types of workers		
	Notionally exposed worker	70 days/year	Reserve Technician working one weekend/month+ one two-week annual tour plus extra person-days for mission requirements
	Flight crew	42 days/year	Based on Reserve Pilot Flight Logs
	Aero-medical evacuation patient	1 days/year	Patient with one aero-medical evacuation/year
	Passenger	3 days/year	Three flights per year
	Airborne	3 days/year	Three flights per year
	Aerospace Maintenance and Regeneration Group personnel	3.5 days/year	Estimation based on author (PAL) observations
	Museum restoration worker	2.5 days/year	Estimation based on author (PAL) Wright-Patterson Air Force Base industrial hygienist experience (2006–2009)

2.3. TCDD airborne concentration using thermodynamic emission models

Finally, we employed a third model, based on theoretical emissions of semivolatile organic chemicals, like dioxin, using first principles of thermodynamics (Weschler and Nazaroff, 2008), to estimate dioxin contamination levels in the interior of the spray aircraft, as illustrated schematically in Fig. 1. We adapted the Little et al. (2012) generalized approach to calculate the extent to which dioxin will either be in the air above the dried residue or will have been adsorbed onto dust in the aircraft, a phenomenon that has been widely observed and for which Little et al. provide essential dioxin-specific parameters.

The concentration of dioxin in the atmosphere above the surface, y, will be a function of y_o, its vapor pressure and the area A of residue in the aircraft capable of emitting the dioxin, as well as the ventilation rate and mass-transfer coefficient, Q and h, respectively (Eq. 3a). While the model does take the ventilation rate Q into account, it is not a critical factor because the surface contamination is a continual sink for emitting gases to be adsorbed onto dust. However, the driving force for potential occupational exposure is not such emission, which will be very low, but rather the adsorption of dioxin onto the dust particles (US National Institute for Occupational Safety and Health, 1984). Dioxin is preferentially and strongly attracted to the dust and will partition onto the solid dust phase from the air phase above the surface. The degree of dust loading will be a function of the total mass of suspended particles, TSP, and K_p, the airborne particle/air partition coefficient (Eq. 3b). A partition coefficient measures the comparative tendency for a substance to reside in one of two neighboring immiscible phases. In our model, the phases are the dust and the air above contaminated surfaces in the aircraft. K_p is the product of how much organic material is present in the dust (F_{om_part}, divided by the density of the dust particles, $\rho_{particle,}$) and the ease with which dioxin preferentially transfers to the dust particles, measured by the octanol/air partition coefficient $K_{oa,}$ which Weschler and Nazaroff (2008) have shown to be the appropriate constant for describing the expected partitioning of a chemical between the gas phase and dust (Eq. 3c).

$$y = (h)(y_o)(A)/(h)(A) + Q^* \tag{3a}$$

$$Q^* = (1 + K_p\ \mathrm{TSP})(Q) \tag{3b}$$

$$K_p = \frac{(F_{om\_part})(K_{oa})}{\rho_{particle}} \tag{3c}$$

Table 6 gives the specific parameters we used for estimating the predicted concentration of dioxin for the UC-123 situation. Because the area of exposure could vary for crew and pilots, we calculated y twice, once with an area of 280 m^2 and a second time with a doubled area of 560 m^2. Also, the Little et al. method is strongly dependent on the value used to estimate the gas-phase concentration at the emission surface, y_o. We thus used three published values for dioxin vapor pressure in our model.

3. Results

3.1. TCDD dermal–oral exposure from direct contact

Based on Eq. 1, the estimated intake factor for the dermal–oral route was 0.92 pg/kg BW day for flight crews and 5.4 pg/kg BW day for maintainers at an assumed 95% upper confidence limit surface wipe concentration of 285 ng/m^2. Both estimates exceed the US EPA acceptable daily intake value of 0.7 pg/kg BW day (US Environmental Protection Agency, 2012). Fig. 2 summarizes the estimated dermal–oral intake by exposure group (flight crew, maintainers, aero-medical evacuation patients, passengers, airborne or paratroopers, Aerospace Maintenance and Regeneration Group, and museum restoration workers). One set of body burden curves is shown at three different body weights, 60, 70 and 80 kg. Three exposure guidelines (2.3, 1.0 and 0.7 pg/kg day, World Health Organization (2002), the Netherlands (Larsen, 2006) and US EPA (2012) respectively, are plotted for comparison. The worst-case maintainer (250 days per year) is also shown.

3.2. TCDD estimates using maximum saturation vapor pressure

Table 5 compares the Conway (1979) air samples to the calculated saturated vapor pressures. The ranges of ratios of observed-to-expected levels were substantially greater than unity: 63–138 and 5–7 for 2,4-D and 2,4,5-T, respectively. The lowest ratio for 2,4,5-T, 5, yielded an estimate of 13–27 pg/m^3 for dioxin, based on observed contamination levels of 13–45 ppm in historic samples.

Table 5
Comparison of maximum vapor concentration to measured airborne concentration and to OSHA permissible exposure limit and German maximum allowable worker concentration.

Compound	Calculated saturated vapor pressure above liquid residue	Reported concentration[a]	Ratio of measured air concentration to saturated vapor pressure	United States[b]	Germany[c]
2,4-D	0.0017 mg/m^3	0.108 to 0.234 mg/m^3	63–138	10 mg/m^3	10 mg/m^3
2,4,5-T	0.0275 mg/m^3	0.135 to 0.194 mg/m^3	5–7	10 mg/m^3	10 mg/m^3

[a] Air samples reported by Conway (1979) and converted from parts per million to mmHg (mm Hg/760 mmHg × 10^6 ppm) × molecular weight/24.45 (mg/m^3/ppm).
[b] Occupational Safety and Health Administration Permissible Exposure Limit. (OSHA, 2013a, 2013b).
[c] German Maximum Allowable Worker Concentration.

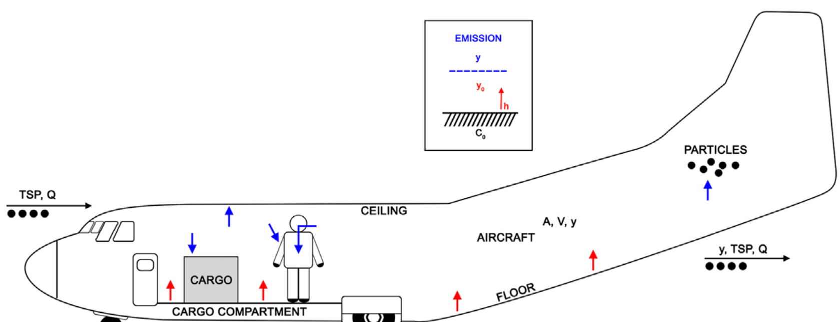

Fig. 1. Schematic showing semivolatile organic compound emissions model applied to a UC-123 spray aircraft. Dioxin present in the surface residue, at a concentration of $c_{0.}$ It is in equilibrium with the atmosphere immediately above the surface, at a concentration y_0, its vapor pressure. Gaseous dioxin molecules are strongly attracted to dust particles, the major source of occupational exposure potential in such a situation (US National Institute for Occupational Safety and Health, 1984). Dust adsorption magnifies dioxin concentration to y. The degree of magnification is also a function of the organic matter present in the total mass of suspended particles, *TSP*, the convective transport coefficient, h, and, to a small extent, the ventilation rate Q. Ventilation is ineffective at reducing y because surface emissions continually replenish the gaseous phase dioxin. Specific equations used in this model are given in Section 2.3 and parameters in Table 6. The figure is adapted from Little et al. (2012).

Table 6
Parameters used to estimate airborne dioxin concentration in UC-123 spray aircraft.

Parameter	Definition		Source/reference
h	Convective mass-transfer coefficient	0.368 m/h	Thibodeaux and Lipsky (1985)
A	Aircraft interior surface: Surface area$=\pi DL+D^2/4$	280 m^2	Assumed cylindrical shape: 15 × 53 feet. D=diameter 4.6 m, L=length=16 m
K_p	Airborne particle/air partition coefficient	0.0045 $m^3/\mu g$	Little et al. (2012)
F_{om_part}	Vol fraction organic matter in airborne particles	0.4	Little et al. (2012)
K_{oa}	Octanol/air partition coefficient	1.12×10^{10}	Åberg et al. (2008)
$\rho_{particle}$	Density airborne particles	1×10^{12} $\mu g/m^3$	Little et al. (2012)
TSP	Total suspended particles	20 $\mu g/m^3$	Little et al. (2012)
Q	Ventilation rate	170 m^3/h	Adapted from Meek (1981)
y_o	Gas-phase concentration in contact with the emission surface	13 pg/m^3 26 pg/m^3 53 pg/m^3	9.74×10^{-13} atm (Podoll et al., 1986) 1.97×10^{-12} atm (National Toxicology Program (NTP), 2011) 4×10^{-12} atm (Weschler and Nazaroff, 2008)

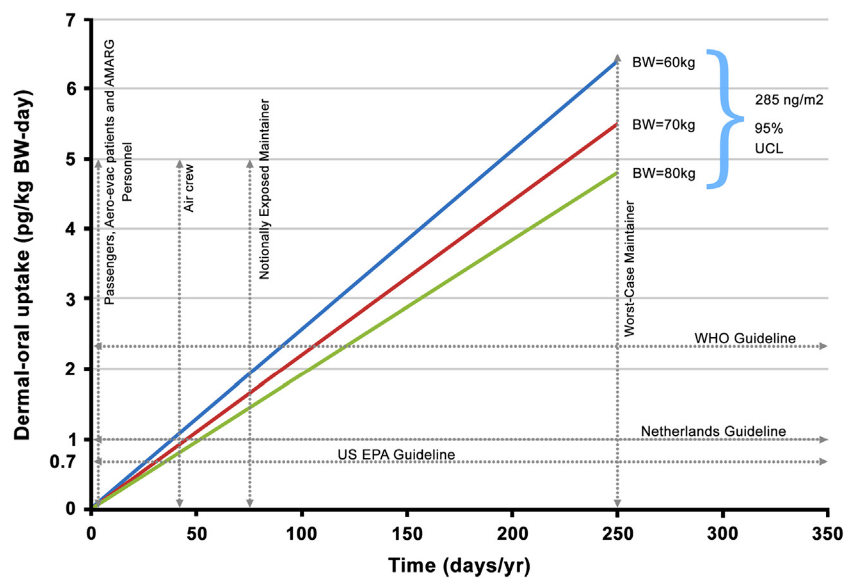

Fig. 2. Estimates of cumulative dermal–oral intake (pg/kg bw day) vs. days per year exposed in UC-123 workers. Using the 95% upper confidence limit mean value of 285 ng/m^2 surface concentration of dioxin for various numbers of work-days per year, we derived estimates using an adaptation of the US Environmental Protection Agency general model for estimating generic intakes (US Environmental Protection Agency, 1989b) to represent likely exposure situations of working conditions in the interior of UC-123 former Ranch Hand aircraft (see Eq. 1). Diagonal lines represent dose-variation as a function of bodyweight. Vertical dashed lines represent typical number of annual 8 h work days used to in the exposure scenarios for dioxin-contaminated surfaces: worst-case maintainer (250 days); reserve maintainer (75 days: 1 two-day-weekend per month, two week annual tour plus 37 extra days); flight crew (42 days); passengers, such as aero-medical evacuation patients and airborne troops (2 days). Intersection of the vertical lines with diagonal lines represents estimated intake, which can be compared to existing guidelines (World Health Organization, 2002, the Netherlands (Larsen, 2006) and US Environmental Protection Agency, 2012), represented by dashed horizontal lines. In this model flight crew have dermal–oral intake exceeding the US Environmental Protection Agency guideline of 0.7 pg/kg BW day; maintainers exceed both US Environmental Protection Agency and Netherlands guidelines and worst-case maintainer exceeds all three guidelines.

3.3. TCDD estimates using thermodynamic models

Using the emission models developed by Little et al. (2012), with the parameters shown in Table 6 and three input values for y_o, the vapor pressure, or gas-phase concentration in contact with the emission surface, we calculated y, the airborne dioxin concentration, to be 11, 22 and 45 pg/m^3, for an area of 280 m^2 and to be 12 pg/m^3, 24 pg/m^3, and 49 pg/m^3 for an area of 560 m^2. These theoretical values are in the same range as the estimates obtained from the saturated vapor pressure model based on the Conway (1979) air samples. Both the theoretical and the experimental models lead to values for dioxin that exceed the only available standard for comparison, the German maximum allowable worker concentration of 10 pg/m^3.

4. Discussion

In this paper we have used three different complementary models to estimate potential occupational exposure to dioxins and military herbicides arising from dried surface residues within contaminated UC-123 Operation Ranch Hand spray planes that had been returned from Vietnam to service in the United States without prior decontamination. Sparse monitoring data (surface wipes and a small number of air samples) were available to us for this modeling. We used the surface wipe data to estimate dermal–oral absorption and the air sample data to estimate the possible concentration of airborne dioxin. As we discuss below, the two models yield levels that exceed recognized guidelines. Similarly, the third method, derived from thermodynamic principles, and not industrial hygiene measurements, also yielded levels that exceed guidelines.

The surface wipe data were used to develop a dermal–oral risk assessment using modification of the U.S. Environmental Protection Agency generic approach for intake, together with parameters defined by May et al. (2002) and the US Army (U.S. Army Center for Health Promotion and Preventive Medicine, 2009) in its analyses of dermal exposure to dried dioxin residues in office workers. The Army's Technical Guidance and its algorithms are, to our knowledge, the only ones available for setting screening levels based on wipe samples. Though developed for occupational exposure to office workers, they are modifiable to other scenarios, using the methods we have applied here. Our calculations yielded occupational exposure estimates of 0.92 pg/kg BW-day for flight crews and 5.4 pg/kg BW day for maintainers, at an assumed 95% upper confidence limit surface wipes concentration of 285 ng/m^2. Other occupational groups were not substantially exposed according to the model. The US Army's surface wipe screening level for dioxin surface wipe contamination is 3.54×10^{-5} μg/100 cm^2 (equivalent to 3.54 ng/m^2), based on a 10^{-6} cancer risk assessment (U.S. Army Center for Health Promotion and Preventive Medicine, 2009) and 10-year working lifetime. Our model uses a 12-year working lifetime. The levels measured in the samples were nearly two orders of magnitude greater than this guidance level.

Our results can also be compared to another set of dioxin exposure guidelines based on an EPA risk assessment paradigm from toxicity studies completed by the National Toxicology Program and validated by the Subcommittee on Dioxin, Committee on Toxicology in their 1988 report "Acceptable Levels of Dioxin Contamination in an Office Building Following a Transformer Fire" (Doull, 1988). The values for re-entry are 25 ng/m^2 and 10 pg/m^3 on surfaces and in air, respectively. At these levels of contamination, it is calculated that a 50 kg office worker working 250 days per year for 30 years would ingest 2 pg/kg dioxin per day for a cumulative lifetime maximum ingestion of 750 ng. The air and surface contamination re-entry values are exclusive; exposure is to either air exclusively or surface contact. If both air contamination and surface contamination exist, then the safe re-entry level for each must be reduced (e.g. if air contamination is 5 pg/m^3, then surface contamination can be no higher than 12.5 ng/ m^2 in order to satisfy re-entry guidelines). Based on our 95% upper confidence limit surface wipes concentration of 285 ng/m^2 and calculated airborne concentrations of 11–49 pg/m^3, we estimate that the lifetime exposure limit of 750 ng would have been reached in less than 3 years for an airman working full-time and this concentration is conservative, as discussed in the methods section.

The estimated daily intake of 0.92 pg/kg BW day for flight crews and 5.4 pg/kg BW day for maintainers exceeds the EPA 0.7 pg/kg BW day acceptable daily intake (US EPA, 2012). The EPA estimate is based on lifetime exposure and our calculations are for a likely occupational exposure period, so the two values are not directly comparable. Our estimates suggest that post-Vietnam flight crew and maintainers will have exceeded their lifetime doses, particularly since expected background exposures are not included. Also, while our dermal–oral model used the worst-case scenario for years of exposure, it is likely to have underestimated the actual time spent in the aircraft, which was based on flight hours logged. Actual residence time was likely to be 25–50% higher (Lurker, 2013).

It is important to emphasize that, because surface wipe and air monitoring samples were collected some thirty and nine years, respectively, after the last spraying of herbicides in Vietnam, our analyses likely underestimate the degree to which aircraft personnel were exposed to dioxin. In the intervening years, surface dioxin contamination would have been substantially reduced through degradation, vaporization and adhesion to dust, mechanical removal from normal wear-and-tear, and cleanup efforts to remove chemical odors. The data showing higher internal dioxin surface contamination in Patches, from samples collected ~24 years after Viet Nam, as compared to data from the aircraft stored under Sonoran desert conditions, from samples taken ~39 years post Viet Nam, supports this notion of time and environmental effects to reduce surface dioxin contamination. Similarly, it is likely that herbicide and insecticide air concentrations were also reduced during the intervening nine years prior to air sampling. Nevertheless, we have used the values from all interior aircraft samples in our dermal to oral route of exposure model. Given the intervening time prior to sampling and sparse available data, it is remarkable that the three models used to estimate dioxin contamination yielded such consistent results.

We used two other models to estimate inhalation exposure of flight crews and maintainers and found that they were likely to have been exposed to airborne concentrations of dioxin that exceed the only available standard for comparison, the German maximum allowable worker concentration limit of 10 pg/m^3.

The first inhalation model, based on a standard industrial hygiene and inhalation toxicology method of saturated vapor pressures, showed that the measured airborne levels of 2,4-D and 2,4,5-T were two orders of magnitude greater than predicted by the saturated vapor pressure, providing strong empirical evidence that the contaminants were adsorbed onto dust particles, which were continually deposited and re-suspended within the aircraft. The US National Institute for Occupational Safety and Health (1984) has noted that dust-adsorbed dioxin is a likely route of exposure, far exceeding exposure from gases arising from vapor pressure alone.

Our extrapolation for the concentration of dioxin present in the atmosphere is also likely to be an underestimate because we used standard temperature and pressure, while the conditions on the aircraft were often not standard. Extremes of temperature, changes in atmospheric pressure, vibration and other factors would have likely increased the vaporization rate, and hence led to higher levels of available dioxin, particularly since the interior of the aircraft was shielded from ultraviolet light, thereby minimizing ultraviolet degradation. This contention is supported by the positive interior wipe samples taken nearly four decades after the last herbicide exposures occurred. Further, the saturated vapor pressure model provides a conservative estimate of maximum exposure based on a closed environment model and based on a liquid. The aircraft had many air exchanges per hour and the residue was dried, yet the levels measured by Conway (1979) were orders of magnitude greater than the saturated vapor pressures. Finally, Conway did not use pre-filters to trap particulates and, therefore, underestimated airborne concentration.

Model 3, based on theoretical emissions from contamination measured in the aircraft yielded results that were consistent with the levels of dioxin estimated by the saturated vapor pressure method. Air samples with levels substantially above saturation, more than a decade after the last herbicide missions, strongly indicate that the aircraft must have been thoroughly coated with a film of herbicides and dioxins during Operation Ranch Hand and that there had never been an opportunity for the chemicals to be cleared by ventilation, either during the War or afterwards in the Air Force Reserves. The herbicides/dioxins had, in effect, become a permanent persistent presence on surfaces, as well as in the dust particles in the air, until the aircraft were destroyed. Given, in essence, an infinite sink for emissions from the legacy surface residue, there would have been a continuous reservoir for adsorption onto dust, even if regular ventilation were present. This is entirely consistent with the behavior of semivolatile organic compounds, as noted by Little et al. (2012). There is no reason to expect dioxin present in the surface residue to behave differently from 2,4,5-T and 2,4-D. In fact, there is good reason to believe that the relative proportion of dioxin present on dust would be greater than the phenoxyherbicides, because the K_{oa} for dioxin is substantially larger than those for the herbicides (Weschler and Nazaroff, 2008) and K_{oa} is an excellent predictor of the compound's adsorption onto dust.

Finally, in most occupations with potential dioxin-exposure, dermal absorption is the primary route of dioxin exposure (Kerber et al., 1995). Our model considered only hand-to-mouth dermal factors and did not include this important source of contamination.

Dermal absorption modeling is difficult and only limited hexane surface data are available to us. The VA has questioned the utility of hexane-based surface sampling: "There is a low probability that transfer of TCDD in food or water or from hand-to-mouth could occur among these crew members, especially given that the sampling for TCDD on the aircraft surfaces required use of a solvent (hexane) to displace and dissolve any residue" (U.S. Dept. of Veterans Affairs, 2012). However, hexane-wipes are a standard sampling method and it is likely that at least some dermal exposure occurred for the following reasons. While hexane can reach chemicals lodged in areas inaccessible to skin contact and overestimate exposure for porous surfaces, the surfaces on the aircraft were not porous. Further, hexane wipes do not completely extract all chemicals, as demonstrated by repeat sampling, and thus can underestimate exposures. While it is true that dioxin is extracted more efficiently by hexane than by skin in laboratory experiments, it is important to note that dioxin uptake always occurred in every experiment. Human skin has a high level of lipids, making it attractive to lipophilic compounds like dioxin, although absorption depends on the area of skin in contact with the chemical, as well as on sweat, number of hours of contact, pressure exerted and other factors (Slayton et al., 1998). The likelihood that absorption through clothing could occur is confirmed in at least one experiment where cotton fabric appears to increase absorption (Midwest Research Institute (MRI), 1994). This route of entry would thus add to the exposures we have also shown likely to occur, namely, dermal-to-oral and inhalation of contaminated dusts.

Our findings, the results of three different modeling approaches, contrast with Air Force and VA conclusions and policies (Smallwood, 2012; Murphy, 2013). The VA concept of a "dried residue" that is biologically unavailable (Dick et al., 2012) is not consistent with widely accepted theories of fugacity and basic thermodynamics of the behavior of surface residues. Aircraft occupants would have been exposed to airborne dioxin-contaminated dust as well as come into direct skin contact, and our models show that the level of exposure is likely to have exceeded several available exposure guidelines.

Acknowledgments

PAL expresses gratitude for the opportunity to have been assigned to work with a team of medical professionals at the United States Air Force School of Aerospace Medicine to identify any post Vietnam UC-123 Ranch Hand exposure data and conduct an exposure assessment (November 2011–April 2012) and also the hard work and long hours the US Air Force Reserve Military Airlift personnel, including the UC-123 staff did to get their passengers, patients and cargo delivered, who facilitated his work as an active duty bioenvironmental engineer conducting in-flight industrial hygiene surveys (1980–1984) on US Air Force Reserve missions.

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.envres.2014.02.004.

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