ESTIMATION OF EXPOSURE OF PERSONS IN CALIFORNIA TO PESTICIDE PRODUCTS THAT CONTAIN

METHOMYL

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ABSTRACT

Methomyl, S-Methyl-N-(methylcarbamoyloxy)thioacetimidate (CAS Reg. # 16752-77-5), is a broad-spectrum *N*-methyl carbamate insecticide with anti-cholinesterase activity. It is used for pest control in field, fruit and vegetable crops; turf; livestock quarters; commercial premises and refuse containers. There are no label-approved, residential uses of methomyl. Methomyl is available in California in four formulation types and 14 commercial products. Methomyl is formulated as a water-soluble powder (WSP) containing 90% active ingredient (AI); water-soluble concentrate/liquid containing 29% AI; dust/powder containing 98.7% AI; and granular/flake fly baits containing 1.0-1.1% AI.

USEPA classifies Methomyl as Restricted Use Pesticide (RUP) because of its high acute oral toxicity to humans. All Methomyl formulations are on the list of Federal restricted use pesticides and California restricted materials except fly baits containing not more than 1% methomyl.

Occupational Exposures: Acute Absorbed daily dosages (ADDs) of methomyl for pesticide handlers ranged from 15 µg/kg/day for mixer/loaders (M/L) for airblast applications to 1760 µg/kg/day for pilots. Annual Absorbed daily dosages (AADDs) for handlers ranged from 5 µg/kg/day for M/L for airblast applications to 630 µg/kg/day for pilots. Lifetime Absorbed daily dosages (LADDs) ranged from 3 µg/kg/day for M/L for airblast applications to 340 µg/kg/day for pilots.

Worker reentry exposure estimates of ADDs ranged from 0.23 µg/kg/day for lettuce harvesters to 308 µg/kg/day for workers harvesting sweet corn by hand. Seasonal Absorbed daily dosages (SADDs) ranged from 0.007 µg/kg/day for lettuce harvesters to 9.62 µg/kg/day for workers harvesting sweet corn by hand. AADDs ranged from 0.007 µg/kg/day for lettuce harvesters to 4.81 µg/kg/day for workers harvesting sweet corn by hand. Reentry worker LADDs ranged from 0.004 µg/kg/day for lettuce harvesters to 2.56 µg/kg/day for workers harvesting sweet corn by hand.

The estimated hourly and daily acute inhalation exposures to application site ambient air levels of methomyl for workers working next to a treated potato field were 0.14 µg/kg/hour and 0.29 µg/kg/day, respectively.

Non-occupational exposures: Acute (one-hour and single day) inhalation exposures of adults and infants were estimated based on the concentrations of methomyl in the air and the inhalation rates for each group. The estimated hourly acute inhalation exposures to application site ambient air levels of methomyl for adults and infants living next to a treated potato field are 0.13 µg/kg/hour and 0.75 µg/kg/hour, respectively. The estimated daily acute inhalation exposures for the same groups of residents were 0.55 µg/kg/day and 1.15 µg/kg/day, respectively. Adult picking sweet corn in a "U-Pick" field would receive a single dermal dose of 150.1 µg/kg/day, if picking nectarines the individual would receive a single dermal dose of 64.6 µg/kg/day. A child picking sweet corn for 2 hours in

a "U-Pick" field would receive a single dermal dose of 68.9 µg/kg/day, if picking nectarines the child would receive a single dermal dose of 29.7 µg/kg/day.

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INTRODUCTION

Methomyl is a broad-spectrum *N*-methyl carbamate insecticide with anti-cholinesterase activity. It is used as an insecticide in field, fruit and vegetable crops; turf; livestock quarters; commercial premises and refuse containers. There are no residential uses of methomyl.

The Department of Pesticide Regulation (DPR) is charged with protecting individuals and the environment from potential adverse effects that may result from the use of pesticides in the State. This is codified in the California Food and Agriculture Code (CFAC), Sections 11501, 12824, 12825, 12826, 13121-13135, 14102, and 14103). As part of DPR's effort to meet this mandate, pesticide active ingredients (AIs) are prioritized for assessment of exposure and risk potential. A description of the risk prioritization process can be found at DPR's website (http://www.cdpr.ca.gov/docs/risk/raprocess.pdf). When comprehensive risk assessments are initiated for particular active ingredients (AI), the evaluations are conducted in accordance with California Code of Regulations Title 3, Section 6158 (3 CCR 6158). Pesticide products containing the active ingredient methomyl are being evaluated on the basis of its widespread agricultural use, its high acute toxicity, the steepness of its acute dose-response curve, its low No Observed Effect Levels (NOELs) for both neurotoxic effects and hematological effects, and the consistency of the hematological effects in different species and study types (Prioritization Scheme Rationale Proposed July, 2005).

Methomyl is highly acutely toxic by the oral route (Toxicity Category I), moderately toxic by the inhalation route (Category II), and slightly toxic by the dermal route (Category III). Methomyl is highly toxic *via* ocular exposure (Category I eye irritant) but it is not considered a skin irritant, dermal sensitizer, or delayed neurotoxicant (USEPA, 1998d). Based on the available chronic toxicity and carcinogenicity studies, which demonstrated no evidence of carcinogenicity, methomyl was classified as a Group E, not likely to be carcinogenic to humans *via* relevant routes of exposure (USEPA, 1998d). The DPR position on the toxicity of methomyl will be addressed in the Risk Characterization Document. Signs and symptoms of acute methomyl overexposure are similar for all anticholinesterase carbamates, and for all mammalian species. Onset and severity of symptoms are dose-related. Signs and symptoms include excessive salivation and increased irregular respiration, followed by lacrimation, urination, defecation, and muscular tremors. Constriction of pupils, nausea, vomiting, pallor, piloerection, bradycardia or tachycardia, are often observed. Either death or signs of recovery are generally observed within one to several hours of exposure (Hayes and Laws, 1991).

Occupational exposure to methomyl can occur during pesticide handling procedures (mixing, loading, application, flagging) and during reentry activities (e.g. scouting, pruning, thinning, harvesting, etc.) in crops that have received methomyl foliar applications. Methomyl has been detected in air in the vicinity of agricultural fields receiving methomyl applications, consequently bystander exposure is possible as well.

PHYSICO-CHEMICAL PROPERTIES AND ENVIRONMENTAL FATE

Methomyl, S-Methyl-N-(methylcarbamoyloxy)thioacetimidate (CAS Reg. # 16752-77-5), is a colorless or white crystalline solid with slightly sulfurous odor (Tomlin, 1997). The structure is shown in Figure 1, and physicochemical properties are listed in Table 1.

Figure 1. Structural formula of methomyl.

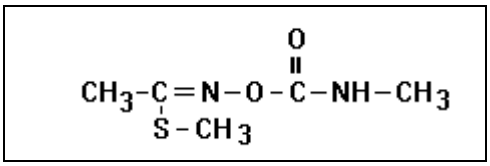


Table 1. Physical and chemical properties of methomyl (Tomlin, 1997).

Chemical Property	Value
Molecular formula	$C_5H_{10}N_2O_2S$
Molecular weight	162.2
Melting Point	78-79°C
Water solubility (g/L, 25°C)	58
Octanol-water partition coefficient (K_{ow}) as logP	0.093
Vapor pressure (25°C)	0.72 mPa = 5.6×10^{-6} mm Hg

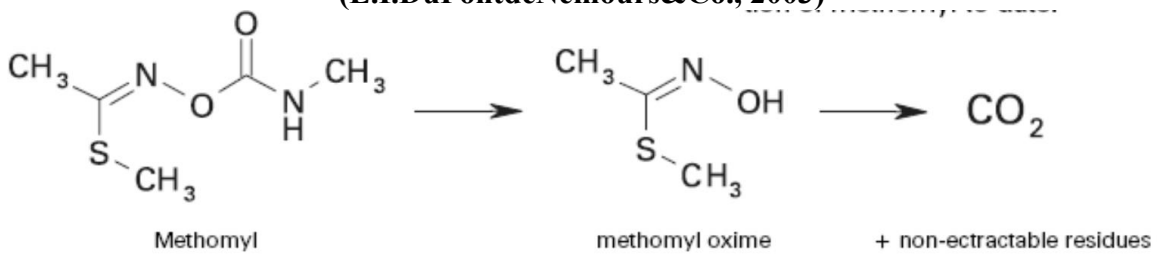
Breakdown in water: Methomyl is stable in the solid state and in slightly acidic or neutral solutions, and hydrolyzes under basic conditions (Van Scoy *et al.*, 2013). Aqueous solutions of methomyl have been reported to decompose more rapidly from aeration, in sunlight, or in alkaline media (Howard, 1991). The hydrolysis product, methomyl oxime, is stable to further hydrolysis, and remains biologically inactive (Howard, 1991). Degradation of methomyl due to reduction by ferrous iron may occur in the ground water and in anaerobic soils (Bromilow *et al.*, 1986; Howard, 1991). Increased rates of carbamate reduction are observed in solutions containing fluoride, carbonate, and phosphate (Strathmann and Stone, 2002). Microbial degradation and indirect photolysis reactions (other chemicals absorb sunlight, and transfer the energy to the pesticide) effectively remove methomyl from surface water systems (E.I.DuPontdeNemours&Co., 2003). Methomyl is not persistent in natural surface waters. The estimated aqueous half-life for the insecticide is 6 days in surface water and over 25 weeks in groundwater (Howard, 1991).

Photostability: Methomyl is not susceptible to direct photolysis in aqueous solution (Van Scoy *et al.*, 2013). The half-life of methomyl on soil surfaces exposed to natural light was 34 days. Under field conditions the rapid mineralization by soil microorganisms is the dominant dissipation mechanism in soil (E.I.DuPontdeNemours&Co., 2003).

Breakdown in soil: In agricultural soils, methomyl has a low persistence and is rapidly mineralized to carbon dioxide (Harvey and Pease, 1973) with methomyl oxime as a minor

transient degradation product (3% of applied active ingredient) (Figure 2). This pathway was observed under aerobic and anaerobic conditions in soil and is identical in terms of nature of the degradants and shows fast mineralization under both conditions. Field studies show varying dissipation rates of the chemical in soils. Dissipation rates were related primarily to differences in soil type and moisture content, which may affect the microbial activity, and rainfall/irrigation, which could influence leaching (Harvey and Pease, 1973). DuPont Co. reports that the average half-life of aerobic soil degradation is 8.5 days, and the methomyl oxime degrades even more rapidly in soil (average half-life = 0.8 days). Under anaerobic conditions methomyl degrades with a half-life of 14 days (E.I.DuPontdeNemours&Co., 2003). Other sources and databases report aerobic soil half-life between 0.5 days and 1.6 months (Van Scoy *et al.*, 2013). Under typical soil conditions present on agricultural fields, 50% of the applied methomyl degraded to innocuous material, such as carbon dioxide, in less than 10 days. Dry soils and low soil temperatures may slow down methomyl degradation. No effects of soil pH have been observed on degradation of methomyl to date (E.I.DuPontdeNemours&Co., 2003).

Figure 2. Degradation pathway of methomyl in aerobic/anaerobic topsoil (E.I.DuPontdeNemours&Co., 2003)



Sorption to soil: Methomyl is poorly sorbed onto soil materials. DuPont Co. reports average K_{oc} of 32 mL/g (E.I.DuPontdeNemours&Co., 2003). Different databases report K_{oc} values from 9 to 160 mL/g, with USDA/ARS Pesticide Properties Database citing an average K_{oc} value of 86 mL/g (http://www.ars.usda.gov/SP2UserFiles/ad_hoc/12755100DatabaseFiles/PesticidePropertiesDatabase/Allchemicals/listallchemicals.doc). The DPR's EM Branch reports methomyl K_{oc} value of 72 mL/g (Van Scoy *et al.*, 2013). Due to the high water solubility and low soil sorption, most methomyl remains in the soil pore water phase and is readily available for mineralization by soil microorganisms (E.I.DuPontdeNemours&Co., 2003).

Volatilization potential: The moderate vapor pressure and high water solubility result in a low Henry's law constant (2.1×10^{-11} atm-m^3/mole (WHO, 1996) = 2×10^{-6} Pa m^3/mol at 25°C (PPDB, 2007, 2008, 2009)) indicating a low potential for volatilization of the active substance from soil under practical conditions of use. After application methomyl is eliminated rapidly from the atmosphere through photochemical oxidative degradation processes in the gas phase with a half-life of 19 hours (E.I.DuPontdeNemours&Co., 2003).

Breakdown in vegetation: Once on the plant surface, methomyl dissipates quickly due to uptake into plant tissue and degradation to volatile metabolites (carbon dioxide and acetonitrile) (Harvey and Reiser, 1973). The average foliar half-life for methomyl is 1.1

days for a variety of crops grown in the USA (E.I.DuPontdeNemours&Co., 2003). Methomyl is also degraded in plants by hydrolytic, oxidative and glutathione conjugation pathways (see pharmacokinetics section). The only residue of concern in all crops studied is methomyl itself (Harvey and Reiser, 1973). Other authors report a 3 to 5 day half-life after application on leaves (Kidd and James, 1991).

REGULATORY STATUS

Federal

Methomyl was first registered in the United States in October 1968 for use as an insecticide. DuPont de Nemours & Co., Inc, Dupont Crop Protection, Newark, Del. is the current manufacturer of methomyl.

Because of advances in scientific knowledge, the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA, Section 4) requires that pesticides first registered before November 1, 1984, be reregistered to ensure that they meet today's more stringent standards. When a pesticide is eligible for reregistration, USEPA explains the basis for its decision in a Reregistration Eligibility Decision (RED) document. The RED for Methomyl was completed in 1998 (USEPA, 1998c). USEPA opened a registration review docket for Methomyl in 2010 (http://www.regulations.gov/#!docketDetail;D=EPA-HQ-OPP-2010-0751).

Methomyl is classified as Restricted Use Pesticide (RUP) by USEPA because of its high acute toxicity to humans (Category I Toxicity). All Methomyl formulations are on the list of Federal restricted use pesticide (40 CFR 152.175) and California restricted materials (3CCRs6400) except fly baits containing not more than 1% Methomyl (http://www.cdpr.ca.gov/docs/enforce/compend/vol_3/entirerep.pdf).

Environmental Standards & Regulations

Acceptable Daily Intakes (ADI): Food and Agriculture Organization of the United Nations /World Health Organization (FAO/WHO): 0–0.02 mg/kg body weight (BW) on the basis of the No Observed Adverse Effect Level (NOAEL) of 0.1 mg/kg BW in the study with human volunteers and a safety factor of 5 (McFarlane *et al.*, 1998; FAO/WHO, 2001).

Federal Drinking Water Guidelines: USEPA 200 µg/L (USEPA/Office of Water; Federal-State Toxicology and Risk Analysis Committee. Summary of State and Federal Drinking Water Standards and Guidelines, 3rd edition. National Library of Medicine's (NLM) Hazardous Substances Data Bank (HSDB) (http://toxnet.nlm.nih.gov).

Occupational Exposure Standards

Occupational Safety and Health Administration (OSHA) Standards: The OSHA Permissible Exposure Limit (PEL) Time Weighted Average (TWA) 2.5 mg/m^3 is enforced in California (Cal/OSHA, 2010).

Threshold Limit Values (TLV): 8 hr TWA: 2.5 mg/m^3. [ACGIH = American Conference of Governmental Industrial Hygienists TLVs and Biological Exposure Indices (BEIs).

Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices. Cincinnati, OH, 2005, p. 37]

NIOSH Recommendations: Recommended Exposure Limit (REL): 10 Hr TWA 2.5 mg/m^3. [NIOSH. NIOSH Pocket Guide to Chemical Hazards & Other Databases. U.S. Department of Health & Human Services, Public Health Service, Center for Disease Control & Prevention. DHHS (NIOSH) Publication No. 2001-145 (CD-ROM) August 2001].

California registration and status

1. Section 3 of the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) labels: there are 14 actively registered products in California as of August 2013 (Table 2).
2. Special Local Needs (SLN) registrations (Registration of pesticide product under FIFRA section 24(c) by a state agency for a specific use that is not federally registered (however, the active ingredient must be federally registered for other uses)): Currently there are 4 SLN registrations of Lannate® SP in California (http://apps.cdpr.ca.gov/sln). More on SLN will be discussed in the section dealing with exposure scenarios.
3. One California special requirement about the restricted reentry interval (Restricted Entry Interval, REI, is the period of time after a field is treated with a pesticide during which restrictions on entry are in effect to protect persons from potential exposure to hazardous levels of pesticide residues. An REI may be found on pesticide product labeling or in regulation) should be noted here, and will receive more attention further in the document. According to the most recent methomyl labels, the REI for grape is 7 days. However, the California Code of Regulations also states: "Applications of methomyl made after August 15, have a 21-day restricted entry interval. This interval may be terminated after 10 days if leaf samples tested pursuant to Section 6774 (c)(4) show 0.1 micrograms per square centimeter or less of dislodgeable foliar residue of methomyl"(3CCR6772(b)). The restriction imposed by 3CCR s.6772(b) is not mentioned on the Lannate labels.

FORMULATIONS, PRODUCTS AND USES

Currently, methomyl is registered on a wide variety of sites including field, vegetable, and orchard crops; turf (sod farms only); livestock quarters; commercial premises; and refuse containers. All uses are agricultural, industrial, or commercial. There are no residential uses of methomyl. In 1995, as part of a risk mitigation plan, the USEPA imposed limitations on fly baits including restricted use to certain commercial agricultural production areas where children would not be present, incorporating an embittering agent into the formulation, and using only colors unattractive to children for the final bait formulation. The ornamental and greenhouse uses were voluntarily cancelled in July 1998 (USEPA, 1998d).

As of September 2013, methomyl is available in California in four formulation types and 14 commercial products. Methomyl is formulated as a water-soluble powder (WSP) in

water-soluble (WS) bags; water-soluble liquid; dust/powder; and granular/flake fly bait. WS concentrate/liquid contains cyclohexanone and methanol as inert ingredients. Fly baits contain additional active ingredient, (Z)-9-Tricosene, CAS Reg. No. 27519-2-4 (sex attractant) in concentration 0.040-0.049 %.

Methomyl can only be applied to crops using mechanical ground and aerial application equipment or chemigation. Hand held equipment is prohibited for crop application. Methomyl technical is intended only for formulation into end use insecticide products and is outside the scope of the exposure assessment. Table 2 summarizes the formulations and products available for agricultural and commercial use in California.

Table 2. Methomyl formulations and products registered in California.

Formulation	Concentration of active ingredient	Name of products /Registration #	Signal word
Water soluble powder	90.0 %	Lannate® SP (352-342-ZB)	DANGER/POISON
Water soluble liquid	29.0 %	Lannate® LV (352-384-AA)	DANGER/POISON
Soluble powder	90.0 %	Nudrin™ SP (83100- 28-AA- 83979)	DANGER/POISON
Water soluble liquid	29.0 %	Nudrin™ LV (83100- 27-AA- 83979)	DANGER/POISON
Water soluble powder	90.0 %	M1 SP (352- 342-AA- 85588)	DANGER/POISON
Water soluble liquid	29.0 %	M1 LV (352- 384-AA- 85588)	DANGER/POISON
Water soluble powder	90.0 %	Corrida 90 WSP (82557-3-AA)	DANGER/POISON
Water soluble liquid	29.0 %	Corrida 29 SL (82557-2-AA)	DANGER/POISON
Water soluble powder	90.0 %	Annihilate SP (82557-3-AA-400)	DANGER/POISON
Water soluble liquid	29.0 %	Annihilate LV (82557-2-AA-400)	DANGER/POISON
Dust/powder [a]	98.7 %	Methomyl technical (352-366-AA)	DANGER/POISON
Granular/flake	1.0-1.1 %	Starbar Golden Malrin® Fly Bait with muscamone fly attractant (2724-274-ZC) Stimukil® Fly Bait (53871-3-AA) Deosect II Fly Bait (53871-3-AA-66114)	Caution

[a] Intended for formulation use only

Application methods for methomyl include aircraft (rotary and fixed wing), airblast, ground sprayer, chemigation, bait box or scatter bait.

LABEL PRECAUTIONS AND REQUIREMENTS

Methomyl has been assigned Toxicity Category I due to its high, acute oral toxicity. The signal word on the label is DANGER for water-soluble powder and liquid concentrate (Lannate® SP and Lannate® LV, respectively), and CAUTION for the granular fly baits.

1. Labels of concentrated methomyl formulations Lannate® SP and Lannate® LV require that:

- Pilots are not allowed to assist in mixing/loading operations with Lannate®.
- Human flaggers must be in enclosed cabs.

Lannate® SP and Lannate® LV labels carry the following requirements for personal protective equipment (PPE):

1A. Applicators and others exposed to the diluted spray solution must wear:

Long-sleeved shirt and long pants.
Chemical-resistant gloves, such as barrier laminate or butyl rubber.
Shoes plus socks.
Protective eyewear.

1B. Mixers, loaders, cleaners, repairers of application equipment, and others exposed to the concentrate must wear:

Long-sleeved shirt and long pants.
Chemical-resistant gloves, such as barrier laminate or butyl rubber.
Socks and chemical resistant footwear.
Protective eyewear.
Chemical resistant apron.
Respirator as outlined below:

For exposures in enclosed areas, a respirator with either an organic vapor-removing cartridge with a prefilter approved for pesticides (MSHA/NIOSH approval number prefix TC-23C), or a canister approved for pesticides (MSHA/NIOSH approval number prefix TC-14G), or NIOSH approved respirator with an organic vapor (OV) cartridge or a canister with any R, P, or HE prefilter.

For exposures outdoors, Dust/mist filtering respirator (MSHA/NIOSH approval number prefix TC-21C), or a NIOSH approved respirator with any R, P, or HE prefilter. Discard clothing or other absorbent materials that have been drenched or heavily contaminated with this product's concentrate. Do not reuse them. Follow manufacturer's instructions for cleaning/maintaining PPE. If no such instructions for washables, use detergent and hot water. Keep and wash PPE separately from other laundry.

For early entry to Lannate® LV - treated areas that is permitted under the Worker Protection Standard (WPS) and that involves contact with anything that has been treated, such as plants, soil, or water, PPE required is:

Coveralls.
Chemical-resistant gloves, such as barrier laminate or butyl rubber.
Shoes plus socks.
Protective eyewear.

For early entry to Lannate® SP - treated areas that is permitted under the WPS and that involves contact with anything that has been treated, such as plants, soil, or water, PPE required is:

Coveralls.
Chemical Resistant Gloves Category A (such as butyl rubber, natural rubber, neoprene rubber or nitrile rubber), all ≥14 mls.
Shoes plus socks.
Protective eyewear.

As a Toxicity Category I pesticide, methomyl has additional requirements under the California Worker Safety Regulations. A closed system is required during mixing and loading, unless one gallon or less is handled per day from the original one gallon container (3 CCR 6746).

When handlers use closed systems, enclosed cabs, or aircraft in a manner that meets the requirements listed in the WPS for agricultural pesticides [40 CFR part 170.240 (d)(4-6)], the handler PPE requirements may be reduced or modified as specified in the WPS. Water-soluble packets (Lannate® SP), when used correctly, qualify as a closed loading system under the WPS. Handlers handling this product while it is enclosed in intact water-soluble packets are permitted to wear long-sleeved shirt, long pants, shoes plus socks, chemical-resistant gloves, and chemical-resistant apron, provided the other required PPE is immediately available in case the bag is opened. Additionally, under the WPS, "Persons using a closed system that operates under pressure shall wear protective eyewear".

The corresponding California regulations list the following PPE requirements (3 CCR 6738): "Persons using a closed system to handle pesticide products with the signal word 'DANGER' or 'WARNING' may substitute coveralls, chemical resistant gloves, and a chemical resistant apron for personal protective equipment required by pesticide product labeling." Also, "Persons using a closed system that operates under positive pressure shall wear protective eyewear in addition to the personal protective equipment listed…... Persons using any closed system shall have all personal protective equipment required by pesticide product labeling immediately available for use in an emergency."

In preparing worker exposure estimates, the following assumptions were made for mixer/loaders (M/L):

- Closed systems were assumed for M/L per California Worker Safety Regulations.
- Reduced or modified PPE, during use of a closed system was assumed, consisting of long-sleeved shirt, long pants, chemical resistant gloves, shoes plus socks, and a chemical resistant apron (95% protection of chest/stomach, front half of thighs, HS-1612) (3 CCR 6738(i)).
- Both short-term and annual exposures were assumed to occur (see Exposure Assessment section).

In preparing worker exposure estimates, the following assumptions were made for applicators:

- Human flaggers are in enclosed cabs per label requirement. Reduced or modified PPE was assumed, consisting of long-sleeved shirt, long pants, and shoes plus socks.
- Pilots are in open cockpits; airblast and groundboom applicators are in open cabs. Long-sleeved shirt, long pants, shoes plus socks, chemical resistant gloves, and protective eyewear (vented goggles, 75% protection, HS-1612) were assumed.
- Both short-term and annual exposures were assumed to occur (see Exposure Assessment section).

2. The labels for fly bait methomyl formulations require the following PPE:

- Long-sleeved shirt, long pants, shoes, socks, and gloves during loading, application, repairing, and cleaning of application equipment and disposal of the pesticide.

In preparing exposure estimates, the following assumptions were made for fly bait applicators:

- Long-term exposures were assumed to occur during twelve months of the year (see Exposure Assessment section).

PESTICIDE USE AND SALES

As of January 2014, 14 methomyl products were registered for use in California. Methomyl is used in both agricultural and non-agricultural situations. The non-agricultural uses of methomyl include applications to animal husbandry premises, storage areas, dumpsters, industrial and institutional establishments. Agricultural uses are numerous and they include field crops, vegetables, fruit, nuts, and nursery/greenhouse crops.

California requires reporting of all agricultural pesticide uses, as well as other uses when pesticides are applied by a licensed applicator. The reporting requirements include pesticide applications to parks, golf courses, cemeteries, rangeland, pastures, and along roadside and railroad rights-of-way. In addition, all post harvest pesticide treatments of agricultural commodities must be reported, along with all pesticide treatments in poultry and fish production, as well as some livestock applications. The primary exceptions to the full use reporting requirements are home and garden use and most industrial and institutional uses. The pesticide use data are collected in the Pesticide Use Report (PUR) database (http://www.cdpr.ca.gov/docs/pur/purmain.htm). Under California law, DPR also assesses a fee – called mill assessment - on all pesticide sales at the point of first sale into the state. Pesticide sales are reported by pesticide registrants, licensed pest control dealers and licensed pesticide brokers. The pesticide sale data are collected in the Mill Assessment data (http://www.cdpr.ca.gov/docs/mill/nopdsold.htm). Knowing the amounts of methomyl used in agriculture and sold in California, it is possible to calculate approximately the proportion of methomyl used for agricultural vs. non-agricultural uses. These databases were intended for different purposes, and the data are not directly comparable (e.g., pesticides sold in one year may be used in a different year, and sales data include sales to distributors). Examination of the 2010 Mill Assessment sales data

(DPR, 2012a) and the 2010 PUR (DPR, 2011b) suggests that in 2010 about 80% of the amount of methomyl sold (131,924 kg) were used in agriculture (104,839 kg).

Table 3 shows PUR data for top crops/commodities groups and use sites for methomyl in 2006 – 2010, based on kilograms AI applied. Methomyl was used most often in leafy greens; 31% of the amount of methomyl recorded in the PUR for 2006 – 2010 was applied to leafy greens crops. Of these, lettuce received the most methomyl, average 32,532 kg, or 27% of the total amount of methomyl used (data not shown). The crops in Table 3 represent total average annual use of 115,971 kg or 96% of the total amounts of methomyl reported in the PUR for these years.

Table 3. Agricultural and commercial use of methomyl by crop/site for 2006-2010 [a].

Crop	Kilograms applied					Average 2006-2010	
	2006	2007	2008	2009	2010	Kilograms applied	% of total use
Leafy greens [b]	40,061	39,793	36,098	31,938	36,968	36,972	30.6
Forage grasses [c]	19,273	23,733	16,653	21,611	23,586	20,971	17.4
Corn (all types)	19,731	11,558	10,896	4,244	5,301	10,346	8.6
Legumes [d]	7,140	10,249	8,996	9,573	10,372	9,266	7.7
Tomato [e]	10,654	10,732	7,216	6,255	4,362	7,844	6.5
Onion [f]	11,991	9,096	6,706	3,818	3,372	6,997	5.8
Grapes (all types)	7,295	7,902	4,923	4,541	5,194	5,971	4.9
Potato (root vegetables) [g]	6,618	7,297	4,921	2,769	1,459	4,613	3.8
Cucurbits [h]	5,426	5,250	2,617	2,746	2,805	3,769	3.1
Strawberry	3,561	3,925	3,275	3,138	3,694	3,519	2.9
Cabbage [i]	2,456	3,194	4,237	2,278	2,650	2,963	2.5
Stone Fruit [j]	3,162	2,490	3,522	2,671	1,862	2,741	2.3
Total of listed crops	137,368	135,219	110,060	95,582	101,625	115,971	96.1
Other crops	6,361	4,940	3,965	4,790	3,397	4,691	3.9
Chemical Total	143,728	140,160	114,025	100,372	105,022	120,661	100

[a] (DPR, 2007; DPR, 2008; DPR, 2009b; DPR, 2010b; DPR, 2011b). Crop groups are arranged in descending order by 5-year average.

[b] Includes celery, chicory, collards, dandelion, endive (escarole), fennel, head lettuce, kale, leaf lettuce, mint, mustard greens, parsley, spinach, Swiss chard, turnip greens.

[c] Includes alfalfa, Bermuda grass, sorghum, Sudan grass.

[d] Includes beans all types, lentils, peas, soybean.

[e] Includes eggplant, peppers, tomato.

[f] Includes onion dry, onion green and garlic.

[g] Includes carrot, horseradish, potato, radish, sugar beet, sweet potato, table beets, turnip.

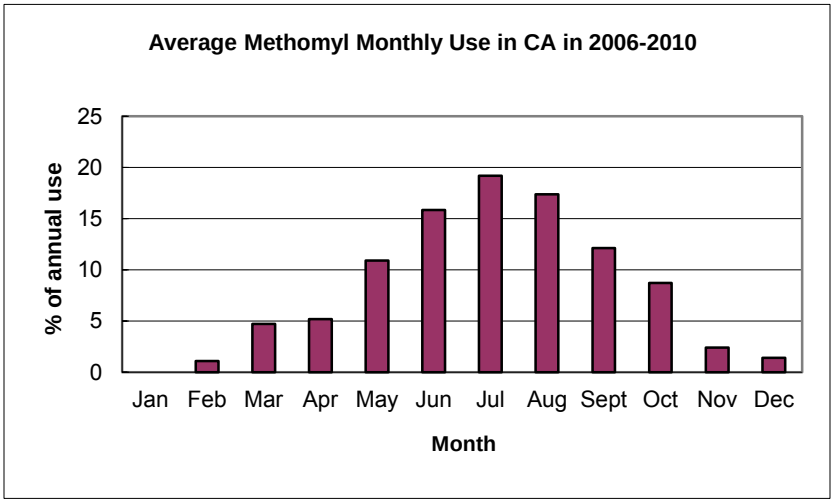
[h] Includes cantaloupe, cucumbers, melons, pumpkins, squash and watermelon.

[i] Includes Bok Choy, broccoli, Brussels sprouts, cabbage, cauliflower, Chinese cabbage.

[j] Includes apricots, avocado, nectarines, peaches, plums and prunes.

Methomyl is typically applied several times per season mostly during the summer months (Fig. 3).

Figure 3. Average methomyl monthly use in California in 2006-2010.



PHARMACOKINETICS

The term ^{14}C-methomyl in this section refers to S-methyl-(1-^{14}C)-N-(methylcarbamoyloxy)thioacetimidate, unless otherwise stated.

Dermal and inhalation absorption

For methomyl, no *in vivo* or *in vitro* human studies on dermal penetration and inhalation absorption are available. The only available dermal study deals with *in vivo* absorption in rodents and is part of a bigger project involving several other insecticides (Shah *et al.*, 1981). This study is described in detail below.

^{14}C-methomyl (specific activity 0.72 mCi/mol) was applied in acetone to a 1 cm^2 shaved area of skin (upper shoulder) of female mice (7-8 weeks old, n=3) at a rate of 1 mg/kg. The authors did not specify if the shaved skin area was covered but noted that no evidence of grooming was observed. The mice were then placed in metabolism chambers and killed for radioactivity measurements at intervals up to 48 h. Within 5 min, ^{14}C activity was detected in blood and liver. In 60 min, 3% of the original ^{14}C dose was present in blood, 5% was in the liver, 13% had been excreted (urine plus CO_2 plus faeces) and 56% in the remaining carcass. Very little methomyl remained at the application site after 60 min, when penetration was estimated to be approximately 85%. The half-life, as a measure of penetration rate, was approximately 13 min. After 8 h the distribution was 55% excreted (urine plus CO_2 plus faeces), 6% in blood, 3% in liver, 4% in the gastro-intestinal tract and smaller amounts (<1%) in other individual tissues. The remaining carcass contained 15% of the original dose (Shah *et al.*, 1981).

In their paper Shah *et al*. reported dermal penetration above 65% after 8 hours for all fourteen insecticides they tested (Shah *et al.*, 1981) but these high numbers were not confirmed by other investigators. The data on *in vivo* dermal absorption of fourteen

pesticides in rats and humans published in journal articles and monographs, was summarized by Ross *et al.,* and four of the compounds investigated by Shah *et al*. in mice showed about 10% or less dermal absorption in humans (Ross *et al.*, 2001) (see also the discussion in (Beauvais and Johnson, 2006). For this reason, and for deviations from the USEPA acceptability guidelines discussed below, it is believed that the figures of Shah *et al.* for methomyl absorption were overestimated.

Requirements for acceptability of dermal absorption studies have been outlined in (USEPA, 1998a). Some of these criteria are: use of water-based vehicles and not organic solvents; doses and durations should be similar to those expected during field use; young adult male rat is the required testing animal; four doses are recommended with four animals per dose per exposure duration; the minimal treated skin area is 10 cm^2 (USEPA, 1998a). The study of Shah *et al*. deviates significantly from the USEPA guidelines outlined above thus undermining the reliability of the findings. For example, the use of acetone as methomyl solvent might overestimate the dermal absorption because acetone has been shown to increase significantly skin permeability by compromising skin barrier (Tsai *et al.*, 2001). Another shortfall in the study of Shah *et al*. (Shah *et al.*, 1981) is the practice of testing on a very small surface area (1 cm^2) using only single dose of the chemical. Experience has shown that absorption is not dose-linear - as the dose per unit area increases the flux increases to a lesser degree. Some compounds have shown saturation of the absorption process (no increase of flux with dose) (USEPA, 1998a). Choice of mouse skin to model human dermal absorption could also overestimate this value. Higher permeability has been demonstrated for some chemicals, including pesticides, in mouse skin than the skin of rats or humans (USEPA, 1992; Baynes *et al.*, 1997).

In view of these deficiencies, the study of Shah *et al*. (Shah *et al.*, 1981) was regarded as inappropriate for determining the dermal absorption of methomyl. In the absence of chemical-specific human dermal absorption data and acceptable animal studies, DPR policy is to use a default value of 50% (Donahue, 1996), and this value was utilized for calculations of dermal exposures in the present document.

As no inhalation absorption data were available for methomyl, this document utilizes the DPR default value of 100% to calculate absorbed doses by the inhalation route (Frank, 2008).

Animal metabolism

Methomyl is metabolized in animals to volatile metabolites (CO_2 and acetonitrile), which are mostly exhaled. In an initial investigation, two male rats were fed a diet containing 200 mg methomyl/kg for 8 days, followed by intra-gastric intubation of 1.2 mg ^{14}C-methomyl (=5 mg/kg). One male rat was treated similarly except that the ^{14}C-methomyl was given after 19 days. Urinary and volatile metabolite identification was carried out 1 or 3 days after the ^{14}C dose. Volatile products, trapped in caustic soda solution or in cold traps, were identified as carbon dioxide and acetonitrile, the latter confirmed by mass spectroscopy (Harvey *et al.*, 1973).

Another proposed pathway involves the conversion of the *syn*-isomer of methomyl (the insecticide form which is more stable) to its *anti*-isomer (Fig. 4). The latter has been shown to produce acetonitrile as the main volatile metabolite when given orally to rats (Huhtanen and Dorough, 1976).

Methomyl is also degraded via a glutathione conjugation pathway in animals (Fig 4). Further metabolism of acetonitrile also occurs leading to polar metabolites that are excreted or to the incorporation of one and two carbon units into a variety of natural products, such as fatty acids, cholesterol, sugars and amino acids (Fig. 4).

Acetonitrile, CO_2 and reincorporation products derived from acetate found after the application of methomyl to plants are similar to those identified in the above animal studies (Harvey and Reiser, 1973).

Figure 4. Proposed metabolic pathway of methomyl in mammalian species, from (WHO, 1996).

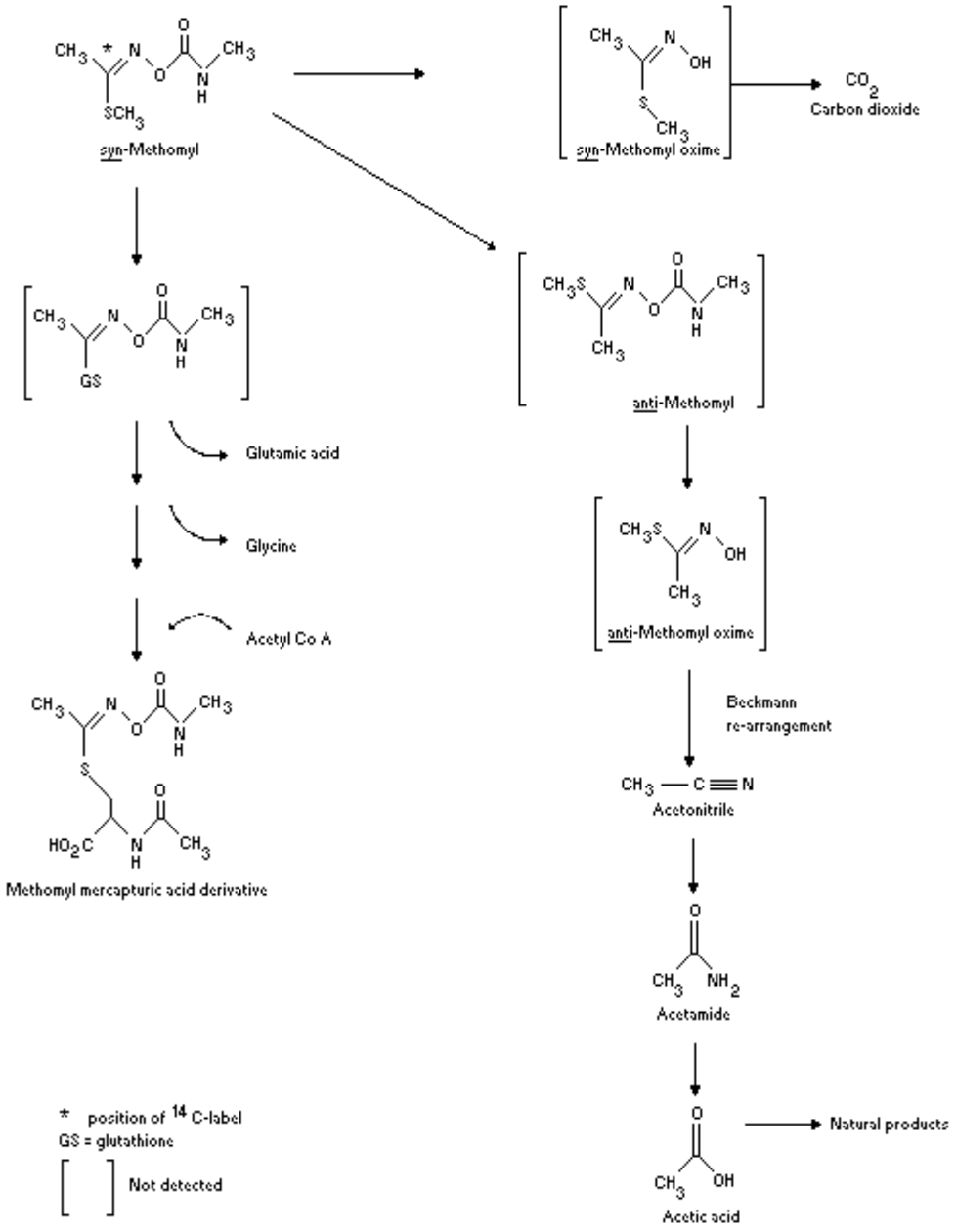


Fig. 1. Proposed metabolic pathway of methomyl in mammalian species

REPORTED ILLNESSES

The Pesticide Illness Surveillance Program (PISP) in the California Department of Pesticide Regulation (DPR) maintains a database of pesticide-related illnesses and injuries - California Pesticide Illness Query (CalPIQ). Reports come from health care facilities, poison control centers, and local health officers throughout the state, and DPR supplements them through workers' compensation records in cooperation with the Department of Industrial Relations and the Department of Health Services. The county

agricultural commissioners investigate these incidents and send their completed investigation reports to DPR, where PISP scientists evaluate the cases and abstract relevant information into a database. Database queries support identification of trends in pesticide illness, responses to public inquiries, and evaluation of the adequacy of safety regulations.

PISP defines a "case" as the program's representation of a pesticide exposure and its apparent effects on one individual's health (WH&SStaff, 2007). Depending on the likelihood that a case is associated with pesticide exposure, cases are classified as definite, probable and possible. A definite relationship indicates that both physical and medical evidence document exposure and consequent health effects. A probable relationship indicates that limited or circumstantial evidence supports a relationship to pesticide exposure. A possible relationship indicates that health effects correspond generally to the reported exposure, but evidence is not available to support a relationship (WH&SStaff, 2007).

PISP defines an "episode" as an event in which a single source appears to have exposed one or more people (cases) to pesticides (WH&SStaff, 2007).

Between the years 2005 and 2009, PISP scientists evaluated 17 individual cases stemming from 13 episodes in which an injury was definitely, probably, or possibly related to methomyl exposures (Table 4). Methomyl was implicated as the sole causal pesticide in six case reports that resulted from five episodes. The remaining 11 cases, stemming from 8 episodes, involved methomyl used in combination with other pesticides. Two of the episodes involved more than one person (two and four cases, resp.). Four cases resulted in total of 18 days of disability. No hospitalizations for more than 24 hours were recorded. Violations were identified in some cases, including early reentry, lack of notification of pending or finished pesticide application, or careless application which resulted in bystander exposures.

Table 4. Individual illnesses and number of episodes associated with methomyl exposure for the years 2005-2009[1]

Year	Number of Episodes	Number of Illnesses (cases)	Number of cases/days with disability
2005	3	4	2 cases/3 days
2006	2	2	-
2007	5	8	1 case/13 days
2008	2	2	1 case/2 days
2009	1	1	-
Total	13	17	4 cases/18 days

[1]Data generated August 2012 by Miglena Stefanova-Wilbur, Worker Health and Safety Branch, DPR, and March 2013 by April Holland, Worker Health and Safety Branch, DPR.

Four of the cases involved pesticide handlers (2 applicators and 2 mixer/loaders) and eleven cases involved field workers. The rest two cases involved residents (Table 5). All

but one exposure were related to the agricultural use of methomyl. The one exception was accidental methomyl ingestion in a single family home. A man stored a Mexican pesticide powder in his garage. He found his developmentally disabled daughter in the garage with pesticide powder on her hands and a pesticide smell to her breath. She was taken to a hospital where she was observed overnight. The other residential exposure occurred when a resident was exposed to pesticide drift. He heard a tractor and went outside to stop the application from overspraying pesticides onto his property. Methomyl was one of multiple pesticides applied. The resident felt spray mist on his face and his eyes immediately burned. His symptoms lasted for an hour. Clothing, swab and foliar residues confirmed drift. This is a violation of pesticide safety requirements because methomyl should not be applied in a way that will expose other persons to the pesticide.

Table 5. Methomyl-related exposures according to activity at the time of exposure, 2005-2009

Activity[1]	Exposure[2]						
	Residue	Drift	Spill/Other Direct	Ingestion	Other	Unknown	Total
Applicator	-	-	-	-	1	1	2
Field Worker	8	3	-	-	-	-	11
Mixer/Loader	-	1	1	-	-	-	2
Routine Indoor	-	-	-	1	-	-	1
Other	-	1	-	-	-	-	1
TOTAL	8	5	1	1	1	1	17

[1]Activities:

- Applicator: Applies pesticides by any method or performs tasks associated with application (e.g., cleans spray nozzles in the field, cleans and stores equipment after application).
- Fieldworker: Works in an agricultural field performing tasks such as advising, scouting, harvesting, thinning, irrigating, driving tractor (except as part of an application), field packing, conducting cultural work in a greenhouse, etc. Researchers performing similar tasks in an agricultural field are also included.
- Mixer/loader: Mixes and/or loads pesticides. This includes: (1) removing a pesticide from its original container; (2) transferring the pesticide to a mixing or holding tank; (3) mixing pesticides prior to application; (4) driving a nurse rig (pesticide transfer vehicle); and (5) transferring the pesticide from a mix/holding tank or nurse rig to an application tank.
- Routine Indoor: Conducts activities in an indoor environment with minimal expectation for exposure to pesticides. This includes people in offices and businesses, residential structures, etc. who are not handling pesticides.
- Other: Activity is not adequately described by any specifically defined activity category. This includes: 1) engagement in two or more defined activities during exposure to pesticides; 2) exposure during routine activity inside a vehicle; 3) an activity causing increased risk of pesticide exposure in some way not expressed by any defined activity, (e.g. dog groomers who did not handle pesticides, individuals who handled preservative-treated wood).

[2]Exposure:

- Residue: The part of a pesticide that remains in the environment for a period of time following an application or drift. This includes odor after the completion of an application.
- Drift: Spray, mist, fumes, or odor carried by air from a pesticide application or mix/load procedure. This excludes exposure to pesticide that air picked up from any source other than an application/mix/load procedure (e.g. from residue after application was complete or from a spill that occurred during transport or storage.)
- Spill/Other Direct: Any of the following: (1) contact made during an application or mixing/loading operation where the material is not propelled by the equipment; (2) expected direct contact during use (e.g., washing dishes in a disinfectant solution); and (3) leaks, spills, etc. not related to an application.

- Ingestion: Any intentional or unintentional oral ingestion. This can include ingestion of products directly from their containers, residue on food products, or any other incident resulting in oral ingestion.
- Other: Other known route of exposure not included in other defined categories. One example would be exposure to smoke or pyrolitic products from a fire where pesticides are burning.
- Unknown: Route of exposure is not known.

Table 5a summarizes the types of exposure illnesses attributed to methomyl used alone or in combination with other pesticides.

Table 5a. Types of symptoms reported in California that are related to methomyl exposure for the years 2005-2009.

Methomyl exposure	Types of symptoms reported[1]			
	Skin	Eye	Respiratory	Systemic
Methomyl used alone (6 cases)	2	1	0	4
Methomyl used in combination with other pesticides (11 cases)	4	3	3	6

[1]Illnesses are characterized as relating to the skin, to the eye, and/or to the respiratory system. Any other or additional manifestation is identified as being systemic. More than one type of symptoms were reported in some cases.

- Skin effects include itching, rashes, and burns.
- Eye effects include irritation, burning, itching and watery eyes.
- Respiratory illnesses include irritation of nose, throat, and lungs; coughing; wheezing; lung congestion; asthma and other breathing difficulties.
- Systemic illnesses include symptoms such as nausea, dizziness, headache, numbness.

Pesticide Handler Cases

All four pesticide handler cases were single-person. Three of them were related to methomyl as a single active ingredient and one involved multiple active ingredients. After completing an application (multiple pesticides applied), a pesticide applicator washed off and changed his clothes. While driving his truck to the next job, he rubbed his eyes which began to sting (exposure type “other”). The examining doctor noted a mildly injected sclera of the right eye and a pterygium on the nasal side of the left eye.

In the second case, a self-employed farmer applied methomyl for 6 hours and later that evening experienced sweating, chills, nausea and vomiting (exposure type ”unknown”). On the following morning he sought medical attention but could not be reached for an interview.

As a mixer/loader added water-soluble bags of methomyl to a supposed closed mix tank system, he noted a damaged bag. The tank agitator caused powder from the damaged bag to waft into the air which he inhaled (exposure type “drift”). He did not wear a respirator as none was required for a closed system mixing/loading. His symptoms included lower eyelid and cheek fasciculations, upset stomach, dizziness, blurred vision, and chemical taste in the mouth.

The fourth and final case involved a mixer/loader who tried to retrieve a methomyl bag inside a half-full mix tank and fell in (exposure type “spill/other direct”). He washed and

soaped himself in a nearby water fill. He changed into clean coveralls but kept on his pants, shoes and socks. He developed symptoms 30 minutes later and sought care. The symptoms included dizziness, weakness, nausea, vomiting, slurred speech, difficulty keeping eyes open. Upon examination, the doctor noticed the odor of pesticides.

Fieldworker Exposure

Eleven cases stemming from seven episodes involving field workers' exposure to methomyl were documented between 2005 and 2009. This accounted for 65% of the overall methomyl exposures. In the first case, an onion harvester broke out in an itchy rash on his body, hands and forearms after cleaning the harvesting machine (exposure type "residue"). The field was treated 5 and 23 days prior to harvest with a combination of methomyl and other pesticides.

The second episode involved two fieldworkers who developed symptoms after an applicator in an adjacent cornfield drifted methomyl on them (exposure type "drift"). Both sought medical attention. They had itchy face and arms, and later one of the workers experienced red skin on the chest. This worker lost two days of work, while the other worker lost one day of work. The applicator did not see the fieldworkers. This is a label violation because methomyl should not be applied in a way that will contact workers or other persons. The workers declined to provide clothing to be analyzed for pesticide residue.

In the third episode, a fieldworker experienced painful skin on the arms, tiredness, dizziness, shakiness and unstable feeling 15 minutes after starting to pick up trash near the edge of a field treated with methomyl and other pesticides the day before (exposure type "residue"). The worker had no contact with the foliage. The doctor said he had a high temperature and probably had the flu.

Another incident happened when a field worker developed spotty rash and swelling on his right arm after hoeing and pulling weeds in an onion field (exposure type "residue"). He sought medical care two days later when he had itchy and irritated skin, and the doctor noted blisters on his arm. A week after the incident the doctor noted small blood-filled blisters and a discolored, swollen, non-draining area by the elbow with excoriations. An Ag pest control operator (PCO) had applied methomyl and three other pesticides to the onion field 8 days earlier, but the REIs had already expired (methomyl REI for onions is 2 days). This worker lost 13 days from work.

A worker began furrow irrigating a corn field 9 hours into a 48-hour REI. The field was treated with multiple pesticides including methomyl. The worker entered the field without PPE and used a shovel to direct the water flow in the rows. He worked in the field for 2 days and developed skin problems for which he sought care (exposure type "residue"). The skin on his hands was painful, swollen, red, dry, cracked and peeling. On exam 2 days later the doctor noted moderate swelling and injection of the hands, more severe on the left hand. This is a label violation because on the first day of work the worker entered the field before the expiration of the REI. There is no information whether the field was posted for the pesticide application.

After an Ag PCO completed a nearby aerial pesticide application (methomyl not included), four farm workers developed symptoms while working in a lettuce field (exposure type "residue"). Their supervisor transported them to the clinic and waited an hour for the clinic to open. Their symptoms included to a various degree headache, stomachache, raspy throat, salivation, numb mouth, swollen tongue and lips, difficulty swallowing, nausea, dizziness, weakness, and anxiety. One of the workers also had sore throat, hyper-salivation, sleepiness, diarrhea after having lunch, and abdominal pain. The doctor administered an injection of atropine to this person. All four workers reported smelling an odor when they entered the lettuce field. The nearby application occurred about 1,000 feet away. The grower applied methomyl and four other pesticides to the lettuce field 3 days earlier. Of those, methomyl had the longest REI of 48 hours. It is not clear whether the symptoms experienced by the field workers were due to the adjacent pesticide application at the moment of reentry, or due to the pesticides applied previously to the field.

The last episode of field worker exposure was due to drift. The worker took his open cab corn topper out at night to avoid heat. He felt mist from an aerial application a quarter mile upwind and left the field until the application ended. He got sick a few hours later, experiencing headache, nausea, vomiting, diarrhea, throat irritation, chest pain, shortness of breath and blurred vision. On examination, bowel sounds were found somewhat hyperactive, but pupils were said to be normal. His diarrhea lasted several days. He missed two workdays as a result of his exposure. This worker was not notified of the pending application.

Methomyl Illnesses outside California

Most of methomyl-related illnesses were result of accidental or suicidal poisoning.

An outbreak of gastrointestinal illness was associated with the consumption of food seasoned with methomyl-contaminated salt among patrons at a Thai restaurant in central California between December 1998 and January 1999. Twenty-six persons (24%) visited the emergency department or were treated by a physician; no person required hospitalization. Patients reported nausea, dizziness, abdominal cramps, headache, vomiting, chills, and diarrhea. Illness was statistically associated with several foods and ingredients, but no single dish or ingredient explained a substantial number of cases. Methomyl was identified in a sample of vomitus (20 ppm) and in salt taken from containers in the storeroom (mean, 5600 ppm) and the stovetop (mean, 1425 ppm). The oral toxic dose causing illness in 50% of those exposed to methomyl was estimated to be 0.15 mg/kg of body weight (estimated range, 0.09-0.31 mg/kg of body weight) (Buchholz *et al.*, 2002).

A 61-year old male farmer was found comatose in his greenhouse with completely wet clothes with garlic odor (Tsatsakis *et al.*, 2001). He was admitted to a hospital 3.5 hours after he was found in the greenhouse. Upon admission the patient was unresponsive, with lowered blood pressure and body temperature, methomyl was detected in blood (1.6 mg/L) and urine but not in stomach content, cholinesterase activity was inhibited 89%.

The patient died in hospital 3 days after admission of multiple organ failure syndrome (liver and renal failure, haemodynamic instability, coagulation disorders and coma). The farmer has been spraying methomyl in his greenhouse for a week prior to the incident. His poisoning could not be attributed to ingestion since no methomyl was found in the stomach. Consequently, the poisoning was caused by inhalation and transdermal absorption. Interview with the relatives revealed that the patient used to wear the same clothes each time he had to spray, and would not take precautions such as respirator, gloves or ventilation of the greenhouse.

In one case, three fishermen in Jamaica became critically ill within 5 min of eating a meal including roti, unleavened bread made from flour, water, and salt. Symptoms were perspiration, visual disturbances, trembling, vomiting, and defecation, progressing to convulsions and coma. The men were taken to a hospital about 3 hr later and pronounced dead on arrival. Postmortem exams revealed congestion of the stomach lining, lungs, trachea, and bronchi. One of two other men who had shared the meal showed generalized twitching, fasciculations, and severe bronchospasms, but recovered within 2 hr after treatment; the fifth was asymptomatic. Poisoning was traced to a small, unlabeled bag of pure methomyl powder found in a tin in the fishermen's hut; the powder was probably used instead of salt in preparing the roti, which contained methomyl at about 11,000 ppm. The lethal doses were estimated at 12-15 mg/kg (Liddle *et al.*, 1979; Morse *et al.*, 1979).

A 31 yr old housewife committed suicide with her 3 children by taking Lannate refreshments. Her 9 yr old son survived, while the other children were dead at the scene. Autopsies of the mother and her 6 yr old son revealed congestion of the stomach lining and lungs, with edema and hemorrhages of various tissues due to acute circulatory failure. The estimated doses ingested were approx 55 mg/kg (2.75 g) to the mother and approx 13 mg/kg (0.26 g) to her son, respectively (Hayes and Laws, 1991).

Food-related methomyl intoxication produced a rapid onset (5 min) of significant clinical toxicity in 124 patrons of seafood restaurant in Taiwan in 2002. 59 dinners were hospitalized. Twenty-four patients recovered completely within 7 days. Thirty-one patients had residual symptoms 7 days after ingestion. The food history and chemical analysis of the poison indicated methomyl was the cause of this outbreak. High levels of methomyl in leaf vegetables of "leaf vegetables stir-fried with crab claws" (380 ppm) and fried mussels (1113 ppm) were found by the Food Inspection Center at the Department of Health. The most commonly reported clinical effects were general weakness, ataxia, dizziness, vomiting, sweating, floating sensation, headache, dyspnea, and blurred vision (Tsai *et al.*, 2003).

A 50-year-old Japanese man was admitted to the emergency room complaining of oppression on his chest, sweating and vomiting. He had drunk a 30 ml volume nutrition supplement 60 minutes before. As myosis and decrease of serum choline esterase activity were observed on admission examination, poisoning was suspected. Toxicological analysis of the drink revealed the presence of methomyl at concentration 2.1 mg/ml. Methomyl concentration in the serum collected 6 hours after ingestion was 0.63 µg/ml, and that in the urine collected 7-20 hours after ingestion was 0.10 µg/ml. Based on these

values and reported data, the amount of methomyl contaminated to the drink was considered to be a toxic dose (Kudo *et al.*, 2005).

SIGNIFICANT EXPOSURE SCENARIOS

An exposure scenario describes a situation in which people may contact pesticides or pesticide residues, such that the nature of the exposure as well as its magnitude (apart from variability among individuals and occasions) are relatively homogeneous. The following types of exposure scenarios are possible due to label-approved uses: occupational handlers exposed during methomyl applications in agricultural settings; occupational reentry scenarios; airborne exposures of bystanders (persons living, working or performing other activities adjacent to an application area); and "U-Pick" non-occupational exposures.

Occupational Handler Scenarios

Handler exposures depend on formulation, application method, and amount handled. Occupational (agricultural and commercial) handler activities include mixer/loader (M/L), applicator, and flagger (Table 6). Flaggers may be used to assist aerial applicators (pilots), although use of human flaggers is becoming increasingly rare as newer technologies are adopted. Handlers may be growers or professional applicators; professional applicators may treat crops for many different growers in many different counties.

Handler scenarios are listed in Table 6. There are no wettable powder applicator scenarios because wettable powder formulations are mixed with water and applied as liquids. Only one M/L scenario is considered for chemigation, because only the liquid formulation is intended for chemigation use. Applicator scenario is not considered for chemigation, as handlers are not present during the application.

Table 6. Agricultural and commercial handler scenarios for methomyl, based on product labels registered by DPR.

Activity	Formulation Type		
	Liquid	Water soluble powder	Bait (Granular or Pellet)
Aerial M/L	X	X	
Aerial Applicator	X		
Flagger	X		
Airblast M/L	X	X	
Airblast Applicator	X		
Groundboom M/L	X	X	
Groundboom Applicator	X		
Chemigation M/L [a]	X	X	
Hand Spread of Bait			X

[a] Chemigation is allowed through overhead sprinkler and drip, and not for all crops.

In preparing occupational handler exposure estimates, the following assumptions were made:

1. Average body weight of an adult handler is 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al.*, 1993a).
2. Dermal absorption is 50% (Donahue, 1996), inhalation absorption is 100% (Frank, 2008).
3. Protection factors for use of PPE and engineering controls are from HS-1612 (Thongsinthusak *et al.*, 1993a).
4. A person is assumed to do the same job for 40 years, life expectancy is assumed to be 75 years.
5. Concentrated methomyl formulations for agricultural use (liquid and water soluble powder):
    a. Agricultural M/L:
        i. Closed systems were assumed for M/L per California Worker Safety Regulations.
        ii. Reduced or modified PPE, during use of a closed system was assumed, consisting of long-sleeved shirt, long pants, chemical resistant gloves (90% protection of hands), shoes plus socks, and a chemical resistant apron (95% protection of chest, front half of thighs).
    b. Agricultural applicators:
        i. Human flaggers are in enclosed cabs (90% protection) as per label requirement. Reduced or modified PPE was assumed, consisting of long-sleeved shirt, long pants, and shoes plus socks.
        ii. Pilots are in open cockpits; airblast and groundboom applicators are in open cabs. Long-sleeved shirt, long pants, shoes plus socks, chemical resistant gloves (90% protection of hands), and protective eyewear (vented goggles, 75% protection of head) were assumed.
    c. Maximum application rate of 0.9 lb AI/a allowed on product labels for most crops (Table 7) was assumed.
    d. Acres treated per day were as follows: 1200 acres for aerial application (M/L and pilots), 350 acres for aerial application (flaggers), 40 acres for airblast application, 200 acres for groundboom application, and 350 acres for chemigation. All values were from (Haskell, 1998) using upper range for high-acre crops (e.g. alfalfa, corn), based on methomyl use in 2002-2006 (Table 3).
    e. Annual exposures were assumed to occur during the year as professional applicators may move from county to county (see Exposure Assessment section).
6. Fly baits (hand spreading):
    a. Chemical resistant gloves, long-sleeved shirt, long pants, shoes and socks were assumed as normal PPE.
    b. Formulations with 1% AI in fly baits.
    c. Maximum application rate of 1/4 lb product per 500 ft^2 was assumed as per label requirement. The amount handled per day is based on 43,560 ft^2 (1 acre) treated per day (USEPA, 2001) and is equivalent to 21.8 lb formulated bait or 0.218 lb AI per day.

d. Long-term exposures were assumed to occur during twelve months of the year (see Exposure Assessment section).

Occupational Reentry Scenarios

Occupational reentry scenarios are considered differently depending on whether the reentry is regulated under the Worker Protection Standard (WPS). Federal WPS regulations are listed under Title 40 of the Code of Federal Regulations (CFR), Parts 156 and 170, and California WPS regulations are listed under 3 CCR 6760 – 6778. The WPS regulates "occupational exposures to pesticides used in the production of agricultural plants on farms or in nurseries, greenhouses, and forests, and also from the accidental exposure of workers and other persons to such pesticides" (40 CFR 170.1). Under the WPS, reentry into treated fields and other production agricultural areas is restricted for a specific interval (the restricted entry interval, or REI) following pesticide applications. Because of the REI, agricultural reentry regulated under the WPS is assessed differently than non-agricultural reentry. (Although the WPS applies to handlers as well as reentry workers in agricultural settings, all occupational handlers must comply with the same set of label requirements regardless of setting.)

Agricultural Reentry Scenarios (Activities in Production Agriculture)

Agricultural reentry scenarios are based on crops/sites and related agricultural practices, application rates, pre-harvest and reentry intervals. Pre-harvest interval (PHI) is the minimum required interval between the last application of a specific pesticide and harvest of the crop. PHI is specified on the product label.

Crops listed on methomyl product labels registered in California as of January 2014, and associated reentry activities/scenarios are listed in Table 7. Special local needs (SLN) use is listed in Table 7 as well. Rows are sorted by site category (FC = Field Crops; FN = Fruits and Nuts; OT = Ornamental; V = Vegetables), then by use sites.

Table 7. Occupational reentry scenarios in crops for methomyl uses in California.

Site Cat	**Use Site/Crop**	**Rate** (lb AI/a)	**REI** (days)	**PHI** (days)	**Tier I Activities** (High)	**Tier II Activities** (Medium)	**Tier III Activities** (Low)
FC	Alfalfa	0.9	2	7	None	None	Irrigating, Scouting, Swathing, Harvesting (Mech.)
FC	Barley	0.45	2	7	None	None	Irrigating, Scouting, Swathing (Mech.), Harvesting (Mech.)
FC	Bermuda grass (Pasture)	0.9	2	3	None	None	Irrigating, Scouting, Swathing, Weeding
FC	Corn (Field, Popcorn, Seed)	0.45	2	10	**Scouting**	None	Irrigating, Harvesting (Mech.), Weeding
FC	Corn (Sweet)	0.45	2	0	**Harvesting** (Hand), **Scouting**	None	Irrigating, Weeding, Harvesting (Mech.)

Site Cat	Use Site/Crop	Rate (lb AI/a)	REI (days)	PHI (days)	Tier I Activities (High)	Tier II Activities (Medium)	Tier III Activities (Low)
FC	Cotton	0.68	3	15	**Scouting**	Irrigating, Hand Weeding/Roguing, Harvesting (Mech.)	None
FC	Oats	0.45	2	7	None	None	Irrigating, Harvesting (Mech.), Scouting, Swathing (Mech.)
FC	Rye	0.45	2	7	None	None	Irrigating, Harvesting (Mech.), Scouting, Swathing (Mech.)
FC	Sorghum, Sudan grass	0.45	2	14	None	Irrigating, **Scouting**	Harvesting (Mech.), Scouting, Weeding/ Rouging
FC	Soybeans	0.45	2	3	None	Irrigating, **Scouting**	Weeding, Harvesting (Mech.)
FC	Tobacco	0.45	2	5	**Harvesting** (Hand)	**Scouting**	Irrigating, Harvesting (Mech.), Pruning, Stripping, Thinning, Topping, Weeding, Reset
FC	Turf (Sod Farms only)	0.9	2	0	None	Harvesting (Hand and Mech.), **Transplanting**	Irrigating, Scouting, Weeding
FC	Wheat	0.45	2	7	None	Irrigating, **Scouting**	Harvesting (Mech.), Swathing (Mech.), Weeding
FN	Apples	0.9	3	14	**Thinning**	**Harvesting** (Hand), Pruning (Nondormant), Propping	Animal Control (Field Baits/Traps), Irrigating, Pruning and Tying (Dormant), Scouting, Transplant/Propagate[a], Weeding (Hand, Mech.)
FN	Avocado	0.9	2	1	**Harvesting** (Hand), Thinning	**Pruning**	Irrigating, Scouting, Weeding (Hand, Mechanical), Transplant/Propagate
FN	Blueberry	0.9	2	3	None	**Harvest** (Hand), Pruning, Thinning,Training /Tying/Trellising	Irrigating, Harvest (Mech.), Hedging, Scouting, Weeding (Hand, Mech.), Transplant/Propagate
FN	Citrus (Grapefruit, Lemon, Orange, Tangelo, Tangerine)	0.9	3	1	**Harvesting** (Hand), Baiting/Trapping (In Tree), Chopping (Brush)	**Pruning** (Hand)	Irrigating, Pruning (Mech.), Scouting, Transplant/Propagate, Weeding (Hand, Mech.)
FN	Nectarine	0.9	3	1	**Thinning**	**Harvesting** (Hand), Pruning	Irrigating, Scouting, Training/Pruning (Dormant), Transplant/Propagate, Weeding (Hand)

Site Cat	Use Site/Crop	Rate (lb AI/a)	REI (days)	PHI (days)	Tier I Activities (High)	Tier II Activities (Medium)	Tier III Activities (Low)
FN	Peaches	0.9	4	4	**Thinning**	**Harvesting** (Hand), Pruning (Nondormant)	Scouting, Irrigating, Weeding (Hand), Training/Pruning (Dormant), Transplant/Propagate
FN	Pomegranate	0.9	2	14	**Thinning**	**Harvesting** (Hand), Pruning (Nondormant)	Irrigating, Pruning (Dormant), Scouting, Sucker/Shoot Removal, Transplant /Propagate, Weeding (Mech.)
OT	Mint (Peppermint, Spearmint)	0.9	2	14	None	None	Irrigating, Harvesting (Mech.), Scouting, Weeding
V	Anise (Fennel)	0.9	2	7	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Transplanting
V	Asparagus (Spears, Ferns, etc.)	0.9	2	1	None	Irrigating, **Scouting**, Harvesting **(**Hand)	Weeding, Transplanting
V	Beans (Dry)	0.9	2	14	Harvesting (Hand)	Irrigating, **Scouting**	Weeding, Transplanting, Harvesting (Mech.)
V	Beans, Succulent	0.9	2	1	Tying, Staking, **Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Transplanting, Harvesting (Mech.)
V	Beans and Soybeans [b]	0.45	2	1	Tying, Staking, **Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Transplanting, Harvesting (Mech.)
V	Beets (Table)	0.9	2	0	None	None	Irrigating, Harvesting (Mech.), Scouting, Thinning, Weeding, Transplanting
V	Broccoli	0.9	2	3	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting, Harvesting (Mech.)
V	Broccoli Raab [c]	0.9	2	3	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting, Harvesting (Mech.)
V	Brussels Sprouts	0.9	2	3	Irrigating, Topping, **Harvesting** (Hand)	**Scouting**	Harvesting (Mech.), Weeding, Thinning, Transplanting
V	Cabbage	0.9	2	1	Head Breaking, **Harvesting** (Hand)	Irrigating, **Scouting**	Harvesting (Mech.), Weeding, Thinning, Transplanting
V	Carrots	0.9	2	1	None	Harvesting (Hand)	Harvesting (Mech.), Irrigating, Scouting, Weeding

Site Cat	Use Site/Crop	Rate (lb AI/a)	REI (days)	PHI (days)	Tier I Activities (High)	Tier II Activities (Medium)	Tier III Activities (Low)
V	Cauliflower	0.9	2	3	Tying, Irrigating, Banding, **Harvesting** (Hand)	**Scouting**	Harvesting (Mech.), Transplanting, Weeding
V	Celery	0.9	2	7	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Transplanting
V	Chicory	0.9	2	80	None	None	Harvesting (Mech.), Irrigating, Scouting, Weeding
V	Chinese Broccoli [d]	0.9	2	3	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting, Harvesting (Mech.)
V	Chinese Cabbage	0.9	2	10	Head Breaking, **Harvesting** (Hand)	Irrigating, **Scouting**	Harvesting (Mech.), Weeding, Thinning, Transplanting
V	Collards (Fresh market only)	0.9	2	10	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting
V	Cucumber	0.9	2	3	**Thinning**, Staking, Harvesting (Hand)	Irrigating, **Scouting**	Harvesting (Mech.), Weeding, Thinning, Transplanting
V	Eggplant	0.9	2	5	**Harvesting** (Hand), Pruning (Hand)	Irrigating, **Scouting**	Weeding, Transplanting
V	Endive, Escarole	0.9	2	10	**Harvesting** (Hand)	Irrigating, **Scouting**	Harvesting (Mech.), Weeding, Thinning, Transplanting
V	Garlic	0.45	2	7	None	**Harvesting** (Hand)	Harvesting (Mech.), Irrigating, Scouting, Thinning, Transplanting, Weeding
V	Horseradish	0.45	2	65	None	Harvesting (Hand)	Scouting, Irrigating, Weeding, Harvesting (Mech.)
V	Leafy greens: Beet (tops), Dandelion, Kale, Mustard Greens, Parsley, Swiss Chard, Turnip greens	0.9	2	10	**Harvesting** (Hand)	Irrigating, **Scouting**	Harvesting (Mech.), Thinning, Weeding, Transplanting
V	Lentils	0.9	2	21	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Transplanting, Harvesting (Mech.)
V	Lettuce (Head and Leaf)	0.9	2	10	Head Breaking (For Head), **Harvesting** (Hand)	Irrigating, **Scouting**	Thinning, Weeding, Transplanting

Site Cat	Use Site/Crop	Rate (lb AI/a)	REI (days)	PHI (days)	Tier I Activities (High)	Tier II Activities (Medium)	Tier III Activities (Low)
V	Melons	0.9	2	3	**Harvesting** (Hand), Pruning (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting
V	Onions, Dry	0.9	2	7	None	Harvesting (Hand)	Irrigating, Harvesting (Mech.), Scouting, Thinning, Weeding, Transplanting
V	Onions, Green	0.9	2	7	None	Banding, Harvesting (Hand), **Thinning**	Irrigating, Scouting, Weeding, Transplanting
V	Peanuts	0.9	2	21	None	Irrigating, **Scouting**	Weeding, Harvesting (Mech.)
V	Peas	0.9	2	1	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Harvesting (Mech.)
V	Peppers	0.9	2	3	Thinning, **Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Transplanting
V	Potato	0.9	2	6	None	Irrigating, **Scouting**	Weeding, Transplanting, Harvesting (Mech.)
V	Pumpkin [e]	0.9	2	3	**Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting
V	Spinach	0.9	2	7	None	Irrigating, Scouting, **Harvesting** (Hand)	Thinning, Weeding, Transplanting, Harvesting (Mech.)
V	Sugar Beet	0.9	2	21	Harvesting (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Harvesting (Mech.)
V	Summer Squash	0.9	2	3	Leaf Pulling, **Harvesting** (Hand)	Irrigating, **Scouting**, Weeding (Hand)	Weeding (Mech.), Thinning, Transplanting, Harvesting (Mech.)
V	Tomato (Fresh Market)	0.9	2	1	Tying, Training, Staking, Pruning (Hand), **Harvesting** (Hand)	Irrigating, **Scouting**	Weeding, Thinning, Transplanting
V	Tomato (Processing/ Canning)	0.9	2	1	Tying, Training, Staking	Irrigating, **Scouting,** Pruning (Hand)	Weeding, Transplanting, Harvesting (Mech.)

[a] Transplant/propagate activity has little potential for exposure in the field, but may present a potential for exposure during the propagation stage in the nursery setting.
[b] Interplanted with non-bearing almonds, plums, prunes, peaches and walnuts (SLN CA-770431).
[c] SLN CA-900034.
[d] SLN CA-860059.
[e] SLN CA-910011.

Typical reentry activities include pruning, scouting, staking/tying, swathing, thinning, transplanting, weeding, and harvesting. Pruning is removal of branches and stems; depending on the crop, pruning may involve minimal or substantial contact with foliage (heavy gloves are usually worn while pruning, in contrast to thinning). Scouts walk through fields examining leaves and other plant parts for evidence of pests or damage

caused by pests. Staking and tying in peppers and tomatoes are done to keep fruit off the ground, and may be done intermittently as plants grow. Swathing in alfalfa is done mechanically, and involves cutting plants and leaving them in windrows (swaths) to dry before harvest. Thinning involves removal of immature fruit or plants; fruit is often thinned by hand, and crops such as lettuce and cabbage are thinned using hoes to remove excess young plants. Transplanting of young plants is done in apples, pears, lettuce and other vegetable crops if initially planted in greenhouses or nurseries. Hand weeding may be done using hoes or by pulling individual plants; roguing in cotton is removal of cotton plants that are diseased or defective, and may also be done by hand. Harvesting is typically done mechanically in field crops, including alfalfa and cotton; hand harvesting is done in fruit and vegetable crops where product appearance is important, including sweet corn. Fresh market tomatoes are hand harvested, and tomatoes for processing/canning are harvested mechanically. Mechanical harvesting by shaking and sweeping to drop and collect fruits/nuts, respectively, has potential for dermal and/or inhalation exposure to dust and debris (falling leaves, branches, produce).

Table 7 was prepared by reviewing methomyl product labels. Maximum application rates and minimum preharvest intervals were listed when they varied within the crops depending on how the crop will be used (e.g. PHI for peas is 1 day for succulent, 5 days for forage and 14 days for hay. In this case PHI of 1 day will be listed in the table). Multiple applications per crop per season (3 to 7) are allowed on most crops (28 on corn) at intervals varying from 0 to 7 days.

Each crop/site was listed along with the respective reentry activities. Tiers of reentry activities are as follows (based on possible exposure):

- Tier I: Most of the body (around >50 % of the body surface) is in contact with residues.
- Tier II: Some of the body (around 25-50 % of the body surface) is in contact with residues (e.g., hands, arms and face; or hands, forearms, feet, and lower legs).
- Tier III: Very little of the body (<25 % of the body surface) is in contact with residues (e.g., hands only; or hands and feet only).

Representative activities in Tiers I and II were determined based on available information about crops/sites or groups of crops. Tier III activities are considered to have exposures that will be less than Tiers I and II activities.

Irrigation can be an activity in Tier I, II or III, depending on the irrigation technique and crop height (18 inches height is the cut-off):

- drip irrigation is Tier III (low);
- sprinkler irrigation
    - for crops 18 inches or taller is Tier I (high),
    - for crops less than 18 inches high is Tier II (moderate);
- flood or furrow irrigation
    - for crops 18 inches or taller is Tier II (moderate),
    - for crops less than 18 inches high is Tier III (low).

Within Tiers I and II, suggested representative activities are shown in **bold**. These are activities that bear the highest exposure potential, and generally should be addressed

specifically in an exposure assessment. For several crops, more than one activity is shown in bold – most often harvesting and scouting. This table is intended for use with all available information and with professional judgment.

Methomyl is registered for use on many crops, and a variety of reentry activities are practiced in each crop. Ideally, it would be advantageous to have exposure estimates for each of the site/activity combinations (scenarios) listed in Table 7. However, little or no exposure data is available for the majority of those scenarios, and several scenarios are likely to result in similar exposures. For this reason, representative reentry exposure scenarios were selected based on available information about the extent of foliar contact for each activity, and the resulting potential for residue transfer. Exposure estimates generated for representative scenarios are anticipated to be the best available for other scenarios. Not all represented scenarios will have identical exposures; but the representative scenario is anticipated to involve exposures similar to, or greater than all represented scenarios. In other words, representative scenarios might overestimate exposure for the represented scenarios, but should not underestimate it. For example, cotton scouting is the representative scenario that covers all reentry activities in cotton and tobacco. That way, protection of workers in representative scenarios would be anticipated to protect other reentry workers in represented scenarios.

Representative scenarios for occupational reentry activities were determined by first grouping crops, then by selecting activities within each group that would be anticipated to have the highest potential for exposure. Crops were grouped by growth form, by comparable application rates, pre-harvest and reentry intervals, and by similar agricultural practices. For example, lettuce and other leafy vegetables are close to the ground, and were considered together. Tomatoes, peppers and eggplants, which have fruit above ground, were assessed as a group, as were root crops such as potatoes, carrots, and peanuts, which are underground. Strawberries were not considered because the registrant withdrew methomyl use on strawberries. These crop groups are summarized in Table 8.

Table 8. Crop groups for selecting representative reentry scenarios[a, b].

Category [c]	Representative Crop	Crops included in this group
FC	Alfalfa	Alfalfa, Bermuda grass, sorghum, Sudan grass; barley, oats, rye, wheat; soybeans (incl. SLN [d])
FC	Corn, Sweet	Corn, human consumption and forage-fodder
FC	Cotton	Cotton, tobacco
FC	Turf	For use on sod farms only. Only crop in this group
FN	Apple	Pome, citrus and stone fruits: Avocado, apples, nectarines, peaches; pomegranate; grapefruit, lemon, orange, tangelos, tangerines; all non-bearing fruit, grape and nut nursery stock (field grown) (SLN)
FN	Blueberry	Only crop in this group
V	Anise	Mint, parsley, fennel
V	Asparagus	Only crop in this group
V	Beans	Beans (dry and succulent) all types (incl. SLN), lentils, peas
V	Cabbage	Bok Choy, broccoli, broccoli raab (SLN), Brussels sprouts, cabbage, cauliflower, Chinese broccoli (SLN), Chinese cabbage
V	Cucumber	Cantaloupe, cucumbers, melons, pumpkins (SLN), squash and watermelon
V	Lettuce	Celery, chicory, collards, dandelion, endive (escarole), head lettuce, kale, leaf lettuce, mustard greens, spinach, Swiss chard, turnip greens
V	Onion, green	Onion dry, onion green and garlic
V	Potato	Root vegetables: Carrot, horseradish, peanuts, potato, sugar beet, table beets, turnip
V	Tomato	Eggplant, peppers, tomato

[a] Crops were grouped by growth form, by comparable application rates, pre-harvest and reentry intervals, and by similar agricultural practices.
[b] Rows are sorted by site category.
[c] FC = Field Crops; FN = Fruits and Nuts; OT = Ornamentals; V = Vegetables.
[d] SLN = Special Local Needs registrations.

After crops were grouped, representative reentry exposure scenarios were selected for each group based on available information about the extent of foliar contact for each activity (Table 9).

Table 9. Representative agricultural reentry scenarios for methomyl[a].

Crop [b]	Activity [c]	Represented crops/sites and activities [d]
Alfalfa	Scouting (REI: 2)	Cereal grains, hay and grass crops; soybeans (incl. SLN); all activities
Anise	Hand Harvest (PHI: 7)	Mint, anise, parsley, outdoor field plants (nursery grown); harvest
Anise	Scouting (REI: 2)	Mint, anise, parsley, outdoor field plants (nursery grown); all activities except harvest
Apple	Thinning (REI: 3)	All tree fruits and nuts; all activities
Asparagus	Scouting (REI: 2)	All activities in asparagus
Beans, Succulent	Hand Harvest (REI: 2)	All activities in beans, peas and soybeans
Blueberry	Hand Harvest (PHI: 3)	All activities
Cabbage	Hand Harvest (REI: 2)	Broccoli, cauliflower, etc.
Corn, Sweet	Hand Harvest (REI: 2)	Corn, human consumption and forage-fodder; all activities
Cotton	Scouting (REI: 3)	Cotton, tobacco; all activities
Cucumber	Thinning (REI: 2)	All melons, pumpkins, squash; all activities
Lettuce	Scouting (REI: 2)	Celery, collards, etc., leafy greens; all activities except harvest
Lettuce	Hand Harvest (PHI: 10)	Celery, collards, etc. leafy greens; harvest
Onion, green	Thinning (REI: 2)	Onion (dry, succulent, green), garlic; all activities
Potato	Scouting (REI: 2)	All root vegetables; all activities
Tomato	Hand Harvest (REI: 2)	Eggplant, tomato, pepper; all activities
Turf	Transplanting (REI: 2)	All occupational reentry activities in sod

[a] Maximum application rate allowed on all crops is 0.9 pounds of active ingredient per acre (lb AI/a), except corn (0.45 lb AI/a), cotton (0.68 lb AI/a).
[b] Representative crops from Table 8. Sorted by alphabetical order.
[c] PHI, Pre-harvest interval, days; REI, days.
[d] All scenarios covered by the representative crop and activity are anticipated to have exposure equivalent or less than that of the representative scenario. See Table 8 for specific crops covered by each scenario.

For most crops, hand harvesting is the activity having the greatest contact with treated foliage, which can result in the highest exposure potential. However, if the PHI was longer than the REI, other Tier I reentry activities were selected as representative (e.g. cucumber, training, Table 9). If the PHI is much longer than the REI, then less foliar residue is available for transfer at harvest, which would result in a lower actual exposure. In this case, a second reentry activity (tier II) also is included to ensure that the scenario having the highest exposure estimate is assessed (e.g. lettuce, anise, scouting). For many crops the PHI is shorter than the REI. In this case, if hand harvesting is chosen as representative scenario, it will fall under the requirements of the REI duration (e.g. corn, Tables 7 and 9). Alternatively, an activity other than harvesting can be selected as representative scenario (e.g. sod, Tables 7 and 9).

The WPS REI for methomyl is generally between 2 and 7 days depending on the crop. Methomyl is typically applied several times per season mostly during the summer months

(Fig. 3). The inhalation exposure accounted for less than 1% of the total exposure at reentry activities in vineyards (Merricks, 1989). As a result, only dermal exposures were evaluated in the post application worker exposure assessment.

Reentry workers are not required to wear protective clothing unless entering before expiration of the restricted entry interval (REI). As a matter of fact, in California's warm climate fieldworkers often do not wear protective clothing since reentry work often occurs in warm or hot weather and for several hours each day. Consequently, fieldworker exposure estimates were based on the assumption that no protective clothing or equipment was used.

Other assumptions made in preparation of reentry worker exposure estimates, were as follows:

1. Work day is 8 hours.
2. Dermal absorption is 50% (Donahue, 1996).
3. Average body weight is 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al.*, 1993a).
4. A person is assumed to do the same job for 40 years, life expectancy is assumed to be 75 years.
5. Maximum application rate of 0.9 lb AI/a allowed on product labels for most crops (Table 7) was assumed.
6. Seasonal use of 6 months per year on most crops was assumed (Figure 3), except lettuce where the use was assumed to be 12 months per year (see Exposure Assessment section).

Considerations for SLN crops:
Reentry activities for maintaining beans/soybeans interplanted with non-bearing almonds, plums, prunes, peaches and walnuts will be covered by the respective scenarios for field grown beans and soybeans according to Section 3 labels since the latter require higher application rates than the SLN label.

Harvesting (Tier I activity) of existing almonds, plums, prunes, peaches and walnuts where beans and soybeans are interplanted is not expected from those trees since they are non-bearing by label requirement. However, crop maintenance will require other Tier I reentry activities such as thinning of plums, peaches. Those scenarios will be covered by a different fruit/nut tree scenario (apple).

Non-Occupational and Non-Crop Occupational Scenarios

When methomyl is applied to agricultural fields, bystanders (people who live, work, or otherwise spend time near fields where pesticides are being applied or have been applied) can be exposed to airborne pesticide residues. Therefore, the potential for inhalation exposure of bystanders being in vicinity to methomyl agricultural applications will be evaluated in this document.

One possible non-occupational reentry scenario is "U-Pick" or similar operations. Methomyl labels state that the restricted entry interval and preharvest interval for the

respective crops must be followed in those cases. Therefore, a short-term non-occupational dermal exposure to methomyl-treated "U-Pick" crops should be considered. Table 10 lists California crop sites that are listed as having "pick-your-own" farms by Pickyourown.org (http://www.pickyourown.org/CAharvestcalendar.htm) and are also on methomyl labels. Rows are sorted by site category (Site Category: FC = Field Crops; FN = Fruits and Nuts; V = Vegetables), then by use sites.

Table 10. "U-Pick" non-occupational reentry scenarios in California.

Site Category	Use Site	Application Rate (lb AI/a)	REI (days)	PHI (days)
FC	Corn, Sweet	0.45	2	0
FN	Apples	0.9	3	14
FN	Blueberries	0.9	2	3
FN	Nectarines	0.9	3	1
FN	Peaches	0.9	4	4
V	Asparagus	0.9	2	1
V	Green Beans	0.9	2	1
V	Peas	0.9	2	1
V	Tomatoes	0.9	2	1

Other non-crop occupational and non-occupational use sites include animal premises, barns, farms, food-handling facilities (incl. bakeries; eating establishments; food/beverage processing, marketing, storage and distribution facilities), dumpster areas, commercial storages or warehouses, commercial, institutional or industrial areas. Reentry or working in those out-doors and in-door areas and facilities where fly baits have been applied, are presumably of similar magnitude between those locations. Having in mind the low vapor pressure of methomyl (5.6×10^{-6} mm Hg), those activities are anticipated to have low potential for inhalation exposure for workers/bystanders. The risk for incidental dermal or oral exposure to fly baits seems also low. For this reason reentry scenario for workers or bystanders (visitors) in facilities when methomyl bait has been spread will not be assessed separately, but are covered by bait handler exposures.

Another possible non-occupational, residential exposure scenario is the dermal and inhalation exposure to a pesticide in water during bathing, showering, or during swimming in public pools/spas.

Residential Handler and Reentry Scenarios

Residential handler and reentry scenarios are not considered in this document because methomyl products are intended primarily for occupational use only and not for homeowner use.

ENVIRONMENTAL CONCENTRATIONS

Air

As part of DPR's comprehensive risk assessment, the EAD addresses scenarios where members of the public can be exposed to airborne pesticide residues. Bystander exposures are possible to individuals who are spending time next to fields during or following

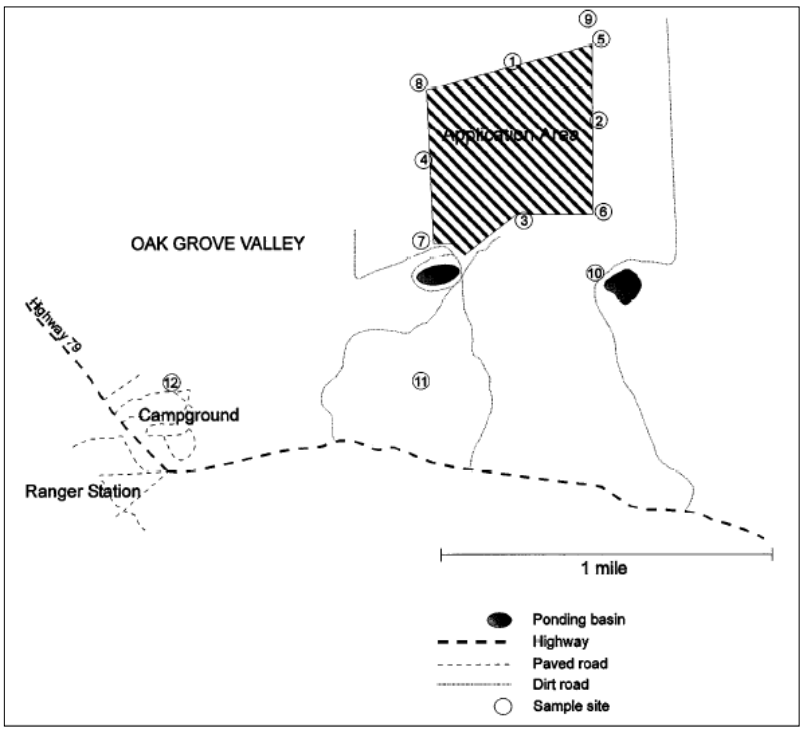
pesticide applications. Also, community exposures to ambient air concentration of pesticide are also possible in areas that are far from application sites. Individuals can be handlers, reentry workers, or members of the public (handlers and reentry workers can also be bystanders if they work adjacent to pesticide application).

Knaak et al. (Knaak *et al.*, 1980) measured the air concentrations of methomyl associated with closed transfer/mixing/loading and ground application (rear mounted spray boom). Methomyl formulations were water-soluble powder in water-soluble bags and liquid concentrate. One ground applicator was monitored using a glass impinger (0.014 m^3/min) that was tractor mounted near the breathing zone of the driver. Air concentrations of methomyl for a worker engaged in closed transfer/M/L was monitored using an air sampler (0.566 m^3/min) held near his breathing zone. Methomyl was not detected in air samples from the breathing zones of operators during normal closed transfer, mixing-loading operations. During ground application, methomyl air concentration of up to 8 $\mu g/m^3$ was found in applicator working zones (Knaak *et al.*, 1980). This study could not be used for applicator inhalation exposure as there was no direct correlation between the amounts of methomyl handled and the measured air concentrations of methomyl in applicators breathing zone.

DPR's Environmental Hazards Assessment Program (EHAP) monitored the air concentrations of methomyl during an aerial application to an 80-acre potato field near Oak Grove, San Diego County (Segawa, 1998). The application took place on August 9, 1996. Methomyl, esfenvalerate, and mancozeb were applied in a tank mix at rates of 0.73, 0.5, and 1.8 pounds active ingredient per acre, respectively. The application occurred in the morning, using a helicopter equipped with a 32-foot boom. EHAP established eight sampling sites around the perimeter of the treatment site (Fig. 5). Four of these sites (sites 1, 2, 3, and 4) were at 10 m from the edge. The remaining four sampling sites (5, 6, 7 and 8) were located 40 m from the corners of the field. EHAP placed additional samplers on a hill above the filed (site 10), and two residences (sites 9 and 11), and a campground adjacent to the ranch (site 12). These additional samplers were between 80-1500 m from the field. EHAP collected air samples using high-volume air samplers calibrated to one cubic meter per minute. Each air sampler was positioned approximately 1.2 meters above ground level and fitted with a glass jar containing XAD-2 resin. Samples were collected for approximately 36 hours before, during and after application: one 12-hour interval before application to measure any background levels, one sample (2.75 hour) during application (application lasted approximately one hour), and two consecutive 10-11-hour samples following application. The air samplers were protected from the direct application spray with plastic bags (Segawa, 2008). Meteorological data (wind direction and speed, air temperature, and relative humidity) was collected for 24 hours prior to application and the duration of the monitoring period. Values for these variables were recorded at one-minute intervals but not reported in the Memorandum by Segawa (Segawa, 1998). Methomyl was extracted from the XAD-2 resin with ethyl acetate and then analyzed using a high-pressure liquid chromatograph equipped with a fluorescence detector and post-column derivatization system. Results are reported in micrograms per cubic meter ($\mu g/m^3$) of air; with application period limit of detection (LOD) 0.0008 $\mu g/m^3$ and post-application period LOD 0.0002 $\mu g/m^3$ for methomyl (Segawa, 2008). LOD is the minimum

concentration of an analyte that, in a given matrix and with a specific method, can reliably be identified and reported to be greater than zero. In accordance with DPR policy samples below LOD are reported as one-half of the detection limit (Andrews, 2000).To account for chemical breakdown of the parent compound, EHAP adjusted the sampling results by using the data from field spikes.

Figure 5. Locations of sampling sites for the potato field air monitoring in San Diego County, 1996, from (Segawa, 1998).



Background samples collected the day before application contained no detectable methomyl. Table 11 shows the methomyl monitoring results during and following approximately 24 hours after application. Air concentrations ranged from no detectable to 2.4 µg/m^3. The highest concentrations were detected during application, but only three of the 12 sampling sites were positive. Air concentrations following application were lower, but a greater number of sampling sites were positive, 11 of 12. These results are also consistent with the weather patterns recorded during the monitoring period. During application the wind was from the southeast and the positive sites were located to the northwest. Following application winds shifted direction several times. With no predominant wind direction methomyl was detected all around the field. Air concentrations decreased over time. The highest concentration detected during the first sampling period was 2.4 µg/m^3, and 1.6 µg/m^3 during the second sampling period. The highest concentration detected 12 - 24 hours post-application during the third sampling period was 1.1 µg/m^3. Air concentrations at the remote sites (sites 9, 10, 11, 12) were lower than concentrations detected next to the field. The highest concentration detected at a remote site (more than 80 meters from the application site) was 0.04 µg/m^3 (Segawa, 1998).

The methomyl application rate used for this study was 0.73 lb AI/a. This is 1.23 times lower than the maximum application rate allowed on methomyl labels (0.9 lb AI/a). Bystanders near a field receiving a maximum application rate would be expected to be exposed to 0.9/0.73=1.23 times higher air concentration of methomyl. Hence all methomyl air concentrations were adjusted by a factor of 1.23 to account for the sub-maximal application rate in the study. The data in Table 11 was also corrected for Non-Detects (ND) as described in the footnotes to the table.

Table 11. Methomyl air concentrations during three sampling periods beginning with the start of the application (6:45 am), Oak Grove (San Diego County), August 9, 1996. Modified from (Segawa, 1998).

Sampler Location [a]			Methomyl in air [b] (µg/m^3)			Methomyl in air, corrected [c] (µg/m^3)			24-h TWA (µg/m^3)[e]
Site	Direction	Distance (m)	06:45-09:30 Application (2.75 hrs)[d]	09:30-20:30 Post-application (11 hrs)	20:30-07:00 Post-application (10.5 hrs)	06:45-09:30 Application (2.75 hrs)	09:30-20:30 Post-application (11 hrs)	20:30-07:00 Post-application (10.5 hrs)	
1	North	10	0.42	0.37	0.09	0.5178	0.4562	0.1110	0.3616
2	East	10	ND	0.38	0.002	0.0005	0.4685	0.0025	0.1572
3	South	10	ND	0.96	0.30	0.0005	1.1836	0.3699	0.5180
4	West	10	1.99	1.64	1.11	**2.4534**[f]	**2.0219**	**1.3685**	**1.9479**
5	NE	40	ND	0.04	ND	0.0005	0.0493	0.0001	0.0168
6	SE	40	ND	0.40	0.01	0.0005	0.4932	0.0123	0.1687
7	SW	40	ND	1.11	0.52	0.0005	1.3685	0.6411	0.6701
8	NW	40	2.44	0.42	0.44	**3.0082**	0.5178	0.5425	1.3562
9	NE	80	ND	ND	ND	0.0005	0.0001	0.0001	0.0006
10	SE	270	ND	0.03	0.002	0.0005	0.0370	0.0025	0.0134
11	SW	650	ND	0.04	0.002	0.0005	0.0493	0.0025	0.0175
12	SW	1460	ND	0.002	ND	0.0005	0.0025	0.0001	0.0012

[a] Direction and distance relative to the edge of the field. See Fig. 5 for exact locations.

[b] Original data from (Segawa, 1998).

[c] Original data was corrected for the following:

- By a factor of 1.23 for maximal application rate (0.9 lb AI/a) *vs*. actual application rate used in study (0.73 lb AI/a) (0.9/0.73 =1.23).
- For Non-Detects (ND). In accordance with DPR policy (Andrews, 2000) all NDs were replaced by 1/2 LOD = 1/2 0.0008 µg/m^3 = 0.0004 µg/m^3 for the application period, and by 1/2 LOD = 1/2 0.0002 µg/m^3 = 0.0001 µg/m^3 for the post-application period.

[d] Duration of sampling period shown in parentheses.

[e] TWA=Time weighted average of air concentrations that were already corrected (see footnote [c] above).

[f] Values in bold are used for Exposure assessment.

At the request of DPR, the California Air Resources Board (ARB) staff conducted two studies for sampling airborne concentrations of methomyl in 2007. The first study was performed in Fresno County in October 2007. Air samples were collected before, during and after aerial application of methomyl on corn grown for human consumption (Adler, 2009). The application rate was not reported. Quality control results raised questions

about the validity of the data: although laboratory spikes and field study trip spikes reported good recoveries (80-90%), field spike recoveries were very poor - between 305 and 192%. Also, the collocated samples collected during the field study reported high degree of variability (+-50%). The study author recommended that the data reported in this study should not be used for decision making purposes. The second study was an ambient air monitoring performed over a six weeks period in July-August 2007 (Adler, 2008). The study took place in Fresno, Kings and Tulare Counties. The monitoring sites were located in areas with historically high use of methomyl. One hundred eighty two (182) twenty four (24) hour integrated ambient air samples were collected from six different locations throughout the three counties. Only five samples - from the Mendota, Fresno County - monitoring site were greater than the method LOQ of 1.5 ng/m^3. These samples varied from 3.2 to 8.8 ng/m^3. A total of thirty ambient air samples were taken in Mendota. The laboratory spikes and field study trip spikes reported good recoveries: 103% and 100%, respectively. However, the field spike recoveries were very low, ranging from 23% to 62%, and were 45% on average, thus raising questions about the data quality. These two studies will not be used for estimating human exposures.

Four other studies deal with methomyl air monitoring data but none of them could be used for estimating worker or bystander inhalation exposures because all were below the detection limit. The first study was conducted by EHAP in 1985, and was designed to determine the levels of several agricultural chemicals present in ambient air collected at residential sites adjacent to agricultural lands. The study was conducted in June, which is historically a high pesticide use month in the Salinas Valley. Methomyl was not detected at the minimum level of detection (MDL) of 0.035 µg/m^3 (96% spike recovery) (Sava, 1985). The second and third study are summarized in the report of Kollman on pesticide air monitoring data that have been collected and published in reports by the California Air Resources Board (ARB) from 1986 to 1995 (Kollman, 1995). Ambient air monitoring for methomyl was conducted four days a week throughout the month of August 1987, at 5 sites in Fresno County (in Selma, Parlier, San Joaquin and Tranquility). The background site was located at the ARB air monitoring station in Fresno. Monitoring was scheduled to coincide with expected applications to grape vineyards and alfalfa. None of the 98 samples analyzed had detectable-residues of methomyl (minimum detection limit 0.02 µg/m^3). Application site monitoring was conducted in September 1989 before, during, and for 72 hours after an application to a lettuce field in Fresno County. Methomyl was applied by ground equipment at the rate of 0.5 lb AI/a. All 20 samples analyzed had no detectable methomyl residues (minimum detection limit 0.19 µg/m^3) (Kollman, 1995). In the fourth study, the under-canopy air in grape vineyards was sampled at 7 and 18 days post methomyl application. Methomyl was applied at a rate 0.675 lb AI/a. Sampling was done thru two air pumps (air flow 1.9 L/min) located up inside the foliar canopy. The MDL for the two pumps was 0.57 and 0.77 ng/L, respectively. A total of 20 air samples were collected but all were below the MDL. In addition to air samplings, leaf punch samples were taken on the same day as the air samples. The leaf punches confirmed the presence of methomyl in the vineyards (DFR 0.026 µg/cm^2) (Fong, 1989).

Ground and Surface Water

When considering representative non-dietary residential exposure scenarios, one must have in mind the dermal and inhalation exposure to an AI in drinking water supplies (which may be drawn from either surface water, ground water, or both). Such exposure can occur during bathing or showering, or during swimming in public pools/spas.

Data on pesticide concentrations in ground and surface water in California can be found in many databases. The Environmental Monitoring Branch (EM) of DPR conducts surface and ground water monitoring of pesticides used in the state of California (http://www.cdpr.ca.gov/docs/emon/pubs/index.htm). Another useful database is that of the US Geological Survey National Water Quality Assessment Program (USGS NAWQA).

- **Ground water**

Environmental Monitoring Branch (EM) of DPR maintains a statewide database of California ground water wells sampled for pesticide active ingredients (http://www.cdpr.ca.gov/docs/emon/grndwtr/gwp_sampling.htm). The wells include public and private drinking water wells and/or wells of unknown type. A search of the annual reports (http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps.htm?filter=grndwater) showed that between 2004 and 2012 an average of 588 wells in over 40 counties were sampled for methomyl annually. This search did not find confirmed methomyl detections in well samples (Schuette *et al.*, 2004; Schuette *et al.*, 2005; Nordmark *et al.*, 2006; Nordmark *et al.*, 2008; DPR, 2009a; DPR, 2010a; DPR, 2011a; DPR, 2012b; DPR, 2013), suggesting that well water contamination is unlikely.

- **Surface water**

The Environmental Monitoring Branch (EM) of DPR conducts surface water monitoring and reporting of pesticides used in the state of California (http://www.cdpr.ca.gov/docs/emon/pubs/index.htm). The original data can be found in the DPR Surface Water Database (http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdata.htm). The data contains monitoring results for pesticides in samples taken from California rivers, creeks, urban streams and agricultural drains. As of December 2013, the database contained results from 75 studies conducted by federal, state, and local agencies, private industry, and environmental groups. Nearly 13,000 samples were taken in 50 counties (over 900 sampling sites) between August 1990 and October 2010. The database contains over 384,000 chemical analysis records. Each chemical analysis record is the result of one analysis for a pesticide active ingredient or breakdown product (http://www.cdpr.ca.gov/docs/emon/surfwtr/surfdes.htm). The query of the database for methomyl returned 3390 samples tested for methomyl (query on December 11, 2013). Of those, 369 samples or 11%, had methomyl detections in the range 0.046-55.3 µg/L (1 µg/L = 1 ppb), the rest had no detections. The LOQ of the detection methods ranged from 0.017 to 0.7 µg/L.

- **US Geological Survey National Water Quality Assessment Program**

The extensive databases of the US Geological Survey (USGS) (http://pubs.usgs.gov/of/index-water.html) including the one dedicated to the water resources of California (http://ca.water.usgs.gov) were searched for detections of methomyl. The most recent analysis is a compilation of USGS water and sediment data in

the Sacramento-San Joaquin Delta region collected between 1990 and 2010 (Orlando, 2013). Of the 323 samples analyzed for methomyl, 13 water samples (4%) had estimated methomyl detections in the range 0.004-0.209 µg/L, and only one of the water samples collected between 2003 and 2010 was positive for methomyl (0.025 µg/L).

Panger and Echeverria (Panger and Echeverria, 2007) studied the Surface water monitoring data for the State of California from the USGS National Water Quality Assessment (NAWQA) program. A total of 346 water samples were analyzed for methomyl. They found that of these samples, 18 (5.2%) had positive detections of methomyl at four sites. The maximum concentration detected was 0.67 µg/L in the Salt Slough at Highway 165 near Stevinson, CA. Lower concentrations of methomyl were also detected in the San Joaquin River near Vernalis, CA (3 samples ranging in concentration 0.0052 – 0.0723 µg/L), and the Orestimba Creek at River Road near Crows Landing, CA (10 samples ranging in concentration 0.0043 – 0.33 µg/L). The reported levels of detection (LODs) ranged within several orders of magnitude: from 0.0044 µg/L to 1.22 µg/L (Panger and Echeverria, 2007). The time frame of the samplings is not specified in this report and all positive detections were within the concentration range of the surface water findings discussed above.

In conclusion, there is no reliable evidence of methomyl presence in California ground waters in the past 20 years (after 1993). The data on methomyl contamination of surface waters is spotty and the majority of the detections were in the low µg/L range. For this reason the scenario for human exposure to methomyl in water during bathing, showering, or during swimming will not be assessed in this document. This is consistent with the USEPA approach to consider swimmer scenario only for pesticide products that are directly applied to water (USEPA, 1997b). Methomyl labels state that the product should not be directly applied to water. In similar situations, DPR has previously determined swimmer exposure to pesticides in surface water to be extremely low, and the risk of such exposure negligible (Beauvais *et al.*, 2010).

Dislodgeable Foliar Residues

Post application dermal exposure resulting from contact with contaminated surfaces can be estimated by direct measurement with dosimeters, or it can be estimated indirectly using a transfer coefficient (TC) and dislodgeable foliar residue (DFR) measurements.

The TC is the rate of transfer from a contaminated surface to a person. TC is usually expressed in cm^2/hr and can be thought of as the area of surface whose total DFR would be transferred to the person in one hour of activity. TC depends on the amount and intensity of contact with the contaminated surface, and thus is highly activity-specific.

Dislodgeable foliar residue (DFR) is defined operationally as the pesticide residue that can be removed from both sides of treated leaf surfaces using an aqueous surfactant. DFR is assumed to be the portion of an applied pesticide available for transfer to humans from leaf and other vegetative surfaces. The DFR is reported as residue per leaf area (µg/cm^2). Measurements of DFR can be used, along with the appropriate transfer coefficient, to estimate the amount of pesticide adhering to clothing and skin surfaces following entry

into a previously treated field. DFRs dissipate (decrease) over time, due to various factors such as volatilization, wash-off in rain or irrigation water, absorption into plant, degradation into other compounds, etc.

Direct dosimetry studies for methomyl exist only for grapes and will be discussed in the Exposure Assessment section.

DFR samples are usually collected by standardized leaf-punch technique. Samples consist of forty 2.52 cm (1 inch) diameter leaf punches. Methomyl is dislodged from samples with aqueous surfactant solution, and extracted with dichloromethane. The extracts are analyzed by HPLC using a fluorescence or UV detector.

The amount of dislodgeable foliar residues after methomyl application has been examined for various crops. Studies used for exposure estimates were evaluated for acceptability based on criteria described in Iwata *et al.* (Iwata *et al.*, 1977) and USEPA (USEPA, 1996). For example, each was performed under climate conditions typical of California growing season; there were no rain events during the study; samples were collected on more than one day extending at least through the restricted entry interval (REI); replicate samples were collected; residues were dislodged from leaf surfaces with a detergent solution (rather than an organic solvent); and the application rate was at or near the maximum stated on the product label for the crop (although application rates might not affect the dissipation rate, the relationship has not been studied for methomyl).

DFR values at Day 0 and at the REI for each crop used in acute exposure estimates were back calculated from equations using study data, as explained in a policy memorandum (Andrews, 2000). The log-linear regression model was used to fit the data (Andrews, 2000) using the following equation:

$$\ln DFR_t = \ln (DFR_0) - kt \qquad (1)$$

where k is the slope of the log-linear, first-order dissipation curve, t represents the time interval (days) and ln is a normal logarithm (with base e). Day 0 refers to the day of application, Day 1 is the first post-application day, and subsequent post-application days are similarly identified. Because the experimentally determined DFR at day 0 (DFR_0) are often not very reliable, DFR_0 was not used for the regression analysis. The dissipation half-life $T_{1/2}$ can be determined from the slope of the regression curve:

$$T_{1/2} = (\ln 0.5)/k \qquad (2)$$

The group of Ware studied methomyl dissipation on cotton for several years in a row (Ware *et al.*, 1974; Cahill *et al.*, 1975; Ware *et al.*, 1978; Ware *et al.*, 1980; Ware *et al.*, 1983). All trials were conducted in Arizona during the months of July or August with no rainfall under meteorological conditions similar to California. With the exception of (Ware *et al.*, 1983) all studies were acceptable and were used for half-life determination and/or DFR values for the purposes of this EA.

The first study was performed in July on a cotton farm near La Palma, AZ (Ware *et al.*, 1974). Methomyl spray was applied by a ground equipment at a rate of 0.75 lb AI/a. Triplicate leaf samples were collected in each treated and one control plot at 0, 24, 48, 72, and 96 hours after treatment. Each sample consisted of 100 36-mm diameter leaf disks. Extraction was with distilled water. The analytical method, method sensitivity and recovery were not reported.

In the study of (Cahill *et al.*, 1975) methomyl was applied at a rate of 0.5 lb AI/a using a ground sprayer. The cotton plots were located near La Palma, AZ and treated in August 1973. Triplicate leaf samples were collected in each treated and one control plot at 0, 24, 48, 72, and 96 hours after treatment. Each sample was composed of 75 leaves, no stems. Cotton leaf surface was determined by obtaining imprints on blueprint paper of leaves collected in the same manner as those to be extracted. The leaf samples were extracted with tap water. No information was provided on the analytical method, sensitivity and recovery.

Ware et al. (Ware *et al.*, 1978) reported the dislodgeable residues of various insecticides on cotton foliage over a 4-day period after application. Methomyl was applied at a rate of 0.5 lb AI/a by ground sprayer to cotton test plots located at La Palma, AZ. The application took place in August 1975 and no rain was reported during the experiment. Leaf disc samples, 25 mm diameter, were collected in triplicate from each plot, using a leaf punch at 0, 24, 48, 72 and 96 hours after treatment. Each sample consisted of 100 leaf discs. Each 100-disc methomyl sample was extracted by tap water. The analytical method, method sensitivity and recovery were not reported.

In July 1979, Ware et al. (Ware *et al.*, 1980) studied the dissipation of seven insecticides on cotton foliage over 96-h post-application interval. Test plots were located near Marana, AZ. Applications were performed using a man-pulled ground rig. Methomyl was applied at a rate of 0.45 lb AI/a. Triplicate samples were collected in each treated plot at 0, 24, 48, 72, and 96 hours after treatment. Each sample consisted of 100 leaf discs, 2.54-cm diameter. Each methomyl sample replicate and controls were dislodged with tap water in the field and analyzed by gas liquid chromatography with flame photometric detection. The method recovery was 70-83%.

The last trial of the group of Ware (Ware *et al.*, 1983) contained very few quality data points that were not enough to construct a meaningful dissipation curve, and the data from this study was not used.

Two studies of methomyl DFR on corn were performed at the Worker Health and Safety Branch of DPR. In the first trial, methomyl decay on two sweet corn fields in Riverside County, CA was studied 7-9 days prior to harvest, in May (Maddy *et al.*, 1976c). The first application of Field 1 was made May 14 with Lannate L and Lannate 90WP using 0.33 lb AI/a. The control sample was taken on May 17, finding trace amounts of methomyl. Field 1 was treated a second time with the same amount of pesticide by ground rig on May 18. A single sample of sweet corn leaves was taken from Field 1 at intervals of 5 and 24 hours after second application. Duplicate DFR samples were taken thereafter at 2, 3, 7 and 9

days post-application. 0.33 lb AI/a was applied to Field 2 on May 20 by ground rig. Duplicate DFR samples were collected from Field 2 about 18 hours and 4 days after application. Each sample consisted of about 100 leaf discs, 2.5 cm in diameter. Residues were dislodged in aqueous surfactant solution and analyzed by HPLC. No information was provided on the LOQ and recovery. There was no precipitation during the study period.

The second corn study was conducted in Orange County, CA (Gibbons and Richmond, 1985). Four sweet corn fields were treated with methomyl at 0.45 lb AI/a. Between two and seven applications were made to each field. Triplicate samples were taken prior to application and 1 and 2 days after the application. Each sample consisted of 48 leaf discs, 2.54 cm in diameter. The dislodgeable residues were removed by aqueous surfactant solution and analyzed by HPLC. The season of the study, rainfall conditions, analytical method LOQ and recovery were not reported.

Methomyl residues following application to head lettuce were studied by Maddy et al. (Maddy *et al.*, 1976a; Maddy *et al.*, 1976b; Maddy *et al.*, 1977). In the first study, methomyl was applied by air equipment to two lettuce fields in Imperial County, CA, in February 1975 (Maddy *et al.*, 1976a; Maddy *et al.*, 1977). The application rate was 0.68 lb AI/a and 0.45 lb AI/a for Field 1 and Field 2, respectively. Phosdrin was applied to the fields as well. Duplicate DFR samples were taken at intervals beginning 1 hour after application and then at approximately 24-h intervals for five days. Each sample consisted of approximately 100 leaf discs, 2.5 cm in diameter. Methomyl residues were dislodged with aqueous surfactant solution and analyzed by HPLC. The method sensitivity and recovery were not reported. There was no precipitation during the study.

The second lettuce study was conducted in Imperial County, CA in January 1976 (Maddy *et al.*, 1976b). Samples were taken immediately after the application (0.68 lb AI/a methomyl) and then at approximately 24-h intervals for four days. Thimet and Thurcide were also applied to the filed at the same time. Three samples, each consisting of about 100 leaf discs, 2.5 cm in diameter, were collected form the leaves of young lettuce plants. There was no rainfall during the study period. The dislodgeable residues were extracted by aqueous surfactant solution and analyzed by HPLC. The method sensitivity and recovery were not reported.

In response to USEPA data call-in, the Agricultural Reentry Task Force (ARTF) reported methomyl residues on lettuce and cabbage (Bruce, 2001). The study was designed to evaluate the statistical distribution of DFR values 1 day after pesticide application and to compare the initial DFR levels (on the day of application) on two crops with different leaf types, among other objectives. The field portion of the study was conducted in the San Joaquin Valley near Porterville, CA, in February 2001. Extraction was in aqueous surfactant solution (0.01% Aerosol OT 75). Methomyl was applied at 0.9 lb AI/acre using a tractor-mounted boom sprayer. Each DFR sample consisted of 40 leaf punches (1 inch diameter) for a total of ~400 cm^2 leaf surface area (counting both sides of the foliage). Leaf samples obtained on the day prior to application from control plots served as laboratory controls and fortifications. No adjustments were made to row data for any

laboratory recovery results since individual recoveries were generally 90% to 110% throughout the study. Field fortifications were deemed unnecessary since previous ARTF field fortification data indicated good methomyl stability. Extracts were analyzed by HPLC using post-column derivatization/fluorescence detection. The analytical LOQ was 1 µg/DFR sample.

Kiigemagi and Deinzer (Kiigemagi and Deinzer, 1979) studied the dislodgeable residues of methomyl on mint foliage. The study was done in August in Oregon. Methomyl 90% WSP was applied by air at 0.9 and 1.8 lb AI/a (the latter being twice as much the label-allowed application rate). Leaf discs, 1.3 cm in diameter, were punched from 100 leaves per sample. Leaf samples were collected at 4, 24 and 48 h post-application, extracted in water–based surfactant solution, and analyzed by gas chromatography using flame photometric detector in the sulfur mode. Laboratory fortified samples indicated a 78% average recovery, and the data was corrected for the analytical recovery. The sensitivity of the analytical method was 0.01 $\mu g/cm^2$. The methomyl residues found in the samples at two tested application rates were proportional to the amount of methomyl applied, and the study deemed useful for exposure assessment.

Other dissipation and DFR studies could not be used to estimate exposure following methomyl applications because they did not satisfy the acceptability criteria as laid out in (Iwata *et al.*, 1977; USEPA, 1996). E.g. DFR values were expressed in *ppm* without the ability to convert them to $\mu g/cm^2$, and/or data were collected only for the first 24 hours post-application which makes them unreliable (Pease, 1971b; Pease, 1971a; E.I.DuPontdeNemours&Co, 1976a; E.I.DuPontdeNemours&Co, 1976b; E.I.DuPontdeNemours&Co, 1976c; Leidy *et al.*, 1977). Some of those data sets could be used only to calculate the dissipation half-life (E.I.DuPontdeNemours&Co, 1976a; E.I.DuPontdeNemours&Co, 1976b; E.I.DuPontdeNemours&Co, 1976c; Leidy *et al.*, 1977) and are outlined below.

A replicated field experiment was conducted at two locations in North Carolina in May and July 1974 to determine the disappearance of methomyl from tobacco (Leidy *et al.*, 1977). Experimental plots at each location were treated with 0.5 b or 1 lb AI/a methomyl. A sample was taken from each control plot (untreated) before spraying, and samples were collected from treated plots within 10 min after spraying. Subsequently, leaf samples were collected from all plots 1, 3, 5, and 9 days after spraying. Each sample contained two hundred 5-cm diameter leaf discs. Methomyl was extracted with chloroform/methanol and analyzed by gas chromatograph equipped with a flame photometric detector in the sulfur mode. Recoveries of known amounts of methomyl added to green tobacco (recoveries) and aqueous solutions containing no tobacco (spikes) were 66% and 61%, respectively. Rainfall occurred on day 6 in both locations so only data from days 1, 3 and 5 were used to construct the dissipation curve which correlated very well with the predicted values. DFRs were presented in ppm and were not used for exposure calculations.

Two registrant studies dealt with the dissipation of methomyl dislodgeable residues on peach, nectarine and orange leaves (E.I.DuPontdeNemours&Co, 1976b; E.I.DuPontdeNemours&Co, 1976c). One to four sprayings of Lannate were made to

Naval and Valencia oranges, and to peaches at a rate 1.8 lb AI/a (E.I.DuPontdeNemours&Co, 1976b; E.I.DuPontdeNemours&Co, 1976c) which is twice the maximum allowed on oranges and peaches. The plots were located near Fresno, CA. Samples were collected after 4 hours and 1, 2, 3, 4 and 7 days post-application. Nectarine plots were located near Newmark, CA (E.I.DuPontdeNemours&Co, 1976c). The application rate was 1.8 lb AI/a again twice the maximum allowed on nectarines. Sampling was done after 4 hours and 1, 2, 3, 4 and 6 days post-application. In both studies the season, sampling and analytical methodology were not reported. The dissipation rate for the three crops was determined after the fourth application. DFRs were expressed in ppm and were not used for exposure calculations.

Chemical-specific DFR data from studies involving crops where methomyl is likely to be used in California are summarized in Table 12. DFR and dissipation half-life ($T_{1/2}$) values used for exposure assessment of reentry activities are in **bold**.

As shown in Table 12, the half-life of methomyl residues on foliage ranged from 0.5 to 3.7 days and was approximately 1 day on average.

Methomyl dissipation on grapes has been studied extensively because of its use on this crop in the past, and because of the importance of the grape and wine industry in the California economy. Grapes are no longer listed on methomyl labels. However, DFR data from grapes can be used as a surrogate re-entry scenario for other crops (e.g. fruit and nut scenario).

Three registrant studies determined the methomyl DFR and dissipation rate on grape foliage (Powley, 1989; Powley, 1990; Powley, 1991). All samples were taken in three or four replicates and consisted of forty 2.54 cm (1 inch) diameter leaf punches per sample. Extraction was done with an aqueous detergent solution, and analysis was by reversed-phase HPLC with UV detection. This sampling and dislodging procedure was consistent with that described by (Iwata *et al.*, 1977).

In the first study, tests were performed in one farm with table grapes in late May 1988 during caning/girdling operations (removal of a strip of bark on either the trunk or cane to advance maturity or produce larger fruit, http://www.vacashears.com/The_Practice_of_Girdling.htm) and in two farms of wine grapes during harvesting in October 1988 (Powley, 1989). Both tests were conducted near Bakersfield, Kern County. Methomyl was sprayed at a rate of 0.9 lb AI/a using airblast equipment with application volume of 25-50 gal of water per acre. A single application was made. Samples were taken 2-7 days later at one day intervals in May, and over a 14-day time period in September. The limit of quantitation (LOQ) was 0.0012 $\mu g/cm^2$. The limit of quantitation is the minimum concentration of an analyte that, in a given matrix and with a specific method, can reliably be quantified. Recoveries ranged from 75 to 105%. No rainfall was reported during this study.

The second study (Powley, 1990) was performed in the central San Joaquin Valley which is a major grape-producing area. Three sites treated in June 1989, during the course of a

worker reentry study to evaluate exposure due to girdling, were near Reedley (two sites) and Parlier (one site). These sites received no rainfall during the course of the study. Two sites treated in September 1989, for the purpose of evaluating table grape harvesting, were near Terra Bella. These sites received traces of rainfall on days 3-4 and 2-3 after methomyl treatment, respectively. Each site was certified to have no recent history (previous 21 days) of methomyl treatments. A single methomyl application was made at the rate of 0.9 lb AI/a using boom spray or airblast equipment typical of grape vineyard use. A control plot was established at each site which had no recent history of carbamate insecticide applications, and which was not downwind of the treated plot. Foliar disc samples were collected at day 0 (pre-application), and at various intervals after each treatment. At each sampling interval at each site, two foliage samples from the untreated plot and four samples from the treated plot were taken. One of the duplicate control samples taken on each day was fortified with methomyl. Samples taken on Day 0 or 1 were fortified at a level corresponding to 1 $\mu g/cm^2$, all other samples were fortified at a level corresponding to 0.1 $\mu g/cm^2$. The recovery for the fortified samples ranged from 70 to 122% for the harvesting studies and from 75 to 125% for the girdling studies. The quantitation limit was 0.01 $\mu g/cm^2$.

In the third study, methomyl was applied by a high-volume, high-pressure U-bottom type sprayer, to three blocks of Perlett grapes at the rate of 0.9 lb AI/a in early May 1991 (about four weeks before grape harvest) in the Coachella Valley near Mecca, CA (Powley, 1991). Leaf punch samples were collected after the spray dried (0 day), and 2, 5, 7, 10, 14, and 22 days after application. Three samples were taken from each of the treated blocks, and six samples were collected from the control block. Extracts from three of the control samples were fortified with methomyl at a level corresponding to 0.1 $\mu g/cm^2$. There was no rainfall during the course of the study. The quantitation limit was 0.01 $\mu g/cm^2$ and the recovery for the fortified samples ranged from 71 to 119%. The study yielded lower initial deposition rate compared to other reports (Table 12). As the authors pointed out, the increased application volume of 485 gal of water per acre may have contributed to the above observation. This volume of water is typical for this type of application in this location but significantly exceeds the volumes used in the Central Valley (25-200 gal/acre depending on the season (Powley, 1989; Powley, 1990)). Secondly, samples were dislodged 72 hours after collection which exceeded the normal 24-h delay, and this could also explain the apparent low initial DFR. This study was not used in the EA.

Table 12. DFR dissipation data for methomyl.

Crop	Location	Initial DFR (µg/cm^2)	DFR at REI (µg/cm^2)	Half-life ($T_{1/2}$) (days)	Reference
Cabbage [a]	San Joaquin Valley, CA	**0.65**	0.16	ND	(Bruce, 2001)
Corn	Riverside County, CA	0.22	0.15	3.7	(Maddy *et al.*, 1976c)
Corn	Riverside County, CA	**1.27**	0.32	1.1	(Maddy *et al.*, 1976c)
Corn	Orange County, CA	0.99	0.24	1.6	(Gibbons and Richmond, 1985)
Cotton	Arizona	**0.72**	0.07	0.9	(Ware *et al.*, 1980)
Cotton	Arizona	4.19	0.08	0.5	(Ware *et al.*, 1978)
Cotton	Arizona	0.08	0.01	0.9	(Cahill *et al.*, 1975)
Cotton	Arizona	0.14	0.04	1.7	(Ware *et al.*, 1974)
Lettuce	Imperial County, CA	0.80	0.40	1.8	(Maddy *et al.*, 1977)
Lettuce	Imperial County, CA	0.94	0.20	0.8	(Maddy *et al.*, 1977)
Lettuce	Imperial County, CA	0.65	0.15	0.9	(Maddy *et al.*, 1976b)
Lettuce [a]	San Joaquin Valley, CA	**1.59**	0.40	ND	(Bruce, 2001)
Mint	Oregon	**1.71**	0.43	1.0	(Kiigemagi and Deinzer, 1979)
Nectarine	Newmark, CA	ND [b]	ND [b]	**1.3**	(E.I.DuPontdeNemours&Co, 1976c)
Orange	Fresno, CA	ND [b]	ND [b]	0.9	(E.I.DuPontdeNemours&Co, 1976b)
Peach	Fresno, CA	ND [b]	ND [b]	1.4	(E.I.DuPontdeNemours&Co, 1976c)
Tobacco	North Carolina	ND [b]	ND [b]	1.0	(Leidy *et al.*, 1977)
				1.2 Average for all crops except grape	
Grape	Bakersfield, CA, May	0.88	N/A [c]	1.9	(Powley, 1989)
Grape	San Joaquín Valley, CA, June	0.76	N/A [c]	1.3	(Powley, 1990)
Grape	Coachella Valley, CA, May	0.13	N/A [c]	2.6	(Powley, 1991)
Grape	Bakersfield, CA, September	1.03	N/A [c]	3.1	(Powley, 1989)
Grape	San Joaquín Valley, CA, September	**1.14**	N/A [c]	3.4	(Powley, 1990)

[a] The DFR values were calculated based on the assumption of half-life 1 day as found average for all

crops except grape. ND = Not determined.
[b] DFR reported in ppm.
[c] N/A = Not applicable

EXPOSURE ASSESSMENT

Handler and reentry exposure to concentrated methomyl formulations is anticipated to be limited to workers engaged in agricultural tasks. The possible exposure routes for handlers and reentry workers are dermal and inhalation. However, bystanders to pesticide agricultural applications (e.g. handlers and reentry workers in adjacent fields, and residents in nearby buildings) may be exposed to airborne methomyl via the inhalation route, as suggested by results of air monitoring studies summarized in the Environmental Concentrations section. Significant exposure scenarios are discussed in the following sections.

The non-agricultural (industrial or institutional) use of methomyl is restricted only to baits containing 1.0% to 1.1% methomyl. This EAD will deal only with scenarios for professional handlers spreading bait. As discussed in the Exposure Scenarios section earlier, the potential for bystander inhalation and dermal exposure to methomyl bait or for accidental ingestion of methomyl bait is considered to be very low, and reentry scenarios for workers or bystanders (visitors) in facilities where methomyl bait has been spread are covered by handler exposures.

Methomyl labels do not permit greenhouse and residential use hence those handler and reentry scenarios are not considered in this document. A reentry scenario for dermal exposure of persons harvesting at "U-Pick" sites will be taken into account.

For each scenario, estimates are provided for short-term and intermediate to long-term (seasonal, annual, and lifetime) exposures. DPR considers short-term (or acute) exposure to be any exposure that persists for seven days or less. The acute worker exposure typically estimated by DPR for occupational scenarios is the amount received in one full workday; unless otherwise stated, this is assumed to be 8 hours. Acute bystander and ambient air exposures state the dosage received in a one-hour period of heavy activity and in a 24-hour day. Acute exposure estimates are important. While an organism can generally tolerate a higher exposure for a short period than it can for a longer period, some adverse effects can be produced in a short period of time if the exposure is sufficient (Beauvais, 2007). Seasonal exposure is defined as a period of frequent exposure lasting more than a week but substantially less than a year, whether the exposure is constant or intermittent during the period. Annual exposure integrates all exposure periods during the year. Lifetime exposures integrate all exposure periods over several years (Beauvais, 2006). For occupational scenarios, two assumptions are used in calculating lifetime exposure, that the average life expectancy is 75 years (U.S.BureauOfTheCensus, 1995), and that a person does the same job for 40 years (Beauvais, 2006).

Handlers

In 1996, WH&S conducted an exposure monitoring study to estimate the potential dermal and inhalation exposures of workers spraying pesticides in grape operations in California

(Schneider *et al.*, 2004). The intent of the study was to evaluate whether exposures could be greater for mixers/loaders/applicators when spraying vineyards using the arbor trellis *vs*. T-type support system. Methomyl was applied by ground boom and airblast. However there were too many variables in this study involving five worker observations that confound any comparison between the different work tasks, application methods and different canopy types: the factor of enclosed cabs for two workers; the applicator treating the arbor trellised vineyards also performing mixing and loading activity; the use of airblast and high pressure sprayers, the low number of repeats. This study was not used for estimating handler worker exposure.

Use of surrogate data to estimate handler exposure

As no acceptable chemical-specific data were available for estimation of handler exposure, exposure estimates were instead derived using the Pesticide Handlers Exposure Database (PHED, 1995). PHED is a computerized database containing monitoring data from multiple studies of inhalation and dermal exposure of pesticide handlers performing mixing, loading, application and flagging tasks with a variety of AI. PHED was developed by the U.S. Environmental Protection Agency (USEPA), Health Canada and the American Crop Protection Association to provide non-chemical-specific pesticide handler exposure estimates for specific handler scenarios. The user selects a subset of the data having the same or a similar application method and formulation type as the target scenario. The use of non-chemical-specific (or "generic") exposure estimates is based on two assumptions (Versar, 1992): (1) that exposure is primarily a function of the pesticide application method/equipment and formulation type and not of the physical/chemical properties of the specific AI; and (2) that exposure is proportional to the amount of AI handled (Reinert *et al.*, 1986; Versar, 1992). These assumptions are supported by comparisons of exposure across several studies (Rutz and Krieger, 1992; van Hemmen, 1992).

PHED has limitations as a generic database. It combines measurements from diverse studies involving different protocols, analytical methods and residue detection limits. Most dermal exposure studies in PHED use the patch dosimetry method of Durham and Wolfe (Durham and Wolfe, 1962); residues (in $\mu g/cm^2$) on small patches placed on different parts of the body are multiplied by the surface area of the body part to estimate its exposure (in µg). These partial estimates are then summed to provide a total body exposure estimate. Some studies measured exposure only to selected body parts such as the hands, arms and face. As a consequence, the dermal exposure estimates for different body parts may be based on data from different studies. Further, for some handler scenarios, the number of matching observations in the PHED is so small that the possibility they do not represent well the target scenario is substantial.

When using PHED to assess short-term exposure, DPR uses as the exposure estimate the 90% upper confidence limit (UCL) on the 95th percentile of daily exposure. (Confidence limits on percentiles, also called tolerance limits, are described by Hahn and Meeker (Hahn and Meeker, 1991). DPR believes upper-bound estimates are appropriate for short-term exposures because high-end exposures are possible and because DPR has an obligation to protect all individuals exposed as a result of legal uses of pesticides (not just individuals with "average" exposures). It is often the case that the upper bound is 3-5

times the size of the mean; this should not be surprising because in highly skewed distributions such exposures can happen.

When using PHED to assess intermediate or long-term exposure, DPR uses as the exposure estimate the 90% UCL on the arithmetic mean of daily exposure.

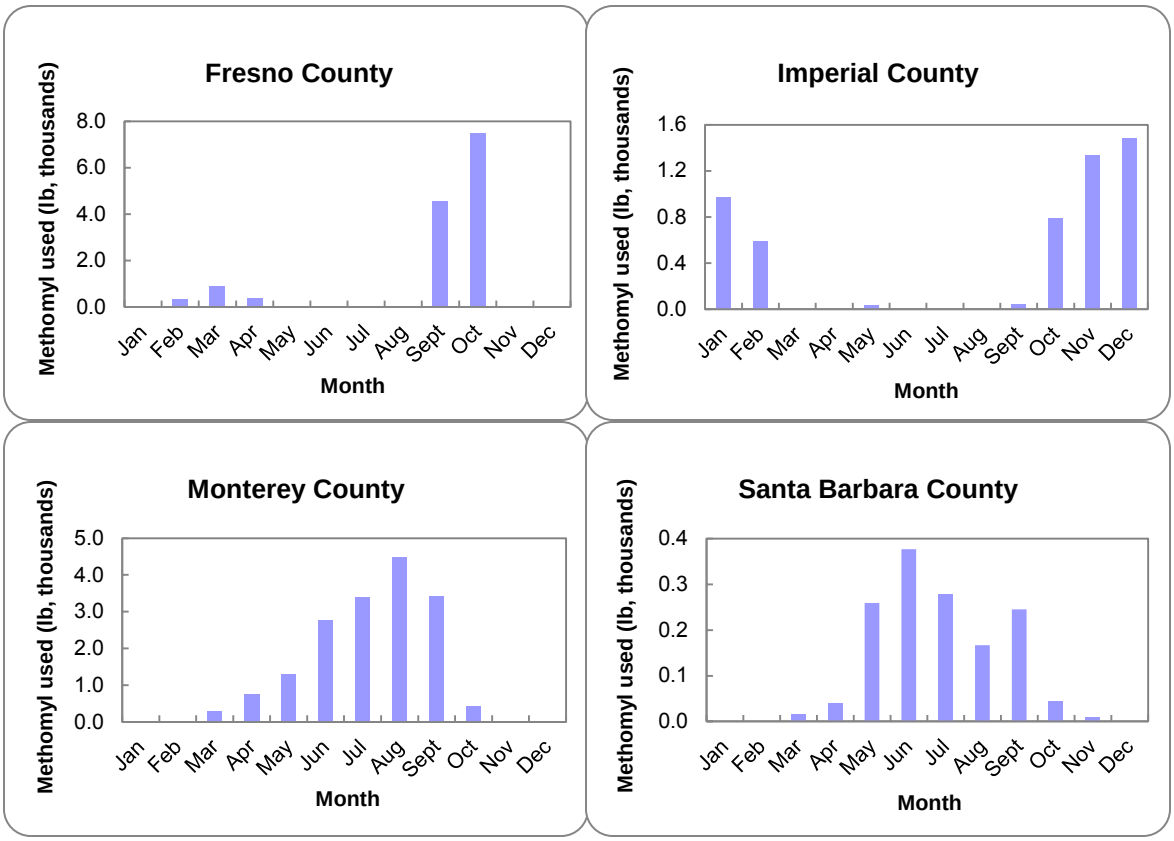
Estimating the confidence limit requires knowing the mean and standard deviation. PHED reports the mean of total dermal exposure, but only the coefficients of variation for separate body regions. Because the sample sizes per body region differ and because the correlations among body regions are unknown, the standard deviation of total dermal exposure cannot be calculated. In order to approximate the confidence limit for the 95th percentile, DPR makes the assumption that the population of total exposure is lognormally distributed across persons and has a coefficient of variation of 100 percent. The method of approximation is described in Powell (Powell, 2007), and uses the fact that in any lognormal distribution with a given coefficient of variation, the confidence limit for the 95th percentile is a constant multiple of the arithmetic mean. The value of the multiplier depends only on sample size. These multipliers have been calculated for a large range of sample sizes (Powell, 2007); to find the UCL for a 95th percentile, arithmetic mean exposure is multiplied by a multiplier corresponding to the sample size.

The 90% UCL on the arithmetic mean of daily exposure is approximated making the same assumptions as for short-term exposure. The UCL is a multiple of the arithmetic mean (a different multiple than for the 95th percentile). These multipliers have also been calculated for a large range of sample sizes (Powell, 2007); to find the UCL for a mean, arithmetic mean exposure is multiplied by a multiplier corresponding to the sample size.

In order to estimate intermediate or long-term occupational and non-occupational exposure we need to know the duration of methomyl use in agriculture. An overall view on the methomyl monthly use in California on all crops in a 5-year period is presented in Figure 3 and shows seasonal pattern with peak in the summer months. As previously discussed in the section on Pesticide Use and Sales, in the years 2006-2010 the crop that received most methomyl was lettuce: an average of 32,532 kg per year, or 27% of the total amount of methomyl used. Lettuce is a crop that is produced year-round in the state of California. In 2010, methomyl use on head lettuce was highest in Fresno County, followed by Monterey, Imperial and Santa Barbara counties. Examination of the 2010 methomyl monthly use on lettuce shows an overlapping, year-round pattern of applications between those counties (Figure 6). E.g. in Fresno County 88% of methomyl was applied in the peak months of September and October. In Imperial County, the highest methomyl use was more evenly distributed between the cold months of the year (January, February, and October-December). Monterey and Santa Barbara counties also had the highest methomyl use in 5 months of the year, but in the summer. The amount of methomyl used in 2010 in Fresno and Imperial counties combined (18,899 lb) was virtually the same as in Monterey and Santa Barbara counties (18,186 lb). A consultation with Exposure Monitoring Program staff at Worker Health and Safety Branch of DPR suggests that pesticide handlers and harvesters can and do move from one location to another within the state (from the Arizona border to Northern California) following their job assignments as they

occur during the year. It would be reasonable and health protective to expect that such workers could be exposed to pesticide year-round. That is why, for the purpose of this Exposure assessment all handlers were assumed to apply methomyl on lettuce fields (conservative presumption), and the annual rather than seasonal methomyl exposures for all handler scenarios were calculated. Annual exposure for occupational reentry scenarios in lettuce was based on 12 months per year methomyl use, while occupational reentry scenarios for crops other than lettuce were estimated on a seasonal basis (6 months of use throughout the year) according to data from Figure 3.

Figure 6. Methomyl use on head lettuce in top four California counties, 2010.



Tables 13 and 14 show the exposure estimates and acute and long-term Absorbed daily dosage (ADD) for M/L and applicators according to exposure scenarios based on methomyl labels. Assuming that a M/L/A spends part of a workday mixing/loading and part making the application, exposure of the M/L/A should be less than the applicator exposure and greater than that of the M/L (Beauvais and Johnson, 2006).

Table 13. Data used for calculating exposure estimates for methomyl handlers[a].

Scenario[b] (PHED Scenario # is in parentheses)	Acute Exposure (µg/lb AI handled)		Long-Term Exposure (µg/lb AI handled)	
	Dermal	Inhalation	Dermal	Inhalation
Aerial				
M/L[b] WSP (3)	54.8	1.05	19.7	0.38
M/L Liquid (6)	57.5	0.44	20.7	0.16
Pilot [c](17)	224	2.12	80.5	0.76
Flagger [d](7)	15.1	0.07	5.44	0.02
Airblast				
M/L WSP (3)	54.8	1.05	19.7	0.38
M/L Liquid (6)	57.5	0.44	20.7	0.16
Applicator [e](9)	1437	17.6	517	6.32
Groundboom				
M/L WSP (3)	54.8	1.05	19.7	0.38
M/L Liquid (6)	57.5	0.44	20.7	0.16
Applicator [e](11)	78.3	4.12	28.2	1.48
Chemigation				
M/L WSP (3)	54.8	1.05	19.7	0.38
M/L Liquid (6)	57.5	0.44	20.7	0.16
Hand Spreader Bait[f]				
With Gloves (15)	351,000	1,270	126,000	457

[a] Data for acute and long-term exposure (in µg/lb AI handled) were from PHED (PHED, 1995). 90% upper confidence limit (UCL) on the 95th percentile of daily exposure data from PHED were used for acute exposure. 90% UCL on the arithmetic mean of daily exposure data from PHED were used for long-term exposure. PHED subsets and exposure calculations are described in detail in Appendix I. Estimates were rounded to three significant figures. Protection factors for using PPE and engineering controls were from HS-1616 (Thongsinthusak *et al.*, 1991).

[b] Mixer/Loader (M/L): Closed systems were assumed for handling of concentrated methomyl formulations as required by California Worker Safety Regulations. Reduced or modified PPE during use of a closed system was assumed, consisting of long-sleeved shirt, long pants, chemical resistant gloves (90% protection of hands), shoes plus socks, and a chemical resistant apron (95% protection of chest and front half of thighs);

[c] Pilots are in open cockpits; long-sleeved shirt, long pants, shoes plus socks, chemical resistant gloves (90% protection of hands), and protective eyewear (vented goggles, 75% protection of head) were assumed;

[d] Human flaggers are in enclosed cabs (90% protection) as per label requirement. Reduced or modified PPE was assumed, consisting of long-sleeved shirt, long pants, and shoes plus socks;

[e] Airblast and groundboom applicators are in open cabs; long-sleeved shirt, long pants, shoes plus socks, chemical resistant gloves (90% protection of hands), and protective eyewear (vented goggles, 75%

protection of head) were assumed;

[f] The following assumptions were made for handlers of fly baits: chemical resistant gloves, long-sleeved shirt, long pants, shoes and socks as required by labels were assumed as normal PPE.

Table 14. Acute, long-term and life-time average daily dosage (ADD) for methomyl handlers[a, b].

Scenario (PHED Scenario # is in parentheses)	Acute ADD[c] (µg/kg/day)			Long Term ADD[d] (µg/kg/day)			Life-Time ADD[e] (µg/kg/day)
	Dermal	Inhalation	Total	Dermal	Inhalation	Total	
Aerial[f]							
M/L WSP (3)	422.7	16.2	438.9	152.0	5.9	157.9	84.2
M/L Liquid (6)	443.6	6.8	450.4	159.7	2.5	162.2	86.5
Pilot (17)	1728.0	32.7	1760.7	621.0	11.7	632.7	337.4
Flagger (7)	34.0	0.3	34.3	12.2	0.1	12.3	6.6
Airblast[g]							
M/L WSP (3)	14.1	0.5	14.6	5.1	0.2	5.3	2.8
M/L Liquid (6)	14.8	0.2	15.0	5.3	0.1	5.4	2.9
Applicator (9)	370.3	9.1	379.4	132.9	3.3	136.2	72.6
Groundboom[h]							
M/L WSP (3)	70.5	2.7	73.2	25.3	1.0	26.3	14.0
M/L Liquid (6)	73.9	1.1	75.0	26.6	0.4	27.0	14.4
Applicator (11)	100.7	10.6	111.3	36.3	3.8	40.1	21.4
Chemigation[i]							
M/L WSP (3)	123.3	4.7	128.0	44.3	1.7	46.0	24.5
M/L Liquid (6)	129.4	2.0	131.4	46.6	0.7	47.3	25.2
Hand Spreader of Bait [j]							
With Gloves (15)	546.6	4.0	550.6	196.2	1.4	197.6	105.4

[a] Data for acute and long-term exposure (in µg/lb AI handled) are from Table 13. Estimates were rounded to four significant figures.

[b] In preparing worker exposure estimates, the following assumptions were made for occupational handlers:

- Maximum application rate of 0.9 lb AI/a allowed on product labels for most crops (Table 7);
- Acres treated per day for agricultural scenarios varied by scenario (footnotes f-i) and were from (Haskell, 1998) using upper range for high-acre crops (e.g. alfalfa, corn), based on methomyl use in 2002-2006 (Table 3).
- Dermal absorption was 50% (Donahue, 1996), inhalation absorption was 100%; body weight assumed to be 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al*., 1993a).

[c] The following equation was used for calculating the acute absorbed daily dosage (ADD):

- Acute ADD = [(Acute exposure) x (Absorption) x (Area treated/day) x (Application rate)]/(body weight).
- Acute ADD is an upper-bound estimate calculated from the acute exposure.

[d] The following equation was used for calculating the Long-Term Average daily dosage (ADD):

- Long-term ADD = [(Long-term exposure) x (Absorption) x (Area treated/day) x (Application rate)]/(body weight).
- Long-Term ADD is a 90% upper confidence limit on the mean calculated from the long-term

exposure estimate.

- Long-term exposures were assumed to occur during twelve months of the year.

[e] The following equation was used for calculating the Life-Time Average daily dosage (ADD):

- Life-Time ADD = Long-term ADD x 40 /75.
- A person is assumed to do the same job for 40 years, life expectancy is assumed to be 75 years.

[f] Area treated was 1200 acre/day for M/L and for pilot, 350 for flagger.

[g] Area treated was 40 acre/day.

[h] Area treated was 200 acre/day.

[i] Area treated was 350 acre/day.

[j] The following assumptions were made for handlers of fly baits:

- Formulations with 1% AI in fly baits;
- Maximum application rate of 1/4 lb formulated product per area of 500 ft^2 as stated on labels. The amount AI handled per day is based on 43,560 ft^2 (1 acre) treated area per day (USEPA, 2001), and is equivalent to 21.8 lb formulated bait or 0.218 lb AI per day;

Reentry workers

Reentry workers are subject to occupational exposure primarily from dermal contact with dislodgeable pesticide residues that have accumulated on treated foliage. By convention and based on evidence from multiple exposure monitoring studies, the inhalation exposure during reentry activities is not considered to be significant (Fong, 1989; Merricks, 1990). Worker exposure estimates may be derived directly from patches or other passive dosimeters. Biological monitoring can also be used when the pharmacokinetic profile of a pesticide is well understood. When acceptable chemical-specific monitoring data are not available, another, indirect method for estimating exposure of field workers who come in contact with foliage, is through the use of dislodgeable foliar residues (DFR) with a crop- and activity-specific transfer coefficient (TC) (USEPA, 2000).

Representative exposure scenarios for reentry workers were selected based on crop-activity groupings and PUR data. For each of these scenarios, exposure of workers reentering fields following foliar applications of methomyl was estimated from chemical specific DFR and an appropriate transfer coefficient.

<u>Exposure monitoring – Turf</u>

Rosenheck and Sanchez evaluated the turf reentry exposure to a broadcast application of Ronstar® 50WP (oxadiazon) (Rosenheck and Sanchez, 1995). The study was reviewed by Dr. Sheryl Beauvais (Worker Health and Safety Branch, DPR) (Beauvais, 2011), and she proposed use of this study as a surrogate exposure study in the risk assessment of carbaryl. This study was found suitable as surrogate data for calculating the post-application occupational exposure to methomyl for professional landscapers transplanting sod. In the discussion of this surrogate study, the following presumptions were made:

1. Human exposure is proportional to the amount of pesticide applied, regardless of chemical nature, formulation, or application method (as long as pesticide is applied as a spray).
2. Pesticide dissipation rate, as determined from residues on foliage, is chemical-specific.

3. Human exposure is proportional to residues on foliage, and decrease of exposure over time is proportional to the pesticide dissipation rate.
4. Long-term exposures were estimated at an assumed average reentry of REI (or PHI if longer than REI) + 5 days as discussed previously.

The primary review of the study of Rosenheck and Sanchez (Rosenheck and Sanchez, 1995) can be found in the Memo HSM-11005, authored by Dr. Sheryl Beauvais (Beauvais, 2011), and only a brief description will be presented in this document. Dermal and inhalation reentry exposures were monitored on the day of application on two treated plots, with or without irrigation after the spray has dried. Ronstar® 50WP (active ingredient oxadiazon) was applied with a boom sprayer to both plots at an application rate of 3 lb AI/acre. Dermal exposure was assessed by using outer whole-body dosimeters, cotton gloves & hand wash, face/neck wipes and cotton socks. The surrogate reentry activity was Jazzercise®. Inhalation exposure was assessed by using personal air samplers mounted above the plots. Two samplers were used on each treated plot, one which sampled at 6 inches above the turf to represent an infant's breathing zone, and one which sampled 36 inches above the turf to represent the breathing zone of an older child or adult sitting on the turf.

Dr. Beauvais provided dermal exposure estimates for normalized application rates (1 lb active ingredient/acre) of oxadiazon as a surrogate active ingredient (AI). Exposure estimates for occupational reentry assumed 90% protection factor for body areas covered by long-sleeved shirt, long pants and shoes. The average occupational hourly dermal exposure to oxadiazon on the day of application (day 0) was 4,030 µg/h per pound AI applied for the non-irrigated plot. The non-irrigated plot was chosen as surrogate data because the methomyl label does not require irrigation after pesticide application. Adjusting this value for the maximal methomyl application rate of 0.9 lb AI/acre gives dermal exposure of 3,627 µg/h on day 0. Next, methomyl exposure was amortized for days 2 (REI) for short-term exposures, and 7 (REI+5) post-application for long-term exposures. This was done by using modified equation (1) where DFR was replaced by exposure data, and assuming chemical specific dissipation half-life of 1 day as found for methomyl on all crops except grape (Table 12). If $t_{1/2}$ = 1 day, then the regression slope *k* in equation (1) equals -0.6931. Thus, the short-term hourly methomyl dermal exposure was calculated to be 907 µg/h (on day 2), and the long-term hourly methomyl dermal exposure was calculated to be 28 µg/h (on day 7).

The level of airborne oxadiazon residues was low, and oxadiazon above the LOQ of 0.100 µg was recovered from only one pair of duplicate samples, collected 6 inches above the non-irrigated plot. The amounts collected from these samples were 0.102 µg and 0.144 µg, for a mean of 0.123 µg oxadiazon per 89.4 L of sample, or 0.00138 µg/L. The occupational hourly inhalation exposure, based on average human breathing rate of 16.7 L/min for light activity (Andrews and Patterson, 2000) , is 0.46 µg/h oxadiazon per pound AI applied for the non-irrigated plot. The inhalation exposure accounts for only 0.01% of the total hourly oxadiazon exposure, and specific calculations for methomyl inhalation exposure are not presented here.

The Acute absorbed daily dosage (Acute ADD) was calculated from Equation (3) below (Zweig *et al.*, 1980; Zweig *et al.*, 1985) using the methomyl hourly dermal exposure on the day of REI (907 µg/h) instead of the multiplier (DFR x TC) in Equation (3).

$$\text{ADD } (\mu g/kg/day) = \frac{DA \times DFR\ (\mu g/cm^2) \times TC\ (cm^2/h) \times ED\ (h/day)}{BW\ (kg)} \qquad (3)$$

The calculation assumes a default dermal absorption rate (DA) of 50% (Donahue, 1996), an exposure duration (ED) of 8 hours, and a body weight (BW) of 70 kg (Thongsinthusak *et al.*, 1993a) based on mean for adult (male and female) U.S. population.

Thus, the Acute ADD for landscaping workers laying sod will be **51.8 µg/kg/day** (Table 15).

The Seasonal Average daily dosage (SADD) for sod transplanting was calculated from Equation (3) using the long-term hourly dermal exposure (28 µg/h) instead of the multiplier (DFR x TC). The other assumptions were the same as for Acute ADD. SADD was calculated at **1.6 µg/kg/day** (Table 15).

The Annual Average daily dosage (AADD) for sod laying was calculated using the formula:

AADD (µg/kg/day) = SADD x (annual use months/year) / (12 months in a year).

It is reasonable to assume that sod can be grown and transplanted year round in California. The annual use for methomyl is assumed to be 12 months/year and the AADD for sod laying will be equal to the SADD **(1.6 µg/kg/day)** (Table 15).

The Lifetime Average daily dosage (LADD) for sod transplanting was calculated using the formula:

LADD (µg/kg/day) = AADD x (40 yrs of work in a life time) / (75 yrs in a lifetime)

and was (1.6 µg/kg/day x 40yrs) / 75 yrs = **0.9 µg/kg/day** (Table 15).

Table 15 summarizes the acute and long-term exposures to methomyl for agricultural workers performing reentry activities with harvested sod.

Table 15. Acute and long-term exposure[a] to methomyl for landscaping workers transplanting sod.

Exposure	Methomyl Hourly Dermal Exposure (µg/h)	Acute ADD (µg/kg/day)	SADD (µg/kg/day)	AADD (µg/kg/day)	LADD (µg/kg/day)
Acute [b]	907	51.8	N/A	N/A	N/A
Long-term [c]	28	N/A	1.6	1.6	0.9

[a] Calculations of exposure:

- The Acute absorbed daily dosage (Acute ADD) and Seasonal ADD (SADD) were calculated using the equation:

$$\text{ADD (µg/kg/day)} = \frac{\text{DA x Hourly Dermal Exposure (µg/h) x ED (h/day)}}{\text{BW (kg)}}$$

- Assumptions: dermal absorption rate (DA) 50% (Donahue, 1996), default exposure duration (ED) 8 hours, default body weight (BW) 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al.*, 1993a).
- Annual Average daily dosage (AADD) (µg/kg/day) = SADD x (annual use months/year) / (12 months in a year). The annual use is 12 months/year.
- Lifetime Average daily dosage (LADD) (µg/kg/day) = AADD x (40 yrs of work in a life time) / (75 yrs in a lifetime).

[b] Calculated for day 2 after application using oxadiazon data as described in text above.
[c] Calculated for day 7 after application using oxadiazon data as described in text above.
[d] N/A = Not applicable.

Exposure derived from DFR

In the absence of chemical-specific monitoring data for workers reentering treated fields, dislodgeable foliar residue data for methomyl from several studies (Table 12) and default transfer coefficients (TC) from surrogate chemicals (Frank, 2009) were used to estimate reentry worker exposure. Each TC estimate was based on the crop type and the activity of the reentry worker. Crop-specific DFR data for methomyl is available only for several crops and is listed in Table 12. In order to cover all representative agricultural reentry scenarios (Table 9), surrogate crops were selected from Table 9 to match the represented crops as closely as possible.

The absorbed daily dosage (ADD) was calculated using Equation (3) (Zweig *et al.*, 1980; Zweig *et al.*, 1985). The calculation assumes a dermal absorption rate (DA) of 50% (Donahue, 1996), a default exposure duration (ED) of 8 hours, and a default body weight (BW) of 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al.*, 1993a). The acute exposure estimates are summarized in Table 18.

All TC used for estimating the acute and long-term exposure of reentry workers were from (Frank, 2009). Reentry workers are not required to wear protective clothing unless entering before expiration of the restricted entry interval (REI). Therefore, fieldworker exposure estimates were based on an assumption that no protective clothing or equipment was used. Acute exposures were estimated at the expiration of the REI for all activities in

most crops (Table 16). Additionally, exposure was calculated at the end of the PHI for hand harvesting of lettuce and anise because hand harvesting assumes higher TC than scouting. Half-life ($T_{1/2}$) values were from Table 12, or default $T_{1/2}$ of 1 day was used when chemical-specific data was not available (see Environmental Concentrations section). When surrogate DFR values were used they were adjusted if the study with the surrogate crop used different application rate. E.g. application rate used to determine DFR value on cotton was 0.68 lb AI/a, but cotton DFR was used as a surrogate on potato, tomato and others, after adjusting for the maximal application rate allowed on those crops, typically 0.9 lb AI/a.

Table 16. Acute exposure to methomyl for agricultural reentry workers.

Crop	Activity (day)	TC [a] (cm^2/h)	DFR_{day} [b] (µg/cm^2)	Acute ADD [c] (µg/kg/day)	DFR from Surrogate Crop
Alfalfa	Scouting (REI 2)	1,500	0.4279	36.68	Mint
Anise	Hand harvesting (PHI 7)	2,500 [d]	0.0134	1.91	Mint
Anise	Scouting (REI 2)	1,500 [d]	0.4279	36.68	Mint
Apple	Thinning (REI 3)	3,000	0.1425	24.43	Grape
Asparagus	Scouting (REI 2)	500	0.2387	6.82	Cotton
Beans	Hand harvesting (REI 2)	2,500	0.2387	34.10	Cotton
Blueberry	Hand harvesting (PHI 3)	1,500	0.1425	12.21	Grape
Cabbage	Hand harvesting (REI 2)	5,000	0.1622	46.34	N/A [e]
Corn, sweet	Hand harvesting (REI 2)	17,000	0.3173	308.23	N/A
Cotton	Scouting (REI 3)	2,000	0.0716	8.18	N/A
Cucumber	Thinning (REI 2)	2,500	0.2387	34.10	Cotton
Lettuce	Hand harvesting (PHI 10)	2,500	0.0016	0.23	N/A
Lettuce	Scouting (REI 2)	1,500	0.3968	34.01	N/A
Onion, green	Thinning (REI 2)	2,500	0.2387	34.10	Cotton
Potato	Scouting (REI 2)	1,500	0.2387	20.46	Cotton
Tomato, fresh	Hand harvesting (REI 2)	1,000	0.2387	13.64	Cotton

[a] Transfer coefficients (TC) are from (Frank, 2009).

[b] DFR as estimated for the respective REI or PHI. If dissipation data was not available for the respective crop or surrogate crop, then Half-life of 1 day (average for all crops except grape, Table 12) was used in calculations of DFR.

[c] Acute absorbed daily dosage (Acute ADD) calculated from Equation (3).

$$\text{ADD (µg/kg/day)} = \frac{\text{DA} \times \text{DFR (µg/cm}^2\text{)} \times \text{TC (cm}^2\text{/h)} \times \text{ED (h/day)}}{\text{BW (kg)}} \quad (3)$$

Assumptions include:

- Dermal absorption (DA) was 50% (Donahue, 1996);
- Exposure duration (ED) 8 hours;
- Body weight (BW) assumed to be 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al.*, 1993a).

[d] DPR Policy (Frank, 2009) does not provide a TC for anise. TC for parsley was used instead.

[e] N/A = Not applicable.

For long-term, repetitive exposure estimates it was assumed that workers would not always enter fields at the expiration of the REI or PHI. Long-term exposures were estimated at an assumed average reentry of REI (or PHI if longer than REI) + 5 days. These assumed averages were not based on data; rather, they were based on the reasonable, health-protective assumption that workers may enter fields an average of 3-10 days after expiration of the REI or PHI (Beauvais and Johnson, 2006). Long-term exposures are listed in Table 17. As it was already mentioned in the Handler exposure section, the annual methomyl exposure on all crops except lettuce is calculated for 6 months per year methomyl use, based on data in Figure 3 (section Pesticide Use).

Table 17. Long-term exposure to methomyl for agricultural reentry workers[a].

Crop	Activity	DFR_{day+5} [b] (µg/cm^2)	SADD [c] (µg/kg/day)	AADD [d] (µg/kg/day)	LADD [e] (µg/kg/day)
Alfalfa	Scouting	0.0134	1.1486	0.5743	0.3063
Anise	Hand harvesting	0.0004	0.0571	0.0286	0.0152
Anise	Scouting	0.0134	1.1486	0.5743	0.3063
Apple	Thinning	0.0045	0.7714	0.3857	0.2057
Asparagus	Scouting	0.0075	0.2143	0.1071	0.0571
Beans	Hand harvesting	0.0075	1.0714	0.5357	0.2857
Blueberry	Hand harvesting	0.0045	0.3857	0.1929	0.1029
Cabbage	Hand harvesting	0.0051	1.4571	0.7286	0.3886
Corn, sweet	Hand harvesting	0.0099	9.6171	4.8086	2.5646
Cotton	Scouting	0.0015	0.1714	0.0857	0.0457
Cucumber	Thinning	0.0075	1.0714	0.5357	0.2857
Lettuce	Hand harvesting	0.00005	0.0071	0.0071	0.0038
Lettuce	Scouting	0.0124	1.0629	1.0629	0.5669
Onion, green	Thinning	0.0075	1.0714	0.5357	0.2857
Potato	Scouting	0.0075	0.6429	0.3214	0.1714
Tomato, fresh	Hand harvesting	0.0075	0.4286	0.2143	0.1143

[a] DFR from same surrogate crops as in Table 16. Transfer coefficients (TC) are the same as in Table 16.

[b] DFR calculated on the respective day of REI or PHI + 5 days (see discussion in text).

[c] Seasonal Average daily dosage (SADD) calculated from Equation (3).

$$\text{ADD (µg/kg/day)} = \frac{\text{DA x DFR (µg/cm}^2\text{) x TC (cm}^2\text{/h) x ED (h/day)}}{\text{BW (kg)}} \quad (3)$$

Assumptions include:

- Dermal absorption was 50% (Donahue, 1996);
- Exposure duration 8 hours;
- Body weight assumed to be 70 kg based on mean for adult (male and female) U.S. population (Thongsinthusak *et al.*, 1993a).

[d] Annual Average daily dosage (AADD) = SADD x (annual use months/year) / (12 months in a year). The annual use is 12 months/year for lettuce and 6 months/year for all other crops.

[e] Lifetime Average daily dosage (LADD) = AADD x (40 yrs of work in a life time) / (75 yrs in a lifetime).

Non-occupational reentry scenarios

One possible non-occupational reentry scenario is "U-Pick" or similar operations. "U-Pick" is an operation in which the general public is allowed to enter an orchard or a field to pick fruit, nuts or other produce for their own use. Of the sites where methomyl can be used, the crops with highest exposure potential and interest for the general public would be sweet corn, fruit and nut trees, and blueberries. Methomyl use on nut trees is restricted only to SLN for non-bearing nursery stock (Table 7). The factors that are used in considering the "U-Pick" exposure scenario are listed in Table 18 below, along with the calculated DFR_t at REI or PHI (see explanation below). Of these surrogate crops, chemical-specific data for DFR is available only for sweet corn (Table 12). For the other crops, grape DFR_0 = 1.14 μg/cm^2 was used as a surrogate (most conservative grape DFR from Table 12). Table 12 also shows that the initial DFR_0 on grape was usually in the range 0.8-1.1 μg/cm^2. That is why the DFR_0 of 0.13 μg/cm^2 from Coachella valley (Powley, 1991) is regarded as atypical. The half-life that was calculated from crop-specific data (Table 12) was used for sweet corn, nectarine and peach, while for blueberries and apples the half-life was considered 1 day, which is the average value for all crops except grape, calculated from Table 12. DFR_t at reentry (day 2 or 3, sweet corn or nectarine, respectively) or at PHI (day 3, 4 or 14 for blueberry, peach or apple, respectively) is calculated using equation (1). Because of the longest PHI (14 days) apples have very low DFR ($7x10^{-5}$ μg/cm^2) at the time residents are allowed to enter an orchard, and this data was not included in Table 18. An adult TC of 10,000 cm^2/h for all surrogate crops, except for sweet corn, was used for the purpose of this exposure scenario. This value was derived from the respective TC for fruit tree harvesting (1,500 cm^2/h) (Frank, 2009) used for workers, having in mind the surface area of additionally exposed body parts (arms, feet and legs) for residents compared to workers who wear long-sleeves, long pants and closed shoes. Using similar extrapolation for sweet corn hand harvesting from occupational TC of 17,000 cm^2/h (Frank, 2009) to residential TC gives an unrealistically high value (110,000). Therefore, the occupational TC of 17,000 cm^2/h was used herein for this residential scenario. The presumption was that because of the harsh nature of the corn plants a person picking corn would have more clothing on their body (not only shorts/t-shirt), and/or would not work as vigorously as a professional harvester. USEPA assumed that the TC for children is 50% of the TC for adults (USEPA, 1997b). Therefore, the TC for children was assumed to be 8,500 cm^2/h for sweet corn, and 5,000 cm^2/h for all other surrogate crops. The most protective assumptions in Table 18 are in **bold**.

The absorbed daily dosage (ADD) was calculated using Equation (3) (Zweig *et al.*, 1980; Zweig *et al.*, 1985). The calculation assumes a dermal absorption rate (DA) of 50% (Donahue, 1996), an exposure duration (ED) of 4 hours for adults and 2 hours for children (10-12 years) (USEPA, 1997b), and a default body weight (BW) of 71.8 kg for adult residential and 39.1 kg for children (USEPA, 1997b).

Table 18. "U-Pick" scenario for non-occupational reentry exposure to methomyl [a].

Crop/age group	Rate (lb AI/a)	REI (days)	PHI (days)	$T_{1/2}$ (days)[b]	DFR_t (µg/cm^2)[c]	TC Hand Harvesting (cm^2/h)	ADD (µg/kg/day[d])
Sweet corn/adult	0.45	**2**	0	1.1	**0.317**	17,000	**150.1**
Sweet corn/child	0.45	**2**	0	1.1	**0.317**	8,500	**68.9**
Blueberry/adult	0.9	2	**3**	1.0	0.142	10,000	39.6
Blueberry/child	0.9	2	**3**	1.0	0.142	5,000	18.2
Nectarine/adult	0.9	**3**	1	1.3	**0.232**	10,000	**64.6**
Nectarine/child	0.9	**3**	1	1.3	**0.232**	5,000	**29.7**
Peaches/adult	0.9	4	4	1.4	0.167	10,000	46.5
Peaches/child	0.9	4	4	1.4	0.167	5,000	21.4

[a] REI, reentry interval; PHI, preharvest interval; $T_{1/2}$, dissipation half-life; DFR_t , dislodgeable foliar residue at reentry or at PHI.
[b] The half-life ($T_{1/2}$) for sweet corn, nectarine and peach was calculated from crop-specific data (Table 12), the half-life ($T_{1/2}$) for blueberry was considered 1 day (the average value as calculated in Table 12).
[c] DFR_t at reentry (day 2 or 3, sweet corn or nectarine, respectively) or at PHI (day 3 or 4 for blueberry or peach, respectively) was calculated based on grape DFR_0 = 1.14 µg/cm^2 as a surrogate (Table 12), and using equation (1). Note that the chemical-specific data for DFR for peach and nectarine was reported in ppm in (E.I.DuPontdeNemours&Co, 1976c) (footnote [b] in Table 12). The data allowed for determination of $T_{1/2}$ for peach and nectarine, but not for calculating the value of DFR.
[d] Acute absorbed daily dosage (Acute ADD) calculated from Equation (3).

$$\text{ADD (µg/kg/day)} = \frac{\text{DA} \times DFR_t\ (\mu g/cm^2) \times \text{TC}\ (cm^2/h) \times \text{ED (h/day)}}{\text{BW (kg)}} \quad (3)$$

Assumptions include:

- Dermal absorption (DA) was 50% (Donahue, 1996);
- Exposure duration (ED) 4 hours for adults and 2 hours for children (USEPA, 1997b);
- Body weight (BW) assumed to be 71.8 kg for adult residential, and 39.1 kg for youth (10-12 years) (USEPA, 1997b).

Assuming an adult with BW 71.8 kg is picking sweet corn for 4 hours, the individual would receive a single dose of 150.1 µg/kg/day, if picking nectarines the individual would receive a single dose of 64.6 µg/kg/day. Assuming a child with BW 39.1 kg is picking sweet corn for 2 hours, the child would receive a single dose of 68.9 µg/kg/day, if picking nectarines the child would receive a single dose of 29.7 µg/kg/day.

Bystanders at application sites

The labels for Lannate LV and SP do not require buffer zones from residential areas or adjacent fields where people are present. It can be expected that there could be bystanders - residents, workers performing reentry or unrelated agricultural or non-agricultural activities - in close proximity to an application field. Having in mind the low concentrations of pesticide in the air (micrograms per cubic meter, table below), it is reasonable to assume that the methomyl bioavailability via the dermal route would be very small, and inhalation would be the major exposure route in this scenario.

A study on application site air concentrations of methomyl was conducted in San Diego County in August 1996 (Segawa, 1998), and is described in detail in Environmental Concentrations section. Air monitoring stations were located at various distances from the edge of a potato field receiving aerial methomyl application. Information obtained from those sampling sites is used to assess the acute exposure of bystanders to methomyl aerial application.

Table 19 summarizes the acute bystander (worker and residential) exposure estimates based on these data. Existing data suggest that short duration exposures (5-60 min) can result in toxicity (see Illnesses section). Therefore 1-hour exposure estimates were calculated based on the highest measured concentration during pesticide application, and assuming heavy activity. The maximum air concentration detected during the first monitoring period of 2h 45 min during the application, was at the NW monitoring station located 40 m from the field (Table 11). This maximum concentration was used as a surrogate for 1-hour air concentration when calculating bystander 1-hour exposure estimates.

For the purpose of this EAD bystander residents are assumed to spend 24 hours in vicinity to pesticide application while bystander workers are assumed to spend 8 hours. Therefore the air concentrations used for daily exposure estimates were calculated differently for residents and workers: The highest 24-h air time-weighted average (TWA) obtained from the west station at 10 m from the field (Table 11) was used to estimate the 24-h bystander residential daily exposure. The highest 14-h air time-weighted average (TWA) obtained from the west station at 10 m from the field (Table 11) was used as a surrogate value for 8-h TWA to estimate the bystander worker daily exposure.

The inhalation rates for 1-hour absorbed dose estimates were calculated from hourly values reported in (Andrews and Patterson, 2000), assuming heavy activity (3.2 m^3/h for adult and 1.9 m^3/h for infant) and dividing by the mean body weight for males and females: 71.8 kg for adult residential, 70 kg for occupational (worker), and 7.6 kg for infant residential.

Daily (24 hour) inhalation rates for residents were default values from (Andrews and Patterson, 2000). We assumed that the occupational activity for the bystanders is not necessarily agricultural – it could vary from office work to construction work.

The inhalation rate for 8 hour occupational exposure was calculated by using a daily rate that factors in proportions of the day engaged in light, moderate, and heavy activity levels (excluding sleep), according to an average daily activity pattern from surveys conducted by California Air Resources Board and referenced in (Andrews and Patterson, 2000). Inhalation rate was calculated for the duration of each activity, i.e. 13.2 hours of light activity at 1 m^3/h = 13.2 m^3, 1.4 hours of moderate activity at 1.6 m^3/h = 2.24 m^3, and 0.27 hours of heavy activity at 3.2 m^3/h = 0.864 m^3. The total volume of 16.3 m^3 summed for all activities of 14.9 hours (13.2 m^3 + 2.24 m^3+ 0.864 m^3 = 16.3 m^3; 13.2 h + 1.4 h + 0.27 h = 14.9 h) was normalized per 1 hour (16.3 m^3 for all activities / 14.9 hours for all activities= 1.1 m^3/h, then air volume breathed for 8-hrs was calculated (8 hours * 1.1 m^3/h

= 8.8 m^3/8 hours) and normalized per kg body weight using 70 kg for occupational activity (8.8 m^3/8 hours/70 kg). The result is 0.13 m^3/kg/8hr work day (Table 19).

Another assumption was that the measured outdoor methomyl air concentration is equal to the indoor methomyl air concentration.

Table 19. Bystander inhalation exposure estimates for methomyl near application sites[a].

	Air concentration (µg/m^3)[b]	Inhalation Rate[c]	Absorbed Dose[d]
1h Absorbed dose (heavy activity for 1h during pesticide application)[e]			
Infant residential	3.0082	0.250 m^3/kg/h	0.75 µg/kg/h
Adult residential	3.0082	0.045 m^3/kg/h	0.13 µg/kg/h
Worker bystander	3.0082	0.046 m^3/kg/h	0.14 µg/kg/h
Acute absorbed daily dosage (Acute ADD)[f]			
Infant residential (24 hours)	1.9479	0.59 m^3/kg/day	1.15 µg/kg/day
Adult residential (24 hours)	1.9479	0.28 m^3/kg/day	0.55 µg/kg/day
Worker bystander (8 hours)	2.2377	0.13 m^3/kg/day	0.29 µg/kg/day

[a] Based on EHAP monitoring of methomyl air concentration during aerial application (Segawa, 1998).

[b] Concentrations used to estimate 1-h absorbed dose and acute ADD were adjusted to estimate exposure when methomyl is applied at the maximum rate. Concentrations were multiplied by a factor of 0.9/0.73=1.23 - the ratio between the maximum application rate allowed (0.9 lb AI/a) and the application rate monitored by EHAP (0.73 lb AI/a) as described in Table 11 in Environmental Concentrations section.

[c] Different inhalation rates were used for the 1-hour, 8-hour and 24-hour absorbed doses. The inhalation rates for 1-hour absorbed dose estimates were calculated from hourly values reported in (Andrews and Patterson, 2000), assuming heavy activity (3.2 m^3/h for adult and 1.9 m^3/h for infant) and dividing by the mean body weight for males and females: 71.8 kg for adult residential, 70 kg for occupational (worker), and 7.6 kg for infant residential. Daily (24 hour) inhalation rates for residents were default values from (Andrews and Patterson, 2000). We assumed that the occupational activity for the bystanders is not necessarily agricultural – it could vary from office work to construction work. The inhalation rate for 8 hour occupational exposure was calculated by using a daily rate that factors in proportions of the day engaged in light, moderate, and heavy activity levels (excluding sleep), according to an average daily activity pattern from surveys conducted by California Air Resources Board and referenced in (Andrews and Patterson, 2000). Inhalation rate was calculated for the duration of each activity, i.e. 13.2 hours of light activity at 1 m^3/h = 13.2 m^3, 1.4 hours of moderate activity at 1.6 m^3/h = 2.24 m^3, and 0.27 hours of heavy activity at 3.2 m^3/h = 0.864 m^3. The total volume of 16.3 m^3 summed for all activities of 14.9 hours (13.2 m^3 + 2.24 m^3+ 0.864 m^3 = 16.3 m^3; 13.2 h + 1.4 h + 0.27 h = 14.9 h) was normalized per 1 hour (16.3 m^3 for all activities / 14.9 h for all activities= 1.1 m^3/h, then air volume breathed for 8-hrs was calculated (8 hours * 1.1 m^3/h = 8.8 m^3/8 hours) and normalized per kg body weight using 70 kg for occupational activity (8.8 m^3/8 hours /70 kg). The result is 0.13 m^3/kg/8h work day.

[d] 1-hour absorbed dosage assumes 1-hour exposure during heavy activity, and are based on the highest methomyl concentration measured (Table 11). This maximum concentration occurred during the first monitoring period of 2h 45 min during the application. Absorbed daily dosage assumes a typical mixture of activity levels throughout the day and are based on the highest 24-hour and 14-hour time-weighted average (TWA) air concentrations (Table 11) for residential and occupational exposure, respectively. Inhalation absorption was assumed to be 100%.

[e] 1-hour absorbed dosage (µg/kg/h) = (highest air concentration during application) x (inhalation rate). The maximum concentration from Table 11 (3.0082 µg/m^3) registered during pesticide application was detected at the Northwest air monitoring station 40m from the application filed. This value was used as a surrogate for 1-hour TWA.

[f] Acute ADD (µg/kg/day) = (TWA air concentration) x (inhalation rate). The highest 24-hour TWA concentration (TWA = 1.9479 µg/m^3) was detected at the West air monitoring station 40m from the application field (Table 11). This value was used for calculating acute daily residential exposure. The highest 14-hour TWA concentration (TWA =2.2377 µg/m^3 = average of 2.4534 and 2.0219, see Table 11) was detected at the West air monitoring station 10m from the application field. This value was used as a surrogate for 8-hour TWA for calculating acute daily worker exposure.

EXPOSURE APPRAISAL

As no acceptable human and animal dermal absorption data are available, the DPR default value of 50% was used in this document for calculations of absorbed dermal doses (Donahue, 1996). This default value is based on a review of data from forty pesticides, twenty-six of which were documented in (Thongsinthusak *et al.*, 1993b). Also, dermal absorption of pesticides in experimental animals can differ significantly from that in humans (Thongsinthusak *et al.*, 1993b). In the absence of human data it is theoretically possible that exposure estimates are underestimated by this default, perhaps by as much as two-fold.

No inhalation retention/absorption studies for methomyl are available. In the absence of these data, DPRs policy is to use a default inhalation absorption value of 100% for calculations of doses absorbed via inhalation. This might overestimate the actual retention/absorption. Data are extremely limited on pesticide uptake via inhalation, and because of this DPR has decided to use a 100% absorption as a health-protective default.

Handler exposure

Because acceptable chemical-specific data were not available to assess exposure of handlers performing mixing/loading and application of methomyl, exposure estimates for these scenarios were derived using generic data from PHED (PHED, 1995). PHED has limitations as a generic database. It combines measurements from diverse studies involving different protocols, analytical methods and residue detection limits. Most dermal exposure studies in PHED use the patch dosimetry method of Durham and Wolfe (Durham and Wolfe, 1962); residues (in $\mu g/cm^2$) on small patches placed on different parts of the body are multiplied by the surface area of the body part to extrapolate its exposure (in µg). These body part estimates are then summed to provide a total body exposure estimate. Some studies measured exposure only to selected body parts such as the hands, arms and face. As a consequence, the dermal exposure estimates for different body parts may be based on data from different studies. Further, for hand exposure of M/L WSP (PHED scenario #3) and Pilot (PHED scenario #17), the number of matching observations in PHED is so small that they may not accurately represent the target scenario. In addition, exposure scenarios are incompletely characterized in the PHED database, confounding assessment of the match between a given subset and the exposure scenario it is intended to represent. Finally, the assumptions underlying the use of generic data, that exposure is primarily a function of the pesticide application method/equipment and formulation type and not of the physical/chemical properties of the specific AI, and that exposure is proportional to the amount of AI handled, may be false in some cases.

To account for some of the uncertainty inherent in using PHED and to increase our confidence that exposures are not underestimated, DPR uses the 90% upper confidence limit (UCL) on an exposure statistic instead of the statistic itself when using PHED to estimate exposure. PHED, however, does not provide all the information needed to calculate confidence limits. Estimating a confidence limit requires knowing the mean and standard deviation. PHED reports the mean of total dermal exposure, but only the coefficients of variation for separate body regions. Because the sample sizes per body

region differ and because the correlations among body regions are unknown, the standard deviation of total dermal exposure cannot be calculated. In order to approximate the confidence limit for the 95th percentile, DPR makes the assumption that the population of total exposure is log normally distributed across persons and has a population coefficient of variation of 100 percent. The method of approximation is described in Powell (Powell, 2007), and uses the fact that in any lognormal distribution with a given coefficient of variation, the confidence limit for the 95th percentile (or for the mean) is a constant multiple of the arithmetic mean, the multiplier depending only on sample size. Any of these underlying assumptions could be incorrect and, to the extent they are, the UCLs would be incorrect.

The level of uncertainty in estimates generated from PHED subsets depends on the quality of data and the number of replicates (sample size) in a subset. Data quality grades and sample size for each PHED scenario data set used in exposure estimates are summarized in Appendix I.

Each study in PHED has been graded from "A" to "E" according to certain Quality Assurance/Quality Control factors. Grades A and B are high-quality grades, with lab recoveries of 90-110% and 80-110%, respectively (field recoveries range 70-120% and 50-120%); grade C represents moderate quality, with lab and field recoveries of 70-120% and 30-120%, respectively; grade D represents poor quality, with lab recovery of 60-120% and field recovery that is either in the range of 30-120% or missing; E is the lowest quality grade, and is assigned to PHED data that do not meet basic quality assurance (USEPA, 1998b).

The quality of data sets used to generate methomyl dermal and inhalation exposure estimates was overall high (grades A and B), except hand data for hand spreading of bait in which all hand data was of moderate quality (grade C).

Most PHED subsets contained satisfactory numbers of observations, in the upper teens and above. Two subsets had lower sample sizes: aerial applicator in open cockpit (9-17 observations) and M/L of WSP containing WP in (6-15 observations). The uncertainty in the estimates generated from those two subsets will be considerably higher compared to the other scenarios.

All handler scenarios assumed methomyl use of 12 months per year as a health protective measure. This was based on the year-round use of methomyl on lettuce and the hypothesis that pesticide handlers can move from one field/county to another throughout the state to follow job assignments. This can be an overestimate of the methomyl handler exposure.

Reentry exposure

The Jazzercise® routine used in the study of Rosenheck and Sanchez (1995) describes well the movements of residents or professional landscapers installing sod. However, the occupational exposures to methomyl-treated sod may be overestimated: because of methomyl's short half-life, the pesticide residues will most likely be very small by the time the harvested sod is installed. Specific calculations for sod exposure to residents are

not presented here because it is considered a rare exposure scenario: the acute exposure is relatively low for the reasons outlined above for occupational exposure; residents are not expected to install sod often, so chronic exposure is not considered.

Exposure estimates for fieldworkers in other crops were based on chemical-specific DFRs, but not necessarily crop-specific values. Surrogate crops were used for many representative scenarios. Residues may dissipate at different rates on different crops, due to factors such as leaf topography and physical and chemical properties of leaf surfaces, and plant metabolism. DFR dissipation can also vary with weather conditions, which is why DPR relies mostly on California-specific data whenever available. For methomyl, DPR used DFR data from studies done in California for corn, lettuce, cabbage and grape. The data for cotton and mint were from field trials in Arizona and Oregon, respectively (Table 12 and references therein). The use of data from surrogate crops increases the uncertainty of the estimate of methomyl residues and hence the uncertainty of the fieldworker exposure estimates derived from those residues.

Non-occupational reentry exposure "U-Pick"

The current Worker Health and Safety Branch default TC for tree fruit harvesting is 1,500 cm^2/hr (Frank, 2009). Agricultural transfer coefficients reflect standard agricultural work clothing worn by adult workers. This clothing typically includes shoes, socks, long-legged pants, and long-sleeved shirts (USEPA, 2000). A person involved in "U-Pick" or similar scenario is not bound by the Worker Protection Standard and may wear shorts and short-sleeved or sleeveless shirt in California, and may even be in sandals. The TC for this activity was calculated by extrapolating the agricultural TC for fruit tree harvesting (1,500 cm^2/hr) and the surface area of head and hands which are directly exposed to surface residues in professional agricultural setting, to the combined surface area of head, upper and lower extremities which could be directly exposed to dislodgeable pesticide residues in a person dressed in shorts and sleeveless shirt. E.g., this calculation resulted in a TC equal to 10,000 cm^2/hr for adults harvesting blueberries and fruit (Table 18). This value is also supported by the USEPA where the Agency used TC of 10,000 cm^2/hr in similar "U-pick" scenario for adult exposure to methomyl (USEPA, 1998d). This TC is not a result of exposure measurements (e.g. body patch dosimetry) during performance of actual harvesting activity and as such can add uncertainty to the value of the exposure estimate.

By-stander inhalation exposure

Bystander exposure to methomyl used in agricultural settings deserves attention because of the likelihood of this exposure. The analysis of California illnesses in the period 2005-2009 showed that three episodes stemmed from drift exposure. All four persons involved - a resident and three field workers - were in vicinity of fields receiving methomyl applications.

The air concentration of methomyl during and following aerial application was determined using the DPR's EHAP study (Segawa, 1998). Methomyl labels require that application should be avoided at wind speeds below 2 mph due to variable wind direction and high inversion potential, and also in windless conditions. Although meteorological data was collected throughout this study the wind speed was not reported in the

Memorandum describing the study results (Segawa, 1998). It is remotely possible that the wind speed was inappropriate for aerial application and this would make the results of this study less reliable. Time of collecting data during application (2.75 h) is longer than the actual application (approximately 1 hour) and may not reflect the highest air concentrations. This could potentially lead to underestimate of bystander exposure.

In order to provide maximal human health protection this Exposure Assessment was based on the most conservative assumptions. E.g. the highest methomyl air concentrations measured downwind of a specific application site were used in exposure calculations. Another conservative hypothesis was that a residential bystander would remain in the area of pesticide application for up to 24 hours without leaving the site, and a worker bystander would spend up to 8 hours continuously near the area where methomyl is applied. These conservative assumptions could lead to overestimate of pesticide exposure. There is no label or regulatory requirement to keep adjacent structures closed during methomyl applications. Since the indoor air concentration of methomyl during and after applications is not known, it was also assumed that it was equivalent to the outdoors when calculating bystander exposure. This assumption brings uncertainty into the Exposure Assessment.

Estimates were calculated solely for exposure via the inhalation route, based on an assumption that dermal exposure to airborne pesticide is insignificant compared to inhalation. While this is generally true for pesticides in the vapor phase, where concentrations impinging on the skin are low, pesticide dissolved in aerosol particles can be deposited on surfaces, and later transferred by contact with the skin. If this occurs to a substantial degree following pesticide applications, exposures omitting the dermal route might underestimate actual exposure (Beauvais, 2007).

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APPENDIX I. PHED SUMMARY STATISTICS TABLES AND SUBSET SPECIFICATIONS FOR EACH PHED SUBSET

Scenario 3: Mixer/Loader, Water Soluble Bags Containing Wettable Powder (With Gloves)

Table 1-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B	A, B
Solid Type	Wettable powder	Wettable powder
Package Type	Water Soluble Bag	Water Soluble Bag

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.
[b] Data quality for Dermal Uncovered, Dermal Covered and Hand are all Grade A or B; Airborne data are all Grade A. Data quality grades are defined in the text and in (Versar, 1992).

Figure 1-1. Summary of Results from the PHED Dermal Subset for Scenario 3 [a]

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	MICROGRAMS PER LB AI MIXED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	3.51	165.0541	1.1942	15
NECK.FRONT	.423	155.9811	.1734	15
NECK.BACK	.2933	167.61	.0978	15
UPPER ARMS	2.619	17.2127	2.5837	6
CHEST	1.8046	83.2317	1.1207	12
BACK	1.8046	83.2317	1.1207	12
FOREARMS	1.089	17.2176	1.0743	6
THIGHS	4.9023	204.1674	1.6636	12
LOWER LEGS	1.19	86.1261	.7092	12

Subset Name:
S3DERMAL.MLOD

[a] Subset criteria included actual and estimated head patches. All 15 head observations were actual.

Table 1-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	14.2 [e]	11	3.836	1.379
Hand (with gloves)	0.056	6	4.299	1.546
Inhalation	0.277	12	3.784	1.361

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).
[b] Median number of replicates was used for Dermal (non-hand).
[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).
[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).
[e] Protection factor of 0.95 applied to exposure of chest and front half of thighs for use of chemical resistant apron.

Table 1-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.836 x 14.2) + (4.299 x 0.056) = 54.8	(1.379 x 14.2) + (1.546 x 0.056) = 19.7
Inhalation	3.784 x 0.277 = 1.05	1.361 x 0.277 = 0.38

[a] Values from Table 1-2. Results rounded to three significant figures.

Scenario 6: Mixer/Loader, Closed System, Liquids

Table 2-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B	A
Liquid Type	Emulsifiable concentrate, aqueous suspension, microencapsulated, solution, or undiluted liquid	All emulsifiable concentrate
Mixing Procedure	Closed, mechanical pump or gravity feed	Closed

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.
[b] Data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A. Data quality grades are defined in the text and in (Versar, 1992).

Figure 2-1. Summary of Results from the PHED Dermal Subset for Scenario 6 [a]

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	MICROGRAMS PER LB AI MIXED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	1.6959	121.3279	.9508	22
NECK.FRONT	1.5225	278.5222	.2418	22
NECK.BACK	.456	280.8991	.0729	22
UPPER ARMS	1.3441	96.6967	.7988	21
CHEST	1.8416	93.4405	1.0577	16
BACK	1.8416	93.4405	1.0577	16
FOREARMS	.5474	98.5203	.3206	21
THIGHS	2.3398	81.9301	1.5773	16
LOWER LEGS	1.292	85.7276	.8778	21

Subset Name:
S6DERMAL.MLOD

[a] Subset criteria included actual and estimated head patches. All 22 head observations were actual.

Table 2-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	10.7 [e]	18	3.576	1.286
Hand (with gloves)	5.72	31	3.369	1.211
Inhalation	0.128	27	3.415	1.228

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).
[b] Median number of replicates was used for Dermal (non-hand).
[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).
[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).
[e] Protection factor of 0.95 applied to exposure of chest and front half of thighs for use of chemical resistant apron.

Table 2-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.576 x 10.7) + (3.369 x 5.72) = 57.5	(1.286 x 10.7) + (1.211 x 5.72) = 20.7
Inhalation	3.415 x 0.128 = 0.44	1.228 x 0.128 = 0.16

[a] Values from Table 2-2. Results rounded to three significant figures.

Scenario 7: Flagger, Liquids

Table 3-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B	A, B
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate or dry floable
Application Method	Fixed- or rotary-wing	All rotary-wing

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.
[b] Data quality for Dermal Covered and Dermal Uncovered are all Grade A; Airborne and Hand data are all Grade A or B. Data quality grades are defined in the text and in (Versar, 1992).

Figure 3-1. Summary of Results from the PHED Dermal Subset for Scenario 7 [a]

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	MICROGRAMS PER LB AI SPRAYED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	11.3028	127.5702	5.6188	18
NECK.FRONT	.9533	134.3334	.5146	18
NECK.BACK	1.4111	215.8529	.4931	18
UPPER ARMS	3.9285	195.1025	.8284	28
CHEST	5.1065	188.8378	1.0384	26
BACK	5.1065	188.8378	1.0384	26
FOREARMS	1.802	179.5283	.3837	28
THIGHS	4.0404	308.6996	.9165	26
LOWER LEGS	2.448	305.6618	.612	28

Subset Name:
S7DERMAL.FLAG

[a] Subset criteria included actual and estimated head patches. All 18 head observations were actual.

Table 3-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure [e] (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	3.74	21	3.510	1.262
Hand (no gloves)	0.597	30	3.379	1.215
Inhalation	0.020	28	3.402	1.223

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).
[b] Median number of replicates was used for Dermal (non-hand).
[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).
[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).
[e] Protection factor of 0.9 applied to dermal (non-hand), hand and inhalation exposure for use of closed cab.

Table 3-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.510 x 3.74) + (3.379 x 0.597) = 15.1	(1.262 x 3.74) + (1.215 x 0.597) = 5.44
Inhalation	3.402 x 0.020 = 0.07	1.223 x 0.020 = 0.02

[a] Values from Table 3-2. Results rounded to three significant figures.

Scenario 9: Airblast Applicator, Open Cab (With Gloves)

Table 4-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B	A, B
Liquid Type or Solid Type	Not specified	Emulsifiable concentrate, dry floable or Wettable powder
Application Method	Airblast	Airblast
Cab type	Open Cab or Closed Cab with Open Window	Open Cab or Closed Cab with Open Window

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.
[b] Data quality for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B. Data quality grades are defined in the text and in (Versar, 1992).

Figure 4-1. Summary of Results from the PHED Dermal Subset for Scenario 9 [a]

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	MICROGRAMS PER LB AI SPRAYED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	778.5762	155.5207	176.2608	42
NECK.FRONT	37.1325	147.948	12.193	38
NECK.BACK	27.8342	159.3144	8.7825	42
UPPER ARMS	42.3987	265.4846	6.4049	40
CHEST	21.8289	177.8784	5.4396	49
BACK	14.7289	174.1332	4.204	49
FOREARMS	7.4511	148.7525	2.0066	38
THIGHS	56.8344	189.968	16.9924	32
LOWER LEGS	17.2699	129.16	7.0944	32

Subset Name:
S9DERMAL.APPL

[a] Subset criteria included actual and estimated head patches. Of the 42 head observations, 41 were actual and 1 was estimated from nearby patches (Versar, 1992).

Table 4-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	429 [e]	42	3.279	1.179
Hand (with gloves)	8.52	18	3.576	1.286
Inhalation	5.41	47	3.249	1.168

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).
[b] Median number of replicates was used for Dermal (non-hand).
[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).
[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).
[e] Protection factor of 0.75 applied to exposure of head for use of vented goggles.

Table 4-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.279 x 429) + (3.576x 8.52) = 1437	(1.179 x 429) + (1.286 x 8.52) = 517
Inhalation	3.249x 5.41 = 17.6	1.168 x 5.41 = 6.32

[a] Values from Table 4-2. Results rounded to three significant figures.

Scenario 11: Groundboom Applicator, Open Cab

Table 5-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B	A, B, C
Liquid Type or Solid Type	Not specified	Emulsifiable or wettable powder
Application Method	Groundboom, Truck or Tractor	Groundboom, Tractor
Cab type	Open Cab or Closed Cab with Open Window	Open Cab or Closed Cab with Open Window

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.
[b] Data quality grades for Airborne, Dermal Uncovered, Dermal Covered and Hand are all Grade A or B, with the exception of one dermal replicate that has Dermal Uncovered Grade C (Dermal Covered for that replicate is Grade B). Data quality grades are defined in the text and in (Versar, 1992).

Figure 5-1. Summary of Results from the PHED Dermal Subset for Scenario 11 [a]

SCENARIO: Long pants, long sleeves, no gloves

PATCH LOCATION	MICROGRAMS PER LB AI SPRAYED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	2.7891	136.1192	1.0464	33
NECK.FRONT	1.5763	167.9503	.3296	23
NECK.BACK	1.0063	173.5765	.2335	29
UPPER ARMS	1.6914	88.749	1.1637	32
CHEST	1.7581	98.5154	1.1329	42
BACK	3.0175	233.2361	1.3959	42
FOREARMS	2.7301	419.1055	.564	32
THIGHS	3.1255	185.5703	1.1806	33
LOWER LEGS	2.1148	172.3425	.7466	35

Subset Name:
S11DERMAL.APPL

[a] Subset criteria included actual and estimated head patches. All 33 head observations were actual.

Table 5-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	18.8 [e]	34	3.340	1.201
Hand (with gloves)	4.56	29	3.391	1.219
Inhalation	1.18	22	3.491	1.255

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).
[b] Median number of replicates was used for Dermal (non-hand).
[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).
[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).
[e] Protection factor of 0.75 applied to exposure of head for use of vented goggles.

Table 5-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.340 x 18.8) + (3.391 x 4.56) = 78.3	(1.201 x 18.8) + (1.219 x 4.56) = 28.2
Inhalation	3.491x 1.18 = 4.12	1.255 x 1.18 = 1.48

[a] Values from Table 5-2. Results rounded to three significant figures.

Scenario 15: Hand Spreading of Bait, Applicator (With Gloves)

Table 6-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B, C	A, B, C
Solid Type	Granular	Granular
Application Method	Other	Other
Study Code	Exclude 1027 [c]	520

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.

[b] Data quality for Airborne, Dermal Uncovered, Dermal Covered are all Grade A or C; Hand data are all Grade C. Data quality grades are defined in the text and in (Versar, 1992).

[c] Study 1027 omitted because applications done with a Lesco spreader (identified in Applicator Make/Model field), rather than by hand. No application equipment is listed in Study Code 520 (field is blank).

Figure 6-1. Summary of Results from the PHED Dermal Subset for Scenario 15 [a]

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	MICROGRAMS PER LB AI SPRAYED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	5911.8638	65.7229	4628.6454	16
NECK.FRONT	788.2688	56.8973	652.267	16
NECK.BACK	500.2346	65.7229	391.6546	16
UPPER ARMS	13233.4796	65.7229	10361.0448	16
CHEST	16143.9356	65.7229	12639.7626	16
BACK	16143.9356	65.7229	12639.7626	16
FOREARMS	5502.5809	65.7229	4308.2008	16
THIGHS	17371.7842	65.7229	13601.0966	16
LOWER LEGS	10823.2582	65.7229	8473.9817	16

Subset Name:

S15DERMAL.APPL

[a] Subset criteria included actual and estimated head patches. All 16 head observations were actual.

Table 6-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	92,000	16	3.631	1.306
Hand (with gloves)	4,660	15	3.663	1.317
Inhalation	350	16	3.631	1.306

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).

[b] Median number of replicates was used for Dermal (non-hand).

[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).

[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).

Table 6-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.631x92,000)+(3.663x4,660)=351,000	(1.306x92,000)+(1.317x4,660)=126,000
Inhalation	3. 631 x 350 = 1,270	1.306 x 350 = 457

[a] Values from Table 6-2. Results rounded to three significant figures.

Scenario 17: Aerial Applicator, Liquids, Open Cockpit

Table 7-1. Description of Pesticide Handlers Exposure Database (PHED) Subsets [a]

Parameter	Specifications used to generate subsets [a]	Actual characteristics of resulting subsets
Data Quality Grades [b]	A, B, C	A, B, C
Liquid Type	Not specified	All emulsifiable concentrate
Solid Type	Exclude granular	None
Application Method	Fixed- or rotary-wing	All fixed-wing
Cab type	Open Cockpit or Closed Cockpit with Open Window	Open Cockpit or Closed Cockpit with Open Window

[a] Subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED). Parameter descriptions are from screens displayed in the PHED program.
[b] Data quality for Dermal Uncovered, Dermal Covered, and Hand were Grade A or C; Airborne data were Grade B or C. Data quality grades are defined in the text and in (Versar, 1992).

Figure 7-1. Summary of Results from the PHED Dermal Subset for Scenario 17 [a]

SCENARIO: Long pants, long sleeves, gloves

PATCH LOCATION	MICROGRAMS PER LB AI SPRAYED Mean	Coef of Var	Geo. Mean	Obs.
HEAD (ALL)	4.212	118.2574	1.2438	10
NECK.FRONT	.414	143.6715	.1169	10
NECK.BACK	.3124	139.1485	.0741	10
UPPER ARMS	8.5554	109.6232	5.7532	10
CHEST	6.3065	158.1987	2.1395	17
BACK	8.7497	141.5614	3.131	17
FOREARMS	2.7901	131.7516	1.1744	17
THIGHS	9.55	157.4126	3.4718	13
LOWER LEGS	7.4494	138.0769	3.3312	10

Subset Name:
S17DERMAL.APPL

[a] Subset criteria included actual and estimated head patches. Of the 10 head observations, 7 were actual and 3 were estimated from nearby patches (Versar, 1992).

Table 7-2. PHED Data from Dermal, Hand, and Inhalation Subsets [a]

Exposure Category	Exposure (µg/lb AI handled)	Replicates in Subset [b]	Short-Term Multiplier [c]	Long-Term Multiplier [c]
Dermal (non-hand) [d]	49.1 [e]	12	3.784	1.361
Hand (with gloves)	9.63	9	3.969	1.427
Inhalation	0.573	14	3.699	1.33

[a] Results from subsets of Mixer/Loader data in the Pesticide Handlers Exposure Database (PHED).
[b] Median number of replicates was used for Dermal (non-hand).
[c] Multipliers are explained in the Exposure Assessment Section and in (Powell, 2007).
[d] Dermal (non-hand) includes addition of default feet value of 0.52 x (value for lower legs); ratio of feet/lower leg surface area (USEPA, 1997a).
[e] Protection factor of 0.75 applied to exposure of head for use of vented goggles.

Table 7-3. Values used in Short-Term and Long-Term Exposure Calculations [a]

	Short-Term (µg/lb AI handled)	Long-Term (µg/lb AI handled)
Total Dermal	(3.784 x 49.1) + (3.969 x 9.63) = 224	(1.361 x 49.1) + (1.427 x 9.63) = 80.5
Inhalation	3.699 x 0.573 = 2.12	1.33 x 0.573 = 0.76

[a] Values from Table 8-2. Results rounded to three significant figures.

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