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Hanford Tank Ventilation System Condensates and Headspace Vapors: An Assessment of Potential Dermal Exposures

J.L. Huckaby
D.L. Springer

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Prepared for the U.S. Department of Energy
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Summary

This study considers whether potential dermal exposures to headspace vapors and their condensates in Hanford Site high-level radioactive waste tanks could result in significant exposure to workers. Three types of potential exposures were evaluated: dermal contact with aqueous condensate, organic condensate, and direct contact with head space vapors. The dermal absorption rates from aqueous and organic condensates were estimated for 56 chemicals of potential concern using a model described by EPA (1992) with a modified correlation for dermal permeability suggested by Wilschut et al. (1995). Dermal absorption rates of vapors were estimated using a model given by AIHA (2000). Results were compared to an "equivalent inhalation dose" calculated by multiplying the inhalation occupational exposure limit by a nominal daily inhalation rate.

Most exposure scenarios considered are hypothetical accident scenarios and do not represent routine working conditions. The study is aimed at identifying those chemicals of greatest concern in each exposure scenario so appropriate industrial hygiene practices and protective equipment can be selected and applied to reduce potential consequences.

Model results indicate relatively large areas of skin would need to be wetted with aqueous condensate or the contact would need to persist for an extended period before the equivalent inhalation dose of any chemical of potential concern is reached. The model identified tributyl phosphate as presenting the greatest risk of exceeding the equivalent inhalation dose, with an allowed exposure (contact) time of less than 1 min. if a very large fraction, 25% of the workers skin (5,000 cm^2), was wetted with the condensate. For a 500-cm^2 area of wetted skin, roughly the area of both palms of a worker's hands, the equivalent inhalation dose of tributyl phosphate would not be exceeded provided the worker could towel-dry his hands within 20 min.

N-nitrosodimethylamine and mercury vapor were found to be the most likely of the chemicals of potential concern to exceed their equivalent inhalation doses via dermal absorption from organic condensate. Exposure of 500 cm^2 of skin, about the surface area of one hand or the palms of both hands, to organic condensate could result in absorption of the equivalent inhalation dose of N-nitrosodimethylamine in less than 5 min., and of mercury in less than 9 min.

Dermal absorption of vapors was modeled to help identify conditions of potential concern. Dermal absorption of vapors present at the tank farms' action limits is predicted to be negligible compared to the dose received via inhalation for most of the chemicals of potential concern.

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Tables

Acronyms and Abbreviations

ACGIH	American Conference of Governmental Industrial Hygienists
AIHA	American Industrial Hygiene Association
CAS	Chemical Abstract Service
cm	centimeter
COPC	chemicals of potential concern
EPA	U.S. Environmental Protection Agency
g	gram
mg	milligram
mL	milliliter
MW	molecular weight
OELs	occupational exposure limits
OSHA	Occupational Safety and Health Administration
PEL	permissible exposure limit
ppm	parts per million
STEL	short-term exposure limits
TLV	threshold limit value

1.0 Introduction

The purpose of this report is to evaluate the potential for unacceptable dermal exposure to Hanford Site waste tank vapors and conservatively estimate dermal absorption rates for chemicals under scenarios of interest. This report is specifically limited to those chemicals in vapor and condensed solution phases identified as chemicals of potential concern (COPC) for tank farms (Honeyman et al. 2004). Dermal absorption of COPC is considered possible from contact with three vehicles: aqueous condensate, organic condensate, and vapor. Each of these entails different exposure scenarios.

Water evaporates from the waste in the tanks and can reach saturated conditions in the headspaces. Air leaving the headspace via the ventilation system and air pathways connected to the tank headspace may be cooled below its dewpoint (due to cool ambient temperatures, cool ground temperatures, etc.), causing the water vapor to condense and collect as condensate in low spots. This condensate absorbs vapors from air leaving the headspace, producing an aqueous solution containing the COPC at concentrations proportional to their vapor-phase concentrations. The concentrations of COPC in the condensate will be at their maximum values when the condensate and vapor are allowed to reach equilibrium. Because many of the tanks are warm and humid, aqueous condensate is relatively common and can be present in certain locations in gallon quantities. It is consequently possible for workers to come in contact with (e.g., via splashing, draining, dripping) enough aqueous condensate to saturate a portion of their clothes and wet their skin.

Analogous to the formation of aqueous condensate from warm humid air in the ventilation system, the concentrations of organic vapors may be high enough in the headspaces of some tanks to cause the formation of an organic condensate. However, because the concentration of organic vapors is always much lower than that of water vapor, the amount of organic condensate formed is very small compared to the amount of aqueous condensate. [1] While the aqueous condensate may form puddles and accumulate as bulk liquid in low spots, the organic condensate forms so slowly that it is present only as a coating on a condensing surface or a sheen on the surface of the aqueous condensate. Worker exposure to organic condensate is consequently limited to very small quantities that might result from handling or rubbing against a coated surface.

Vapors from the tank headspaces released into the air above the tanks may be absorbed through a worker's skin. The dilution of the vapors with ambient air generally makes this exposure very small, but under certain scenarios, such as when workers are present in a radiological containment tent over an open tank riser, dermal absorption of vapors may be important to the total dose.

[1] The highest reported organic vapor concentrations were from tank 241-C-103, for which an average total nonmethane hydrocarbon concentration of 520 mg/m^3 was reported (TWINS 2005). For comparison, the water vapor concentration in 241-C-103 was 54,100 mg/m^3.

2.0 Methodology

This section describes a method for estimating the dose received via absorption through the skin and the models applied to estimate dermal absorption rates. The dermal absorption of COPC from three vehicles (aqueous condensate, organic condensate, and vapor) was examined for different potential exposure scenarios. The approach taken to evaluate exposures depends on the vehicle and scenario as described below.

2.1 Equivalent Inhalation Dose

Dermal occupational exposure limits (OELs) analogous to the American Conference of Governmental Industrial Hygienists (ACGIH) and Occupational Safety and Health Administration (OSHA) inhalation OELs have not been established for any of the COPC. The approach taken here is to assume the dermal absorption of a given mass of COPC has the same health consequences as the same mass absorbed through the lungs. Assuming that 100% of the inhaled vapor is absorbed by the lungs, the equivalent inhalation dose is calculated by multiplying the lower of the OSHA permissible exposure limit (PEL) or ACGIH threshold limit value (TLV) by a nominal 10 m^3/day inhalation rate:

$$Equivalent\ Inhalation\ Dose \quad = \quad (Inhalation\ OEL, mg/m^3\ )(10\ m^3/day)$$

The 10 m^3/day inhalation rate is a commonly used estimate (e.g., AIHA 2000). Table 1 lists the current COPC with their Tank Farms inhalation OELs and calculated equivalent inhalation doses. Two of the current COPC, chlorinated biphenyls and substituted furans, are classes of compounds that include multiple compounds.

Table 1. Equivalent Inhalation Doses for Chemicals of Potential Concern

Chemical	CAS Number	Molecular Weight (g/mol)	Inhalation OEL		Equivalent Inhalation Dose (mg)	Note
			(ppm)	(mg/m^3)		
1,1'-Biphenyl	92-52-4	154.21	0.20	1.3	13	
1,3-Butadiene	106-99-0	54.09	1.0	2.2	22	
1,3-Dinitrate-1,2,3-propantriol	623-87-0	182.09	0.050	0.37	3.7	
1,4-Butanediol dinitrate	3457-91-8	180.12	0.050	0.37	3.7	
1-Butanol	71-36-3	74.12	20	60.6	606	
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	194.28	0.0010	0.0079	0.079	1
2,3-Dihydrofuran	1191-99-7	70.09	0.0010	0.0029	0.029	1
2,4-Dimethylpyridine	108-47-4	107.16	0.50	2.2	22	
2,4-Pentadienenitrile	1615-70-9	79.10	0.30	0.97	9.7	
2,5-Dimethylfuran	625-86-5	96.13	0.0010	0.0039	0.039	1
2-Ethyl-5-methylfuran	1703-52-2	110.16	0.0010	0.0045	0.045	1
2-Ethylhex-2-enal	645-62-5	126.20	0.10	0.52	5.2	
2-Fluoropropene	1184-60-7	60.07	0.10	0.25	2.5	
2-Hexanone	591-78-6	100.16	5.0	20.5	205	

Table 1. Cont'd.

Chemical	CAS Number	Molecular Weight (g/mol)	Inhalation OEL		Equivalent Inhalation Dose (mg)	Note
			(ppm)	(mg/m^3)		
2-Methylbut-2-enal	1115-11-3	84.12	0.030	0.10	1.0	
2-Methylene butanenitrile	1647-11-6	81.12	0.30	0.99	9.9	
2-Methylfuran	534-22-5	82.10	0.0010	0.0034	0.034	1
2-Nitro-2-methylpropane	594-70-7	103.12	0.30	1.3	13	
2-Pentylfuran	3777-69-3	138.21	0.0010	0.0056	0.056	1
3-Buten-2-one	78-94-4	70.09	0.20	0.57	5.7	
3-Methyl-3-buten-2-one	814-78-8	84.12	0.020	0.069	0.69	
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	126.20	0.0010	0.0052	0.052	1
4-Methyl-2-hexanone	105-42-0	114.19	0.50	2.3	23	
6-Methyl-2-heptanone	928-68-7	128.22	8.0	41.9	419	
Acetaldehyde	75-07-0	44.05	25	45.0	450	
Acetonitrile	75-05-8	41.05	20	33.6	336	
Ammonia	7664-41-7	17.03	25	17.4	174	
Benzene	71-43-2	78.11	0.50	1.6	16	
Butanal	123-72-8	72.11	25	73.7	737	
Butanenitrile	109-74-0	69.11	8.0	22.6	226	
Butyl nitrate	928-45-0	119.12	8.0	39.0	390	
Butyl nitrite	544-16-1	103.12	0.10	0.42	4.2	
Dibutyl butylphosphonate	78-46-6	250.32	0.0070	0.072	0.72	
Dichlorinated biphenyls	2050-67-1	223.10	0.0033	0.030	0.30	2
Diethyl phthalate	84-66-2	222.24	0.55	5.0	50	
Dimethylmercury	593-74-8	230.66	0.0012	0.012	0.12	
Formaldehyde	50-00-0	30.03	0.30	0.37	3.7	
Furan	110-00-9	68.08	0.0010	0.0028	0.028	
Heptanenitrile	629-08-3	111.19	6.0	27.3	273	
Hexanenitrile	628-73-9	97.16	6.0	23.8	238	
Mercury	7439-97-6	200.59	0.0030	0.025	0.25	
Methanol	67-56-1	32.04	200	261.9	2619	
Methyl isocyanate	624-83-9	57.05	0.020	0.047	0.47	
Methyl nitrite	624-91-9	61.04	0.10	0.25	2.5	
Monochlorinated biphenyls	2051-60-7	188.66	0.0039	0.030	0.30	2
Nitrous oxide (N_2O)	10024-97-2	44.01	50	89.9	899	
N-Nitrosodimethylamine	62-75-9	74.08	0.00030	0.00091	0.0091	
N-Nitrosomethylethylamine	10595-95-6	88.11	0.00030	0.0011	0.011	
N-Nitrosomorpholine	59-89-2	116.12	0.00060	0.0028	0.028	
Pentanenitrile	110-59-8	83.13	6.0	20.4	204	
Propanenitrile	107-12-0	55.08	6.0	13.5	135	
Pyridine	110-86-1	79.10	1.0	3.2	32	
Tetrachlorinated biphenyls	41464-49-7	291.99	0.0025	0.030	0.30	2
Tributyl phosphate	126-73-8	266.32	0.20	2.2	22	
Trichlorinated biphenyls	16606-02-3	257.55	0.0028	0.030	0.30	2

1. This chemical is a member of the substituted furan class.
2. This entry represents a portion of the chlorinated biphenyl class.

The chlorinated biphenyl COPC class is represented in Table 1 by four entries: monochlorinated, dichlorinated, trichlorinated, and tetrachlorinated biphenyls. These four subclasses include all chlorinated

biphenyls that have been detected in the headspaces; additional highly chlorinated biphenyls exist in the waste but tend to have such low vapor pressures they have not been measurable in the headspaces. The Chemical Abstract Service (CAS) number of the monochlorinated biphenyl having the highest reported headspace concentration is listed as the CAS number for this subclass in Table 1 and elsewhere in this report, and the CAS numbers given for the other three subclasses of chlorinated biphenyls were chosen analogously. The chlorinated biphenyls were divided into these four subclasses to improve specification of physical properties (e.g., solubilities, diffusivities, etc.) needed in the dermal absorption models described below.

The substituted furan class of COPC is represented in Table 1 by the seven members of this chemical class that have been reported in the headspaces. These are noted in Table 1. There are potentially many hundreds of substituted furans, and their physical properties, needed for the dermal modeling below, could vary greatly. The seven that have been reported in the headspaces are considered here to be representative of the possible substituted furans likely to be present in the headspaces.

The OELs listed in Table 1 are generally based on an 8-hr/day occupational exposure. For some chemicals, ACGIH has also established 15-min. time-weighted average short-term exposure limits (STELs) and OSHA has established ceiling guidelines for varying exposure durations. For those chemicals having STEL or ceiling guidelines, a corresponding dermal dose was calculated using the following equation:

$$\text{STEL or Ceiling Dermal Dose} = (\text{STEL or Ceiling, mg/m}^3)(\textit{Time Basis, hr})\left(\frac{10\ m^3/day}{8\ hr/day}\right) \quad \text{(Eq. 1)}$$

Here, the Time Basis is the applicable duration of the exposure associated with the STEL or ceiling value; e.g., ACGIH STELs generally have a 15-min (0.25-hr) Time Basis. Table 2 lists the COPC that have established STEL or ceiling values, the most restrictive of the established values, the time basis, and the calculated STEL or ceiling dermal dose. The STEL or ceiling dermal doses given in Table 2 should be used instead of the 8-hr equivalent inhalation doses (Table 1) if dermal absorption rates are high, as when a large area of skin is contacted by condensate with high concentrations of COPC.

Table 2. Short-Term and Ceiling Dermal Doses for Chemicals of Potential Concern

Chemical	CAS Number	Most Restrictive STEL or Ceiling OEL (ppm)	Most Restrictive STEL or Ceiling OEL (mg/m^3)	Time Basis of STEL or Ceiling OEL (hr)	STEL or Ceiling Dermal Dose (mg)
1,3-Butadiene	106-99-0	5	11.1	0.25	3.45
2-Hexanone	591-78-6	10	40.9	0.25	12.8
Ammonia	7664-41-7	35	24.4	0.25	7.61
Benzene	71-43-2	2.5	7.98	0.25	2.49
Formaldehyde	50-00-0	2	2.45	0.25	0.767
Dimethylmercury	593-74-8	0.00366	0.0345	0.25	0.0108
Ethylamine	75-04-7	10	18.4	0.25	5.76
Methanol	6`7-56-1	250	327	0.25	102

In the remainder of this study, no distinction has made between the equivalent inhalation dose calculated with the 8-hr time-weighted average OEL and the STEL or ceiling dermal dose; the smaller of the two values has been used.

2.2 NonSteady-State Model for Dermal Absorption from an Aqueous Vehicle

The model used to approximate absorption of COPC from aqueous condensate is given in the EPA interim report *Dermal Exposure Assessment: Principles and Applications* (EPA 1992). In that report, EPA recommends the use of a steady state model for inorganic solutes and a nonsteady-state model for organic solutes from an aqueous vehicle:

> "…the new nonsteady-state approach for estimating the dermally absorbed dose from water droplets appears to offer significant advantages (over the traditional steady-state approach) for risk assessment application. First, the method more accurately reflects normal human exposure conditions since the short contact times associated with bathing and swimming generally mean that steady state will not occur. Second, the method accounts for the dose that can occur after the actual exposure event due to absorption of contaminants stored in skin lipids. For these reasons, it is recommended as the preferred approach. However, the nonsteady-state approach was developed for application to organics which exhibit octanol-water partitioning. Thus, it is not applicable to inorganics."

The exclusion of "inorganics" in the EPA nonsteady-state model is apparently not based on consideration of inorganic species in general, but on inorganic electrolytes that tend to have extremely small octanol-water partition coefficients.[2] Most of the inorganic COPC are not strictly ionic species in aqueous solution, and arguably the nonsteady-state model is just as valid for these inorganic as for the organic COPC.

The nonsteady-state model for absorption of organic solutes from an aqueous solution given by EPA (1992) attempts to account for the relatively high absorption rate of solute expected and observed between the initial exposure and the time at which a steady state absorption rate is developed. The form of the model varies depending on whether the duration of the exposure, t_{event}, is less than or greater than the time it takes to approximately develop the steady-state absorption rate, t^*. The absorbed dose per unit area of skin wetted by the liquid per exposure event, DA_{event} , is given by

$$If\ t_{event} < t^*, then \quad DA_{event} = 2K_p^w C_v \sqrt{\frac{6\tau t_{event}}{\pi}} \qquad \text{(Eq. 2)}$$

[2] The EPA nonsteady-state model estimates the partition coefficient of solute between the stratum corneum and water, a parameter rarely measured experimentally, using the octanol-water partition coefficient, a commonly measured parameter (EPA 1992).

$$If\ t_{event} > t^*, then \quad DA_{event} = K_p^w C_v \left[\frac{t_{event}}{1+B} + 2\tau \left(\frac{1+3B}{1+B} \right) \right] \qquad \text{(Eq. 3)}$$

$$\tau = \frac{l_{sc}^2}{6D_{sc}} \qquad \text{(Eq. 4)}$$

in which

l_{sc} = thickness of the stratum corneum (cm), and
D_{sc} = diffusivity of the solute in the stratum corneum (cm^2/hr); and

B = a dimensionless constant from the Cleek and Bunge (1993) model approximated by

$$B \approx \frac{K_{o/w}}{10{,}000} \qquad \text{(Eq. 5)}$$

EPA (1992) recommends using

$$l_{sc} = 0.001\,\text{cm} \qquad \text{(Eq. 6)}$$

and estimating the diffusivity, D_{sc}, from the following expression that is based on the Guy and Potts (1993) model for the permeability coefficient K_p^w:

$$\log\left(\frac{D_{sc}}{l_{sc}} \right) = -2.72 - 0.0061MW \qquad \text{(Eq. 7)}$$

where MW is the molecular weight of the diffusing species (g/mol). However, subsequent to the EPA (1992) report, Wilschut et al. (1995) examined five mathematical models for estimating skin permeability coefficients and found that the revised Robinson model provided the smallest residual variance for a dataset of experimentally measured permeability coefficients. The Robinson model also more accurately reflects the physical mass transfer resistances involved and is specifically recommended by AIHA (2000). It has been adopted here as an improvement of the EPA (1992) formulation. The revised Robinson model, as tested and assigned new optimized constants by Wilschut et al. (1995), is

$$K_p^w = \frac{1}{\frac{1}{K_{psc} + K_{pol}} + \frac{1}{K_{aq}}} \qquad \text{(Eq. 8)}$$

where:

K_{psc} = permeability coefficient of the lipid fraction of the stratum corneum, given by

$$\log(K_{psc}) \quad = \quad -1.326 + 0.6097\log(K_{o/w}) - 0.1786\,MW^{0.5} \qquad \text{(Eq. 9)}$$

in which

$K_{o/w}$ = octanol-water partition coefficient, defined as

$$K_{o/w} \quad = \quad \frac{Concentration\ in\ octanol}{Concentration\ in\ water} \text{ at equilibrium;}$$

K_{pol} = permeability coefficient of the protein fraction of the stratum corneum, given by

$$K_{pol} \quad = \quad \frac{0.0001519}{\sqrt{MW}} \qquad \text{(Eq. 10)}$$

K_{aq} = permeability of the watery dermal layer of the skin, given by

$$K_{aq} \quad = \quad \frac{2.5}{\sqrt{MW}}\,. \qquad \text{(Eq. 11)}$$

Note that, as suggested by the form of Eq. 8, mass transport of solute occurs in parallel through the two fractions of the stratum corneum (protein and lipid fractions) and then in series through the watery dermis layer that lies below the stratum corneum.

Rederiving the expression for the diffusivity of solute through the stratum corneum using Eq. (4.2) and (4.48) of EPA (1992) yields

$$D_{sc} \quad = \quad \frac{l_{sc}\,K_p^w}{K_{o/w}^{0.7}}\,. \qquad \text{(Eq. 12)}$$

The time required to approximately reach a steady state rate of absorption, t^*, depends on the Cleek and Bunge (1993) parameter, B, as follows:

$$If\ \ B \le 0.1,\ then \quad t^* \quad = \quad 2.4\tau\,, \qquad \text{(Eq. 13)}$$

$$if\ \ 0.1 < B \le 1.17,\ then \quad t^* \quad = \quad \left(8.4 + 6\log(B)\right)\tau\,, \qquad \text{(Eq. 14)}$$

$$and\ if\ \ B > 1.17,\ then \quad t^* \quad = \quad 6\left(b - \sqrt{b^2 - c^2}\right)\tau\,. \qquad \text{(Eq. 15)}$$

where:

$$b \quad = \quad \frac{2}{\pi}\left(1 + B\right)^2 - c \qquad \text{(Eq. 16)}$$

and

$$c = \frac{1+3B}{3}. \qquad \text{(Eq. 17)}$$

The nonsteady-state model for COPC absorption from aqueous condensate in contact with the worker's skin is thus given by Eq. 2 through 6 and Eq. 8 through 17. Table 3 lists, for each COPC, the permeability coefficients through the lipid and protein fractions of the stratum corneum and the watery dermal layer, the overall permeability coefficient, and the time to reach steady state. Note that the time to reach steady state varies significantly for the COPC, ranging from about 16 min. for ammonia to more than 1 day for tributyl phosphate. In principle, the longer it takes to reach steady state, the more important it is to account for the transient nonsteady-state period of exposure.

While the nonsteady-state model described by EPA is appealing from the perspective of more accurately estimating absorption during short-time exposures, as is the case for accidental contact with condensates that are washed off quickly, it has not been validated yet. The following is an excerpt from EPA (1992):

> "…calculations performed by EPA have shown that this approach provides a more conservative total absorbed dose over the traditional steady-state equation for organic compounds. Preliminary testing showed that this new approach indicates that the dermal dose resulting from 10-minute showers exceeds the dose associated with drinking 2 L/day for a number of the pollutants listed in Table 6-8. For the fastest penetrating chemicals the dermal dose was predicted to exceed the ingested dose by about two orders of magnitude (see Chapter 9 for further discussion of this comparison). This seems counterintuitive and raises concerns that the model may be overly conservative. …"

Table 3. Permeability Coefficients and Time to Steady-State for COPC

Chemical	CAS Number	Molecular Weight (g/mol)	Log of octanol-water partition coefficient	Permeability coefficient for lipid fraction of stratum corneum (cm/hr)	Permeability coefficient for protein fraction of stratum corneum (cm/hr)	Permeability coefficient for watery dermal layer (cm/hr)	Overall permeability coefficient (Robinson [1993] model) (cm/hr)	Time to Reach Steady-State (hr)
			$\log(K_{o/w})$	K_{psc}	K_{pol}	K_{aq}	K_{ps}^{w}	t^*
1,1'-Biphenyl	92-52-4	154.21	3.98	0.0763	1.22E-05	0.20	0.055	6.3
1,3-Butadiene	106-99-0	54.09	1.99	0.0375	2.07E-05	0.34	0.034	0.45
1,3-Dinitrate-1,2,3-propantriol	623-87-0	182.09	0.71	0.00050	1.13E-05	0.19	0.00051	2.7
1,4-Butanediol dinitrate	3457-91-8	180.12	2.20	0.0042	1.13E-05	0.19	0.0041	2.6
1-Butanol	71-36-3	74.12	0.88	0.00471	1.76E-05	0.29	0.0047	0.59
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	194.28	3.19	0.0135	1.09E-05	0.18	0.013	4.7
2,3-Dihydrofuran	1191-99-7	70.09	0.72	0.00415	1.81E-05	0.30	0.0041	0.56
2,4-Dimethylpyridine	108-47-4	107.16	1.90	0.00963	1.47E-05	0.24	0.0093	0.95
2,4-Pentadienenitrile	1615-70-9	79.10	0.98	0.00482	1.71E-05	0.28	0.0048	0.64
2,5-Dimethylfuran	625-86-5	96.13	2.24	0.0194	1.55E-05	0.25	0.018	0.81
2-Ethyl-5-methylfuran	1703-52-2	110.16	2.95	0.0396	1.45E-05	0.24	0.034	0.99
2-Ethylhex-2-enal	645-62-5	126.20	2.62	0.0184	1.35E-05	0.22	0.017	1.2
2-Fluoropropene	1184-60-7	60.07	1.73	0.02211	1.96E-05	0.32	0.021	0.49
2-Hexanone	591-78-6	100.16	1.38	0.00534	1.52E-05	0.25	0.0052	0.86
2-Methylbut-2-enal	1115-11-3	84.12	1.15	0.00546	1.66E-05	0.27	0.0054	0.68
2-Methylene butanenitrile	1647-11-6	81.12	1.25	0.00672	1.69E-05	0.28	0.0066	0.66
2-Methylfuran	534-22-5	82.10	1.85	0.01526	1.68E-05	0.28	0.014	0.67
2-Nitro-2-methylpropane	594-70-7	103.12	1.17	0.00375	1.50E-05	0.25	0.0037	0.89
2-Pentylfuran	3777-69-3	138.21	3.87	0.0859	1.29E-05	0.21	0.061	4.6
3-Buten-2-one	78-94-4	70.09	0.41	0.00268	1.81E-05	0.30	0.0027	0.56
3-Methyl-3-buten-2-one	814-78-8	84.12	0.96	0.00418	1.66E-05	0.27	0.0041	0.68
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	126.20	2.67	0.0197	1.35E-05	0.22	0.018	1.2
4-Methyl-2-hexanone	105-42-0	114.19	1.66	0.00599	1.42E-05	0.23	0.0059	1.0
6-Methyl-2-heptanone	928-68-7	128.22	2.15	0.0092	1.34E-05	0.22	0.0088	1.3
Acetaldehyde	75-07-0	44.05	-0.34	0.00191	2.29E-05	0.38	0.0019	0.39
Acetonitrile	75-05-8	41.05	-0.34	0.00210	2.37E-05	0.39	0.0021	0.37

Table 3. Cont'd.

Chemical	CAS Number	Molecular Weight (g/mol)	Log of octanol-water partition coefficient	Permeability coefficient for lipid fraction of stratum corneum (cm/hr)	Permeability coefficient for protein fraction of stratum corneum (cm/hr)	Permeability coefficient for watery dermal layer (cm/hr)	Overall permeability coefficient (Robinson [1993] model) (cm/hr)	Time to Reach Steady-State (hr)
Ammonia	7664-41-7	17.03	-1.38	0.00125	3.68E-05	0.61	0.0013	0.27
Benzene	71-43-2	78.11	2.13	0.0248	1.72E-05	0.28	0.023	0.63
Butanal	123-72-8	72.11	0.88	0.00494	1.79E-05	0.29	0.0049	0.58
Butanenitrile	109-74-0	69.11	0.53	0.00325	1.83E-05	0.30	0.0032	0.55
Butyl nitrate	928-45-0	119.12	2.15	0.0109	1.39E-05	0.23	0.010	1.1
Butyl nitrite	544-16-1	103.12	2.35	0.0196	1.50E-05	0.25	0.018	0.89
Dibutyl butylphosphonate	78-46-6	250.32	3.83	0.0153	9.60E-06	0.16	0.014	22
Dichlorinated biphenyls	2050-67-1	223.10	5.06	0.123	1.02E-05	0.17	0.071	9.7
Diethyl phthalate	84-66-2	222.24	2.42	0.0031	1.02E-05	0.17	0.0030	4.8
Dimethylmercury	593-74-8	230.66	2.59	0.0035	1.00E-05	0.16	0.0034	5.4
Formaldehyde	50-00-0	30.03	0.35	0.00810	2.77E-05	0.46	0.0080	0.32
Furan	110-00-9	68.08	1.34	0.0104	1.84E-05	0.30	0.010	0.55
Heptanenitrile	629-08-3	111.19	2.31	0.0158	1.44E-05	0.24	0.015	1.0
Hexanenitrile	628-73-9	97.16	1.66	0.00843	1.54E-05	0.25	0.0082	0.82
Mercury	7439-97-6	200.59	0.62	0.00033	1.07E-05	0.18	0.00034	3.5
Methanol	67-56-1	32.04	-0.77	0.00156	2.68E-05	0.44	0.0016	0.33
Methyl isocyanate	624-83-9	57.05	0.79	0.00641	2.01E-05	0.33	0.0063	0.47
Methyl nitrite	624-91-9	61.04	0.88	0.00653	1.94E-05	0.32	0.0064	0.49
Monochlorinated biphenyls	2051-60-7	188.66	4.58	0.103	1.11E-05	0.18	0.066	6.3
Nitrous oxide (N_2O)	10024-97-2	44.01	0.36	0.00511	2.29E-05	0.38	0.0051	0.39
N-Nitrosodimethylamine	62-75-9	74.08	-0.57	0.00062	1.76E-05	0.29	0.00063	0.59
N-Nitrosomethylethylamine	10595-95-6	88.11	0.04	0.00105	1.62E-05	0.27	0.0011	0.72
N-Nitrosomorpholine	59-89-2	116.12	-0.44	0.00030	1.41E-05	0.23	0.00032	1.1
Pentanenitrile	110-59-8	83.13	1.12	0.00535	1.67E-05	0.27	0.0053	0.67
Propanenitrile	107-12-0	55.08	0.16	0.00279	2.05E-05	0.34	0.0028	0.46
Pyridine	110-86-1	79.10	0.65	0.00303	1.71E-05	0.28	0.0030	0.64
Tetrachlorinated biphenyls	41464-49-7	291.99	6.26	0.273	8.89E-06	0.15	0.095	25
Tributyl phosphate	126-73-8	266.32	4.00	0.0158	9.31E-06	0.15	0.014	31
Trichlorinated biphenyls	16606-02-3	257.55	5.66	0.180	9.47E-06	0.16	0.084	15

2.3 NonSteady-State Model for Dermal Absorption from an Organic Liquid Vehicle

The formulation of the nonsteady-state model presented in the previous section is specific for an aqueous vehicle because the permeability coefficient correlation employed is specific for the transfer of solute from an aqueous vehicle. Specifically, the permeability coefficient includes the partitioning of solute between the solution contacting the skin and the stratum corneum. From EPA (1992) Eq. (4.2):

$$K_p^v = \frac{K_{sc/v} D_{sc}}{l_{sc}} \quad \text{(Eq. 18)}$$

where:

K_p^v = permeability of a solute from an arbitrary vehicle through the stratum corneum; and

$K_{sc/v}$ = partition coefficient of solute between the stratum corneum and the vehicle.

It follows from the definitions of the partition coefficients that the dermal permeability coefficient of a solute from an organic solvent, K_p^{os}, is related to the dermal permeability coefficient from water, K_p^w, by

$$K_p^{os} = \frac{K_p^w}{K_{os/w}} \quad \text{(Eq. 19)}$$

where:

$K_{os/w}$ = partition coefficient of the solute between the organic solvent and water.

Given that the organic condensate of interest is a mixture of volatile and semivolatile organic chemicals, many having polar functional groups like octanol, the approximation is made here that the organic solvent-water partitioning coefficient is equal to the octanol-water partitioning coefficient:[3]

$$K_{os/w} \approx K_{o/w} \quad \text{(Eq. 20)}$$

The nonsteady-state model for dermal absorption of solute from an organic condensate is otherwise identical to that presented above for aqueous condensate. The absorbed dose per unit area of skin wetted by the liquid per exposure event, DA_{event}, is given by Eq. 2 through 7 with K_p^{os}, given by Eq. 19, substituted for K_p^w.

2.4 Steady-State Model for Dermal Absorption from the Vapor Phase

The model used here to estimate dermal absorption of gases and vapors directly from the air is that given by the American Industrial Hygiene Association (AIHA 2000). It is a steady state model (analogous to

[3] This approximation is suggested in EPA (1992).

Eq. 1 that incorporates the revised Robinson (1993) model as given by Wilschut et al. (1995) to estimate the permeability of a vapor from the surface of the skin inwards, and an additional permeability coefficient to address the transport of vapors through air to the skin. The overall permeability coefficient, K_p^{vap}, is given in a form similar to that proposed by Robinson (Wilschut et al. 1995):

$$K_p^{vap} = \frac{1}{\frac{1}{K_{p\,sk}^{vap}} + \frac{1}{K_{p\,air}^{vap}}} \qquad \text{(Eq. 21)}$$

where:

$K_{p\,sk}^{vap}$ = dermal permeability coefficient for absorption of a vapor from air through the skin; and

$K_{p\,air}^{vap}$ = permeability coefficient for transport of a vapor through air (and loose work clothing) to the surface of the skin.

Analogous to Eq. 19, the permeability coefficient for the dermal absorption of vapor from air, $K_{p\,sk}^{vap}$, is estimated by

$$K_{p\,sk}^{vap} = \frac{K_p^w}{K_{air/w}} \qquad \text{(Eq. 22)}$$

where:

$K_{air/w}$ = partition coefficient of a vapor between air and water, defined as

$K_{air/w} = \frac{Concentration\ in\ air}{Concentration\ in\ water}$ at equilibrium.

Values for K_p^w have been tabulated in Table x.2, and values for $K_{air/w}$ are easily established from published Henry's law constants.

The dermal permeability coefficient for transport of a vapor through air to the surface of the skin is estimated by assuming the air around the worker is well mixed except for a thin boundary layer adjacent to the skin, through which vapors diffuse to the skin. Analogous to Eq. 18[4], the permeability coefficient for vapor diffusion through the boundary layer is given in terms of the diffusivity of the vapor in air, D_{air}, and the thickness of the boundary layer, l_{bl}, by

[4] For this particular portion of the mass transfer model, there is no phase change and consequently no partition coefficient is needed as was required in Eq. 19.

$$K_{p\ air}^{vap} = \frac{D_{air}}{l_{bl}} \qquad \text{(Eq. 24)}$$

The thickness of the boundary layer, l_{bl}, depends on the level of activity of the worker and the clothing worn. Lotens and Wammes (1993) examined this issue and estimated the effective thickness of the boundary layer to be 3 cm for light work clothing.

AIHA (2000) recommends the diffusivity of a vapor in air is calculated from the expression

$$D_{air} = 360\sqrt{\frac{76}{MW}}\,. \qquad \text{(Eq. 25)}$$

The absorbed dose per unit area of skin exposed to the vapor per exposure event, DA_{event} , is given by

$$DA_{event} = C_{vap}\ K_p^{vap}\ t_{event} \qquad \text{(Eq. 26)}$$

where C_{vap} is the vapor concentration in the air surrounding the worker.

2.5 Limiting Approximation for Ocular Absorption from the Vapor Phase

No model for absorption of vapor by a human eye was found in the literature. Vapors, particularly those soluble in water, are absorbed by the tear-wetted surface of the eye and transported to blood vessels in the eye. The importance of ocular absorption varies with the eyes' response to each chemical; some vapors are known ocular irritants and this effect may be far more important than the contribution of ocular absorption to the body's systemic dose. Nevertheless, a simple model is developed here to examine the latter.

As a first approximation it is assumed here that vapors are absorbed by the eye at the same rate as by the watery dermal layer of the skin, without the stratum corneum. Assuming a typical eyeball diameter of about 2.5 cm, and that about one-sixth of the eyeball is exposed, the eyes present roughly 6.5 cm^2 of surface area for vapor absorption. Analogous to Eq. 21, the overall permeability coefficient can be expressed as

$$K_{p\ ocular}^{vap} = \frac{1}{\frac{1}{K_{p\ eye}^{vap}} + \frac{1}{K_{p\ air\ eye}^{vap}}} \qquad \text{(Eq. 27)}$$

where the permeability coefficient of the chemical from the surface of the eye to a blood vessel is now given by

$$K_{p\ eye}^{vap} = \frac{K_{eye}}{K_{air/w}} \qquad \text{(Eq. 28)}$$

where K_{eye}, the permeability of a chemical from the surface of the eye to a blood vessel, is set equal to the permeability coefficient of the water dermal layer,

$$K_{eye} = K_{aq} = \frac{2.5}{\sqrt{MW}}, \qquad \text{(Eq. 29)}$$

and the permeability coefficient of vapors from the air to the surface of the eye is given by an expression analogous to Eq. 24:

$$K^{vap}_{p\ air\ eye} = \frac{D_{air}}{l_{bl\ eye}} \qquad \text{(Eq. 30)}$$

where $l_{bl\ eye}$ is the thickness of a stagnant boundary layer of air at the surface of the eye. Based on qualitative considerations of the inherent way that people protect their eyes from wind and the disturbance of the air next to the eye caused by blinking, the air boundary layer next to the eye was specified here to be $l_{bl\ eye}$ = 0.5 cm.

The absorbed dose per exposure event, DA_{event}, is given by

$$DA_{event} = C_{vap}\ K^{vap}_{p\ occular}\ t_{event}\ A_{eye} \qquad \text{(Eq. 31)}$$

where, as above, C_{vap} is the vapor concentration in the air surrounding the worker, and A_{eye} = 6.5 cm^2, the exposed surface area of the eye.

3.0 Results

3.1 Aqueous Condensate

The composition of aqueous condensate is assumed to be that in equilibrium with the highest reported headspace concentration of each COPC. This results in an overestimation of the actual COPC concentrations because the highest reported COPC concentrations are not commonly attained in the headspaces or ventilation systems, and the COPC concentrations in condensate are maximized when the vapor and condensate are in equilibrium. The concentrations given by Meacham et al. (2006) are used here.

Estimated COPC concentrations in the aqueous condensate were first compared to EPA drinking water standards. Table 4 lists the two COPC for which EPA has established drinking water standards, along with their calculated aqueous condensate concentrations, and their EPA standards. The drinking water standards were obtained from the EPA web site at http://www.epa.gov/safewater/mcl.html. As indicated in Table 4, mercury is expected to be at a lower concentration in the aqueous condensate than the EPA standard. Based on this comparison, mercury is considered to present a negligible dermal exposure hazard to workers and is not considered further here. Though calculated to be present at only slightly higher concentrations than its EPA drinking water standard, benzene was included in subsequent analyses here.

Table 4. Comparison of Aqueous Condensate Concentrations with EPA Drinking Water Standards

Chemical	CAS Number	Condensate Concentration (mg/g)	EPA Drinking Water Standard (mg/g)	Comment
Benzene	71-43-2	8.90E-06	5.00E-06	
Mercury	7439-97-6	3.18E-07	2.00E-06	Below EPA Standard

The quantity of aqueous condensate needed to exceed the equivalent inhalation dose of each remaining COPC (assuming 100% of the dissolved COPC is absorbed dermally) was calculated and compared to a nominal maximum condensate volume of 4 L. This 4-L criterion corresponds to approximately 1 gal. of condensate, an estimate of the largest volume with which workers would be contacted. If spread evenly, 4 L would amount to about a 0.2-cm-thick layer of the condensate covering the entire body of a worker. The volume of condensate (in units of L) needed to exceed the most restrictive dose (the smallest of the acceptable 8-hr, STEL, or ceiling dermal dose, in units of mg) is given by

$$Volume\ of\ Condensate = \frac{Equivalent\ Inhalation\ Dose}{C\ \rho}$$

where C is the concentration (mg/g) of the COPC in the condensate, and ρ is the density of the condensate (g/L). Table 5 lists the estimated condensate concentration, the equivalent inhalation dose, and the calculated condensate volume needed to reach the dermal dose for each COPC. Entries in Table 5 are arranged in order of increasing values in the fifth column, “condensate volume containing dermal dose.”

Table 5. Volume of Aqueous Condensate Required to Exceed the Allowable Dermal Dose

Chemical	CAS Number	Condensate Concentration (mg/g)	Equivalent Inhalation Dose (mg)	Condensate Volume (L)	Note
N-Nitrosomorpholine	59-89-2	4.57E-02	0.028	0.0006	
N-Nitrosodimethylamine	62-75-9	8.73E-03	0.0091	0.0010	
Ammonia	7664-41-7	2.63E+00	7.6	0.0029	
Tributyl phosphate	126-73-8	9.60E-01	22	0.0227	
1,3-Dinitrate-1,2,3-propantriol	623-87-0	1.43E-01	3.7	0.026	
N-Nitrosomethylethylamine	10595-95-6	1.51E-04	0.011	0.071	
Formaldehyde	50-00-0	5.67E-03	0.77	0.14	
Methanol	67-56-1	2.68E-01	102	0.38	
1,4-Butanediol dinitrate	3457-91-8	7.47E-03	3.7	0.49	
Furan	110-00-9	4.02E-05	0.028	0.69	
Dibutyl butylphosphonate	78-46-6	1.01E-03	0.72	0.71	
Diethyl phthalate	84-66-2	4.69E-02	50	1.1	
1-Butanol	71-36-3	4.92E-01	606	1.2	
2-Methylfuran	534-22-5	1.49E-05	0.034	2.3	
3-Buten-2-one	78-94-4	1.72E-03	5.7	3.3	
1,1'-Biphenyl	92-52-4	1.10E-03	13	11	> 4-L
2,4-Dimethylpyridine	108-47-4	1.66E-03	22	13	> 4-L
Nitrous oxide (N_2O)	10024-97-2	6.27E-02	899	14	> 4-L
Propanenitrile	107-12-0	7.90E-03	135	17	> 4-L
2-Hexanone	591-78-6	6.39E-04	13	20	> 4-L
Acetonitrile	75-05-8	1.57E-02	336	21	> 4-L
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	3.27E-06	0.079	24	> 4-L
2,3-Dihydrofuran	1191-99-7	1.01E-06	0.029	29	> 4-L
4-Methyl-2-hexanone	105-42-0	6.36E-04	23	37	> 4-L
Pyridine	110-86-1	8.79E-04	32	37	> 4-L
Acetaldehyde	75-07-0	7.92E-03	450	57	> 4-L
Butanenitrile	109-74-0	3.38E-03	226	67	> 4-L
3-Methyl-3-buten-2-one	814-78-8	6.78E-06	0.69	100	> 4-L
2-Methylbut-2-enal	1115-11-3	7.23E-06	1.0	140	> 4-L
Butanal	123-72-8	4.76E-03	737	150	> 4-L
2-Nitro-2-methylpropane	594-70-7	7.95E-05	13	160	> 4-L
Methyl nitrite	624-91-9	1.50E-05	2.5	170	> 4-L
Pentanenitrile	110-59-8	1.17E-03	204	170	> 4-L
2-Ethylhex-2-enal	645-62-5	2.51E-05	5.2	210	> 4-L
Monochlorinated biphenyls	2051-60-7	1.39E-06	0.30	220	> 4-L
2,4-Pentadienenitrile	1615-70-9	4.35E-05	9.7	220	> 4-L
2,5-Dimethylfuran	625-86-5	1.66E-07	0.039	240	> 4-L
Benzene	71-43-2	8.90E-06	2.5	280	> 4-L
Hexanenitrile	628-73-9	7.93E-04	238	300	> 4-L
2-Ethyl-5-methylfuran	1703-52-2	1.40E-07	0.045	320	> 4-L
Tetrachlorinated biphenyls	41464-49-7	8.37E-07	0.30	360	> 4-L
2-Methylene butanenitrile	1647-11-6	2.51E-05	9.9	400	> 4-L
Dichlorinated biphenyls	2050-67-1	7.34E-07	0.30	410	> 4-L
Methyl isocyanate	624-83-9	1.00E-06	0.47	470	> 4-L
6-Methyl-2-heptanone	928-68-7	8.97E-04	419	470	> 4-L
Butyl nitrite	544-16-1	8.59E-06	4.2	490	> 4-L
Trichlorinated biphenyls	16606-02-3	4.78E-07	0.30	630	> 4-L

Table 5. Cont'd.

Chemical	CAS Number	Condensate Concentration (mg/g)	Equivalent Inhalation Dose (mg)	Condensate Volume (L)	Note
Heptanenitrile	629-08-3	3.64E-04	273	750	> 4-L
Mercury	7439-97-6	3.18E-07	0.25	790	> 4-L
2-Pentylfuran	3777-69-3	2.97E-08	0.056	1,900	> 4-L
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1.52E-08	0.052	3,400	> 4-L
2-Fluoropropene	1184-60-7	3.21E-07	2.5	7,700	> 4-L
Butyl nitrate	928-45-0	2.78E-05	390	14,000	> 4-L
1,3-Butadiene	106-99-0	1.64E-07	3.5	21,000	> 4-L
Dimethylmercury	593-74-8	1.44E-10	0.011	75,000	> 4-L

As indicated in Table 5, most of the COPC are expected to be present in aqueous condensate at levels that, even assuming 100% absorption through the skin, would not exceed the equivalent inhalation dose given indefinite contact with 4 L of condensate. These are assumed to present negligible dermal exposure hazard to workers and have been excluded from further consideration.

The 4-L criterion applied above resulted in the identification of 15 COPC that, assuming the condensate is in equilibrium with the highest reported vapor concentrations, could result in exposures that exceeded the equivalent inhalation dose. Whether a dermal exposure actually does result in an unacceptable dose depends on the actual amount of condensate contacting the skin, the rate at which it is absorbed, and the duration of the exposure.

The dermal absorption dose for various scenarios has been estimated for the 15 remaining COPC using the EPA (1992) nonsteady-state model described in Section 2.2. It attempts to account for the relatively high initial absorption rate while properly modeling the lower steady state absorption rates that are developed at larger times. Inasmuch as most tank farm exposure scenarios would involve the removal of the condensate as soon as possible (e.g., doffing wet clothing, toweling, showering, etc.), the proper modeling of short-duration exposures was deemed important. The following subsections consider model results applied to various scenarios.

Scenario 1. Indefinite Contact with Aqueous Condensate

Consider the scenario in which a worker is contacted by a small amount of aqueous condensate, but because of working conditions and the small amount of condensate involved, the worker does not notice it and takes no action to remove it. It is assumed here that the condensate is sufficiently spread out on the worker's skin and left on long enough for essentially 100% of the COPC present in the condensate to be absorbed. Under these circumstances the worker could only exceed the equivalent inhalation dose if the amount of condensate in contact with the skin contains more than the equivalent inhalation doses listed in Table 5.

Inasmuch as it is very unlikely that an exposure of more than 10 mL would go unnoticed, only the first three COPC listed in Table 5 (N-nitrosomorpholine, N-nitrosodimethylamine, and ammonia) could result in an exposure that exceeds its equivalent inhalation dose given this scenario. Though both the

nitrosamines are carcinogens, the proposed limits are expected to be protective under plausible exposure conditions.

Scenario 2. Contact with Aqueous Condensate for Specified Duration

Consider a scenario in which a worker is contacted by a relatively large quantity of aqueous condensate and remains exposed for a period of 30 min, before the condensate can be effectively washed off. For a fixed exposure time such as this, the nonsteady-state model provides an estimated dose absorbed per unit area, and this can be used to estimate the wetted surface area required to reach the equivalent inhalation dose. Table 6 lists the minimum area of contacted skin needed to absorb the equivalent inhalation dose during a 30-minute exposure for each of the 15 COPC of interest. Entries in Table 6 are arranged in order of increasing values of the fourth column, "area of contacted skin."

Table 6. Aqueous Condensate-Skin Contact Area to Reach the Most Restrictive Dermal Dose Given an Exposure Time of 30 Minutes

Chemical	CAS Number	Duration of Exposure (hr)	Area of Contacted Skin (cm^2)	Average Absorption Rate (mg/cm^2-hr)	Equivalent Inhalation Dose (mg)
Tributyl phosphate	126-73-8	0.5	420	1.03E-01	21.8
N-Nitrosomorpholine	59-89-2	0.5	1,500	3.78E-05	0.0285
N-Nitrosodimethylamine	62-75-9	0.5	1,700	1.07E-05	0.00908
Ammonia	7664-41-7	0.5	3,100	4.86E-03	7.61
Dibutyl butylphosphonate	78-46-6	0.5	15,000	9.40E-05	0.716
Formaldehyde	50-00-0	0.5	22,000	6.94E-05	0.767
1,3-Dinitrate-1,2,3-propantriol	623-87-0	0.5	25,000	3.02E-04	3.72
1,4-Butanediol dinitrate	3457-91-8	0.5	59,000	1.25E-04	3.68
N-Nitrosomethylethylamine	10595-95-6	0.5	62,000	3.46E-07	0.0108
Furan	110-00-9	0.5	74,000	7.56E-07	0.0278
Diethyl phthalate	84-66-2	0.5	130,000	7.81E-04	50
2-Methylfuran	534-22-5	0.5	150,000	4.42E-07	0.0336
1-Butanol	71-36-3	0.5	270,000	4.45E-03	606
Methanol	67-56-1	0.5	310,000	6.56E-04	102
3-Buten-2-one	78-94-4	0.5	1,300,000	8.71E-06	5.73

Given a nominal 20,000 cm^2 surface area for the human body (AIHA 2000), only the absorption rates of the first five COPC in Table 6 would be high enough to reach the equivalent inhalation dose in 30 min., even if the worker were completely submerged in condensate. Controls to limit the potential exposure surface area and duration of exposure for tributyl phosphate, N-nitrosomorpholine, N-nitrosodimethylamine, ammonia, and dibutyl butylphosphonate should be considered.

Note that the average absorption rate given in Table 6 is actually the average flux (i.e., mass absorbed per unit time per unit surface area) for a 0.5-hr exposure. The absorbed dose for an exposure of duration t_{event} to any given surface area can be calculated

$$Absorbed\ Dose = (Average\ Absorption\ Rate)(Surface\ Area)(t_{event}) \qquad \text{(Eq. 32)}$$

where *Average Absorption Rate* is itself a function of t_{event}. Values of the average absorption rates for each COPC for selected t_{event} values are tabulated in Table 7 to allow the reader to examine other scenarios.

Table 7. Average Absorption Rates from Aqueous Condensate for Selected Exposure (Event) Durations

Chemical	Chemical Identification Number ↓	Average Absorption Rate (mg/hr cm^2)									
	Event Duration →	5 min	10 min	15 min	20 min	30 min	45 min	1 hr	2 hr	4 hr	8 hr
Nitrous oxide (N_2O)	10024-97-2	1.23E-03	8.67E-04	7.08E-04	6.13E-04	5.24E-04	4.55E-04	4.21E-04	3.69E-04	3.43E-04	3.31E-04
4-Methyl-2-hexanone	105-42-0	2.35E-05	1.66E-05	1.36E-05	1.18E-05	9.60E-06	7.84E-06	6.79E-06	5.34E-06	4.53E-06	4.12E-06
N-Nitrosomethylethylamine	10595-95-6	8.48E-07	5.99E-07	4.89E-07	4.24E-07	3.46E-07	2.91E-07	2.58E-07	2.10E-07	1.85E-07	1.73E-07
1,3-Butadiene	106-99-0	2.30E-08	1.62E-08	1.33E-08	1.15E-08	9.72E-09	8.31E-09	7.61E-09	6.55E-09	6.02E-09	5.76E-09
Propanenitrile	107-12-0	9.19E-05	6.50E-05	5.31E-05	4.60E-05	3.88E-05	3.32E-05	3.04E-05	2.62E-05	2.41E-05	2.31E-05
2,4-Dimethylpyridine	108-47-4	9.27E-05	6.55E-05	5.35E-05	4.63E-05	3.78E-05	3.09E-05	2.76E-05	2.15E-05	1.84E-05	1.68E-05
Butanenitrile	109-74-0	5.04E-05	3.57E-05	2.91E-05	2.52E-05	2.06E-05	1.77E-05	1.60E-05	1.35E-05	1.22E-05	1.16E-05
Furan	110-00-9	1.85E-06	1.31E-06	1.07E-06	9.26E-07	7.56E-07	6.52E-07	5.90E-07	4.97E-07	4.51E-07	4.28E-07
Pentanenitrile	110-59-8	3.14E-05	2.22E-05	1.81E-05	1.57E-05	1.28E-05	1.08E-05	9.67E-06	7.92E-06	7.05E-06	6.62E-06
Pyridine	110-86-1	1.31E-05	9.26E-06	7.56E-06	6.55E-06	5.35E-06	4.54E-06	4.06E-06	3.36E-06	3.01E-06	2.83E-06
2-Methylbut-2-enal	1115-11-3	1.98E-07	1.40E-07	1.15E-07	9.92E-08	8.10E-08	6.83E-08	6.10E-08	4.99E-08	4.43E-08	4.15E-08
2-Fluoropropene	1184-60-7	2.87E-08	2.03E-08	1.66E-08	1.43E-08	1.21E-08	1.03E-08	9.34E-09	7.97E-09	7.29E-09	6.95E-09
2,3-Dihydrofuran	1191-99-7	1.91E-08	1.35E-08	1.11E-08	9.57E-09	7.81E-09	6.71E-09	6.07E-09	5.10E-09	4.61E-09	4.37E-09
Butanal	123-72-8	1.09E-04	7.72E-05	6.31E-05	5.46E-05	4.46E-05	3.82E-05	3.44E-05	2.88E-05	2.60E-05	2.46E-05
Tributyl phosphate	126-73-8	2.53E-01	1.79E-01	1.46E-01	1.26E-01	1.03E-01	8.42E-02	7.29E-02	5.16E-02	3.65E-02	2.58E-02
2,4-Pentadienenitrile	1615-70-9	1.02E-06	7.22E-07	5.89E-07	5.11E-07	4.17E-07	3.54E-07	3.17E-07	2.62E-07	2.34E-07	2.20E-07
2-Methylene butanenitrile	1647-11-6	8.28E-07	5.86E-07	4.78E-07	4.14E-07	3.38E-07	2.86E-07	2.56E-07	2.11E-07	1.88E-07	1.77E-07
Trichlorinated biphenyls	16606-02-3	6.90E-07	4.88E-07	3.98E-07	3.45E-07	2.82E-07	2.30E-07	1.99E-07	1.41E-07	9.96E-08	7.04E-08
2-Ethyl-5-methylfuran	1703-52-2	2.92E-08	2.06E-08	1.68E-08	1.46E-08	1.19E-08	9.72E-09	8.91E-09	6.64E-09	5.50E-09	4.93E-09
Dichlorinated biphenyls	2050-67-1	7.08E-07	5.01E-07	4.09E-07	3.54E-07	2.89E-07	2.36E-07	2.04E-07	1.45E-07	1.02E-07	7.23E-08
Monochlorinated biphenyls	2051-60-7	9.77E-07	6.91E-07	5.64E-07	4.88E-07	3.99E-07	3.26E-07	2.82E-07	1.99E-07	1.41E-07	9.24E-08
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	1.90E-09	1.35E-09	1.10E-09	9.51E-10	7.77E-10	6.34E-10	5.49E-10	4.20E-10	3.42E-10	3.03E-10
1,4-Butanediol dinitrate	3457-91-8	3.06E-04	2.16E-04	1.76E-04	1.53E-04	1.25E-04	1.02E-04	8.82E-05	6.24E-05	4.72E-05	3.86E-05
2-Pentylfuran	3777-69-3	1.36E-08	9.60E-09	7.84E-09	6.79E-09	5.54E-09	4.53E-09	3.92E-09	2.77E-09	1.96E-09	1.56E-09
Tetrachlorinated biphenyls	41464-49-7	1.75E-06	1.24E-06	1.01E-06	8.77E-07	7.16E-07	5.85E-07	5.07E-07	3.58E-07	2.53E-07	1.79E-07
Formaldehyde	50-00-0	1.58E-04	1.12E-04	9.14E-05	8.16E-05	6.95E-05	6.14E-05	5.74E-05	5.13E-05	4.83E-05	4.68E-05
2-(2-Methyl-6-oxoheptyl) furan	51595-87-0	4.54E-07	3.21E-07	2.62E-07	2.27E-07	1.85E-07	1.51E-07	1.31E-07	9.27E-08	6.56E-08	5.29E-08
2-Methylfuran	534-22-5	1.08E-06	7.67E-07	6.26E-07	5.42E-07	4.43E-07	3.75E-07	3.35E-07	2.74E-07	2.44E-07	2.29E-07

Table 7. Cont'd.

Chemical	Chemical Identification Number ↓	Average Absorption Rate (mg/hr cm^2)									
	Event Duration →	5 min	10 min	15 min	20 min	30 min	45 min	1 hr	2 hr	4 hr	8 hr
Butyl nitrite	544-16-1	9.15E-07	6.47E-07	5.28E-07	4.57E-07	3.73E-07	3.05E-07	2.75E-07	2.14E-07	1.84E-07	1.68E-07
2-Hexanone	591-78-6	1.92E-05	1.36E-05	1.11E-05	9.61E-06	7.84E-06	6.40E-06	5.76E-06	4.55E-06	3.95E-06	3.65E-06
Dimethylmercury	593-74-8	7.05E-12	4.98E-12	4.07E-12	3.52E-12	2.88E-12	2.35E-12	2.03E-12	1.44E-12	1.02E-12	7.70E-13
2-Nitro-2-methylpropane	594-70-7	1.72E-06	1.22E-06	9.94E-07	8.61E-07	7.03E-07	5.74E-07	5.15E-07	4.04E-07	3.49E-07	3.22E-07
N-Nitrosomorpholine	59-89-2	9.26E-05	6.55E-05	5.35E-05	4.63E-05	3.78E-05	3.09E-05	2.67E-05	2.09E-05	1.77E-05	1.61E-05
1,3-Dinitrate-1,2,3-propantriol	623-87-0	7.39E-04	5.23E-04	4.27E-04	3.70E-04	3.02E-04	2.46E-04	2.13E-04	1.51E-04	1.14E-04	9.31E-05
Methyl isocyanate	624-83-9	2.67E-08	1.89E-08	1.54E-08	1.33E-08	1.12E-08	9.60E-09	8.77E-09	7.54E-09	6.93E-09	6.62E-09
Methyl nitrite	624-91-9	4.19E-07	2.96E-07	2.42E-07	2.10E-07	1.76E-07	1.49E-07	1.36E-07	1.16E-07	1.06E-07	1.01E-07
2,5-Dimethylfuran	625-86-5	1.67E-08	1.18E-08	9.61E-09	8.33E-09	6.80E-09	5.55E-09	5.03E-09	3.99E-09	3.46E-09	3.20E-09
N-Nitrosodimethylamine	62-75-9	2.63E-05	1.86E-05	1.52E-05	1.32E-05	1.07E-05	9.17E-06	8.25E-06	6.89E-06	6.20E-06	5.86E-06
Hexanenitrile	628-73-9	3.63E-05	2.57E-05	2.10E-05	1.82E-05	1.48E-05	1.21E-05	1.09E-05	8.70E-06	7.58E-06	7.02E-06
Heptanenitrile	629-08-3	3.34E-05	2.36E-05	1.93E-05	1.67E-05	1.37E-05	1.11E-05	9.65E-06	7.65E-06	6.47E-06	5.89E-06
2-Ethylhex-2-enal	645-62-5	2.94E-06	2.08E-06	1.70E-06	1.47E-06	1.20E-06	9.80E-07	8.49E-07	6.49E-07	5.30E-07	4.70E-07
Methanol	67-56-1	1.50E-03	1.06E-03	8.68E-04	7.73E-04	6.56E-04	5.79E-04	5.40E-04	4.82E-04	4.53E-04	4.38E-04
1-Butanol	71-36-3	1.09E-02	7.71E-03	6.29E-03	5.45E-03	4.45E-03	3.80E-03	3.42E-03	2.85E-03	2.57E-03	2.43E-03
Benzene	71-43-2	9.95E-07	7.04E-07	5.75E-07	4.98E-07	4.06E-07	3.46E-07	3.10E-07	2.55E-07	2.28E-07	2.14E-07
Mercury	7439-97-6	1.26E-09	8.93E-10	7.29E-10	6.32E-10	5.16E-10	4.21E-10	3.65E-10	2.58E-10	1.89E-10	1.49E-10
Ethylamine	75-04-7	2.95E-05	2.08E-05	1.70E-05	1.47E-05	1.26E-05	1.09E-05	1.01E-05	8.83E-06	8.21E-06	7.89E-06
Acetonitrile	75-05-8	1.25E-04	8.87E-05	7.24E-05	6.27E-05	5.39E-05	4.70E-05	4.35E-05	3.84E-05	3.58E-05	3.45E-05
Acetaldehyde	75-07-0	5.88E-05	4.16E-05	3.40E-05	2.94E-05	2.51E-05	2.18E-05	2.02E-05	1.77E-05	1.65E-05	1.59E-05
Ammonia	7664-41-7	1.07E-02	7.60E-03	6.20E-03	5.61E-03	4.86E-03	4.36E-03	4.11E-03	3.74E-03	3.55E-03	3.46E-03
Dibutyl butylphosphonate	78-46-6	2.30E-04	1.63E-04	1.33E-04	1.15E-04	9.41E-05	7.68E-05	6.65E-05	4.70E-05	3.33E-05	2.35E-05
3-Buten-2-one	78-94-4	2.13E-05	1.51E-05	1.23E-05	1.07E-05	8.71E-06	7.48E-06	6.76E-06	5.68E-06	5.14E-06	4.88E-06
3-Methyl-3-buten-2-one	814-78-8	1.43E-07	1.01E-07	8.28E-08	7.17E-08	5.86E-08	4.94E-08	4.41E-08	3.60E-08	3.20E-08	3.00E-08
Diethyl phthalate	84-66-2	1.91E-03	1.35E-03	1.10E-03	9.57E-04	7.81E-04	6.38E-04	5.52E-04	3.91E-04	2.76E-04	2.12E-04
1,1'-Biphenyl	92-52-4	5.11E-04	3.61E-04	2.95E-04	2.56E-04	2.09E-04	1.70E-04	1.48E-04	1.04E-04	7.38E-05	5.43E-05
Butyl nitrate	928-45-0	1.89E-06	1.33E-06	1.09E-06	9.43E-07	7.70E-07	6.29E-07	5.44E-07	4.23E-07	3.54E-07	3.19E-07
6-Methyl-2-heptanone	928-68-7	5.52E-05	3.90E-05	3.19E-05	2.76E-05	2.25E-05	1.84E-05	1.59E-05	1.21E-05	9.96E-06	8.89E-06

Scenario 3. Contact with Aqueous Condensate on Specified Dermal Surface Area

If the contact area of the aqueous condensate with a worker's skin is specified, the model can be applied to determine the minimum exposure time required to reach the equivalent inhalation dose. Table 8 lists the calculated duration of exposure for the absorption of the equivalent inhalation dose if the contact area were 5,000 cm^2, nominally 25% of the entire body's surface area. Entries in Table 8 are arranged in increasing order of the duration of exposure required.

Table 8. Exposure Times to Reach the Equivalent inhalation Dose Given an Aqueous Condensate-Skin Contact Area of 5,000 cm^2

Chemical	CAS Number	Duration of Exposure (hr)	Area of Contacted Skin (cm^2)	Average Absorption Rate (mg/cm^2 hr)	Equivalent Inhalation Dose (mg)
Tributyl phosphate	126-73-8	0.0036	5,000	1.22E+00	21.8
N-Nitrosomorpholine	59-89-2	0.045	5,000	1.25E-04	0.0285
N-Nitrosodimethylamine	62-75-9	0.057	5,000	3.17E-05	0.00908
Ammonia	7664-41-7	0.24	5,000	6.31E-03	7.61
Formaldehyde	50-00-0	3.1	5,000	4.91E-05	0.767
Dibutyl butylphosphonate	78-46-6	4.6	5,000	3.08E-05	0.716

As indicated in Table 8, the model predicts that the exposure of such a large portion of the body would very rapidly result in the absorption of an unacceptable dose of tributyl phosphate and the two nitrosamines. Suitable controls should be considered for any working scenario that could result in this type of extensive exposure of a worker to aqueous condensate, particularly from a tank with high tributyl phosphate or nitrosamine headspace concentrations.

The same analysis was applied for an aqueous condensate-skin contact area of 500 cm^2, roughly the surface area of one hand or the palms of both hands. Results are shown in Table 9. Under this more limited exposure scenario, only tributyl phosphate represents a hazard if the condensate is removed within 1 hr of the exposure.

Table 9. Exposure Times to Reach the Equivalent inhalation Dose Given an Aqueous Condensate-Skin Contact Area of 500 cm^2

Chemical	CAS Number	Duration of Exposure (hr)	Area of Contacted Skin (cm^2)	Average Absorption Rate (mg/cm^2 hr)	Equivalent Inhalation Dose (mg)
Tributyl phosphate	126-73-8	0.36	500	1.22E-01	21.8
N-Nitrosodimethylamine	62-75-9	2.8	500	6.49E-06	0.00908
N-Nitrosomorpholine	59-89-2	3.0	500	1.87E-05	0.0285
Ammonia	7664-41-7	4.3	500	3.54E-03	7.61
Formaldehyde	50-00-0	34	500	4.56E-05	0.767
Dibutyl butylphosphonate	78-46-6	153	500	9.33E-06	0.716

3.2 Organic Condensate

The composition of organic condensate is assumed to be that in equilibrium with the highest reported headspace concentration of each COPC. Specifically, the organic condensate concentrations given by Meacham et al. (2006) are used here.

The dermal dose of COPC associated with organic condensate was evaluated using the nonsteady-state model proposed by EPA (1992) with appropriate modifications to address the differences between absorption from aqueous and organic solutions. Details of the model are given in Section 2.3. Results are given in terms of skin surface area and duration of exposure for the following scenarios.

Scenario 4. Indefinite Contact with Organic Condensate

Consider the scenario in which organic condensate contacts the skin of a worker and the worker does not notice or take action to remove it. Analogous to the first aqueous condensate exposure scenario discussed above, the potential for an unacceptable exposure via dermal absorption depends on the volume of condensate contacting the skin and not on the area contacted or duration. Assuming the organic condensate to have been in equilibrium with the highest reported COPC vapor concentrations, the volume of organic condensate needed to reach the equivalent inhalation dose of each COPC has been calculated and tabulated in Table 10. Entries in Table 10 are arranged in order of increasing values in the last column, "condensate volume containing dermal dose."

Table 10. Volume of Organic Condensate Required to Exceed the Allowable Dermal Dose

Chemical	CAS Number	Condensate Concentration (mg/g)	Equivalent Inhalation Dose (mg)	Condensate Volume Containing Dermal Dose (mL)
Tetrachlorinated biphenyls	41464-49-7	4.6E+01	0.30	0.0066
Dibutyl butylphosphonate	78-46-6	8.6E+01	0.72	0.0084
Tributyl phosphate	126-73-8	4.4E+02	22	0.049
Mercury	7439-97-6	4.9E+00	0.25	0.051
1,1'-Biphenyl	92-52-4	1.3E+02	13	0.10
Trichlorinated biphenyls	16606-02-3	1.5E+00	0.30	0.20
Dichlorinated biphenyls	2050-67-1	9.9E-01	0.30	0.30
N-Nitrosodimethylamine	62-75-9	2.1E-02	0.0091	0.44
Monochlorinated biphenyls	2051-60-7	4.0E-01	0.30	0.74
1,3-Dinitrate-1,2,3-propantriol	623-87-0	4.5E+00	3.7	0.83
N-Nitrosomorpholine	59-89-2	2.9E-02	0.028	0.98
Diethyl phthalate	84-66-2	4.7E+01	50	1.1
1,4-Butanediol dinitrate	3457-91-8	1.6E+00	3.7	2.2
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	2.2E-02	0.079	3.6
2-Methylfuran	534-22-5	1.8E-03	0.034	18
Furan	110-00-9	1.3E-03	0.028	22
2-Pentylfuran	3777-69-3	1.0E-03	0.056	55
N-Nitrosomethylethylamine	10595-95-6	1.1E-04	0.011	100
2-Ethyl-5-methylfuran	1703-52-2	2.3E-04	0.045	190
1-Butanol	71-36-3	2.3E+00	606	270

Table 10. Cont'd.

Chemical	CAS Number	Condensate Concentration (mg/g)	Equivalent Inhalation Dose (mg)	Condensate Volume Containing Dermal Dose (mL)
4-Methyl-2-hexanone	105-42-0	6.6E-02	23	350
Ammonia	7664-41-7	2.0E-02	7.6	390
2-Ethylhex-2-enal	645-62-5	9.6E-03	5.2	540
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	8.6E-05	0.052	600
2,5-Dimethylfuran	625-86-5	6.3E-05	0.039	620
2-Hexanone	591-78-6	1.8E-02	13	710
Heptanenitrile	629-08-3	3.0E-01	273	920
6-Methyl-2-heptanone	928-68-7	3.8E-01	419	1,100
2,3-Dihydrofuran	1191-99-7	2.4E-05	0.029	1,200
Benzene	71-43-2	1.8E-03	2.5	1,400
2,4-Dimethylpyridine	108-47-4	1.2E-02	22	1,800
2-Nitro-2-methylpropane	594-70-7	6.9E-03	13	1,800
3-Buten-2-one	78-94-4	3.1E-03	5.7	1,900
Butyl nitrite	544-16-1	1.8E-03	4.2	2,300
Hexanenitrile	628-73-9	1.0E-01	238	2,400
Methanol	67-56-1	3.3E-02	102	3,100
Pentanenitrile	110-59-8	4.3E-02	204	4,700
2-Methylbut-2-enal	1115-11-3	2.1E-04	1.0	5,000
3-Methyl-3-buten-2-one	814-78-8	1.3E-04	0.69	5,200
Propanenitrile	107-12-0	2.1E-02	135	6,300
2,4-Pentadienenitrile	1615-70-9	1.5E-03	9.7	6,400
2-Methylene butanenitrile	1647-11-6	1.5E-03	9.9	6,500
Butanenitrile	109-74-0	3.2E-02	226	7,100
Acetonitrile	75-05-8	2.1E-02	336	16,000
Pyridine	110-86-1	1.6E-03	32	20,000
Butyl nitrate	928-45-0	1.8E-02	390	22,000
Dimethylmercury	593-74-8	3.4E-07	0.011	31,000
Butanal	123-72-8	1.7E-02	737	43,000
Methyl isocyanate	624-83-9	1.0E-05	0.47	45,000
Nitrous oxide (N_2O)	10024-97-2	1.7E-02	899	54,000
2-Fluoropropene	1184-60-7	2.9E-05	2.5	83,000
Methyl nitrite	624-91-9	2.4E-05	2.5	100,000
1,3-Butadiene	106-99-0	2.0E-05	3.5	170,000
Acetaldehyde	75-07-0	2.0E-03	450	220,000
Formaldehyde	50-00-0	1.7E-06	0.77	450,000

Comparison of the volumes of organic condensate needed to reach the most restrictive dose with the corresponding volumes of aqueous condensate (given in the last column of Table 5) indicates the organic condensate to be potentially much more toxic. However, the occurrence of organic condensate is limited to only those few tanks with very high organic vapor headspace concentrations, and the quantities of organic condensate are limited by the tendency for aqueous condensate to displace the organic from any low spots in the ventilation system. Although it is arguably less hazardous than aqueous condensate because of its rarity and low potential quantities, special consideration should be given to any scenario in which a worker could be directly contacted with organic condensate.

Given that only small quantities of organic condensate can accumulate in the ventilation systems, attention is focused here on the 12 COPC for which 2 mL or less of condensate could contain the equivalent inhalation dose.

Scenario 5. Contact with Organic Condensate for Specified Duration

Consider the scenario in which organic condensate contacts the skin of a worker, say by accidental contact with an inner surface of the ventilation system, and 30 min. elapse before the condensate is effectively removed. Under these circumstances the nonsteady-state model proposed by EPA (1992) can be applied to estimate the maximum skin-condensate contact area. Results for the 12 high importance COPC in organic condensate are given in the fourth column of Table 11. Entries in Table 11 are arranged in order of increasing maximum surface area.

Table 11. Organic Condensate-Skin Contact Area to Reach the Most Restrictive Dermal Dose Given an Exposure Time of 30 Minutes

Chemical	CAS [(1)] Number	Duration of Exposure (hr)	Area of Contacted Skin (cm^2)	Average Absorption Rate (mg/cm^2-hr)	Equivalent Inhalation Dose (mg)
N-Nitrosodimethylamine	62-75-9	0.5	190	4.68E-05	0.00908
Mercury	7439-97-6	0.5	260	9.48E-04	0.250
N-Nitrosomorpholine	59-89-2	0.5	860	3.32E-05	0.0285
Dibutyl butylphosphonate	78-46-6	0.5	1,200	5.91E-04	0.716
1,3-Dinitrate-1,2,3-propantriol	623-87-0	0.5	4,000	9.23E-04	3.72
Tributyl phosphate	126-73-8	0.5	9,100	2.39E-03	21.8
1,1'-Biphenyl	92-52-4	0.5	9,600	1.31E-03	12.6
Tetrachlorinated biphenyls	41464-49-7	0.5	28,000	1.08E-05	0.300
Diethyl phthalate	84-66-2	0.5	33,000	1.50E-03	50
Dichlorinated biphenyls	2050-67-1	0.5	180,000	1.70E-06	0.300
Monochlorinated biphenyls	2051-60-7	0.5	200,000	1.52E-06	0.300
Trichlorinated biphenyls	16606-02-3	0.5	300,000	9.93E-07	0.300

As Table 11 indicates, a worker with organic condensate covering roughly 190 cm^2 of skin could, according to the model, absorb the equivalent inhalation dose of N-nitrosodimethylamine from a 30-min. exposure. Protective controls should be considered for any work conducted on the ventilation system or fugitive emission pathways of a tank with very high organic headspace concentrations.

Analogous to the absorption of species from an aqueous solution, the average absorption rate given in Table 11 is actually the average flux (i.e., mass absorbed per unit time per unit surface area) for a 0.5-hr exposure. The absorbed dose for selected exposure (event) durations to any given surface area can be calculated using Eq. 32 and the *Average Absorption Rate* values tabulated in Table 12.

Table 12. Average Absorption Rates from Organic Condensate for Selected Exposure (Event) Durations

Chemical	Chemical Identification Number ↓	Average Absorption Rate (mg/hr cm^2)									
	Event Duration →	5 min	10 min	15 min	20 min	30 min	45 min	1 hr	2 hr	4 hr	8 hr
Nitrous oxide (N_2O)	10024-97-2	1.43E-04	1.01E-04	8.28E-05	7.17E-05	6.13E-05	5.33E-05	4.92E-05	4.32E-05	4.02E-05	3.87E-05
4-Methyl-2-hexanone	105-42-0	5.36E-05	3.79E-05	3.09E-05	2.68E-05	2.19E-05	1.79E-05	1.55E-05	1.22E-05	1.03E-05	9.38E-06
N-Nitrosomethylethylamine	10595-95-6	5.48E-07	3.87E-07	3.16E-07	2.74E-07	2.24E-07	1.88E-07	1.67E-07	1.36E-07	1.20E-07	1.12E-07
1,3-Butadiene	106-99-0	2.86E-08	2.02E-08	1.65E-08	1.43E-08	1.21E-08	1.03E-08	9.46E-09	8.15E-09	7.49E-09	7.16E-09
Propanenitrile	107-12-0	1.73E-04	1.22E-04	9.99E-05	8.65E-05	7.30E-05	6.25E-05	5.72E-05	4.94E-05	4.54E-05	4.35E-05
2,4-Dimethylpyridine	108-47-4	8.65E-06	6.11E-06	4.99E-06	4.32E-06	3.53E-06	2.88E-06	2.58E-06	2.00E-06	1.72E-06	1.57E-06
Butanenitrile	109-74-0	1.39E-04	9.84E-05	8.04E-05	6.96E-05	5.68E-05	4.89E-05	4.42E-05	3.72E-05	3.37E-05	3.20E-05
Furan	110-00-9	2.66E-06	1.88E-06	1.53E-06	1.33E-06	1.08E-06	9.35E-07	8.46E-07	7.13E-07	6.47E-07	6.14E-07
Pentanenitrile	110-59-8	8.79E-05	6.21E-05	5.07E-05	4.39E-05	3.59E-05	3.03E-05	2.70E-05	2.22E-05	1.97E-05	1.85E-05
Pyridine	110-86-1	5.41E-06	3.82E-06	3.12E-06	2.70E-06	2.21E-06	1.87E-06	1.68E-06	1.39E-06	1.24E-06	1.17E-06
2-Methylbut-2-enal	1115-11-3	4.04E-07	2.86E-07	2.33E-07	2.02E-07	1.65E-07	1.39E-07	1.24E-07	1.01E-07	9.02E-08	8.45E-08
2-Fluoropropene	1184-60-7	4.91E-08	3.47E-08	2.83E-08	2.45E-08	2.07E-08	1.75E-08	1.60E-08	1.36E-08	1.25E-08	1.19E-08
2,3-Dihydrofuran	1191-99-7	8.86E-08	6.26E-08	5.11E-08	4.43E-08	3.62E-08	3.11E-08	2.81E-08	2.36E-08	2.14E-08	2.02E-08
Butanal	123-72-8	5.20E-05	3.68E-05	3.00E-05	2.60E-05	2.12E-05	1.82E-05	1.64E-05	1.37E-05	1.24E-05	1.17E-05
Tributyl phosphate	126-73-8	1.17E-02	8.27E-03	6.75E-03	5.85E-03	4.77E-03	3.90E-03	3.38E-03	2.39E-03	1.69E-03	1.19E-03
2,4-Pentadienenitrile	1615-70-9	3.71E-06	2.62E-06	2.14E-06	1.85E-06	1.51E-06	1.28E-06	1.15E-06	9.51E-07	8.51E-07	8.01E-07
2-Methylene butanenitrile	1647-11-6	2.85E-06	2.01E-06	1.64E-06	1.42E-06	1.16E-06	9.84E-07	8.80E-07	7.24E-07	6.46E-07	6.07E-07
Trichlorinated biphenyls	16606-02-3	4.87E-06	3.44E-06	2.81E-06	2.43E-06	1.99E-06	1.62E-06	1.41E-06	9.94E-07	7.03E-07	4.97E-07
2-Ethyl-5-methylfuran	1703-52-2	5.48E-08	3.87E-08	3.16E-08	2.74E-08	2.24E-08	1.83E-08	1.67E-08	1.25E-08	1.03E-08	9.26E-09
Dichlorinated biphenyls	2050-67-1	8.35E-06	5.91E-06	4.82E-06	4.18E-06	3.41E-06	2.78E-06	2.41E-06	1.70E-06	1.21E-06	8.52E-07
Monochlorinated biphenyls	2051-60-7	7.47E-06	5.28E-06	4.31E-06	3.73E-06	3.05E-06	2.49E-06	2.16E-06	1.52E-06	1.08E-06	7.07E-07
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	2.29E-08	1.62E-08	1.32E-08	1.15E-08	9.36E-09	7.64E-09	6.62E-09	5.06E-09	4.12E-09	3.65E-09
1,4-Butanediol dinitrate	3457-91-8	4.22E-04	2.99E-04	2.44E-04	2.11E-04	1.72E-04	1.41E-04	1.22E-04	8.62E-05	6.53E-05	5.34E-05
2-Pentylfuran	3777-69-3	6.28E-08	4.44E-08	3.63E-08	3.14E-08	2.57E-08	2.09E-08	1.81E-08	1.28E-08	9.07E-09	7.20E-09
Tetrachlorinated biphenyls	41464-49-7	5.32E-05	3.76E-05	3.07E-05	2.66E-05	2.17E-05	1.77E-05	1.53E-05	1.09E-05	7.67E-06	5.43E-06
Formaldehyde	50-00-0	2.14E-08	1.51E-08	1.23E-08	1.10E-08	9.37E-09	8.28E-09	7.74E-09	6.93E-09	6.52E-09	6.31E-09
2-(2-Methyl-6-oxoheptyl) furan	51595-87-0	2.01E-06	1.42E-06	1.16E-06	1.00E-06	8.20E-07	6.70E-07	5.80E-07	4.10E-07	2.90E-07	2.34E-07
2-Methylfuran	534-22-5	1.89E-06	1.34E-06	1.09E-06	9.44E-07	7.71E-07	6.53E-07	5.82E-07	4.77E-07	4.25E-07	3.98E-07

Table 12. Cont'd.

Chemical	Chemical Identification Number ↓	Average Absorption Rate (mg/hr cm^2)									
	Event Duration →	5 min	10 min	15 min	20 min	30 min	45 min	1 hr	2 hr	4 hr	8 hr
Butyl nitrite	544-16-1	8.77E-07	6.20E-07	5.06E-07	4.38E-07	3.58E-07	2.92E-07	2.63E-07	2.05E-07	1.76E-07	1.61E-07
2-Hexanone	591-78-6	2.24E-05	1.59E-05	1.30E-05	1.12E-05	9.16E-06	7.48E-06	6.72E-06	5.32E-06	4.61E-06	4.26E-06
Dimethylmercury	593-74-8	4.30E-11	3.04E-11	2.48E-11	2.15E-11	1.76E-11	1.43E-11	1.24E-11	8.78E-12	6.21E-12	4.70E-12
2-Nitro-2-methylpropane	594-70-7	1.01E-05	7.16E-06	5.84E-06	5.06E-06	4.13E-06	3.37E-06	3.02E-06	2.38E-06	2.05E-06	1.89E-06
N-Nitrosomorpholine	59-89-2	1.63E-04	1.15E-04	9.39E-05	8.13E-05	6.64E-05	5.42E-05	4.69E-05	3.68E-05	3.11E-05	2.82E-05
1,3-Dinitrate-1,2,3-propantriol	623-87-0	4.53E-03	3.20E-03	2.61E-03	2.26E-03	1.85E-03	1.51E-03	1.31E-03	9.24E-04	6.96E-04	5.71E-04
Methyl isocyanate	624-83-9	4.46E-08	3.15E-08	2.57E-08	2.23E-08	1.88E-08	1.60E-08	1.47E-08	1.26E-08	1.16E-08	1.11E-08
Methyl nitrite	624-91-9	8.96E-08	6.33E-08	5.17E-08	4.48E-08	3.76E-08	3.19E-08	2.91E-08	2.48E-08	2.27E-08	2.17E-08
2,5-Dimethylfuran	625-86-5	3.66E-08	2.58E-08	2.11E-08	1.83E-08	1.49E-08	1.22E-08	1.10E-08	8.75E-09	7.61E-09	7.03E-09
N-Nitrosodimethylamine	62-75-9	2.30E-04	1.62E-04	1.33E-04	1.15E-04	9.37E-05	8.00E-05	7.21E-05	6.01E-05	5.42E-05	5.12E-05
Hexanenitrile	628-73-9	1.01E-04	7.14E-05	5.83E-05	5.05E-05	4.12E-05	3.36E-05	3.04E-05	2.42E-05	2.10E-05	1.95E-05
Heptanenitrile	629-08-3	1.34E-04	9.47E-05	7.73E-05	6.70E-05	5.47E-05	4.47E-05	3.87E-05	3.06E-05	2.59E-05	2.36E-05
2-Ethylhex-2-enal	645-62-5	2.69E-06	1.90E-06	1.55E-06	1.35E-06	1.10E-06	8.97E-07	7.77E-07	5.94E-07	4.85E-07	4.30E-07
Methanol	67-56-1	1.11E-03	7.82E-04	6.38E-04	5.68E-04	4.83E-04	4.26E-04	3.97E-04	3.54E-04	3.33E-04	3.22E-04
1-Butanol	71-36-3	6.59E-03	4.66E-03	3.80E-03	3.29E-03	2.69E-03	2.30E-03	2.07E-03	1.72E-03	1.55E-03	1.47E-03
Benzene	71-43-2	1.51E-06	1.06E-06	8.69E-07	7.53E-07	6.15E-07	5.23E-07	4.68E-07	3.86E-07	3.44E-07	3.24E-07
Mercury	7439-97-6	4.65E-03	3.29E-03	2.68E-03	2.32E-03	1.90E-03	1.55E-03	1.34E-03	9.49E-04	6.95E-04	5.48E-04
Ethylamine	75-04-7	1.62E-06	1.15E-06	9.37E-07	8.12E-07	6.93E-07	6.01E-07	5.55E-07	4.86E-07	4.52E-07	4.35E-07
Acetonitrile	75-05-8	3.72E-04	2.63E-04	2.15E-04	1.86E-04	1.60E-04	1.39E-04	1.29E-04	1.14E-04	1.06E-04	1.02E-04
Acetaldehyde	75-07-0	3.32E-05	2.35E-05	1.92E-05	1.66E-05	1.42E-05	1.23E-05	1.14E-05	9.99E-06	9.30E-06	8.95E-06
Ammonia	7664-41-7	1.93E-03	1.36E-03	1.11E-03	1.01E-03	8.72E-04	7.82E-04	7.38E-04	6.71E-04	6.37E-04	6.20E-04
Dibutyl butylphosphonate	78-46-6	2.90E-03	2.05E-03	1.67E-03	1.45E-03	1.18E-03	9.65E-04	8.36E-04	5.91E-04	4.18E-04	2.96E-04
3-Buten-2-one	78-94-4	1.47E-05	1.04E-05	8.51E-06	7.37E-06	6.02E-06	5.17E-06	4.67E-06	3.93E-06	3.55E-06	3.37E-06
3-Methyl-3-buten-2-one	814-78-8	3.10E-07	2.19E-07	1.79E-07	1.55E-07	1.26E-07	1.07E-07	9.51E-08	7.78E-08	6.91E-08	6.48E-08
Diethyl phthalate	84-66-2	7.37E-03	5.21E-03	4.25E-03	3.68E-03	3.01E-03	2.46E-03	2.13E-03	1.50E-03	1.06E-03	8.17E-04
1,1'-Biphenyl	92-52-4	6.44E-03	4.55E-03	3.72E-03	3.22E-03	2.63E-03	2.15E-03	1.86E-03	1.31E-03	9.29E-04	6.84E-04
Butyl nitrate	928-45-0	8.63E-06	6.11E-06	4.99E-06	4.32E-06	3.52E-06	2.88E-06	2.49E-06	1.94E-06	1.62E-06	1.46E-06
6-Methyl-2-heptanone	928-68-7	1.68E-04	1.18E-04	9.67E-05	8.38E-05	6.84E-05	5.58E-05	4.84E-05	3.68E-05	3.03E-05	2.70E-05

Scenario 6. Contact with Organic Condensate on Specified Dermal Surface Area

If the contact area of the organic condensate with a worker's skin is specified, the nonsteady-state EPA model can be applied to determine the minimum exposure time required to reach the equivalent inhalation dose. Table 13 lists the calculated duration of exposure for the absorption of the equivalent inhalation dose if the contact area were 500 cm^2, nominally the surface area of one hand or the palms of both hands.

Table 13. Exposure Times to Reach the Equivalent inhalation Dose Given an Organic Condensate-Skin Contact Area of 500 cm^2

Chemical	CAS Number	Duration of Exposure (hr)	Area of Contacted Skin (cm^2)	Average Absorption Rate (mg/cm^2-hr)	Equivalent Inhalation Dose (mg)
N-Nitrosodimethylamine	62-75-9	0.075	500	1.82E-05	0.00908
Mercury	7439-97-6	0.14	500	5.00E-04	0.250
N-Nitrosomorpholine	59-89-2	1.3	500	5.70E-05	0.0285

3.3 Vapors

3.3.1 Dermal Absorption of COPC Vapors

The dermal absorption doses of COPC vapors were evaluated by applying a steady-state model given by AIHA (2002). The use of a steady-state model is justified for vapor exposures because, unlike the dermal exposure to condensates which generally is expected to be no longer than needed to towel or wash the condensate off, a worker may be exposed to COPC vapors as long as he or she is working in the vicinity of the source. The model is described in Section 2.4.

It is assumed in the model development that the worker is in loose work clothing, so that the entire body is exposed. Given a 20,000 cm^2 nominal body surface area and specified COPC vapor concentrations, the model was used to calculate maximum acceptable exposure durations. Table 14 lists vapor absorption model results for each COPC. Two sets of results are listed in Table 14, one for exposures based on the maximum reported COPC headspace concentrations, and one for exposures based on the COPC Tank Farms Action Limits.

The fifth and sixth columns in Table 14 give the calculated dermal absorption rates and maximum acceptable exposure time, respectively, for each COPC assuming exposure to the maximum reported headspace concentrations. Entries are sorted in order of increasing values in the sixth column, so vapors presenting the greatest potential risk are at the top of the table. Maximum acceptable exposure times are less than 1 hr for N-nitrosodimethylamine, ammonia, and N-nitrosomorpholine, and less than an 8-hr working shift for seven other COPC.

The seventh column of Table 14 lists the Tank Farms Action Limit, specified as 50% of the Tank Farms OEL, for each COPC. The vapor dermal absorption model was applied for the scenario of COPC vapor concentrations in the work zone equal to these action limits and estimated the dermal absorption rates and maximum acceptable exposure times are given in the eighth and ninth (last) columns of Table 14.

Maximum acceptable exposure times are generally much longer than when exposures are based on maximum headspace concentrations (compare the sixth and last columns), particularly for the COPC at the top of Table 14. Two notable exceptions are formaldehyde and methanol, for which the model predicts dermal absorption rates that are actually higher than absorption via inhalation. These two compounds are both low-molecular weight chemicals for which transport from the ambient air to the worker's skin is apparently overestimated. These are discussed in Section 4.5.

3.3.2 Ocular Absorption of COPC Vapors

Ocular absorption of COPC vapors was evaluated using the simple model described in Section 2.5. It is based on the AIHA dermal model, with two significant changes. First, the transport of vapors from the ambient air to the surface of the eye is assumed to incur much less resistance, since the dermal model assumes loose work clothing, and this does not apply to the eye. Second, the permeability coefficient from the surface of the eye to the bloodstream is approximated by the watery dermal layer permeability coefficient of the dermal model, thus eliminating from the ocular model the protection of the stratum corneum layer of the skin.

Results of the ocular model are given in Table 15, where the scenarios of exposure to the maximum reported headspace concentration and exposure to the tank farms action level are both considered for each COPC. The ratio of ocular to dermal absorption rates is given in the last column of Table 15 – this value is independent of the COPC concentration in the ambient air and applies to both scenarios. The analysis indicates that ocular absorption rates are quite small compared to dermal absorption rates (less than 10%) for all but mercury. Several factors are responsible for mercury being at the top of Table 15, but it is not that the eye tends to have any special affinity for mercury vapor. Indeed, both dermal and ocular absorption rates for mercury vapor are very small when compared to most other COPC. Given the uncertainties associated with the AIHA dermal model and the results shown in Table 15, the contribution of ocular absorption of COPC to the dose absorbed by a worker is negligible. Note this does not imply irritation and even damage to the eye is not possible, only that the amount of COPC absorbed through the eyes is small compared to the amount absorbed through the skin.

Table 14. Exposure Times to Reach the Equivalent Inhalation Dose Via Dermal Vapor Absorption

Chemical	CAS Number	Equivalent Inhalation Dose (mg)	Worker Exposed to Maximum Headspace Concentration			Worker Exposed to Tank Farms Action Level		
			Maximum Headspace Conc. (mg/m^3)	Absorption Rate (mg/hr)	Maximum Acceptable Duration of Exposure (hr)	Tank Farms Action Level (mg/m^3)	Absorption Rate (mg/hr)	Maximum Acceptable Duration of Exposure (hr)
N-Nitrosodimethylamine	62-75-9	0.00908	0.650	1.03E-01	0.088	0.000908	7.21E-05	130
Ammonia	7664-41-7	7.61	1,730	6.68E+01	0.11	17.4	3.36E-01	23
N-Nitrosomorpholine	59-89-2	0.0285	0.0458	6.80E-02	0.42	0.00285	2.11E-03	13
Tributyl phosphate	126-73-8	21.8	5.89	7.35E+00	3.0	2.18	1.36E+00	16
Dibutyl butylphosphonate	78-46-6	0.716	0.716	2.16E-01	3.3	0.0716	1.08E-02	66
Formaldehyde	50-00-0	0.767	0.0781	2.24E-01	3.4	0.368	5.29E-01	1.5
Furan	110-00-9	0.0278	8.88	8.10E-03	3.4	0.00278	1.27E-06	22,000
N-Nitrosomethylethylamine	10595-95-6	0.0108	0.00263	2.08E-03	5.2	0.00108	4.27E-04	25
1,4-Butanediol dinitrate	3457-91-8	3.68	1.93	5.06E-01	7.3	0.368	4.83E-02	76
2-Methylfuran	534-22-5	0.0336	3.35	4.30E-03	7.8	0.00336	2.15E-06	16,000
1,1'-Biphenyl	92-52-4	12.6	13.9	1.16E+00	11	1.26	5.26E-02	240
Methanol	67-56-1	102	49.8	8.10E+00	13	262	2.13E+01	4.8
1-Butanol	71-36-3	606	177	4.13E+01	15	60.6	7.07E+00	86
1,3-Dinitrate-1,2,3-propantriol	623-87-0	3.72	0.0770	1.10E-01	34	0.372	2.67E-01	14
Diethyl phthalate	84-66-2	50.0	1.17	1.04E+00	48	5.00	2.22E+00	23
3-Buten-2-one	78-94-4	5.73	3.27	9.10E-02	63	0.573	7.98E-03	720
2,4-Dimethylpyridine	108-47-4	21.9	0.458	2.31E-01	95	2.19	5.53E-01	40
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	0.0794	0.00412	7.23E-04	110	0.00794	6.97E-04	110
Nitrous oxide (N_2O)	10024-97-2	899	8,455	6.35E+00	140	89.9	3.38E-02	27,000
Monochlorinated biphenyls	2051-60-7	0.300	0.0349	1.77E-03	170	0.0300	7.61E-04	390
2-Hexanone	591-78-6	12.8	2.44	6.62E-02	190	20.5	2.78E-01	50
Tetrachlorinated biphenyls	41464-49-7	0.300	0.00452	1.24E-03	240	0.0300	4.11E-03	70
Propanenitrile	107-12-0	135	12.0	4.35E-01	310	13.5	2.46E-01	550
4-Methyl-2-hexanone	105-42-0	23.3	5.08	7.39E-02	320	2.33	1.70E-02	1,400
Dichlorinated biphenyls	2050-67-1	0.300	0.00691	9.41E-04	320	0.0300	2.05E-03	150
2,3-Dihydrofuran	1191-99-7	0.0286	0.0716	8.25E-05	350	0.00286	1.65E-06	17,000
Trichlorinated biphenyls	16606-02-3	0.300	0.00348	6.79E-04	440	0.0300	2.92E-03	100
2-Ethyl-5-methylfuran	1703-52-2	0.0450	0.0458	9.49E-05	470	0.00450	4.66E-06	9,700
Acetonitrile	75-05-8	336	22.2	6.57E-01	510	33.6	4.98E-01	670

Table 14. Cont'd

Chemical	CAS Number	Equivalent Inhalation Dose (mg)	Worker Exposed to Maximum Headspace Concentration			Worker Exposed to Tank Farms Action Level		
			Maximum Headspace Conc. (mg/m^3)	Absorption Rate (mg/hr)	Maximum Acceptable Duration of Exposure (hr)	Tank Farms Action Level (mg/m^3)	Absorption Rate (mg/hr)	Maximum Acceptable Duration of Exposure (hr)
Benzene	71-43-2	2.49	2.02	4.05E-03	620	1.60	1.60E-03	1,600
2-Ethylhex-2-enal	645-62-5	5.16	0.144	8.29E-03	620	0.516	1.48E-02	350
Pyridine	110-86-1	32.3	0.396	5.02E-02	640	3.23	2.05E-01	160
2,5-Dimethylfuran	625-86-5	0.0393	0.0366	5.98E-05	660	0.00393	3.21E-06	12,000
Butanenitrile	109-74-0	226	7.24	2.17E-01	1,000	22.6	3.38E-01	700
3-Methyl-3-buten-2-one	814-78-8	0.688	0.0733	5.59E-04	1,200	0.0688	2.62E-04	2,600
Methyl nitrite	624-91-9	2.49	0.793	1.93E-03	1,300	0.249	3.03E-04	8,200
2-Methylbut-2-enal	1115-11-3	1.03	0.0436	7.70E-04	1,300	0.103	9.10E-04	1,100
Butyl nitrite	544-16-1	4.21	2.05	3.13E-03	1,300	0.421	3.21E-04	13,000
Acetaldehyde	75-07-0	450	21.6	3.03E-01	1,500	45.0	3.16E-01	1,400
2-Pentylfuran	3777-69-3	0.0565	0.0143	3.63E-05	1,600	0.00565	7.15E-06	7,900
Butanal	123-72-8	737	22.4	4.61E-01	1,600	73.7	7.58E-01	1,000
Pentanenitrile	110-59-8	204	3.71	1.22E-01	1,700	20.4	3.35E-01	600
Hexanenitrile	628-73-9	238	3.37	1.27E-01	1,900	23.8	4.50E-01	500
2-Nitro-2-methylpropane	594-70-7	12.6	0.973	5.87E-03	2,200	1.26	3.82E-03	3,300
2,4-Pentadienenitrile	1615-70-9	9.70	0.132	4.08E-03	2,400	0.970	1.50E-02	600
Heptanenitrile	629-08-3	273	2.92	1.06E-01	2,600	27.3	4.96E-01	500
6-Methyl-2-heptanone	928-68-7	419	10.8	1.57E-01	2,700	41.9	3.04E-01	1,400
2-Methylene butanenitrile	1647-11-6	9.95	0.143	3.27E-03	3,000	0.995	1.14E-02	900
Methyl isocyanate	624-83-9	0.466	0.0421	1.26E-04	3,700	0.0466	6.98E-05	6,700
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	0.0516	0.00504	5.53E-06	9,300	0.00516	2.83E-06	18,000
2-Fluoropropene	1184-60-7	2.46	1.30	1.33E-04	18,000	0.246	1.25E-05	200,000
1,3-Butadiene	106-99-0	3.45	0.494	1.11E-04	31,000	2.21	2.48E-04	14,000
Butyl nitrate	928-45-0	390	1.75	5.75E-03	68,000	39.0	6.40E-02	6,100
Mercury	7439-97-6	0.250	0.112	2.18E-06	110,000	0.0250	2.43E-07	1,000,000
Dimethylmercury	593-74-8	0.0108	0.000251	9.85E-09	1,100,000	0.0115	2.26E-07	48,000

Table 15. Ocular Absorption of COPC Vapors

Chemical	CAS Number	Worker Exposed to Maximum Headspace Conc.		Worker Exposed to Tank Farms Action Level		Ratio of Ocular to Dermal Absorption Rates
		Maximum Headspace Conc. (mg/m^3)	Absorption Rate (mg/hr)	Tank Farms Action Level (mg/m3)	Absorption Rate (mg/hr)	
Mercury	7439-97-6	0.112	3.64E-07	0.0250	4.06E-08	0.17
Acetaldehyde	75-07-0	21.6	1.69E-02	45.0	1.76E-02	0.06
Acetonitrile	75-05-8	22.2	3.10E-02	33.6	2.35E-02	0.05
Propanenitrile	107-12-0	12.0	1.37E-02	13.5	7.74E-03	0.03
3-Buten-2-one	78-94-4	3.27	2.76E-03	0.573	2.42E-04	0.03
Methanol	67-56-1	49.8	2.45E-01	262	6.43E-01	0.03
Butanenitrile	109-74-0	7.24	5.58E-03	22.6	8.70E-03	0.03
Nitrous oxide (N_2O)	10024-97-2	8,455	1.53E-01	89.9	8.14E-04	0.02
2,3-Dihydrofuran	1191-99-7	0.0716	1.94E-06	0.00286	3.88E-08	0.02
2-Nitro-2-methylpropane	594-70-7	0.973	1.23E-04	1.26	8.01E-05	0.02
3-Methyl-3-buten-2-one	814-78-8	0.0733	1.16E-05	0.0688	5.44E-06	0.02
Butanal	123-72-8	22.4	8.40E-03	73.7	1.38E-02	0.02
2,4-Pentadienenitrile	1615-70-9	0.132	7.02E-05	0.970	2.58E-04	0.02
Pyridine	110-86-1	0.396	8.52E-04	3.23	3.48E-03	0.02
Methyl isocyanate	624-83-9	0.0421	2.13E-06	0.0466	1.18E-06	0.02
Methyl nitrite	624-91-9	0.793	3.10E-05	0.249	4.87E-06	0.02
Dimethylmercury	593-74-8	0.000251	1.54E-10	0.0115	3.55E-09	0.02
2-Methylbut-2-enal	1115-11-3	0.0436	1.20E-05	0.103	1.42E-05	0.02
Pentanenitrile	110-59-8	3.71	1.86E-03	20.4	5.11E-03	0.02
2-Hexanone	591-78-6	2.44	9.40E-04	20.5	3.95E-03	0.01
2-Methylene butanenitrile	1647-11-6	0.143	4.24E-05	0.995	1.47E-04	0.01
4-Methyl-2-hexanone	105-42-0	5.08	9.21E-04	2.33	2.11E-04	0.01
1-Butanol	71-36-3	177	4.41E-01	60.6	7.54E-02	0.01
Furan	110-00-9	8.88	7.90E-05	0.00278	1.24E-08	0.01
Hexanenitrile	628-73-9	3.37	1.20E-03	23.8	4.23E-03	0.009
6-Methyl-2-heptanone	928-68-7	10.8	1.25E-03	41.9	2.41E-03	0.008
Butyl nitrate	928-45-0	1.75	4.11E-05	39.0	4.57E-04	0.007
1,4-Butanediol dinitrate	3457-91-8	1.93	3.56E-03	0.368	3.39E-04	0.007
2-Methylfuran	534-22-5	3.35	2.66E-05	0.00336	1.33E-08	0.006

Table 15. Cont'd.

Chemical	CAS Number	Worker Exposed to Maximum Headspace Conc.		Worker Exposed to Tank Farms Action Level		Ratio of Ocular to Dermal Absorption Rates
		Maximum Headspace Conc. (mg/m^3)	Absorption Rate (mg/hr)	Tank Farms Action Level (mg/m3)	Absorption Rate (mg/hr)	
N-Nitrosomethylethylamine	10595-95-6	0.00263	1.10E-05	0.00108	2.25E-06	0.005
2-Fluoropropene	1184-60-7	1.30	6.72E-07	0.246	6.35E-08	0.005
Heptanenitrile	629-08-3	2.92	5.35E-04	27.3	2.50E-03	0.005
2,4-Dimethylpyridine	108-47-4	0.458	1.07E-03	2.19	2.55E-03	0.005
2,5-Dimethylfuran	625-86-5	0.0366	2.74E-07	0.00393	1.47E-08	0.005
Butyl nitrite	544-16-1	2.05	1.37E-05	0.421	1.41E-06	0.004
2-Ethylhex-2-enal	645-62-5	0.144	3.40E-05	0.516	6.09E-05	0.004
Benzene	71-43-2	2.02	1.63E-05	1.60	6.45E-06	0.004
2-(2-Methyl-6-oxoheptyl)furan	51595-87-0	0.00412	2.89E-06	0.00794	2.79E-06	0.004
4-(1-Methylpropyl)-2,3-dihydrofuran	34379-54-9	0.00504	2.20E-08	0.00516	1.13E-08	0.004
1,3-Butadiene	106-99-0	0.494	3.63E-07	2.21	8.11E-07	0.003
Dibutyl butylphosphonate	78-46-6	0.716	6.63E-04	0.0716	3.32E-05	0.003
Diethyl phthalate	84-66-2	1.17	3.01E-03	5.00	6.44E-03	0.003
N-Nitrosomorpholine	59-89-2	0.0458	1.73E-04	0.00285	5.38E-06	0.003
Formaldehyde	50-00-0	0.0781	5.62E-04	0.368	1.32E-03	0.003
2-Ethyl-5-methylfuran	1703-52-2	0.0458	2.16E-07	0.00450	1.06E-08	0.002
1,3-Dinitrate-1,2,3-propantriol	623-87-0	0.0770	2.32E-04	0.372	5.62E-04	0.002
Tributyl phosphate	126-73-8	5.89	1.45E-02	2.18	2.68E-03	0.002
N-Nitrosodimethylamine	62-75-9	0.650	1.76E-04	0.000908	1.23E-07	0.002
Ammonia	7664-41-7	1,730	8.43E-02	17.4	4.24E-04	0.001
1,1'-Biphenyl	92-52-4	13.9	1.40E-03	1.26	6.35E-05	0.001
2-Pentylfuran	3777-69-3	0.0143	4.10E-08	0.00565	8.08E-09	0.001
Monochlorinated biphenyls	2051-60-7	0.0349	1.62E-06	0.0300	6.97E-07	0.0009
Dichlorinated biphenyls	2050-67-1	0.00691	7.66E-07	0.0300	1.66E-06	0.0008
Trichlorinated biphenyls	16606-02-3	0.00348	4.59E-07	0.0300	1.97E-06	0.0007
Tetrachlorinated biphenyls	41464-49-7	0.00452	7.41E-07	0.0300	2.46E-06	0.0006

4.0 Discussion

This study indicates dermal exposures to COPC via aqueous and organic condensates and vapors have the potential to exceed acceptable doses to workers in certain scenarios. This section attempts to summarize and qualify the study findings.

4.1 Equivalent Inhalation Dose

The equivalent inhalation dose, described and tabulated for each COPC in Section 2.1, is the occupational exposure parameter used in this study to identify unacceptable risk. It is calculated by multiplying the inhalation OEL by a typical volume of air that a worker would breathe over the applicable time period. It is a parameter developed to compensate for the fact that occupational dermal absorption exposure guidelines do not exist for any of the COPC, and it is based on the premise that the inhalation and dermal routes of entry into the body can be treated as equivalent. This approach is not novel to this study (e.g., AIHA 2002). As with the inhalation OELs from which they are derived, the consequences of exceeding the equivalent inhalation dose may differ markedly between COPC.

There are two issues that should be understood and considered. First, the inhalation OELs of some COPC are based on irritation of the nose, throat, and lungs, and these COPC may or may not have comparable dermal effects. Conversely, some COPC may have dermal effects that were not considered significant in the development of the inhalation OEL. Second, calculation of the equivalent inhalation dose assumes that 100% of the inhaled species is indeed absorbed by the lungs and that workers' bodies can safely handle all the vapor present in the air they inhale over the applicable period. This is not necessarily true; different vapors are absorbed with different efficiencies by the lungs, and to assume it is safe to absorb 100% when the vapor is present at its OEL concentration may not be justified. Nevertheless, it is assumed here that numerical adjustments to address these two issues are not warranted, given the variability in response between workers and the uncertainties in the inhalation OELs, the dermal absorption models, and the model inputs.

Note also that the equivalent inhalation dose does not include any correction for the dose a worker may get simultaneously via inhalation. The simultaneous dose from inhalation is assumed to be negligible in this study but should be evaluated and may need to be addressed as part of the acceptable total dose.

4.2 Dermal Absorption Models

The models on which this study is based are believed to generally overestimate dermal absorption rates and the potential to exceed COPC equivalent inhalation doses, as evidenced by the quotation from EPA (1992) given in Section 2.2. One reason for their tendency to overestimate absorption rates is the assumption that the concentration of the absorbing species is essentially zero within the body; this enhances the diffusion gradients and increases the absorption rate. For most COPC this approximation may not be significant, but for others, such as formaldehyde which is normally present in the blood at about 2 ppm (Heck et al. 1985), this assumption may lead to an unrealistic dermal absorption rate.

The models themselves employ standard engineering mass transport principles and equations and well-accepted approximations. The primary limitation of the models in this study is thought to be the lack of

experimentally determined permeability coefficients for the COPC and the corresponding reliance on empirical approximations for these parameters.

No accommodations are made in the models for the potential effects of different ambient air humidities, skin lesions, or the age of the worker on dermal absorption rates. Though the models incorporate many approximations, they are still the best available means for estimating dermal absorption rates and absorbed doses.

4.3 Aqueous Condensate

The nonsteady-state EPA dermal absorption model, with the modified Robinson formulation of the permeability coefficient, was applied to estimate absorption rates of COPC from direct contact with aqueous condensate. The aqueous condensate was assumed to be at equilibrium with the maximum reported COPC headspace concentrations, resulting in reasonably conservative estimates of the likely COPC concentrations in the condensate. Though the model is sound, it does appear to generally over estimate dermal absorption rates (EPA 1992), and the numerical results given in Tables 6, 8, and 9 are judged to be conservative from a worker-protection perspective.

Model results suggest that relatively large areas of skin would need to be wetted with aqueous condensate or the contact would need to persist for an extended period before the equivalent inhalation dose of any COPC is reached. The model identified tributyl phosphate as presenting the greatest risk of exceeding the equivalent inhalation dose, with an allowed exposure (contact) time of less than 1 min. if a very large fraction, 25% of the workers skin (5,000 cm^2), was wetted with the condensate. For a 500-cm^2 area of wetted skin, roughly the area of both palms of a worker's hands, the equivalent inhalation dose of tributyl phosphate would not be exceeded provided the worker could towel-dry his hands within 20 min.

4.4 Organic Condensate

Dermal absorption of COPC from organic condensate was modeled using the same EPA nonsteady-state model as applied to aqueous condensate, with permeability coefficients modified to account for the partitioning of species between an organic liquid and the stratum corneum. As with the aqueous condensate modeling, the organic condensate was assumed to be at equilibrium with the maximum reported COPC headspace concentrations, resulting in reasonably conservative estimates of the likely COPC concentrations in the condensate.

Based on the compositions calculated by Meacham et al. (2006), the organic condensate is significantly more toxic than the aqueous condensate (see Tables 5 and 10). However, organic condensate is expected to be present in much smaller quantities and will not form except in the ventilation systems of tanks with exceptionally high organic vapor levels. Potential exposures are consequently limited to operations on the ventilation systems of a very tanks and to small areas of skin.

Model results indicate N-nitrosodimethylamine and mercury vapor to be the most likely to exceed their equivalent inhalation doses via dermal absorption from organic condensate. Exposure of 500 cm^2 of skin, about the surface area of one hand or the palms of both hands, to organic condensate could result in absorption of the equivalent inhalation dose of N-nitrosodimethylamine in less than 5 min., and of mercury in less than 9 min.

4.5 Vapors

Dermal absorption of COPC vapors was modeled to help identify conditions of potential concern. Full-body exposure to the maximum reported headspace concentrations of COPC was determined to result in unacceptable absorption rates. Ammonia, for example, has been reported at 1,730 mg/m^3 (about 2,500 ppm) in the tank headspaces or roughly 200 times the tank farms' action limit. At this concentration, the model predicts a worker would dermally absorb an equivalent inhalation dose in about 6 min. Consideration of the model results given in the sixth column of Table 14 and/or the application of the dermal model to evaluate other concentrations is advised any time a work zone could potentially contain levels of COPC greater than the tank farms' action limits.

Dermal absorption of vapors present at the tank farms' action limits is predicted to be negligible compared to the dose received via inhalation for most of the COPC. Notable exceptions to this are formaldehyde and methanol, which were both found to be absorbed via the skin faster than via inhalation. These two chemicals are both low molecular weight, highly water-soluble species that the model predicts will be transferred rapidly through the effective 3-cm boundary layer of air surrounding the body.

It is suggested here that the expression for mass transport of light species from the workplace air through clothing and to the surface of the skin, Eq. 24, is inappropriately based entirely on the diffusivity of the species in air; the actual transport depends on body motions that cause clothing to breathe and convection to occur between the clothing and the skin. While Eq. 24. with a 3-cm effective boundary layer, may be suitable for larger molecules, it apparently overestimates the transport rates of smaller molecules. An additional issue for both formaldehyde and methanol is that the model assumes the baseline concentration of the absorbing species is zero inside the body and in the blood. Both formaldehyde and methanol are endogenous to the body, being present at about 2 ppm in blood (Heck et al. 1985, Batterman and Franzblau 1997). Inasmuch as the model assumes a larger-than-actual concentration gradient between the surface of the skin and the blood stream, it overestimates the absorption rate.

As noted in Section 3.3.2, the estimated ocular absorption of COPC vapors is small compared to dermal absorption and, given uncertainties in the dermal model, can be considered negligible in the evaluation of dermal dose. This should not be construed as indicating irritation and/or damage to the eye could not occur from direct exposure to headspace COPC concentrations, only that ocular absorption has a small contribution to the allowable dermal dose.

4.6 Recommendations

The models and modeling results presented above are intended to provide guidelines for the tank farms industrial hygiene worker protection program. The models are admittedly inexact, with the apparent bias of overestimating dermal absorption rates in at least some cases.

Tabulated condensate exposure results apply to the scenario of direct contact of aqueous and organic condensates with a worker's skin, with no remediation until the specified exposure duration is over. Clearly, this scenario can be avoided by suitable selection of worker clothing, awareness training to prevent the possibility of such contact, and response training to ensure appropriate actions are quickly taken in the event a worker is contacted by condensate.

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