A Proposition 65 No Significant Risk Evaluation of 1,4-dioxane in @@ Dish Liquid

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@@

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1. Overview and Introduction

A recent notice[1] alleges that use of @@ Dish Liquid poses a significant risk of cancer. In particular, it is claimed or implied that the presence in these products of the chemical 1,4-dioxane, at a concentration of @@ micrograms per gram, or @@ parts per million [@@ μg/g; @@ ppm] or less, would result in a dose larger than California's "no significant risk level" (NSRL) for this compound. On its face, this claim is not credible, in that it implies that typical use of dish liquid is somehow tantamount to drinking, and completely absorbing, the 1,4-dioxane in @@ of full-strength dish liquid every day. Further exposure assessment, presented below, demonstrates that even worst-case conditions, let alone those pertaining to the average user, do not result in any significant dose of 1,4-dioxane, and so do not result in the alleged violation.

1,4-dioxane is present at low concentrations in @@ dish liquids because of the use of sodium laureth sulfate.[2] Its presence has been known to @@, and the concentration is controlled at sufficiently low levels by the specifications demanded by @@ of its suppliers of sodium laureth sulfate products.

The US Food and Drug Administration (FDA) has been aware of the presence of 1,4-dioxane in many cosmetic products (which, all other things being equal, would present greater opportunities for absorption across the skin than would dish liquid) using the same ingredient for some time. FDA has discounted the importance of 1,4-dioxane as a health issue, based on the low concentrations found in cosmetic studies, the ready evaporation of 1,4-dioxane, and the small

[1] Notice of Violation of the Safe Drinking Water and Toxic Enforcement Act of 1986, from @@, on behalf of @@, to @@, Re: Consumer Personal Care Products; @@ @@, 2008.
[2] See @@ for product varieties, @@ for lists of all ingredients, and @@ to obtain Material Safety Data Sheets for these products.

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fraction of 1,4-dioxane that penetrates the skin even from products that remain on the skin for hours (Bronaugh, 1982).[3]

A detailed exposure assessment, presented below, indicates that the presence of 1,4-dioxane in @@ Dish Liquid products is of no toxicologic significance.

2. Proposition 65 "No Significant Risk" dose

The Reproductive and Cancer Hazard Assessment Branch of OEHHA is the lead agency for the implementation of the Safe Drinking Water and Toxic Enforcement Act of 1986 (Proposition 65), and in that role has established no significant risk levels (NSRLs) for carcinogens and maximum allowable dose levels (MADLs) for chemicals causing reproductive toxicity. The latest available list of these levels is dated January 2008 (OEHHA, January 2008), and indicates an NSRL of 30 μg/day for 1,4-dioxane. This compound is not known to cause reproductive toxicity, so there is no MADL for 1,4-dioxane (OEHHA, March 2008).

The NSRL for 1,4-dioxane was derived by OEHHA in the late 1980's, using data from a laboratory rat study performed in the late 1970's, and applying a standard, linearized, multistage procedure (OEHHA, December 2002). More recent data and toxicologic analysis suggest that OEHHA's NSRL estimate is a substantial underestimate, in that doses of 1,4-dioxane much larger than 30 μg/day also likely present no significant risk of cancer (Stickney *et al*., 2003).[4]

In assessing NSRLs for carcinogens, the relevant time-frame for exposure is the long-term average, where long term is typically taken to be a 70-year lifetime.[5] Thus, although some days of product-use (such as when one has many dirty dishes to wash) will involve larger-than-average exposures, other days will, of course, involve smaller-than-average exposures. In what follows, most of our exposure estimates are larger than would be expected for an average day (sometimes substantially so), so that we have, overall, overestimated doses for average consumers (and average workers) over the long term. Moreover, we assume, in the analysis that follows, that the "average" consumer will engage in heavy use of this dish liquid every day for 70 years, but such use is unlikely to start until one is at least as old as a teenager, and otherwise constitutes a larger-than-typical exposure.

[3] See http://www.cfsan.fda.gov/~dms/cosdiox.html, dated July 3, 2007, accessed April 16, 2008.
[4] The products at issue result in doses much smaller than 30 μg/day, so further toxicologic arguments, although valid, are not presented herein.
[5] See http://www.oehha.ca.gov/prop65/law/pdf_zip/RegsArt7.pdf, accessed May 13, 2008.

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3. Concentration of 1,4-dioxane in @@ dishwashing products

3.1. Measured concentrations

The Organic Consumers Association[6] recently announced that they had measured 1,4-dioxane in @@ Dish Liquid at a concentration of @@ µg/g, and in @@ Dish Liquid at @@ µg/g. The 1,4-dioxane-containing component is present at the same concentration in both varieties of dish liquid, so the two reported values represent an expected, small, sample-to-sample variation (in the products, the laboratory analyses, or both). As explained below, these measured concentrations of 1,4-dioxane are consistent with the expectations of the company based on the specifications it sets for its ingredients, and the composition of the subject products (@@, personal communication, April 2008).

3.2. Product specifications

The ingredient containing 1,4-dioxane is sodium laureth sulfate. @@, Inc. obtains a solution of this ingredient from suppliers under a contract requiring that the supplied solution contain less than @@ µg/g 1,4-dioxane (@@, personal communication, April 2008). Since the solution is used in the product at a concentration near @@%, it is expected that the concentration of 1,4-dioxane in the product may range up to about @@ µg/g. This is consistent with the observed measurements noted in Section 3.1.

4. Initial screening evaluation

Given a concentration of @@ µg/g in these dishwashing liquids, to exceed the NSRL dose of 30 µg/day (see Section 2) would require complete absorption into the body of the 1,4-dioxane in @@ g/day of the product (about @@ tablespoon/day) — such as one might get by drinking that amount of full-strength dish liquid.[7] Such a scenario clearly does not correspond to average behavior; the typical direct contact with dish liquid is through skin contact with a dilute solution (when washing dishes), and through occasional use of undiluted dish liquid as hand soap.

While the total daily *use* of dish liquid for an average user may be around @@/day, the user could not absorb the total amount of 1,4-dioxane within the liquid except by drinking it or by using it in some other extremely unlikely and unhealthful way. Absorption through the skin of 1,4-dioxane dissolved *in skin lotion* has been demonstrated experimentally to be minimal —

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[6] Press release March 14, 2008; available at http://www.organicconsumers.org/bodycare/DioxaneRelease08.cfm,; with results posted at http://www.organicconsumers.org/bodycare/DioxaneResults08.cfm and http://www.organicconsumers.org/bodycare/DioxaneAlert080314.pdf (accessed April 21, 2008).

[7] The density of these dish liquids is close enough to that of water, approximately 1 g/mL, that the difference can be ignored for this discussion, so that grams and milliliters can be used interchangeably here. For food labeling purposes a tablespoon (a measure of volume) is defined as 15 mL, a teaspoon as 5 mL, and 1 fluid ounce as 30 mL by 21CFR101.9(b)(5)(viii), and we use these definitions here. An ounce (a measure of weight) is strictly 28.35 grams, so for this discussion is not appreciably different from a fluid ounce.

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0.3% from a lotion[8] applied to the skin and *left on for 3 hours* (Bronaugh, 1982) and 3.4% from a lotion *left on for 24 hours* (Marzulli, 1981)[9] — partly because of the rapid evaporation of 1,4-dioxane. Of course, even people using full-strength dish liquid as liquid soap to wash their hands do not leave this material on their hands for anything close to 3 hours. Moreover, even if they did, they would have to use @@ g/0.3% = @@ grams, or about @@ bottles (@@ ounce size) of dish liquid every day in order to exceed the NSRL for 1,4-dioxane. Clearly, average users do not do this.

5. Detailed evaluation of exposure pathways

Average users' most extensive exposure to 1,4-dioxane from dish liquids will result from its intended use in dishwashing. During this use, users failing to use gloves will be exposed through penetration of some of the 1,4-dioxane through the skin. Some users might also, on occasion, use dish liquid neat (that is, full strength) as hand soap (but clearly not using the amounts required for exposures to approach the NRSL exposure, see Section 4). In addition, some of the 1,4-dioxane will evaporate, so the dishwasher may also be exposed via inhalation during dishwashing and subsequently in the general household atmosphere. The following sections make conservative (*i.e.* deliberately high) estimates of exposures that might be achieved by users via these pathways. In all cases, estimates for average users would be lower than those presented here. The Notice of Violation (footnote 1) mentions exposure via ingestion as well, but that route is readily shown to be insignificant (see Section 5.5 below).

5.1. Dermal exposure during dishwashing

Methods for evaluating dermal exposure to soluble organic chemicals in aqueous solutions have been extensively evaluated by the U.S. EPA and reviewers, as documented in the *Risk Assessment Guidance for Superfund, Volume 1E* (U.S. EPA, July 2004). They are based on solutions of the differential equation for diffusion through skin proposed and evaluated by Cleek and Bunge (1993), Bunge and Cleek (1995), Bunge, Cleek, and Vecchia (1995), and Reddy, Guy, and Bunge (2000), together with analysis of and comparison with a large experimental database on dermal permeation of chemicals.

To a reasonable approximation, the total amount of dissolved organic compound absorbed per event can be estimated by

$$\begin{aligned} D &= 2F_a K_p C_w A_s \sqrt{\frac{6\tau t}{\pi}} \qquad \text{for} \quad t \le t^* \\ &= F_a K_p C_w A_s \left[\frac{t}{1+B} + 2\tau \frac{1+3B+3B^2}{(1+B)^2} \right] \quad \text{for} \quad t > t^* \end{aligned} \tag{1}$$

where the symbols represent

D mass of dissolved organic material absorbed per event,

[8] Dermal absorption of dioxane from a lotion is assumed here and in Section 5.2 (for comparison with the absorption modeling), to be a good analog for dermal absorption of dioxane from neat dish liquid when it is used as hand soap; but it clearly is not a good analog for the dilute solution of product in dishwashing water (addressed in Section 5.1).

[9] The measured 0.3% was for human skin, but *in vitro*; while the 3.4% was *in vivo*, but in monkeys.

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F_a fractional absorption due to sloughing of the epidermis (set to unity),
K_p dermal permeability coefficient for the organic compound,
C_w concentration of the organic compound in the water,
τ the lag time for absorption,
t the time of immersion of skin,
t^* the time to reach steady state,
A_s the area of skin immersed, and
B the ratio of the permeability coefficient in the stratum corneum to that in the viable epidermis.

These equations are approximations to the exact solution of the differential equation, and are valid using any consistent set of units for the symbols. The permeability K_p may be estimated using the correlation (U.S. EPA, July 2004, equation 3.8)

$$\log_{10}\left(K_p/(\text{cm/hr})\right) = -2.80 + 0.66\log_{10}\left(K_{ow}\right) - 0.0056\,M/(\text{g/mole}) \tag{2}$$

where the symbols represent

K_{ow} octanol/water partition coefficient, with $\log_{10}(K_{ow})$ = –0.27 for 1,4-dioxane (*op. cit.*, Exhibit B-2),
M molecular weight, 88.1051 g/mole for 1,4-dioxane.

The estimated permeability coefficient, K_p, is then 3.4×10^{-4} cm/hr, compared with a measured permeability coefficient of 4.3×10^{-4} cm/hr from a water solution (Bronaugh, 1982). U.S. EPA (July 2004) discusses the use of measured versus estimated permeability coefficient, and suggests the likely greater accuracy of the estimate compared with a single measured value, because of the variation of measured values between experimenters and experiments. The difference here is minor, and we use the estimated value.

The ratio B may be estimated from the approximation (U.S. EPA, July 2004, equation A.1)

$$B \approx \frac{\left(K_p/(\text{cm/hr})\right)\sqrt{M/(\text{g/mole})}}{2.6} \tag{3}$$

giving a value $B \approx 0.0012$ for 1,4-dioxane, and τ from the correlation (U.S. EPA, July 2004, equation A.4)

$$\left(\tau/\text{hr}\right) = 0.105\times 10^{0.0056(M/\text{g/mole})} \tag{4}$$

which gives $\tau = 0.33$ hr for 1,4-dioxane. Finally, t^* is obtained from

$$\begin{aligned} t^* &= 2.4\tau && \text{for} \quad B \le 0.6 \\ &= 6\tau\left(b - \sqrt{b^2 - c^2}\right) && \text{for} \quad B > 0.6 \end{aligned}$$

where (5)

$$c = \frac{1 + 3B + 3B^2}{3(1+B)} \quad \text{and} \quad b = \frac{2(1+B)^2}{\pi} - c$$

For dishwashing, the skin immersed is highly unlikely to exceed both hands and forearms, with an area of about $A_s = 1980$ cm^2 (average value for men, U.S. EPA, 1997, table 6-4; the value for

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women is smaller) and the exposure time *t* for an average user is unlikely to exceed 30 minutes per dishwashing event. A typical dishpan has a useful volume of about 18 liters (15″ × 12″ × 6″), but may contain much less water, perhaps as little as 1 gallon (3.785 liters) at any time during dishwashing (although such a small quantity would almost certainly have to be replenished during a 30 minute dishwashing session). The quantity of dishwashing liquid used is a personal choice: we found that 1 teaspoon of dish liquid in 1 gallon of tap water gives highly sudsy water, and corresponds to a typical squirt from a @@ @@ oz plastic dish liquid container. This yields a somewhat larger concentration than the American Society for Testing and Materials (ASTM, 1997) "standard concentration" for hand dishwashing liquid in water of "0.10% product," which amounts to 0.76 teaspoons per gallon. To be conservative, we use the larger concentration, 1 teaspoon (5 grams) dishwashing liquid per gallon of dishwashing water (or 0.13%), and a 1,4-dioxane concentration of @@ μg/g, to yield an estimated concentration of 1,4-dioxane in the dishwashing water of 0.@@ μg/mL.

Inserting these values into the equations above, the estimated amount of 1,4-dioxane absorbed through the skin per dishwashing event is 0.@@ μg, so if a person washes dishes in this way three times per day (for a total time of 90 minutes of hand dishwashing daily) the amount absorbed is 0.@@ μg/day, or about 1/@@ of the NSRL exposure.[10]

Although these products are not sold for commercial use (@@, personal communication), it is possible that some workers might use them to hand-wash dishes. Under commercial conditions requiring longer hours of dishwashing by hand, the average commercial user will use gloves that will prevent dermal exposure. Even in the absence of gloves, exposure would only amount to 0.@@ μg/day for 8 hours dishwashing, using the same methodology as described above; giving a lifetime average of 0.@@6 μg/day (again about 1/@@ of the NSRL) when taking account of a 40 hour work-week, 50 weeks year, and a 40 year working lifetime.

5.2. Dermal exposure during handwashing

Some users might use dishwashing liquid as hand soap. The typical quantity used for this purpose is a personal choice, and may vary from much less than 1 gram (1/5 teaspoon) to the amount in a typical squirt from a plastic dishwashing liquid container (about 5 grams, 1 teaspoon).[11] Experimentally, we found that even 0.1 gram of @@ dish liquid is sufficient to provide a good lather for hand washing.

Even if a user were to use 5 grams (1 teaspoon) five times a day,[12] took 1 minute before washing off the liquid, and wetted the total area of both hands (840 cm^2 for an adult male; U.S. EPA, 1997, table 6-4) with the neat dishwashing liquid, the estimated absorption of 1,4-dioxane would

[10] At the rate of use assumed here (and assuming use only for dishwashing), if the dishpan was not refilled during dish washing, a @@ oz. container of dishwashing liquid would last @@ days. With one refill of the dishpan per dishwashing, as we assume in Section 5.4, it would last @@ days. With more dish liquid used per dishwashing the container would last proportionately less time.

[11] Typical residential hand soap pump dispensers squirt about 0.5 g/pump, while commercial wall-mounted ones may dispense 1.5 g/pump, based on a few ad-hoc measurements.

[12] This would use up a @@ oz container of dishwashing liquid every @@ days, if it were used for no other purpose.

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be 0.@@ μg/day using the same approach as described in Section 5.1, or 1/@@ of the NSRL exposure. As noted above, an experimental *in vitro* measurement of absorption through human skin (Bronaugh, 1982) indicates absorption of about 0.3% of the 1,4-dioxane in the applied lotion; that gives an estimate of about 0.@@ μg/day under similar conditions, or about 1/@@ of the NSRL exposure.

Although, as noted above, these products are not sold for commercial use, it is possible that some workers might use them to wash their hands. Under commercial conditions hand washing should ideally be more frequent in some industries (*e.g.* food preparation or serving) than for domestic conditions. Using the same conservatively high estimates as above for domestic hand-washing, but assuming fifteen hand-washings per day, and prorating to a 40 hour (5-day) week, 50 weeks per year, and 40 year lifetime, yields a lifetime average estimate of 0.@@ μg/day, about 1/@@ the NSRL.

5.3. Inhalation exposure during dishwashing

1,4-dioxane is a moderately volatile compound that is completely soluble in water at all concentrations. It will evaporate from water solutions at a rate that is governed both by the physical situation of turbulently mixed water with substantial surface area exposed and by its Henry's law constant (ratio of equilibrium air-to-water concentrations; for 1,4-dioxane, this ratio is quite small).

Absent direct relevant measurements for 1,4-dioxane volatilizing into air during hand dishwashing, we can use measurements of other, more volatile organic compounds released during hand dishwashing as an overestimate. Even overestimating (indeed, overestimating substantially, as explained below), we find no significant exposures *via* inhalation.

Nuckols *et al.* (2005) measured airborne concentrations of four trihalomethanes commonly found in public water supplies (chloroform, bromodichloromethane, dibromomethane, and bromoform) in people's breathing zones during various indoor activities, simultaneously measuring the concentration of trihalomethanes in the water used. Included in the activities sampled was dishwashing by hand, and the measurements taken are used here to overestimate concentrations of 1,4-dioxane in the breathing zone during dishwashing, hence the potential exposures to and doses of 1,4-dioxane during this activity.

Table 1 summarizes the measurements and shows that the air/water concentration ratio had an average of 0.13 $L/m^3 = 1.3 \times 10^{-4}$ for chloroform and bromodichloromethane combined. The air/water concentration ratio for 1,4-dioxane would be much less than this, because the (dimensionless) Henry's law constants[13] for chloroform and bromodichloromethane are approximately 0.14 and 0.09 respectively, whereas that for 1,4-dioxane is approximately

[13] These values were obtained from the NIST Chemistry Webbook compilation at http://webbook.nist.gov/chemistry. The values there are the water/air ratios given in units of mole/kg-bar. To obtain the dimensionless air/water ratios used here, take the inverse of 22.4 times the values given on the NIST site.

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2.2×10^{-4}, or some 500 times smaller.[14] As it happens, the measured air/water concentration ratios for chloroform and bromodichloromethane are only slightly lower than the *equilibrium* air/water concentration ratio for 1,4-dioxane, and so must be overestimates for 1,4-dioxane during dishwashing, no matter how different the configurations and conditions of sink, basin, and dishwasher for an average consumer may be from the test conditions of Nuckols *et al.* (2005).

Table 1 Measured concentrations in water and breathing zone air during hand dishwashing

	Median water concentration, μg/L		Median air concentration, μg/m^3		Ratio, air/water concentration ratio, L/m^3	
	NC	TX	NC	TX	NC	TX
Chloroform	95	22	8	5	0.08	0.23
Bromodichloromethane	19	10	2	1	0.11	0.10
Dibromochloromethane	7	3	BDL	BDL		
Bromoform	N/A	N/A	BDL	BDL		
N/A: not provided; BDL: below detection limit NC: North Carolina site; TX: Texas site Note: median water concentrations are approximate, as estimated from graphs.						

In Section 5.1, the concentration of 1,4-dioxane in dishwashing water was estimated as approximately 0.@@ μg/mL, or @@ μg/L, so the air concentration during dishwashing would be less than about 0.@@ μg/m^3 based on the measurements in Table 1. With a breathing rate of about 1 m^3/hr (U.S. EPA, 1997, section 5.2.4, recommended estimate for adults for light activities), and an exposure time of 1.5 hours per day (3 dishwashing sessions of 30 minutes each), the amount of inhaled 1,4-dioxane would amount to less than 0.@@ μg, or less than 1/@@ the NSRL exposure, assuming 100% absorption of all inhaled 1,4-dioxane.

Some workers might use these dish liquids to hand-wash dishes. Even doing so for 8 hours per day, assuming inhalation of 10 m^3 air/working day, at a rate of 40 hours per week, 50 weeks per year, and 40 working years, given the conservative assumptions above, the amount of inhaled 1,4-dioxane would amount to less than @@ μg/day as a lifetime average, or less than 1/@@ the NSRL exposure.

As small as it is, our estimate that intended use of this product could result in airborne concentrations of 1,4-dioxane on the order of 0.@@ μg/m^3 is likely to be a substantial overestimate for several reasons. Primarily, this is because 1,4-dioxane, unlike chloroform and other quite volatile substances, does not readily vaporize once dissolved in water. Attempts to *intentionally* liberate vapors of 1,4-dioxane from contaminated water have met with limited success, at most. U.S. EPA reports that 1,4-dioxane in groundwater, for example, is not removed

[14] These are at 25° C. At higher temperatures the Henry's law constants for all the compounds will be higher.

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(that is, vaporized) by the air stripper that does remove other dissolved, more volatile contaminants.[15] Similarly, 1,4-dioxane is some 100 times less readily vaporized by standard, laboratory "purge and trap" methods (which involve bubbling an inert gas through an aqueous sample) than are readily volatile compounds.[16] Moreover, experimental measurements (Rathbun and Tai, 1981, 1982) of the rate of volatilization of volatile organics from well-mixed water in bowls that are slightly larger than typical dishwashing bowls indicate that even with high air flow rates the half-life for volatilization from water may exceed 1/2 hour even for highly volatile chemicals like chloroform, under conditions designed so that the liquid-side resistance dominates. The emission rate for highly volatile chemicals like chloroform is governed primarily by the liquid side resistance under most conditions, whereas for materials like 1,4-dioxane with low Henry's law constant, the resistance of the air side will likely dominate (and add to the liquid-side resistance), decreasing the volatilization rate and air concentrations in the vicinity of the liquids.

In addition, the trihalomethanes measured by Nuckols *et al.* (2005) were present in the *tap water*, not in the detergent, and so would have volatilized from both wash water and whatever rinse water was used during the experiment. Thus, even were 1,4-dioxane as likely to evaporate as the trihalomethanes, the measurements of Nuckols *et al.* (2005) would overestimate concentrations arising from evaporation from just the wash water.

5.4. General inhalation exposure

Besides inhaling 1,4-dioxane evaporated out of dishwashing water during dishwashing, a user may also be generally exposed by inhalation within the room where dishwashing is performed. Using the approach of Section 5.1, total use of dishwashing liquid would be 5 g (1 teaspoon) per gallon of sudsy dishwashing water, and one could envision using two gallons of this during each of three dishwashings,[17] for a total daily use of as much as 30 g dishwashing liquid (2 tablespoons dish liquid used per day).[18]

At a concentration of @@ µg/g of dishwashing liquid, the total amount of 1,4-dioxane in the dishwashing liquid used is then @@ µg/day: to be as conservative as possible, we assume that all of this evaporates into the room. To overestimate the effect on an average user, we take the

[15] Concerning property in Bally, PA at which groundwater had been contaminated with several organic compounds, U.S. EPA notes: "the compound 1,4-dioxane was identified at low concentrations in the Bally municipal water system. This contaminant is not removed by the air stripper currently in-place." This air stripper had been successful in reducing concentrations of more volatile contaminants, such as trichloroethane, trichloroethylene (TCE), and dichloroethene. See http://www.epa.gov/reg3hscd/npl/PAD061105128.htm.

[16] *Per* U.S. EPA, 1,4-dioxane has "poor purging efficiency" (http://www.epa.gov/sw-846/pdfs/5030c.pdf). And Walsom and Tunnicliffe (2002) note, "Due to the poor purging efficiency of 1,4-dioxane, conventional purge and trap methods employed by the commercial laboratories produced detection limits about 100 times greater than for the more volatile organic compounds (VOCs) http://www.esemag.com/0502/tca.html."

[17] Total water use for dishwashing would be considerably higher, since this omits the water used for rinsing.

[18] This corresponds to using up a @@ oz container of dishwashing liquid in @@ days, assuming no other use.

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effective volume of the "kitchen" zone into which it evaporates equal to the 25th percentile of the distribution of the "kitchen" zone[19] volume measured in the Los Angeles area, 113 m^3 (Murray, 1997), an air change rate in that zone equal to 0.4 air changes per hour, the 25th percentile of the all-season air change rates measured in region 4 of U.S. as defined by Murray and Burmaster (1995), and assume the user stays in the kitchen area *for 12 hours*, breathing a total air volume of 10 m^3. With such extreme assumptions, the average kitchen zone air concentration is 0.@@ μg/m^3, and the average daily amount inhaled is about @@ μg/day, about 1/@@ of the NSRL exposure even if all inhaled 1,4-dioxane were to be absorbed.

This exposure scenario also may occur for a commercial user; however, such a user would be present typically for 8 hours rather than 12, and would be less exposed than the commercial users who continuously washed dishes, as described in Section 5.3.

5.5. Exposure via ingestion

The Notice of Violation (Footnote 1) claims, without further justification, that ingestion is a route of exposure for average users of dish liquid. The only plausible ingestion routes would involve residues remaining on dishes after rinsing (or after drying without rinsing), or occasional "hand-to-mouth" transfer of sudsy water.

However, 1,4-dioxane would not remain in residues on dishes or cutlery even if they were not rinsed; it is sufficiently volatile to evaporate rapidly from thin films of either liquid (while still wet) or solid residues (after drying). For hand-to-mouth transfer, suppose that a user managed to effectively drink 1 teaspoon of sudsy water per dishwashing event (3 times a day), at a concentration of 0.@@ μg/ml (see Section 5.1). This would require frequent sucking of sudsy fingers, not the behavior of an average user; but nevertheless would contribute a dose of only about 0.@@ μg/day, 1/@@ of the NSRL.

Although, as noted above, these products are not sold for commercial use, it is possible that some workers might use them and be exposed by ingestion through sucking of sudsy fingers. Direct ingestion of as much as 5 teaspoons/day of sudsy liquid appears unlikely;[20] however, even this would only give a lifetime average dose of 0.@@ μg/day, about 1/@@ of the NSRL.

Direct ingestion of neat dishwashing liquid is highly unlikely, so cannot be considered a pathway of exposure for the average user and is not further evaluated here (see Section 4).

5.6. Total exposure

Overall, then, an **average domestic user** of @@ dishwashing liquid, using 30 g/day (2 tablespoons/day) for dishwashing and 25 g/day (1 tablespoon and 2 teaspoons per day) for hand

[19] This is larger than any single room, because rooms are connected.

[20] The most frequent direct cause of hand-to-mouth activity leading to potential ingestion of contaminants is smoking; however ingestion of liquids is less likely due to such smoking-induced hand-to-mouth activity, since liquid on the fingers would result in soggy smoking materials.

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washing,[21] staying in the dishwashing area 12 hours of every day, and breathing at a rate corresponding approximately to light exercise all the time, would be exposed to at most 0.@@ μg/day from skin exposure during dishwashing, 0.@@ μg/day from skin exposure during hand washing, 0.@@ μg/day from inhalation during dishwashing, @@ μg/day from inhalation during the rest of the day, and 0.@@ μg/day from direct ingestion of sudsy water. The total is **less than @@ μg/day, substantially below the NSRL exposure of 30 μg/day.**

For an **average commercial user** (even though these products are not sold for commercial use), the corresponding estimates for lifetime average exposures are 0.@@ μg/day from skin exposure during dishwashing, 0.@@ μg/day from skin exposure during hand washing, @@ μg/day for inhalation exposure during dishwashing (and the worst case is dishwashing all the time, so there is no other inhalation component), and 0.@@ μg/day from direct ingestion of sudsy water. The total is **less than @@ μg/day (lifetime average), substantially below the NSRL exposure of 30 μg/day.**

6. Conclusion

A cursory examination of dermal exposure to 1,4-dioxane in dishwashing liquid suffices to show that such exposure would be far below the NSRL exposure. More detailed examination of other potential pathways of exposure indicates that inhalation exposures may dominate, although we have deliberately overestimated this case. Regardless, worst case estimates for all pathways combined show that an average user, whether in a household or in a commercial setting, of @@ Dish Liquid would have intakes of 1,4-dioxane substantially smaller than the NSRL of 30 μg/person/day.

7. References

ASTM D 4009 – 92 (Reapproved 1997). Standard Guide for Foam Stability of Hand Dishwashing Detergents. ASTM, 100 Bar Harbor Drive, West Conshohocken, PA 19428-2959, USA.

Bronaugh, R.L. 1982. Percutaneous Absorption of Cosmetic Ingredients. Chapter 35 In *Principles of Cosmetics for the Dermatologist*, Frost, P., and Horwitz, S., Eds. St. Louis, Toronto, London: The C.V. Mosby Company, 1982.

Bunge, A.L., and Cleek, R.L., 1995. A new method for estimating dermal absorption from chemical exposure. 2. Effect of molecular weight and octanol-water partitioning.. Pharmaceutical Res. 12(1):88–95.

Bunge, A.L., Cleek, R.L., and Vecchia, B.E., 1995. A new method for estimating dermal absorption from chemical exposure. 3. Compared with steady-state methods for prediction and data analysis. Pharmaceutical Res. 12(7):972–982.

Cleek, R.L, and Bunge, A.L., 1993. A new method for estimating dermal absorption from chemical exposure. 1. General approach. Pharmaceutical Res. 10(4):497–506.

[21] This would be a good customer for @@, needing to purchase a new @@ oz container of dishwashing liquid every @@ days.

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Marzulli, F.N., Anjo, D.M., and Maibach, H.I., 1981. *In vivo* skin penetration studies of 2,4-toluenediamine, 2,4-diaminoanisole, 2-nitro-*p*-phenylenediamine, *p*-dioxane and *n*-nitrosodiethanolamine in cosmetics. Fd. Cosmet. Toxicol. 19(6):743–747.

Murray, D.M., 1997. Residential house and zone volumes in the United States: empirical and estimated parametric distributions. Risk Analysis 17(4):439–446.

Murray, D.M., and Burmaster, D.E. 1995. Residential air exchange rates in the United States: empirical and estimated parametric distributions by season and climatic region. Risk Analysis 15(4):459–465.

Nuckols, J.R., Ashley, D.L., Lyu, C., Gordon, S.M., Hinckley, A.F., and Singer, P. 2005. Influence of tap water quality and household water use activities on indoor air and internal dose levels of trihalomethanes. Environ. Health Perspect. 113(7):863–870.

OEHHA, December 2002. Air Toxics Hot Spots Program. Risk Assessment Guidelines. Part II. Technical Support Document for Describing Available Cancer Potency Factors. Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, January, 2008. Available at http://www.oehha.ca.gov/air/hot_spots/pdf/TSDNov2002.pdf, accessed April 15, 2008.

OEHHA, January 2008. Proposition 65 Safe Harbor Levels: No Significant Risk Levels for Carcinogens and Maximum Allowable Dose Levels for Chemicals Causing Reproductive toxicity. Reproductive and Cancer Hazard Assessment Branch, Office of Environmental Health Hazard Assessment, California Environmental Protection Agency, January, 2008. Available at http://www.oehha.ca.gov/prop65/pdf/Feb2008StatusReport.pdf, accessed April 16, 2008.

OEHHA, March 2008. Chemicals known to the state to cause cancer or reproductive toxicity. March 21, 2008. Office of Environmental Health Hazard Assessment. Available at http://www.oehha.ca.gov/prop65/prop65_list/files/032108list.pdf, linked from http://www.oehha.ca.gov/prop65/prop65_list/Newlist.html, accessed April 16, 2008.

Rathbun, R.E., and Tai, D.Y., 1981. Technique for determining the volatilization coefficients of priority pollutants in streams. Water Res. 15(2):243–250.

Rathbun, R.E., and Tai, D.Y., 1982. Volatilization of ketones from water. Water, Air, and Soil Pollution 17(3):281–293.

Reddy, M.B., Guy, R.H., and Bunge, A.L., 2000. Does epidermal turnover reduce percutaneous absorption. Pharmaceutical Res. 17(11):1414–1419.

Stickney J.A., Sager S.L., Clarkson J.R., Smith L.A., Locey B.J., Bock M.J., Hartung R., and Olp S.F., 2003. An updated evaluation of the carcinogenic potential of 1,4-dioxane. Regul. Toxicol. Pharmacol. 38(2):183–95.

U.S. EPA, 1997. Exposure factors handbook. Available at http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=12464 (accessed April 21, 2008).

U.S. EPA, July 2004. Risk Assessment Guidance for Superfund. Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment). Final. EPA/540/R/99/005, OSWER 9285.7-02EP, PB99-963312. July 2004. Available with

spreadsheets at http://www.epa.gov/oswer/riskassessment/ragse/index.htm (accessed April 21, 2008).

Walsom, D.G. and Tunnicliffe, B., 2002. 1,4-dioxane – a little known compound. Environ. Sci. Eng. Available at http://www.esemag.com/0502/tca.html.

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