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Kenneth S. Fink, MD, MGA, MPH Director of Heath Hawai'i State Department of Health 1250 Punchbowl Street Honolulu, Hawai'i 96813

Dear Dr. Fink:

Subject: Honolulu Board of Water Supply (BWS) Comments on the State of Hawai'i Department of Health (DOH) Spring 2024 Draft Environmental Action Levels (EALs) for Total Petroleum Hydrocarbons (TPH)

BWS offers the following comments on the revised EALs for TPH as presented in the DOH Spring 2024 draft document *Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater* (DOH, 2024).

We provide these comments to highlight several issues for DOH to address and to help improve the accuracy and protectiveness of the EALs, particularly for TPH middle distillates (TPH-d). BWS has long supported lowering the TPH-d EALs (Lau 2018a,b; 2019; 2022a,b; 2023) so that these levels can serve their intended purpose to screen for health risks or adverse aesthetic properties of our irreplaceable drinking water resources.

Calculation of the Health-Based EALs for TPH-d is Less Protective than for Other EALs

BWS notes that DOH has incorporated the updates in the recent U.S. Environmental Protection Agency (EPA) toxicity factors for hydrocarbon fractions, as we previously recommended (Lau, 2023). The revised EALs are thus 91 parts per billion (ppb) for undegraded TPH-d, 127 ppb for 50% degraded TPH-d, and 193 ppb for totally degraded TPH-d, compared to the 2023 EALs for TPH-d (JP-5) of 266 ppb, 346 ppb, and 450 ppb, respectively (Brewer, 2022).

However, the undegraded and 50% degraded TPH-d EALs would be even lower if they were calculated using the same parameters DOH used to calculate EALs for other volatile chemicals with inhalation exposure. Although the 2024 draft documents do not

mention that the inhalation exposure time in the home was reduced by DOH from 24 hours to 4.5 hours per day for TPH-d, the EAL values themselves indicate that this reduction was made for undegraded TPH-d (half degraded TPH-d is also partially affected). The risk based EALs for other volatile chemicals, however, do not appear to incorporate this reduction in exposure and follow the EPA equations with default EPA input parameters (presented in the draft 2024 document Volume 2 Appendix 1, Methods). If the EAL for undegraded TPH-d were also calculated as DOH did for other volatile chemicals, the EAL for degraded TPH-d would be reduced to 57 ppb. The EAL for 50% degraded TPH-d would likewise decrease. *Please explain if these calculations are in error or, alternatively, why DOH used less conservative EAL calculations for TPH-d compared to other chemicals*.

Inhalation Exposure in the Home should be 24 Hours Rather than 4.5 Hours

BWS also reiterates our previous comments that DOH's reduction in exposure time in the home is not justified (Lau, 2023). DOH has modified the EPA assumption of 24 hours to 4.5 hours for exposure to the average concentration in the home resulting from volatile emissions from water over a day. Previous DOH memos on the JP-5 EALs (e.g., Brewer 2022, 2023) assumed that the air concentration of volatile TPH emissions in EPA's calculations is only when water is being used in the home. This assumption is incorrect, as documented in sources cited by EPA (EPA, 2024).

Specifically, DOH (2024, Vol. 2, Appendix 2) and Brewer (2022, 2023) cite the use of the standard EPA Regional Screening Level (RSL) equations to calculate oral, dermal, and inhalation exposure in developing screening levels or EALs (EPA 2024). As noted above, the EPA equation assumes an *average* air concentration of contaminants over time in a house that off-gas from daily water use.¹ DOH (2024; Brewer 2022, 2023), however, appears to misinterpret EPA's 24-hour average air concentration as the air concentration of volatile contaminants only when water was being used for showering, washing, etc. DOH (DOH, 2024; Brewer, 2023) thus reduced the inhalation exposure time to 4.5 hours per day (4.2 hours per day in Brewer, 2022) when bathing and washing occurred in the home.

However, applying this reduced exposure time to the standard EPA equation that calculates exposure to daily average air concentrations, in effect, assumes that a resident is only in their house for 4.5 hours per day. Although not everyone would spend 24 hours a day in a house, some people, such as young children, people with

¹ EPA (2024, section 2.2 Exposure Assumptions) cites EPA (1991) as the basis of the equations. EPA (1991, Chapter 3, p. 20), specifies that factor K in the equation approximates the *average indoor air concentration* along with assumptions on a certain amount of daily water use (not constant water use) from showers, dishwashing, toilet flushing, laundry, etc.; house size; air exchange; for a family of four, citing Andelman (1990) (Attachment 1). Andelman (1990, p. 495) notes the basis of this factor as a volume-use weighted mean over a day, which approximates the 24-hour average air concentration of a volatile contaminant from daily water use in a home (p. 500; equation 23). Andelman (1990, p. 500, equation 25) notes that exposure for a 24-hour residence period in a house can be calculated by multiplying by 24 (not 4.5), and also specifically states (p. 500-501) that this factor does *not* include direct inhalation exposure at the point of water use such as in the shower.

illnesses, or the elderly, could spend more time in their home, up to 24 hours a day. In addition, some people may use more water and have more exposure to volatile emissions (e.g., while showering) than assumed by the standard EPA equation.

The input assumptions to EPA's equation combine average (e.g., air concentration over 24 hours in a home) and high-end exposure assumptions (e.g., 24-hour residency) to ensure reasonable and health protective screening level calculations. If this equation is being used, the DOH adjustment of exposure time to 4.5 or 4.2 hours at home is inappropriate and not sufficiently protective of human health for calculating conservative screening levels. DOH drinking water EALs use the same equations and are derived to be protective of the same exposure pathways as EPA tap water RSLs: ingestion, dermal, and inhalation exposure to chemicals in water used in the household. EPA applied an exposure time of 24 hours per day for inhalation exposure specifically to be protective for people who spend up to 24 hours each day in their home, not because they believe people are using water constantly every day. DOH should not deviate from EPA's reasonable assumptions and, as a result, afford less protection to the people of Hawai'i. As noted above, using the correct exposure time of 24 hours per day, the EAL for TPH-d would be **57 ppb** instead of 91 ppb.

Lack of Transparency and Errors in Reported Parameter Values for EAL Calculations

The DOH EAL calculations for TPH are very difficult to comprehend since the information on the methodology and model inputs is spread out over several places in the document volumes and appendices. Moreover, errors, ambiguity, and inconsistencies in the text, table footnotes, and input parameters make it extremely difficult to verify the calculated EALs. For example, based on the methodology and parameters specified in the documents, we calculated the EAL for undegraded TPH-d as 28 ppb. However, this is based on what appears to be an error in the dermal parameter Kp listed in Table D (0.495; Vol. 2 Appendix 6, p. 25) which is the same as for tevent. Using 0.079 for Kp instead, as presented for gasoline (Vol. 2 Appendix 6, p. 18),² results in an EAL of 90 ppb.³ Similarly, we were unable to verify the scientific bases for the 50% degraded EALs for gasoline, diesel, and Bunker C of 108 ppb, 127 ppb and 106 ppb based on the input parameters provided.

We identified a number of additional errors and inconsistencies in the Draft 2024 DOH documents.⁴ As noted in our previous comments (Lau, 2023) on the Exposure

² Weighted average of dissolved hydrocarbon constituents assumed for gasoline and diesel are the same; assuming no contribution from volatile aliphatic compound as noted by DOH.

³ The difference between this calculated value of 90 ppb and the TPH-d EAL of 91 ppb is likely because of rounding of parameter values listed in the document.

⁴ A few examples include: 1) Vol. 2 Appendix 1, p. 6-17, the volatilization factor VF is stated to be reduced to **0.25 0.5** L/m³. (emphasis added); 2) Table D dermal parameters (Vol. 2 Appendix 6, p. 18) for Gasoline lists factors for TPH (JP-5); 3) footnote to Table A in the Diesel section (Vol. 2 Appendix 6, page 22) notes that the weighted percent of constituents in diesel fuel is based on the average composition of gasolines; 4) Vol. 2 Appendix 6 repeats the same table numbering (Tables A through E) for each of the petroleum types (e.g., Gasoline, Diesel, Bunker C), making it confusing when specific tables are cited elsewhere in the document or in other reports.

Assessment of JP-5 and calculation of EALs (Brewer, 2023), a complete editorial and technical review should be conducted of the Draft 2024 DOH documents. In the interim, we would appreciate greater transparency with respect to the methodology and calculations utilized by DOH in connection with the EAL update process. Specifically, DOH should provide a concise accounting of the relevant equations, input calculations, calculations, and results for public review. The Excel spreadsheet calculations used for the TPH EALs should also be provided with all inputs and equations.

Other Issues with the Health-Based TPH EAL Calculations

The health based TPH EAL calculations include only the dissolved fraction of TPH. However, a sheen on the water (as was reported in Joint Base Pearl Harbor Hickam [JBPHH] housing) might indicate less soluble fractions are present. As result, more of the volatile aliphatic fractions may be present in the water than assumed. DOH should make note of this potential for underestimation of risk.

Dermal toxicity factors (DOH, 2024 - Vol. 2, Appendix 6, p. 2) for non-degraded mixtures focus on more soluble and less volatile, C13+ aromatic compounds. A footnote in Table E (weighted toxicity factors for dissolved phase diesel; Vol. 2, Appendix 6, p. 26) indicates that volatile aliphatic compounds are assumed to be lost during water use and are not considered for dermal exposure. However, the inhalation part of the exposure equation assumes for all compounds present in water, including the volatile aliphatic fraction, that 50% volatilizes into the air and 50% remains in the water. Therefore, for consistency, 50% of the volatile aliphatic portion should be assumed to be present in water for dermal absorption.

The TPH EAL for Odor and Taste should also be Re-evaluated

The TPH EAL for odor and taste has not been revised and remains at the unacceptably high level of 500 ppb (raised in 2017 from 100 ppb) (DOH, 2024 - Volume 2. Appendix 1, p. 6-15). BWS has previously commented on the uncertainty regarding this increased level (Lau, 2018b; 2019). The scientific support for this higher level is, at best, poor. While BWS recognizes that available studies addressing hydrocarbon taste and odor are from decades old literature with considerable uncertainty, no clear scientific evidence supports 500 ppb as free of taste and odor for the general population. Indeed, other studies suggest that lower levels, including the previous 100 ppb threshold is appropriate for odor and taste. For example, DOH (DOH, 2017, 2024 - Vol. 2, Appendix 1, p. 6-15) acknowledges a wide range in odor threshold values for drinking water from 10 ppb to 2,000 ppb for gasoline and 82 ppb to 667 ppb for kerosene and heating oil (citing McKee and Wolfe, 1963).

DOH (DOH, 2017, 2024) does not mention additional information presented in McKee and Wolfe (1963) concerning the water dilution ratio necessary to meet the odor threshold for different types of petroleum products. Among the products presented, the middle distillate, fuel oil no. 2, is most similar to diesel and jet fuel, and had the lowest

odor threshold (required the largest dilution with water). The data presented for all products also indicated that odor threshold was greatly affected by the temperature of the water, with warmer temperatures substantially lowering the odor threshold. These data strongly indicate that the 500-ppb taste and odor EAL lacks sufficient scientific basis to be confident that it would be protective of the aesthetic properties of TPH in household water for various uses, including use of warm water for showering, bathing, washing, as well as hot water for cooking or in beverages.

DOH (DOH, 2024), continues to note: "The adequacy of this threshold should be verified if impacts to actively used sources of drinking water are identified", as previously confirmed by DOH (Anderson, 2019). However, this guidance has not been followed in the aftermath of the November 2021 release from the Red Hill Bulk Fuel Storage Facility (RHBFSF). In Dr. Brewer's December 12, 2022, presentation at the BWS Board meeting, the footnote to Slide No. 6 states that residents impacted by the November 2021 release were "unable to initially identify contamination of tap water at concentrations much higher than 500 micrograms per liter (μ g/L)." However, neither the DOH nor Dr. Brewer have presented the results of any representative survey of residents' ability to smell or taste changes at specific hydrocarbon concentrations measured in their water as the drinking water contamination at JBPHH began in late November and early December 2021.

Comments on DOH Recommendations on Use of the TPH EALs

DOH (DOH, 2024) and Dr. Brewer (Brewer, 2024) note that 91 ppb would be less than the typical laboratory method reporting limit (MRL) of 200 ppb for TPH-d, and that for concentrations below the MRL: "the laboratory is both unable to verify that the detected compound is associated with petroleum and that the estimated concentration of the compound is accurate". Dr. Brewer (Brewer, 2024) states: "Concentrations of organic matter below the MRL should not be reported as 'TPH' until such verification has been made," and specifies that such samples from a current or potential source of drinking water should receive additional analysis to verify whether the sample contains "petroleum-related contamination or other, nonpetroleum-related organic matter in the water."

DOH, however, used a laboratory (Eurofins, 2021; Attachment 2) with a method reporting limit of 47-50 ppb in their analysis of water samples in December 2021.

The Navy appears to use methods with higher laboratory reporting limits based on the EAL:

- 290 to 300 ppb in December 2021 when the EAL was 400 ppb
- 200 ppb after the EAL was lowered to 266 ppb.

Dr. Brewer (Brewer, 2023) stated "HIDOH guidance recommends the use of the laboratory MRL as the screening (action) level when the risk-based screening level is lower unless a more detailed analysis of the sample can be carried out (HIDOH 2017)"

(p. 24). However, DOH should acknowledge that a lower MRL than 91 ppb is available and has been used by laboratories for analysis of DOH samples. This lower reporting limit would also be sufficient for the recalculated EAL of 57 ppb, based on an exposure time of 24 hours per day in the home, as described above.

BWS has repeatedly commented on the lack of protectiveness of the revised TPH-d EALs of 400 ppb and 266 ppb as compared to the previous toxicity-based limit of 160 ppb and aesthetic limit of 100 ppb (Lau 2018a,b; 2019; 2022a,b; 2023). BWS again urges DOH to make clear that compliance with the updated EALs for TPH-d/JP-5 cannot be avoided merely by using laboratory analytical methods with higher limits of detection, rather than the technically achievable, lower levels already used by DOH and others to detect lower-level concentrations of TPH-d in the JBPHH water system. Higher detection limits effectively result in less complete data as well as reduced early warning of potential contamination, and likewise do little to aid in the understanding of contaminant migration either in the JBPHH water system or in the aquifer.

Thank you for considering our comments. We look forward to a revised EAL document. If you have any questions, please contact Erwin Kawata, Deputy Manager at (808) 748-5066.

Very truly yours,

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Attachments

 Andelman, J.B. 1990. Total exposure to volatile organic compounds in potable water, Chapter 20 in Significance and Treatment of Volatile Organic Compounds in Water Supplies. Ram, N.M, Christman, R.F., and K.P. Cantor (eds). Lewis Publishers, Chelsea, MI. pp. 485-504.

> 2. Eurofins. 2021. Analytical report. Laboratory Job ID: 570-77576-1. Client Project/Site: Red-Hill Incident, Hawai'i DOH. December 7, 2021. Eurofins Calscience LLC, Garden Grove, California.

References

- Anderson, B.S. 2019. Response to Hawai'i Department of Health (DOH) Reply to Honolulu Board of Water Supply (BWS) Request for an Explanation of the Basis for the Increase in the Environmental Action Levels (EALs) for the Total Hydrocarbon Middle Distillate Fraction (TPH-d). August 26.
- Andelman, J.B. 1990. Total exposure to volatile organic compounds in potable water, Chapter 20 in Significance and Treatment of Volatile Organic Compounds in Water Supplies. Ram, N.M, Christman, R.F., and K.P. Cantor (eds). Lewis Publishers, Chelsea, MI. pp. 485-504.
- Brewer, R. 2022. Recommended Risk-Based Drinking Water Action Levels for Total Petroleum Hydrocarbons (TPH) Associated with Releases of JP-5 Jet Fuel (revised February 12, 2022, revised April 20, 2022). State of Hawaii, Department of Health.
- Brewer, R. 2023. Exposure Assessment: November 2021 Release of JP-5 Jet Fuel into the Joint Base Pearl Harbor Hickam Drinking Water System. Last updated June 26, 2023.
- Brewer, R. 2024. Comparison of HIDOH Total Petroleum Hydrocarbon (TPH) Action Levels to Data for Water Samples. Draft. March 25, 2024.
- Eurofins Calscience, LLC (Eurofins). 2021. Analytical report. Laboratory Job ID: 570-77576-1. Client Project/Site: Red-Hill Incident, Hawai'i DOH. December 7, 2021.
- Hawai'i State Department of Health (DOH). 2021. Eurofins test reports from DOH collections on 11/30/2021; 12/03/2021; 12/05/2021; and 12/06/2021. Email with attachments from Joanna L. Seto, Hawai'i Department of Health to Ernest Lau, Ellen E. Kitamura, and Erwin Kawata, Honolulu Board of Water Supply. December 9.
- Hawai'i State Department of Health (DOH). 2024. Evaluation of Environmental Hazards at Sites with Contaminated Soil and Groundwater. Hawai'i edition. Spring 2024 (draft).
- Lau, Ernest Y.W. (Lau). 2018a. Honolulu Board of Water Supply (BWS) Request to Hawai'i State Department of Health (DOH) for an Explanation of the Basis for the Increase in the Environmental Action Levels (EALs) for Total Petroleum Hydrocarbon Middle Distillate Fraction (TPH-d). Honolulu Board of Water Supply. August 20.
- Lau, Ernest Y.W. (Lau). 2018b. Response to Hawai'i State Department of Health (DOH) Reply to Honolulu Board of Water Supply (BWS) Request for an Explanation of the Basis for the Increase in the Environmental Action Levels (EALs) for Total

Petroleum Hydrocarbon Middle Distillate Fraction (TPH-d). Honolulu Board of Water Supply. December 28.

- Lau, Ernest Y.W. (Lau). 2019. Honolulu Board of Water Supply (BWS) Response to Hawai'i State Department of Health (DOH) for an Explanation of the Basis for the Increase in the Environmental Action Levels (EALs) for Total Petroleum Hydrocarbon Middle Distillate Fraction (TPH-d). Honolulu Board of Water Supply. October 7.
- Lau, Ernest Y.W. (Lau). 2022a. Honolulu Board of Water Supply (BWS) Request the Hawai'i State Department of Health (DOH) Revisit its Environmental Action Levels (EALs) for Total Petroleum Hydrocarbon Middle Distillate Fraction (TPHd). Honolulu Board of Water Supply. January 31.
- Lau, Ernest Y.W. (Lau). 2022b. Honolulu Board of Water Supply (BWS) Response to Hawai'i State Department of Health (DOH) Recommended Risk-Based Drinking Water Action Levels for Total Petroleum Hydrocarbons (TPH) AAnderson, B. 2020. Request for Additional Consideration of the Toxicity-Based and Taste and Odor Threshold for Total Petroleum Hydrocarbons (TPH) in Drinking Water. State of Hawai'i, Department of Health. February 13.
- Lau, Ernest Y.W. (Lau). 2023. Honolulu Board of Water Supply (BWS) Comments on the Hawaii Department of Health (DOH) June 2023 Exposure Assessment of the November 2020 Release of JP-5 Jet Fuel into the Joint Base Pearl Harbor Hickam Drinking Water System
- United States Environmental Protection Agency (EPA).1991. EPA Risk Assessment Guidance for Superfund, Part B Manual, Chapter 3. Available at: <u>https://www.epa.gov/sites/default/files/2015-09/documents/chapt3.pdf.</u>
- United States Environmental Protection Agency (EPA). 2024. Regional screening levels (RSLs)—user's guide. Available at: <u>https://www.epa.gov/risk/regional-screening-levels-rsls-users-guide#exposure.</u> Last updated: March 22, 2024.

Significance and Treatment of Volatile Organic Compounds in Water Supplies

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CHAPTER 20

Total Exposure to Volatile Organic Compounds in Potable Water

Julian B. Andelman

INTRODUCTION

Traditionally the regulation and concern about exposures to potentially toxic chemicals and other constituents of potable water supplies have focused on the ingestion route. However, there is an increasing awareness that other routes of exposure from various potable water uses are potentially harmful as well, such as the inhalation of constituents emitted as vapors or aerosols from the water, as well as skin contact, such as in bathing.

Inhalation exposure to volatile organic chemicals (VOCs) in indoor air has been receiving increased attention, such as in the Total Exposure Methodology (TEAM) study of personal exposures of 600 residents of seven U.S. cities during the period 1981 through 1984.^{1.2} This study used personal samplers to analyze their exposures to airborne toxic organic chemicals. For 11 VOCs, including chlorinated hydrocarbons, toluene, and benzene, the indoor exposures exceeded those outdoors by factors of 2 to 5, while the highest indoor concentrations exceeded the highest outdoor concentrations by factors of 10 to 20. In the New Jersey study the median value of chloroform in drinking water was found to be 67 μ g/L, and in air 3.2 μ g/m³. Although it was not clear from the study that the chloroform in air originated only from the indoor water uses, it was hypothesized that hot showers were such a source.²

Recent studies of volatilization of VOCs from indoor water uses have shown that often 50% or more of common contaminants of water supplies, such as chloroform and trichloroethylene (TCE), will volatilize and constitute inhalation exposures, both at the point of water use in the home, as well as to inhabitants elsewhere as the air moves throughout the home.³⁻⁹ These studies have involved air measurements in

homes using water contaminated with VOCs, laboratory experiments with scaleddown model shower and bath systems, full-size showers in an experimental house, and theoretical models of volatilization and transport within houses.

Additionally, several studies have assessed the inhalation route of exposure to radon volatilizing from indoor water uses, and have predicted air exposures based on the concentration of radon in the water; the nature and quantity of the indoor water uses; and the characteristics of homes, such as their size and ventilation rates.¹⁰⁻¹³ One can conclude from these studies that about 50% of the radon volatilizes from all the indoor water uses, and that the typical air concentration of radon due to volatilization from all indoor water uses in homes is about 10^{-4} times that of the radon in the water entering the homes, based on the same concentration units for air and water.

This chapter will consider several of the key studies that have assessed these noningestion routes of exposures to VOCs, namely, skin absorption and inhalation, and review the principal factors that can influence these exposures.

SKIN ABSORPTION OF WATER CONTAMINANTS

To date, limited attention has been given to the potential for direct exposure to volatile organic chemicals by absorption through skin in contact with contaminated water, such as in bathing. Data to confirm such exposures has been minimal, and estimates as to their extent have often been speculative. Nevertheless, it is of interest to examine the possibility of these exposures and compare them to those from the ingestion of contaminated water.

The principles of the absorption of toxicants through the skin have been discussed by Klaassen¹⁴ who notes that in spite of the lipoid barrier, "some chemicals can be absorbed by the skin in sufficient quantities to produce systemic effects." Passive diffusion, not active transport across the stratum corneum, is the mechanism of such movement in mammals in percutaneous absorption. Polar substances (e.g., ethanol) "diffuse through the outer surface of protein filaments . . . while non-polar molecules (e.g., carbon tetrachloride) dissolve in and diffuse through the nonaqueous lipid matrix between the protein filaments." For these nonpolar toxicants the rate of such diffusion is related directly to their lipid solubility and inversely to molecular weight. Klaassen notes further that water plays an important role in skin permeability. The normal water content of the stratum corneum (90 grams of water per gram of dry tissue) increases the permeability by 10-fold compared to that of "perfectly dry" skin. Additional contact with water (presumably such as from bathing) will increase the amount of tightly bound water, resulting in an additional two- to threefold increase in permeability. Variations in cutaneous permeability among species have been observed, with man being similar to the guinea pig, pig, and monkey.

The toxicity following dermal contact exposure to a given quantity of chemical in comparison to that via the oral route is of interest. An example of such a Table 1. Comparison of Oral and Dermal LD₅₀ in Rats for Cyclodiene Insecticides

	Oral LD	50 (mg/kg)	Dermal LD _{so} (mg/kg)		
Substance	Male	Female	Male	Female	
Aldrin	39	60	98	08	
Dieldrin	46	46	90	64	
Photodieldrin	9.6	_	50	04	
Endrin	17.8	7.5	_	15	
Chlordane	335	430	840	690	
Heptachlor	100	162	195	250	
Heptachlor epoxide	46.5	61.3		200	
Endosullan	43	18	130	74	

Source: Drinking Water and Health.15

comparison is the acute toxicity of cyclodiene insecticides. As shown in Table 1, a study of the oral and dermal LD_{50} for rats found that they were "roughly equivalent."¹⁵

In summary, organic and other chemicals can be absorbed through the human skin; contact with water can enhance this absorption; variations in such absorption can be expected among different chemicals; and toxic effects from such absorption may occur.

Brown et al.¹⁶ reviewed skin absorption as a route of exposure of chemicals in water and assessed it for several volatile organic chemicals in comparison with the corresponding doses expected from ingestion. They noted that little attention has been paid to skin absorption as a route of entry of such chemicals outside of occupational settings, in spite of the fact that there have been many investigations of the toxicity and high penetration rates of volatile organics. Skin absorption rates can vary among.individuals and even for the same individual with time. Soaps and surfactants can increase skin permeability.

Brown et al.¹⁶ discussed the evidence for the applicability of a Fick's law diffusion model to describe the dermal absorption of solutes from dilute aqueous solution. They noted that the flux or transport across the skin is proportional to a permeability constant, the skin surface area, and the concentration of the chemical in the aqueous solution. They focused on one particular human volunteer study where the skin absorption rates were based on a 1-hour hand immersion. The results for three chemicals are shown in Table 2, indicating that the flux (skin absorption rate) for each chemical is essentially proportional to its aqueous concentration, and thus that the permeability constant is approximately independent of concentration in the range studied. This is consistent with a Fick's law model. Also, as shown in Table 2, the permeability constants for two of them, ethylbenzene and toluene, are about the same, while that for styrene is significantly smaller.

Brown et al.¹⁶ estimated the relative doses via the ingestion and skin absorption routes for these three chemicals at specific concentrations in water using the permeability constants shown in Table 2. For adults, they assumed the ingestion of 2 liters of water per day—for children, 1 liter—and that the gastrointestinal absorption

Table 2. Average Skin Absorption Rates of Chemicals from Human Volunteer Studies

	Experin	Calculated	
Chemical	Aqueous Conc. (mg/L)	Flux (mg/cm²/h)	Constant (L/cm²/h)
Ethylbenzene	112	0.11	0.001
	158	0.21	0.001
Styrene	66.5	0.04	0.0006
	269	0.16	0.0007
Toluene	180	0.16	0.0009
	600	0.60	0.001

Source: Brown et al.16

efficiency is 100%. Body surface areas of 1.8, 0.88, and 0.4 m^2 were used for an adult, child, and infant, respectively, to calculate absorption. For the adult and infant, the skin absorption calculation was based on bathing for 15 minutes per day; for the child, swimming 1 hour per day.

The results of their calculation are shown in Table 3, along with the exposure conditions, the concentration of each organic chemical being $5 \mu g/L$. In each case the calculated dermal dose is at least comparable to the ingested dose; in cases 1 and 3 the dermal doses are substantially greater. Although these calculated doses are for aqueous concentrations of $5 \mu g/L$, because both the dermal and oral intakes are likely to be proportional to the concentration, the relative oral and dermal doses are expected to be independent of the latter.

It should be noted that the estimate of the ingestion of 2 and 1 liter of water per day for an adult and child, respectively, as utilized in the analyses of Brown et al.,¹⁶ is likely to be high. If, on the contrary, one assumes that the only contaminated water ingested is that piped into the home and that uncontaminated waters are also consumed (e.g., bottled beverages), then the oral doses shown in Table 3 should be lower, increasing the relative impact from bathing or swimming. Also, they assumed that the gastrointestinal absorption of each chemical would be 100%, which is unlikely. Less than complete absorption would also reduce the effective oral dose.

Harris et al.¹⁷ have also estimated the doses from chemicals in water via ingestion and skin absorption for a specific infant exposed to four chlorinated hydrocarbons from well water used in a home. Although the exposure history was complex and it was judged that there was also exposure *in utero* from the mother consuming the water, the calculations are nevertheless of interest and are shown in Table 4. They indicate that for each chemical the calculated skin absorption dose from bathing is 25% to 40% higher than that for ingestion.

Unlike the calculation of Brown et al.,¹⁶ the Harris et al.¹⁷ study assumed simply that 10% of the contaminant in the water to which the infant came in contact was absorbed by the skin, based on information they cited. Although the approach and the assumptions in the calculations were quite different from those of Brown et al., the results are very similar in that both studies show that for an infant (Tables 3 and 4), the dermal and oral doses are comparable.

Table 3. Estimated Daily Doses for Skin Absorption Veraus Ingestion for Individual Compounds at Aqueous Concentrations of 5 Micrograms per Liter

Chemical	Dose (µg/kg)								
	Case 1* (Adult)		Case 2 ^b (infant)		Case 3° (Child)				
	Dermal	Oral	Dermal	Oral	Dermal	Oral			
Ethylbenzene	0.3	0.1	0.4	0.5	2	0.2			
Styrene	0.2	0.1	0.2	0.5	1	0.2			
Toluene	0.2	0.1	0.4	0.5	2	0.2			

Source: Brown et al.16

*70 kg adult bathing 15 minutes, 80% immersed (skin absorption); 2 liters water consumed per day (ingestion).

•10.5 kg infant bathed 15 minutes, 75% immersed (skin absorption); 1 liter water consumed per day (ingestion).

\$21.9 kg child swimming 1 hour, 90% immersed (skin absorption); 1 liter water consumed per day (ingestion).

Table 4. Comparison of Estimated Doses of Four Chlorinated Hydrocarbons to an Infant via Ingestion and Skin Absorption from Contaminated Groundwater

Route	Average Daily Dose (mg/kg/day)						
	Carbon Tetrachloride	Chloroform	Chloro- benzene	Tetrachloro- ethylene			
Drinking water	0.78	0.068	0.0015	0.00083			
Skin	1.0	0.091	0.0021	0.0011			

Source: Harris et al.17

Wester et al.¹⁸ studied the binding of aqueous solutions of organic chemicals to human'stratum corneum and their *in vitro* percutaneous absorption using fresh human skin from surgical reduction, as well as *in vivo* percutaneous absorption using the rhesus monkey. The chemicals they studied were ¹⁴C-labeled *p*nitroaniline, benzene, and PCB, all in the range of about 0.5-20 mg/L. They noted in general that the greater the lipid solubility of a chemical, the more it would partition from the water into the skin. Typically in a 30-minute period 2% to 5% of the aqueous organic chemicals was absorbed by the skin. When the concentration was varied for *p*-nitroaniline, the percent absorbed was essentially independent of concentration. They concluded that their study suggests that during a 30-minute bath or swim, chemical contaminants in the water will be absorbed by the stratum corneum; also that, based on their research, "it must be assumed that the chemical bound to the skin," and not rinsed off, "will then be absorbed by the skin and into the body."

Wester et al.¹⁸ did a hypothetical calculation of percutaneous absorption of a chemical contaminant during a 30-minute swim or bath, assuming 5% absorption suggested by their experiments. For an adult they used a skin surface area of 17,000 cm². Assuming a 1.0 mg/L concentration of absorbing organic chemical in the water, they calculated an absorbed dose of 224 μ g. In comparison, if the adult were to ingest 2 liters of the water daily, the exposure by the ingestion route would be 2.0 mg, about nine times greater.

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Although the data base is limited and the estimates are speculative regarding the absorption of VOCs from direct human skin contact with contaminated water, nevertheless there is sufficient information to conclude that such exposures may not be insignificant in comparison with those from direct ingestion. The reasonable consistency of the skin absorption estimates suggest the need to consider such dermal contact in both assessing the impacts from the exposures to chemicals in water, as well as giving guidance to the public about water uses during the event of a short-term contamination.

QUESTIONS CONCERNING VOLATILIZATION EXPOSURES

In assessing the possible inhalation exposures to potentially toxic volatile chemicals from indoor water uses, several questions should be addressed.

1. Do human inhalation exposures occur from chemicals volatilizing from indoor water uses? That is, are such volatile organic and other chemicals present in potable waters used domestically; if so, do they volatilize to such an extent, and do they have a sufficiently large residence time indoors, that they are inhaled by the inhabitants of the homes, either at the point of water use, or elsewhere in homes as air moves among the rooms?

2. If these exposures occur, how large are they compared to those from the direct ingestion of the contaminated water containing the same concentration of volatile chemical pollutant? That is, how much air is breathed in by the occupants of a home compared to the water they ingest, and what are the relative volatile chemical concentrations in the air and the water. For the purpose of this discussion, the term exposure will be defined as the quantity of a chemical inhaled or ingested, irrespective of the amount of the exposure that is subsequently absorbed either by the lungs or the gasirointestinal tract.

3. What are the characteristics of the chemicals that influence the extent to which they volatilize in indoor water uses? This includes parameters that affect both the rate at which these chemicals will volatilize as well as the equilibria that are attained between the water and air phases, such as vapor pressure, water solubility, and diffusion coefficient.

4. What factors in water uses, as well as water quality, affect the extent of volatilization? Water temperature can be expected to have a substantial impact since it will affect both equilibria and rate processes. The use of soaps and detergents may also be important since they are surface active and will affect the nature of the water-air interface across which volatilization occurs. The quantity of water and duration of its specific use will obviously have a major effect on the quantity of chemical that volatilizes, in that the process is likely to be a rate-limited one; dependent both on the time the water is exposed to the air as well as the quantity of chemical available to volatilize. Since the volatilization rate will depend on the amount of surface area at the water-air interface, each domestic water use will have to be assessed separately as to the extent of its contribution to indoor volatilization

exposures. Also, whether the water is quiescent or turbulent should have an impact on the quantity of the exposed surface area of the water.

5. How do the ventilation and other house characteristics affect the volatilization, the resulting air concentrations, and subsequent transport of the airborne chemicals throughout the house; also, are there time and spatial variations in air concentrations that will affect the human exposures? If the airflow at the point of use is low, a buildup in volatilized chemical concentration could inhibit subsequent volatilization as equilibrium between the air-water concentrations is approached. Thus increased airflow will dilute the air concentrations for a given rate of volatilization but consequently may be less inhibitory of continued volatilization. The extent to which rooms are interconnected with respect to air movement will determine whether a source of volatilizing chemical from a specific water use will result in a high exposure primarily at the point of use but very low exposures elsewhere in a house because of low air movement from the source room; or, alternatively, with high air flows among rooms, the volatilized chemical could be rapidly disseminated such that the resulting air exposures might not be very different for the inhabitants of different rooms. The specific construction of rooms and water appliances will affect both the volatilization and the human exposures. The extent of air movement between the shower/bath chamber and the bathroom, and the ventilation of the latter, will be primary factors in the exposure of the bather, both while taking a bath or shower and during the subsequent period in the bathroom.

6. What are the personal water uses and residence occupancy factors that affect the source emission quantities from volatilization, as well as the subsequent individual inhalation exposures? It is obvious that the time spent at home will affect a person's exposures to indoor-air contaminants. However, the shower/bath times, water flows, and individual's proximity to the water appliance or use will also affect them. These may vary considerably, even among residents of a given house.

7. What are the fates of these volatilized chemicals in the home environment, and are there specific interactions with materials in the home that could affect the inhalation exposures? Many of the chemicals of interest, such as low molecularweight, halogenated organics, are not likely to be unstable in home air. However, even though it is expected that they will be transported outdoors by exfiltration, there is the possibility that they may interact with or adsorb onto surfaces in a home, such as fabrics of carpets, furniture, and drapes. To the extent that this occurs, the variability in indoor-air concentrations could be mitigated or dampened.

8. What are the public health and regulatory implications of these waterborne, indoor-air inhalation exposures? Are they of sufficient magnitude compared to that of direct ingestion that they should be considered explicitly in setting maximum contaminant limits in drinking water guidelines and regulations? For a water supply contaminated with a volatile chemical such that public health authorities advise against direct ingestion of the water, should other indoor water uses also be eliminated or curtailed?

Currently there is not sufficient published information to answer all of these questions. Nevertheless many have been addressed. The rest of this chapter will

Table 5. Henry's Law Constants and Related Data at 25°C

Chemical		Vapor Pressure (atm)	Water Sol. (mol/m³)	н
n-Octane	10.00	• 0.019	5.8 × 10 ⁻³	49
Tetrachloroethylene		0.025	0.84	0.93
Carbon tetrachloride		0.15	7.5	0.81
Benzene		0.13	23	0.22
Chloroform		0.25	66	0.15
Naphthalene		1.1 x 10 ⁻⁴	0.27	0.017
Anthracene		1.4 × 10-4	4.2 × 10 ⁻⁴	0.0024
Lindane		8.3 × 10 ⁻⁸	2.5 × 10 ⁻²	1.3 × 10-4

Source: Calculated from selected data of Mackay and Shiu.19

summarize some of the key relevant studies to provide a perspective of the issues that they raise.

NATURE OF VOLATILIZATION PROCESS

To assess the potential for VOCs to volatilize from water used indoors, it is useful to consider the equilibrium and rate processes involved. The relevant relationship describing the volatilization of a chemical and its subsequent equilibrium between the air and water phases is Henry's law:

$$H = C_{\rm s}/C_{\rm w} \tag{1}$$

where H is the dimensionless Henry's law constant, and C_a and C_w (mass/volume) are the concentrations of the volatilized chemical in the air and water phases, respectively, at equilibrium.

Table 5 is a list of H constants at 25°C for several organic chemicals of environmental concern along with their vapor pressures and solubilities, the values being approximate, either calculated or taken directly from the compilation by Mackay and Shiu.¹⁹ The H constants shown there encompass a range greater than 5 orders of magnitude. Their vapor pressures and water solubilities are also quite different. Since the H values are predicted fairly well by the ratio of the vapor pressure of the pure material to its aqueous solubility, compounds such as carbon tetrachloride and tetrachloroethylene, with quite different solubilities and vapor pressures, can nevertheless have similar H values. Also it is essential to recognize that even a low-vapor-pressure chemical, by virtue of its low solubility in water, has the potential to volatilize to the same extent as a high-vapor-pressure chemical.

The maximum extent to which a chemical may be expected to volatilize in the home from indoor water uses can be estimated by considering the average quantities of water used within a home, F_w (L/h), along with typical air flow or infiltration rates F_a (L/h). For a family of four a typical ratio of F_a/F_w may be taken as 10⁴ (reference 4). The ratio of masses of volatilized chemicals, r, in the two phases is given by

 $\mathbf{r} = (\mathbf{C}_{a}/\mathbf{C}_{w})(\mathbf{V}_{a}/\mathbf{V}_{w}) \tag{2}$

where V_a and V_w are the quantities of air and water, respectively, used in a given period of time in the home. In the steady state one can assume that V_a/V_w equals F_s/F_w , and r_{MAX} is the maximum expected value for r when C_a/C_w equals H, such that

$$r_{Max} = H(F_e/F_w) = 10^4 \text{ H.}$$
 (3)

This indicates that in the steady state, as water is used within the typical home and air infiltrates through it, for a chemical with an H value as low as 10^{-4} , r_{MAX} is unity, or about 50% volatilization will occur. Since all the chemicals in Table 5 have H values greater than 10^{-4} , in each case, *assuming Henry's law equilibrium is attained*, one would expect substantial volatilization to occur in the home from normal uses of contaminated water as it is exposed to the indoor air.

The H constant will increase with temperature. Munz and Roberts²⁰ showed that for several volatile organic chemicals the temperature effect is given by

$$\log H = A' - B'/\Gamma \tag{4}$$

where A' and B' are constants for each chemical, and T is absolute temperature. For chloroform, the measured A' and B' values were found to be 4.990 and 1729, respectively, and for carbon tetrachloride, 5.853 and 1718, respectively, the measurements being taken over the range of 10°C to 30°C. For example, using this equation for chloroform, the H values are 0.076 and 0.19 at 10°C and 30°C, respectively. The comparable values for carbon tetrachloride are 0.606 and 1.52. Thus the maximum extent of volatilization that can occur will increase markedly with temperature.

As discussed by Mackay and Yeun,²¹ the rate of volatilization of a chemical from water is dependent on its molecular-diffusivity properties. Often a two-resistance model is used to describe the process in which the volatilizing chemical has to first diffuse across a liquid film at the air-water interface, followed by diffusion across the air film. Mackay and Yeun measured volatilization rates in a wind wave tank for 11 organic compounds with varying Henry's law constants. They confirmed the validity of the two-resistance model, and showed the effects of solute diffusivity and temperature. The chemicals studied included several halogenated VOCs, including chlorobenzene, carbon tetrachloride, 1,2-dibromoethane, and 1,2-dichloropropane as well as benzene and toluene and several ketones and alcohols. They showed that no interactions occur when solutes volatilize simultaneously and concluded that the mass-transfer rate was predominantly liquid-phase resistant for many of these chemicals.

The two-resistance model expressing the mass flux, F_m (mol/m²s), can be written as

$$F_m = K(C_w - C_e/H)$$
⁽⁵⁾

where K is the overall, two-resistance mass-transfer coefficient (m/s), C_{\bullet} is the solute concentration in air (mol/m³) and C_{w} that in water. The overall mass transfer is a product of the flux and the surface area exposed so that, for example, small droplets in a shower with a greater surface area would be expected to have a greater rate of volatilization per unit time than would the same mass of larger droplets with a lower surface area/mass ratio.

Mackay and Yeun concluded that the mass-transfer coefficient in either the liquid or gas phase was most likely dependent on the Schmidt number, Sc, which is the dimensionless ratio of viscosity/(density \times diffusivity), in the respective phase. The two-resistance model describes the K in terms of liquid- and gas-phase transfer coefficients, K_L and K₀, respectively, such that

$$1/K = 1/K_{L} + 1/HK_{G}$$
 (6)

They showed that for their data K_L was proportional to 3.41 \cdot 10⁻³ Sc_L^{-0.5}, while K_G was proportional to $4.62 \cdot 10^{-2}$ Sc_G^{-0.67}. The Sc_G and Sc_L values for the 12 compounds did not differ greatly, ranging from 0.72 to 1.07 for Sc_G, and 939 to 1177 for Sc_L at 20°C. However, the H values varied considerably, almost 4 orders of magnitude. For the smallest H-value compound, 1-butanol, the K_{α} term dominated to establish the overall K, while for the high H-value compounds like benzene and carbon tetrachloride, liquid-film transfer was the dominant rate-controlling step, the 1/HK_o term being negligible in Equation 8. The overall mass-transfer coefficients measured were thus quite different at these two extremes. For example, the ratio of mass-transfer coefficients for benzene to that of 1-butanol varied from 14 to 20. In contrast, for those compounds where K_L dominated, the K values did not vary much, as expected, since their Sc_1 values were quite similar, and H no longer played a significant role in determining K. Thus, in one series of determinations of mass-transfer coefficients, Mackay and Yeun measured K values of 51.1, 51.1, and 45.3 (10⁶ m/s), respectively, for benzene, carbon tetrachloride, and 1,2-dibromoethane, their Sc, values being 1021, 1062, and 1075, respectively.

This analysis indicates that one should be able to compare and predict the K values among compounds based on fundamental molecular properties and H values, to the extent that this two-resistance model applies to the volatilization from indoor water uses. They observed that the use of the K_L dependency on $Sc_L^{-0.5}$ predicts a 2.8% temperature increase in K per degree.

Equation 5 for the mass-transfer or flux at the water-air interface predicts that when the air concentration, C_a , is negligible, meaning a small buildup of chemical in the receiving air, then the rate of mass transfer is directly proportional to the concentration of volatilizing chemical in the water. This is of importance in that one could then extrapolate the percent volatilization at a high concentration in the feed water to predict the same fractional volatilization at a low-feed concentration. At the same time, even if the buildup in the air did occur, however, and its removal were first order in concentration, one could still extrapolate to the lower feed concentration.

Table 6. Transfer Efficiencies for Radon for Various Water Uses in a Typical House

Water Use	Daily Quantity (L)	Transfer Efficiency (%)
Showers	150	63
Tub baths	150	47
Toilet	365	30
Laundry	130	90
Dishwasher	55	90
Drinking and kitchen	30	30
Cleaning	<u> 10 </u>	90
TOTAL	890	

Source: Prichard and Gesell.¹⁰

There is independent evidence in laboratory studies that the mass-transfer coefficient may be reasonably constant over several orders of magnitude of concentration.²² For 1,2-dichloroethane in the range of 1 g/L to 10 μ g/L the coefficient of variation of mass-transfer coefficient was found to be $\pm 6.31\%$; for 1,1,1-trichloroethane it was $\pm 5.42\%$ over a range of concentration of 0.05 g/L to 30 μ g/L.

In summary, the H constant will limit the maximum volatilization that can occur in indoor water uses. However, except for a few still-water systems in the home, such as water in a toilet bowl, many water uses are flowing or are of short duration in which the rate of volatilization will be limiting and equilibrium will not be reached. In those instances the mass-transfer coefficients become the principal controlling factor for the relative releases of different volatile and semivolatile chemicals. Even here, however, the H constant is of importance in that it will influence the magnitude of the mass-transfer coefficient as well as the extent to which the flux for volatilization at the water-air interface will be reduced as the air concentration builds up.

Finally, the water-air interfacial areas and temperatures of the water uses are critical determining factors in the rate of mass transfer; certainly the H constants will also increase with temperature. Thus, one can expect that since the various indoor water uses involve different quantities and flows of water; residence times in the water appliances; degrees of mixing and turbulence; and temperatures, the extents of volatilization among the water uses, even for a given chemical, should vary.

Values for transfer efficiencies among water uses in a typical home have been determined for radon by Prichard and Gesell.¹⁰ As shown in Table 6, the transfer efficiencies (percent volatilization) were found to vary from 30% to 90% among the water uses, the volume use-weighted mean being about 50%.

LABORATORY SHOWER EXPERIMENTS

We have performed studies on volatilization of chemicals from laboratory and full-size shower and bath systems in which chemicals have been added to the water.³⁻⁸ In our typical laboratory shower experiments with chloroform, shown in

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Figure 1. Chloroform air concentrations in laboratory shower. From Jackman.23

Figure 1,²³ the concentration of the chemical in the air pumped from the chamber is measured continuously as the shower water flows and continues to be measured after the chemical injection is terminated, but with the shower still flowing. The peak concentrations shown in Figure 1 occur shortly after terminating the injection of chemical. In these studies we have also monitored the drainwater leaving the shower chamber for mass-balance purposes.

For this system the equation describing the rate of change of air concentration, C_a (mg/L), can be expressed as⁶

$$V_{a}(dC_{e}/dt) = k(C_{w} - C_{e}/H) - F_{a}C_{a}$$
⁽⁷⁾

where $V_a(L)$ is the volume of the shower chamber, C_w (mg/L) the concentration of the chemical in the feed water, $F_a(L/min)$ the air flow rate through the chamber, and k (L/min) the volatilization mass-transfer coefficient. When the feed concentration is terminated, the volatilization source term becomes zero and Equation 7 reduces to

$$V_{a}(dC_{a}/dt) = -F_{a}C_{a}$$
(8)

the integrated form being

$$\ln C_a = \ln C_{alNITIAL} - (F_a/V_a)t.$$
(9)

As expressed by Equation 7, we find that the volatilization source term $k(C_w - C_e/H)$ does indeed reduce significantly with time as C_a increases. For example, in the experiment with a chloroform feed of 1.84 mg/L shown in Figure 1, at 10, 30, and 50 min, the instantaneous fractional rate of volatilization, f, was 0.82, 0.70, and 0.62, respectively. This is consistent with our experimental observation that the C_e/C_w ratio for air and water leaving the chamber was found to be less than the H value for chloroform, but that the latter value of about 0.15 was gradually approached during the shower experiment,²³ thus gradually inhibiting the volatilization rate.

We have also found in our experiments with both chloroform and trichloroethylene (TCE) that during the decay period (following the termination of the chemical in the shower feed) significant quantities of the volatilized chemical in the shower chamber air redissolves in the flowing water, as measured in the drainwater. Thus, Equations 8 and 9 are not quite accurate, since there is this additional decay route.

As shown in Figure 1 for chloroform, as expected the air concentration due to volatilization increases with temperature and concentration of the feed water in the shower experiments. Also as expected, we have found that increased air flow reduces the concentration of volatilized chemical in the chamber air and at the same time increases the rate of volatilization, since the rate of approach to Henry's law equilibrium is reduced. Rates of volatilization for chloroform and TCE ranged from about 50% to 90%, depending on temperature and other shower conditions, with chloroform volatilization typically lower than that for TCE.

MODELING SHOWER AND WHOLE-HOUSE EXPOSURES

One can estimate the shower and whole-house exposures by the use of simple, one-compartment modeling. For example, integrating Equation 7 and assuming that C_e/H is negligible compared to C_w , one obtains an expression for the change in C_a with time in a chamber:

$$\ln (1 - C_{a}F_{a}/kC_{w}) = -(F_{a}/V_{a})t.$$
(10)

The assumption that C_a/H is negligible implies that the rate of volatilization in the shower is constant. In that case it can be shown that k equals fF_w , where f is the fraction of chemical that volatilizes from the feedwater whose flow rate is F_w (V/t). Although, as noted above, there is a gradual decrease in f values with time during the shower experiments, this will not substantially affect the estimated average values of C_a that will be used to calculate exposures. Using Equation 10 one can calculate the maximum air concentration that will be achieved in a one-compartment shower or bath. For small values of (F_a/V_a) t (the magnitude of which will be considered below), Equation 10 reduces to a simple linear form

$$C_a = ktC_w/V_a. \tag{11}$$

Thus, after a given shower period, t, this is also the maximum concentration, C_{aMAX} ,

$$C_{aMAX} = ktC_w/V_a.$$
(12)

Also, the average concentration, C_{aAVG} , would be $C_{aMAX}/2$ since C_a increases linearly with time:

$$C_{aAVG} = ktC_w/2V_a.$$
(13)

For the purpose of estimating possible shower exposures, it will be assumed that the concentrations during the shower itself and during the time in the bathroom afterward will be the same in the shower and bathroom. In fact, our measurements in a full-size shower show that there is indeed a difference between the two and that the system should be more appropriately treated as a two-compartment system.²⁴ For precise modeling of the exposures, this difference should be considered, but as an approximation it will be neglected here.

Subsequent to the showering period there will be a decay of the air concentrations in the bathroom due to normal exchange of air. During this period the person in the bathroom will continue to be exposed to the volatilized chemicals in the air. The decay of C_a is represented by

$$\ln \left(C_a / C_{aMAX} \right) = -(F_a / V_a)t.$$
(14)

For small values of (F_{a}/V_{a}) t this equation linearizes to

$$C_a = C_{aMAX} [1 - (F_a/V_a)t].$$
 (15)

The average concentration during this period, C_{BAVG} , is

$$C_{aAVG} = (C_a + C_{aMAX})/2.$$
 (16)

Combining Equations 15 and 16, one obtains

$$C_{uAVG} = C_{aMAX} \left[1 - F_a t / (2V_a) \right].$$
(17)

In many cases, the $F_at/(2V_a)$ term in Equation 17 is likely to be substantially smaller than unity, so that as an approximation during the decay period one can assume that $C_{aAVG} = C_{aMAX}$, at least for the purposes of estimating the magnitude of inhalation exposures.

One can use these equations to estimate the C_{aAVG} values for various showerwater flow and bathroom characteristics. In an Australian survey of water uses, distributions of average shower-water flow rates and duration were reported for about 2,500 households.²⁵ The geometric mean for the shower flow rates, F_w , was about 8 L/min (about 500 L/h), and about 6 min for the shower duration, which will be specified as t_d , and typically taken as 0.1 h. These values will be utilized here to estimate C_a values using the above equations. In a study of modern houses in one heating season the geometric mean for air exchange rates was reported to be 0.53 h⁻¹.¹³ This value will be used for the bathroom, along with a value for its size, V_a , of 10,000 L. Thus, the F_a for the bathroom will be 0.53V_a, or about 5000 L/h. Thus, for a shower period of 0.1 h, or a decay period of 0.2 h, with $(F_a/V_a)t$ values of 0.053 and 0.115, respectively, the approximation of linearizing Equations 10 and 14 involves errors of less than 1%.

The above equations and data can be utilized to estimate the average air concentrations to which people are exposed in bathrooms during and after showering. As discussed earlier, the fractional volatilization rate in our shower experiments has been found to range from 0.5 to 0.9, depending on the specific chemical, water temperature, and other factors. For the purposes of estimating a typical value, we will use an f value of 0.75.

Using Equation 12 and the fact that k equals fF_w yields

$$C_{aMAX} = C_w f F_w t_d / V_a.$$
(18)

One can use typical values for the variables indicated above to obtain

$$C_{aMAX} = C_w(0.75)(500)(0.1)/10^4 = 3.75 \cdot 10^{-3} C_w.$$
 (19)

The value for C_{aAVG} would be one-half this, or $1.9 \cdot 10^{-3} C_w$. It is interesting to note that Prichard and Gesell¹⁰ predicted that for a 5-minute shower using 75 L of water and with 65% volatilization in a 30,000 L room, the average radon air concentration would be $1.6 \cdot 10^{-3} C_w$. Similarly, McCone⁹ modeled several low-molecular-weight organics volatilizing with multiple family use of a bathroom in the early morning hours and calculated typical bathroom air concentrations of $5 \cdot 10^{-3} C_w$.

Such predicted air concentrations will be highly dependent on a variety of factors, including the nature of the volatilizing chemical, geometry and air exchange between the shower and surrounding room, water temperature, and water flow rate. Nevertheless, these can be assessed to determine the likely range of bathroom air concentrations that can be expected in homes.

It is also of interest to estimate the inhalation exposures in the shower and bathroom, and compare them to the likely ingestion exposures. *Inhalation exposure*, E_i (mg), can be defined as the product of C_a , the breathing rate, B (L/h), typically 1000 L/h for an adult, and the exposure time, t:

$$E_{i} = C_{a}Bt.$$
 (20)

As an example, one can use this equation to estimate the exposures during a 0.1 h showering time, using the value of C_{aAVG} above of $1.9 \cdot 10^{-3} C_w$. Also as noted above, during a 0.2 h period subsequent to the shower, the decay will not be significant, so that the C_{aAVG} during this period can be taken to be C_{MAX} , namely, $3.75 \cdot 10^{-3} C_w$. Thus, one can calculate the E_i for the combined 0.1 h shower and 0.2 h subsequent period in the bathroom as the sum of two terms using Equation 20, to give

$$E_{i} = [C_{aAVG}Bt]_{shower} + [C_{aAVG}Bt]_{decay}.$$
 (21)

Inserting the appropriate values, one obtains

$$E_i = 1.875 \cdot 10^{-3} C_w(1000)(0.1) + 3.75 \cdot 10^{-3} C_w(1000)(0.2).$$
 (22)

Thus, E_i has the value $0.94C_w$, where the units of C_w are mass/L. This is the inhalation exposure in the bathroom during the shower and subsequent to it while the bather remains in the bathroom and is approximately equivalent to the exposure that would occur from ingesting 1 liter of the water. However, several occupants of a home may take a shower during a period when the volatile chemical air concentration in a bathroom has not decayed and builds up to levels higher than one would predict for a single bather. In that instance, the exposures could be substantially higher than would be predicted by the above relationship.

Similarly, we have used a simple predictive equation, based on a one-compartment indoor-air model, to describe the range of average indoor-air concentrations that are likely to be encountered from a chemical volatilizing at an average rate of 50% from all water uses, as discussed above to be a typical value for radon. The relationship we have obtained for the expected range of indoor-air concentrations is⁷

$$C_a = (0.1 \text{ to } 5) \cdot 10^{-4} C_w$$
 (23)

where C_s is the average indoor-air concentration (mg/L), generated by the corresponding average water concentration, C_w (mg/L). Thus, for example, a water concentration of 1 mg/L would be expected to generate between $1 \cdot 10^{-3}$ to $5 \cdot 10^{-4}$ mg/L average air concentration in the home. This, of course, does not address the time and space variations that will be encountered throughout the day in the home. It is interesting to note that Nazaroff et al.¹³ have similarly made estimates of the likely indoor-air concentrations of radon for U.S. homes by the water volatilization route. The geometric mean in their factor applicable to Equation 23 is $0.65 \cdot 10^{-4}$, within our range of predicted values. Also, their range of 1 standard deviation around the mean corresponds to the following equation:

$$C_{a} = (0.23 \text{ to } 1.87) \cdot 10^{-4} C_{w}$$
 (24)

also within our predicted range. McKone⁹ has similarly estimated household air concentration for several volatilizing chemicals, predicting an average C_a ranging from $2 \cdot 10^{-5}$ to $1.2 \cdot 10^{-4}$ mg/L in air for a C_w of 1 mg/L in water, also within the range of that predicted by Equation 23.

One can use these air concentration predictions to estimate the likely inhalation exposures, E_1 , for an adult during a 24-hour residence period in a house. Combining Equations 20 and 23 one obtains

 $E_i = (0.1 \text{ to } 5)(10^{-4})(1000)(24) C_w = (0.2 \text{ to } 10) C_w.$ (25)

Since the C_w units here are mass/L, a 1 mg/L water concentration corresponds to a range of inhalation exposures of 0.2 to 10 mg per day, in comparison to 2 mg per day for the ingestion of 2 liters of that water. It should be noted that these inhalation

exposure estimates do not include those that would occur at the point of water use, such as during showering. As discussed above, the latter exposures can be comparable to those from direct ingestion.

There is a remarkable consistency in the above range of likely predicted average indoor-air concentrations from the totality of indoor water sources. Nevertheless, there are a number of factors to be considered in refining these estimates and developing a useful and simple predictive relationship that can be applied by those responsible for exposure assessments in specific situations. They can be categorized as follows:

- chemical characteristics that affect the rate and extent of volatilization, including soap and detergent use
- water use factors that affect the "source strength" and its time and location variability
- chemical characteristics that influence the behavior and interactions of the volatilized chemicals with "sinks," typically high surface area materials in the home; also the specific nature, amounts, and locations of these sinks
- house structure and indoor-air flow regimes that transport the volatilized chemicals throughout the home
- personal behavior and home occupancy factors that determine an individual's exposure.

The simple indoor-air models mentioned above generally are not sufficiently specific to address all the above factors, although they can and have been evaluated for some indoor-air pollution sources other than those from water.²⁶

The potential interactions between surfaces in homes and organic vapors released from water into indoor air have not been studied and need to be evaluated. For some chemicals it may be appropriate to incorporate these interactions into the volatilization, indoor-air exposure model. One study of the interaction of volatile organic chemicals with materials used in the home examined three surfaces:²⁷ plywood, nylon carpeting, and wool carpeting. The study focused on 20 volatile organic chemicals, including alkanes, aromatics, alcohols, esters, ketones, aldehydes, terpenes, and chlorinated hydrocarbons. They showed clear interactions between the gaseous organic chemicals and the surfaces. For example, in one experiment wool carpeting became essentially saturated with lindane within about one day.

In order to determine the role of such "sink" interactions there are three broad questions that need to be addressed:

- 1. Which classes of organic/surface systems demonstrate significant sorption effects?
- 2. What are the appropriate equilibrium and kinetic models for the sorption process for the organic/surface systems of interest?
- 3. How can this equilibrium and kinetic information be incorporated into a watervolatilization, indoor-air quality model?

SUMMARY AND CONCLUSIONS

VOCs have the potential for causing substantial human exposures from indoor uses of contaminated water by noningestion routes, namely, inhalation following volatilization from water, as well as by skin contact. The latter exposures have been estimated to be comparable to those from direct ingestion of water, although published research in this area is scanty.

Measurements in homes have shown that VOCs can be detected in indoor air following the use of contaminated water. Scaled-down and full-size laboratory bath and shower studies for such VOCs as chloroform and trichloroethylene have shown that a variety of factors can affect the extent of volatilization, found to be typically in the range of 50% to 90%. These include the nature of the volatilizing chemical, water temperature, air and water flow rates, and nature of the water use (e.g., bath vs shower).

The Henry's law equilibrium constants, H, predict that even chemicals with low vapor pressures may be expected to volatilize substantially, provided their water solubilities are also low. Thus, so-called semivolatile organic chemicals have the potential to volatilize and cause inhalation exposures. Also, chemicals with varying H values may nevertheless volatilize at comparable rates.

Modeling and estimates of inhalation exposures to VOCs indicate that for the bather these exposures during and directly after a shower can be comparable to that from direct ingestion of the contaminated water. Also, when all water uses are considered, the inhalation exposures to all inhabitants of a home may be substantially larger than that from direct ingestion, even without considering the inhalation exposures at the point of water use. However, additional research is required to more specifically and precisely quantify these exposures to encompass the full range of home characteristics, as well as personal water uses and occupancy factors.

Because the noningestion exposures to VOCs in indoor water uses are likely to be comparable to or greater than those from direct ingestion, it would be prudent to consider this in establishing regulatory limits in drinking water, as well as the need to restrict all indoor water uses when it is judged that there is a significant health risk from the direct ingestion of a contaminated water.

ACKNOWLEDGMENTS

The author would like to acknowledge the fruitful discussions and collaborations with several students and colleagues which have provided useful perspective and data for much of this research. These include Nicholas Giardino, Thomas Jackman, Steve Myers, Lynn Wilder, Amy Couch, and William Thurston at the University of Pittsburgh and John Borrazzo and Cliff Davidson at Carnegie-Mellon University.

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REFERENCES

- Wallace LA, ED Pellizzari, TD Hartwell, R Whitmore, C Sparacino, and H Zelon (1986) "Total Exposure Assessment Methodology (Team) Study: Personal Exposures, Indoor-Outdoor Relationships, and Breath Levels of Volatile Organic Compounds in New Jersey," *Environment International* 12:369–387.
- Wallace, LA (1987) Total Exposure Assessment Methodology (TEAM) Study: Summary and Analysis: Vol. 1 (Washington, DC: U.S. Environmental Protection Agency, Office of Research and Development).
- 3. Andelman, JB (1985) "Human Exposures to Volatile Halogenated Organic Chemicals in Indoor and Outdoor Air," *Environ. Health Pers.* 62:313-318.
- Andelman, JB (1985) "Inhalation Exposure in the Home to Volatile Organic Contaminants of Drinking Water," Sci. Total Env. 47:443-460.
- Andelman, JB, SM Meyers, and LC Wilder (1986) "Volatilization of Organic Chemicals from Indoor Uses of Water," in *Chemicals in the Environment*, JN Lester, R Perry, and RM Sterritt, Eds. (London: Selper Ltd.), 323-330.
- Andelman, JB, A Couch, and WW Thurston (1986) "Inhalation Exposures in Indoor Air to Trichloroethylene from Shower Water," in *Environmental Epidemiology*, FC Kopfler and GC Craun, Eds. (Chelsea, MI: Lewis Publishers, Inc.), 201–213.
- Andelman, JB, LC Wilder, and SM Myers (1987) "Indoor Air Pollution from Volatile Chemicals in Water," in *INDOOR AIR '87, Vol. 1*, Proceedings of the 4th International Conference on Indoor Air Quality and Climate (Berlin: Institute for Water, Soil and Air Hygiene), 37-41.
- Giardino, NJ, JB Andelman, JE Borrazzo, and CI Davidson (1988) "Sulfur Hexafluoride as a Surrogate for Volatilization of Organics from Indoor Water Uses," JAPCA 38(3):278-280.
- McKone, TE (1987) "Human Exposure to Volatile Organic Compounds in Household Tap Water: The Indoor Inhalation Pathway," *Environ. Sci. Technol.* 21:1194–1201.
- Prichard, HM, and TF Gesell (1981) "An Estimate of Population Exposures due to Radon in Public Water Supplies in the Area of Houston, Texas," *Health Physics* 41: 599-606.
- Hess, CT, CV Weiffenbach, and SA Norton (1983) "Environmental Radon and Cancer Correlations in Maine," *Health Physics* 45:339-348.
- Cross, FT, NH Harley, and W Hoffman (1985) "Health Effects and Risks from ²²²Rn in Drinking Water," *Health Physics* 48(5):649-670.
- Nazaroff, WW, SM Doyle, AV Nero, and RG Sextro (1987) "Potable Water as a Source of Airborne ²²²Rn in U.S. Dwellings: A Review and Assessment," *Health Physics* 52(3):281-295.
- Klaassen, CD (1980) "Absorption, Distribution and Excretion of Toxicants," in *Toxicology*, J Doull, CD Klaassen, and MO Amdur, Eds. (New York: Macmillan Publishing Company, Inc.), 28-51.
- 15. Drinking Water and Health (1977) (Washington, DC: National Academy Press).
- 16. Brown, HS, DR Bishop, and CA Rowan (1984) "The Role of Skin Absorption as a

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Route of Exposure for Volatile Organic Compounds (VOCs) in Drinking Water," Am. J. Public Health 74:479-484.

- Harris, RH, JV Rodricks, CS Clark, and SS Papadopulos (1987) "Adverse Health Effects at a Tennessee Hazardous Waste Disposal Site," in *Health Effects from Hazardous Waste Sites*, JB Andelman and DW Underhill, Eds. (Chelsea, MI: Lewis Publishers, Inc.), 221-240.
- Wester, RC, M Mobayen, and HI Maibach (1987) "In Vivo and In Vitro Absorption and Binding to Powdered Stratum Corneum as Methods to Evaluate Skin Absorption of Environmental Chemical Contaminants From Ground and Surface Water," J. Toxicol. Environ. Health 21:367-374.
- 19. Mackay, D, and WY Shiu (1981) "A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest," J. Phys. Chem. Ref. Data 10(4):1175-1199.
- Munz, C, and PV Roberts (1987) "Air-Water Phase Equilibria of Volatile Organic Solutes," J. Am. Water Works Assoc. 79:62-69.
- 21. Mackay, D, and ATK Yeun (1983) "Mass Transfer Coefficient Correlations for Volatilization of Organic Solutes from Water" *Environ. Sci. Technol.* 17(4):211-217.
- Rathbun, RE, and DY Tai (1984) "Volatilization of Chlorinated Hydrocarbons from Water," in Gas Transfer at Water Surfaces, W Brutsaert and GH Jirka, Eds. (Dordrecht, Holland: D. Reidel Publishing Company), 27–34.
- 23. Jackman, T (1988) "Volatilization of Chloroform and Trichloroethylene in a Model Shower System," MSc Thesis, University of Pittsburgh, Pittsburgh, PA.
- Giardino, N (1987) "An Indoor Air Pollution Study Using Sulfur Hexafluoride Volatilized from a Model Shower System," MSc Thesis, University of Pittsburgh, Pittsburgh, PA.
- James, IR, and MW Knuiman (1987) "An Application of Bayes Methodology to the Analysis of Diary Records From a Water Use Study," J. Amer. Stat. Assoc. 82:705– 711.
- 26. Wadden, RA, and PA Scheff (1983) Indoor Air Pollution (New York: John Wiley & Sons, Inc.).
- 27. Seifert, B, and HJ Schmahl (1987) "Quantification of Sorption Effects for Selected Organic Substances Present in Indoor Air," in *INDOOR AIR '87, Vol. 1*, Proceedings of the 4th International Conference on Indoor Air Quality and Climate (Berlin: Institute for Water, Soil and Air Hygiene), 252–256.

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Environment Testing America

ANALYTICAL REPORT

Eurofins Calscience LLC 7440 Lincoln Way Garden Grove, CA 92841 Tel: (714)895-5494

Laboratory Job ID: 570-77576-1

Client Project/Site: RED-HILL INCIDENT, HAWAII-DOH

For:

Eurofins Eaton Analytical 750 Royal Oaks Drive Monrovia, California 91016

Attn: Jaclyn Contreras

Authorized for release by: 12/7/2021 8:15:56 PM

Xuan Dang, Project Manager I (714)895-5494 Xuan.Dang@eurofinset.com

The test results in this report meet all 2003 NELAC, 2009 TNI, and 2016 TNI requirements for accredited parameters, exceptions are noted in this report. This report may not be reproduced except in full, and with written approval from the laboratory. For questions please contact the Project Manager at the e-mail address or telephone number listed on this page.

This report has been electronically signed and authorized by the signatory. Electronic signature is intended to be the legally binding equivalent of a traditionally handwritten signature.

Results relate only to the items tested and the sample(s) as received by the laboratory.



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Definitions/Glossary

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Percent Recovery

Glossary Abbreviation

¤ %R Job ID: 570-77576-1

3
-
5
9

CEI	Contains Free Liquid
CFU	
CNF	Contains No Free Liquid
DER	Duplicate Error Ratio (normalized absolute difference)
Dil Fac	Dilution Factor
DL	Detection Limit (DoD/DOE)
DL, RA, RE, IN	Indicates a Dilution, Re-analysis, Re-extraction, or additional Initial metals/anion analysis of the sample
DLC	Decision Level Concentration (Radiochemistry)
EDL	Estimated Detection Limit (Dioxin)
LOD	Limit of Detection (DoD/DOE)
LOQ	Limit of Quantitation (DoD/DOE)
MCL	EPA recommended "Maximum Contaminant Level"
MDA	Minimum Detectable Activity (Radiochemistry)
MDC	Minimum Detectable Concentration (Radiochemistry)
MDL	Method Detection Limit
ML	Minimum Level (Dioxin)
MPN	Most Probable Number
MQL	Method Quantitation Limit
NC	Not Calculated
ND	Not Detected at the reporting limit (or MDL or EDL if shown)
NEG	Negative / Absent
POS	Positive / Present
PQL	Practical Quantitation Limit
PRES	Presumptive
QC	Quality Control
RER	Relative Error Ratio (Radiochemistry)
RL	Reporting Limit or Requested Limit (Radiochemistry)
RPD	Relative Percent Difference, a measure of the relative difference between two points
TEF	Toxicity Equivalent Factor (Dioxin)
TEQ	Toxicity Equivalent Quotient (Dioxin)
TNTC	Too Numerous To Count

These commonly used abbreviations may or may not be present in this report. Listed under the "D" column to designate that the result is reported on a dry weight basis

Eurofins Calscience LLC

Case Narrative

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Job ID: 570-77576-1

Laboratory: Eurofins Calscience LLC

Narrative

Job Narrative 570-77576-1

Comments

No additional comments.

Receipt

The samples were received on 12/3/2021 10:00 AM. Unless otherwise noted below, the samples arrived in good condition, and where required, properly preserved and on ice. The temperature of the cooler at receipt was 3.5° C.

GC Semi VOA

No analytical or quality issues were noted, other than those described in the Definitions/Glossary page.

Organic Prep

No analytical or quality issues were noted, other than those described in the Definitions/Glossary page.



Job ID: 570-77576-1

Detection Summary

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Job ID: 570-77576-1

Client Sample ID: Mokulele2021113021

Lab Sample ID: 570-77576-1

No Detections.

This Detection Summary does not include radiochemical test results.

Eurofins Calscience LLC

Client Sample Results

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Method: 8015B - Diesel Range Organics (DRO) (GC)

Client Sample ID: Mokulele2021113021						Lab Sample ID: 570-77576-1			
Date Collected: 11/30/21 15:00	D						Matrix	: Water	
Date Received: 12/03/21 10:00)								
Analyte	Result	Qualifier	RL	Unit	D	Prepared	Analyzed	Dil Fac	
C6 as C6	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C7 as C7	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C8 as C8	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C9-C10	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C11-C12	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C13-C14	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C15-C16	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C17-C18	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C19-C20	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C21-C22	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C23-C24	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C25-C28	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C29-C32	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	ા	
C33-C36	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C37-C40	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C41-C44	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
C6-C44	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
Gasoline Range Organics [C6 - C10]	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
Diesel Range Organics [C10-C28]	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
Oil Range Organics (C28-C40)	ND		47	ug/L		12/06/21 11:14	12/07/21 10:42	1	
Surrogate	%Recovery	Qualifier	Limits			Prepared	Analyzed	Dil Fac	
n-Octacosane (Surr)	113		53-151			12/06/21 11:14	12/07/21 10:42	1	

Job ID: 570-77576-1

6

Surrogate Summary

Job ID: 570-77576-1

Prep Type: Total/NA

Method: 8015B - Diesel Range Organics (DRO) (GC)

Matrix: Water

		Percent Surrogate Recovery (Acceptance Limits)					
La bSample ID	Client Sample ID	OTCSN1 (53-151)					
570-77576-1	Mokulele2021113021	113					
570-77576-1 MS	Mokulele2021113021	108					
570-77576-1 MSD	Mokulele2021113021	106					
LCS 570-198844/2-A	Lab Control Sample	109					
LCSD 570-198844/3-A	Lab Control Sample Dup	112					
MB 570-198844/1-A	Method Blank	110					
Surrogate Legend							

OTCSN = n-Octacosane (Surr)

QC Sample Results

Job ID: 570-77576-1

Method: 8015B - Diesel Range Organics (DRO) (GC)

Lab Sample ID: MB 570-198844/1-A	
Matrix: Water	

Client Sample ID: Method Blank Prep Type: Total/NA Prop Batch: 198944

Analysis Batch: 199008							Prep Batch:	198844
	MB	МВ						
Analyte	Result	Qualifier	RL	Unit	D	Prepared	Analyzed	Dil Fac
C6 as C6	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C7 as C7	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C8 as C8	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C9-C10	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C11-C12	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C13-C14	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C15-C16	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C17-C18	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C19-C20	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C21-C22	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C23-C24	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C25-C28	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C29-C32	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C33-C36	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C37-C40	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C41-C44	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
C6-C44	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
Gasoline Range Organics [C6 - C10]	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
Diesel Range Organics [C10-C28]	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
Oil Range Organics (C28-C40)	ND		50	ug/L		12/06/21 11:14	12/07/21 08:24	1
	МВ	МВ						
Surrogate	%Recovery	Qualifier	Limits			Prepared	Analyzed	Dil Fac
n-Octacosane (Surr)	110		53 - 151			12/06/21 11:14	12/07/21 08:24	1

Lab Sample ID: LCS 570-198844/2-A Matrix: Water

[C10-C28]

Analysis Batch: 199008							Prep Batch:	198844
	Spike	LCS	LCS				%Rec.	
Analyte	Added	Result	Qualifier	Unit	D	%Rec	Limits	
Diesel Range Organics	4000	4297		ug/L	-6-	107	70-131	
[C10-C28]				-				

Surrogate	LCS %Recovery	LCS Qualifier	Limits
n-Octacosane (Surr)	109		53 - 151
Lab Sample ID: LCSD 570	-198844/3-A		
Matrix: Water			
Analysis Batch: 199008			
			Spike
Analyte			Added
Diesel Range Organics			4000

Client Sample ID: Lab Control Sample Dup	
Prep Type: Total/NA	
Prep Batch: 198844	

Client Sample ID: Lab Control Sample

Prep Type: Total/NA

Datch. 155000						Ргер Ва	acn: 1	38844
	Spike	LCSD LCSD				%Rec.		RPD
	Added	Result Qualifier	Unit	D	%Rec	Limits	RPD	Limit
e Organics	4000	4322	ug/L		108	70-131	1	20

	LCSD LCSD	
Surrogate	%Recovery Qualifier	Limits
n-Octacosane (Surr)	112	53 - 151

QC Sample Results Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Job ID: 570-77576-1

Method: 8015B - Diesel Range Organics (DRO) (GC) (Continued)

Lab Sample ID: 570-77	576-1 MS					Clien	t San	nple ID:	Mokulei	e20211	13021
Matrix: Water									Prep Ty	pe: Tot	al/NA
Analysis Batch: 199008	Samplo	Sampla	Sniko	MQ	MS				Prep Ba	atch: 19	98844
Analida	Beault	Sample	Added	Desult	Qualifian	l Init		9/ Daa	/ortec.		
Analyte	Result	Quaimer	Added	Result	Quaimer	Unit	-	%Rec	Limits		
Diesel Range Organics [C10-C28]	ND		3840	3238		ug/L		84	33 - 160		
	MS	MS									
Surrogate	%Recovery	Qualifier	Limits								
n-Octacosane (Surr)	108		53-151								
						0				00044	10004
Lab Sample ID: 5/0-//:	576-1 MSD					Clien	t San		MOKUIEI	320211	13021
Matrix: Water									Prep Ty	pe: Tot	al/NA
Analysis Batch: 199008	3								Prep Ba	atch: 19	98844
	Sample	Sample	Spike	MSD	MSD				%Rec.		RPD
Analyte	Result	Qualifier	Added	Result	Qualifier	Unit	D	%Rec	Limits	RPD	Limit
Diesel Range Organics	ND		3990	3843		ug/L		96	33 - 160	17	40
[C10-C28]											
	MSD	MSD									
Surrogate	%Recovery	Qualifier	Limits								
n-Octacosane (Surr)	106		53-151								

QC Association Summary

Job ID: 570-77576-1

GC Semi VOA

Prep Batch: 198844

Lab Sample ID	Client Sample ID		Matrix	Method	Prep Batch
570-77570-1 MD 570 109944/1 A	Mothed Block	Total/NA Total/NA	Water	35100	
WB 570-198644/1-A		TOLAINNA	VValer	35100	
LCS 570-198844/2-A	Lab Control Sample	Total/NA	Water	3510C	
LCSD 570-198844/3-A	Lab Control Sample Dup	Total/NA	Water	3510C	
570-77576-1 MS	Mokulele2021113021	Total/NA	Water	3510C	
570-77576-1 MSD	Mokulele2021113021	Total/NA	Water	3510C	
Analysis Batch: 1990	800				
Lab Sample ID	Client Sample ID	Ргер Туре	Matrix	Method	Prep Batch
570-77576-1	Mokulele2021113021	Total/NA	Water	8015B	198844
MB 570-198844/1-A	Method Blank	Total/NA	Water	8015B	198844
LCS 570-198844/2-A	Lab Control Sample	Total/NA	Water	8015B	198844
LCSD 570-198844/3-A	Lab Control Sample Dup	Total/NA	Water	8015B	198844
570-77576-1 MS	Mokulele2021113021	Total/NA	Water	8015B	198844
570-77576-1 MSD	Mokulele2021113021	Total/NA	Water	8015B	198844

12/7/2021

Lab Chronicle

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Job ID: 570-77576-1

Client Sample ID: Mokulele2021113021

Date Collected: 11/30/21 15:00 Date Received: 12/03/21 10:00

Lab Sample ID: 570-77576-1

Matrix: Water

-										
Pren Tyne	Batch Type	Batch Method	Run	Dil Factor	Initial Amount	Final Amount	Batch Number	Prepared or Analyzed	Analyst	Lab
Total/NA	Prep	3510C		- actor	264.7 mL	2.5 mL	198844	12/06/21 11:14	UFLU	ECL 1
Total/NA	Analysis	8015B		1			199008	12/07/21 10:42	N5Y3	ECL 1
	Instrumer	nt ID: GC47								

Laboratory References:

ECL 1 = Eurofins Calscience LLC Lincoln, 7440 Lincoln Way, Garden Grove, CA 92841, TEL (714)895-5494

Accreditation/Certification Summary

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Job ID: 570-77576-1

Laboratory: Eurofins Calscience LLC

The accreditations/certifications listed below are applicable to this report.

Authority	Program	Identification Number	Expiration Date
California	State	2944	09-30-22
Oregon	NELAP	CA300001	01-30-22

Eurofins Calscience LLC

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

		. (i)		
Method	Method Description	Protocol	Laboratory	
8015B	Diesel Range Organics (DRO) (GC)	SW846	ECL 1	
3510C	Liquid-Liquid Extraction (Separatory Funnel)	SW846	ECL 1	

Protocol References:

SW846 = "Test Methods For Evaluating Solid Waste, Physical/Chemical Methods", Third Edition, November 1986 And Its Updates.

Laboratory References:

ECL 1 = Eurofins Calscience LLC Lincoln, 7440 Lincoln Way, Garden Grove, CA 92841, TEL (714)895-5494

Eurofins Calscience LLC

Sample Summary

Client: Eurofins Eaton Analytical Project/Site: RED-HILL INCIDENT, HAWAII-DOH

Lab Sample ID	Client Sample ID	Matrix	Collected	Received
570-77576-1	Mokulele2021113021	Water	11/30/21 15:00	12/03/21 10:00

		11115	Eaton Analytical						10		ЛГ		501	Nυ										
750 Royal Oaks Drive, Suite 100				_EUROFINS EATON ANALYTICAL USE ONLY LOGIN COMMENTS:									SAMPLES CHECKED AGAINST COC BY											
Phone 626 386 1100 Fax. 626 386 1101			SAMPLE TEMP RECEIVED AT:					°C (Compliance 4±2°C)				SAMPLES REC'D DAY OF COLLECTION? (check for y							eck for yes)					
800 5	566 LAI	BS (800 56)	5227)	Monrovia CONDIT METHO	ION OF B DD OF SI	BLUE ICE: HIPMENT:	Frozen _ Pick-Up	Pa / Walk-In	_°C (artiaily / FedE	Comple Frozen Ex / UF	ance 4: 	±2°C Thay L/A) ved rea Fas	W st / Top L	et ice .ine / C)ther _	No Ice							
0 BE C	OMPLET	ED BY SAMPL	ER:												(chea	ck for y	es)					(check	or yes)	
COMPANY/AGENCY NAME State of Hawaii DOH			PROJECT CODE. HAWAII-DOH					COMPLIANCE SAMPLES - Requires state EDD Type of samples (circle one): POLITERE SECTION						CONFI	NON-COMPLIANCE SAMPLES x REGULATION INVOLVED Response Sampling						se Sampling			
EA CLIENT CODE Job#			SAMPLE GR						SEE ATTACHED BOTTLE ORDER FOR ANALYSES										OR					
Stendan	TAT		1. 1.227	and the second	STD_1	wk 3 day	X_ 2day_	1 day	P	T <u>s</u>			SREQ	UIRED (e			Dotties	sent to	- each	lest				-
SAMPLE DATE	SAMPLE TIME	SAMPLE ID		CLIENT LA	NB ID	MATRIX	Field pH	Source Temp (Ceisuis)	IPH 8015 Deisel : Motor oli	(PH 8015 Daleal I dotor oil chlodradad)	Transmission											SAM	PLER CON	VIMI
1-30-2	1500	Mokulele2021113021				Water				1			1											
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MAT	RIX T	YPES: RSV RGV	V = Raw Surface Wa V = Raw Ground Wa	ater CFW = Chle ater FW = Other	or(am)ına r Finıshed	I Ited Finishe Water	ed Water		II SEA WW	W = Se = Wasi	a Water te Water			BW = SW =	= Bottled	Water Water		SO SL	= Soil = Sludg	je	0=0	1 Other - Ple	ase Identify	1
SAMPLE	SKGNATURE PRINT NAME AMPLED BY Melvin Tokuda									COMPANY/TITLE Hawaii Department of Health				- 1	DATE 11/30/21			1500	1					
				Melvin Tokuda					Hawaii Departm					ment o	ment of Health				12/02/21		0900			
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After printing this label

Use the 'Print' button on this page to print your label to your laser or Inkjet printer
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3 Place label in shipping pouch and affix it to your shipment so that the barcode portion of the label can be read and scanned.

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Login Sample Receipt Checklist

Client: Eurofins Eaton Analytical

Login Number: 77576 List Number: 1 Creator: Vitente, Precy

Question	Answer	Comment
Radioactivity wasn't checked or is = background as measured by a survey meter.</td <td>N/A</td> <td></td>	N/A	
The cooler's custody seal, if present, is intact.	True	
Sample custody seals, if present, are intact.	True	
The cooler or samples do not appear to have been compromised or tampered with.	True	
Samples were received on ice.	True	
Cooler Temperature is acceptable.	True	
Cooler Temperature is recorded.	True	
COC is present.	True	
COC is filled out in ink and legible.	True	
COC is filled out with all pertinent information.	True	
Is the Field Sampler's name present on COC?	True	
There are no discrepancies between the containers received and the COC.	True	
Samples are received within Holding Time (excluding tests with immediate HTs)	True	
Sample containers have legible labels.	True	
Containers are not broken or leaking.	True	
Sample collection date/times are provided.	True	
Appropriate sample containers are used.	True	
Sample bottles are completely filled.	True	
Sample Preservation Verified.	True	
There is sufficient vol. for all requested analyses, incl. any requested MS/MSDs	True	
Containers requiring zero headspace have no headspace or bubble is <6mm (1/4").	True	
Multiphasic samples are not present.	True	
Samples do not require splitting or compositing.	True	
Residual Chlorine Checked.	N/A	

Job Number: 570-77576-1

List Source: Eurofins Calscience LLC