

APPENDIX 1

DEVELOPMENT OF TIER 1 LOOKUP TABLES

[Refer to Appendix 9 for summary of most recent updates]

APPENDIX 1

DEVELOPMENT OF TIER 1 LOOKUP TABLES

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1 Development of Tier 1 Lookup Tables

1.1 Introduction

This appendix describes the compilation and development of action levels for contaminants in indoor air, soil vapor, soil, surface water and groundwater that was used to generate the final, Tier 1 Environmental Action Levels (Tier 1 EALs) presented in Volume 1. The action levels in general reflect guidance published by other sources that was directly referenced or modified for use in Hawai'i. Reference documents include publications of the U.S. Environmental Protection Agency (USEPA) and a number of individual states, as well as guidance from Canada and Europe.

Action levels for the following environmental concerns are presented (refer also to Figure 1):

Indoor Air and Soil Vapor:

- Protection of human health
 - Intrusion of subsurface vapors to building interiors.

Soil:

- Protection of human health
 - Direct/indirect exposure with impacted soil (ingestion, dermal absorption, inhalation of vapors and dust in outdoor air);
 - Intrusion of subsurface vapors to building interiors;
- Protection of groundwater quality (leaching of chemicals from soil);
- Protection against gross contamination concerns (free product, odors, etc.) and general resource degradation.

Groundwater:

- Protection of human health
 - Current or potential drinking water resource;
 - Intrusion of subsurface vapors to building interiors;
- Protection of aquatic habitats (discharges to surface water);
- Protection against gross contamination concerns (free product, odors, etc.) and general resource degradation.

For use in this document, the term "soil" refers to any unconsolidated material found in the subsurface, including actual soil, saprolite, sediment, fill material, etc.

Action levels are organized with respect to groundwater utility and threat to surface water bodies:

| ¹GROUNDWATER UTILITY | ²LOCATION OF NEAREST SURFACE WATER BODY | |
|---|---|--|
| | >150m From Release Site | ≤ 150m From Release site |
| Current or Potential Source of Drinking Water | Soil: Table A-1 Groundwater: Table D-1b | Soil: Table A-2 Groundwater: Table D-1a |
| NOT a Current or Potential Source of Drinking Water | Soil: Table B-1 Groundwater: Table D-1d | Soil: Table B-2 Groundwater: Table D-1c |

1. Based on location of site with respect to UIC line and Aquifer Identification and Classification technical reports (see Appendix 7).

2. Location of downgradient edge of release site from nearest surface water body. Use of groundwater action levels for sites <150m from a surface water body may be necessary if plume is suspected to have moved into this area.

Tables A and B summarize individual action levels compiled for soil overlying groundwater for the environmental concerns noted above. Table C summarizes soil, groundwater and soil vapor action levels compiled specifically for vapor intrusion and indoor-air impact concerns. Action levels for groundwater and surface water are summarized in the Table D series. Tables E, F, G and I summarize action levels for leaching, gross contamination and direct exposure. Table J summarizes potential chronic health effects posed by the chemicals listed. Table K summarizes background metal concentrations for soil. Table H summarizes physiochemical parameter values and toxicity factors used in models.

A common thread between contaminated soil and groundwater is the potential for the intrusion of volatile contaminants into existing or overlying homes and buildings. Chapter 2 provides a brief overview of vapor intrusion hazards and the models used to develop associated action levels. Chapter 3 discusses vapor intrusion action levels for indoor air and shallow (e.g., subslab) soil vapor. A discussion of action levels compiled for soil is then provided in Chapter 3. A detailed discussion of action levels compiled for surface water and groundwater is provided in Chapter 2.

Specific action levels developed for Total Petroleum Hydrocarbon (TPH) are discussed in Chapter 5. This includes an overview of the chemistry and toxicity of the non-specific, aliphatic and aromatic hydrocarbon compounds that make up the overwhelming majority mass of petroleum fuels and vapors associated with these fuels.

As discussed in Volume 1, analysis and evaluation of TPH in conjunction with targeted, individual petroleum compounds such as benzene is required at petroleum-release sites. Contrary to past beliefs, the combined TPH compounds will drive risk posed by petroleum

contamination at many sites, rather than individual chemicals like benzene or naphthalene. Risk is based on a combination of toxicity and mass. While benzene and naphthalene may be more toxic on a relative scale, the overwhelming mass of otherwise less toxic, non-specific, aliphatic and aromatic compounds can ultimately pose a greater risk to human health and the environment.

Other issues pertinent to the lookup tables are discussed in Chapter 7. This includes background concentrations of trace metals in soils, laboratory reporting limits, wet-weight versus dry-weight reporting of soil data, evaluation of salt-impacted soils and the consideration of degradation daughter products for some chemicals.

1.2 Example Selection of Tier 1 EALs for Tetrachloroethylene

Figure 2 illustrates the selection of final Tier 1 soil and groundwater EALs for the chemical tetrachloroethylene (PCE). The example assumes impacts to exposed or potentially exposed soils under an unrestricted (e.g., residential) land-use scenario. Groundwater immediately underlying the site is assumed to be a potential source of drinking water. A surface water body is assumed to be located within 150m of the release site. This scenario places the site under Table A-1 of the Tier 1 lookup tables (refer to Section 1.1).

The Tier 1 EAL for PCE in shallow soil is selected as the lowest of the individual action levels for Direct Exposure (1.1 mg/kg), Vapor Intrusion (0.098 mg/kg), Gross Contamination (170 mg/kg) and Groundwater Protection (leaching concerns, 0.64 mg/kg). The final soil EAL for PCE is the lowest of the individual action levels, or 0.098 mg/kg, based on potential vapor intrusion concerns for buildings overlying contaminated soil (see also Table A-1 in this appendix and Table A in Volume 1).

The process for selection of a Tier 1 PCE EAL in groundwater is similar (refer to Figure 2). Individual action levels for Drinking Water (5.0 µg/L), Vapor Intrusion (190 µg/L), Impacts to Aquatic Habitats (53 µg/L) and Gross Contamination (170 µg/L) concerns are compared and the lowest of these is selected for inclusion in the Volume 1 summary, Tier 1 lookup tables. In this example, the groundwater action level for drinking water concerns drives potential risks and is selected as the Tier 1 EAL (5.0 µg/L).

Selection of EALs for PCE in deep soils is similar. For deep soils, however, potential impacts to terrestrial biota are not considered, the direct-exposure action level is modified to reflect a less stringent, construction/trench worker exposure scenario, and the ceiling level for gross contamination concerns is generally somewhat less stringent. Soil action levels for leaching and groundwater protection concerns remain the same.

The process described above was carried out for each of the 100+ chemicals included in the Tier 1 lookup tables under each combination of groundwater beneficial use, soil depth and land use. The results are summarized in Tables A and B (soil) and Table D (groundwater) of this appendix. As can be seen from a review of these tables, the selection of final, Tier 1 EALs for highly mobile or highly toxic chemicals is typically driven by groundwater protection or vapor intrusion concerns (e.g., see selection process for benzene or vinyl chloride EALs in Table A-1). Final EALs for chemicals that are relatively immobile in soils but highly toxic are typically driven by direct-exposure concerns (e.g., see selection process for polychlorinated biphenyls [PCBs] in Table A-1). In contrast, selection of EALs for heavy metals that are relatively non-toxic to humans is typically driven by ecological concerns or ceiling levels for general resource degradation (e.g., see selection process for copper EAL in Table A-1). For chemicals that have particularly strong odors, selection of EALs may be driven in part by gross contamination concerns ("ceiling levels", e.g., see TPH EALs in Table B-2). The consideration of gross contamination becomes especially important in the selection of alternative action levels for relatively immobile chemicals in isolated, deep soils (e.g., refer to Tables F-3).

1.3 Toxicity Factors and Physiochemical Constants

Toxicity factors and physiochemical constants used in the soil, tapwater and vapor intrusion models for risk to human health are taken directly from the USEPA Regional Screening Levels (RSLs) guidance except as noted in footnotes to Table H (USEPA 2017a). References for constants not included in the RSL guidance include: National Library of Medicine Toxnet database (NLM 2017a), NLM ChemID Plus (NLM 2017b), ATSDR Toxprofiles (ATSDR 2006) and USDOE RAIS database (USDOE 2006), in that order or preference, unless otherwise noted. Refer to footnotes in Table H for additional details on specific chemicals.

Inhalation Reference Concentrations are not available for a number of volatile chemicals included in the USEPA RSLs. Affected chemicals are indicated in the footnotes to Table H. The RSL guidance instead calls for a case-by-case review of these chemicals by a toxicologists. This is highly unlikely to occur given the widespread use of the RSLs by workers not trained in risk assessment, effectively eliminating consideration of the inhalation exposure pathway in most cases where the affected screening levels are applied. The original USEPA Region IX Preliminary Remediation Goals (PRGs), the precursors of the current RSLs, used route-to-route extrapolation to develop an interim, inhalation Reference Concentration from an oral Reference Dose for chemical where studies specific to this pathway were not available or inadequate to develop toxicity factors (USEPA 2004a; see also USEPA 1993, 2011a):

$$\text{Reference Concentration } \left(\frac{\text{mg}}{\text{m}^3} \right) = \text{Reference Dose} \times 70 \text{ kg} \times \left(\frac{1}{20 \frac{\text{m}^3}{\text{day}}} \right).$$

Although confidence in the resulting Reference Concentration is low, the need to include the chemicals in the EAL summary tables and the subsequent need to consider the inhalation exposure pathway in generic action levels outweighs limitations in the use of route-to-route extrapolation methods. Chemicals where this approach was used are noted in the footnotes of Table H. Alternative inhalation toxicity factors can be considered on a site-specific basis.

Note that estimation of Unit Inhalation Risk factors from oral cancer slope factors for volatile chemicals where the latter had been published was discontinued in the 2017 update to this guidance. This was based on discussions with toxicologists and the lack of evidence that the subject chemicals were carcinogenic via the inhalation exposure route. Inhalation toxicity factors based on noncancer risk were available or estimated for the subject chemicals (see Table H).

Several contaminants included in the HDOH EALs are not listed in the USEPA RSLs (e.g., TPH). In these cases alternative sources were referred to for compilation of toxicity factors and physiochemical constants. Chemicals that fall in this category and references used to compile toxicity factors and constants are discussed in the footnotes of Table H.

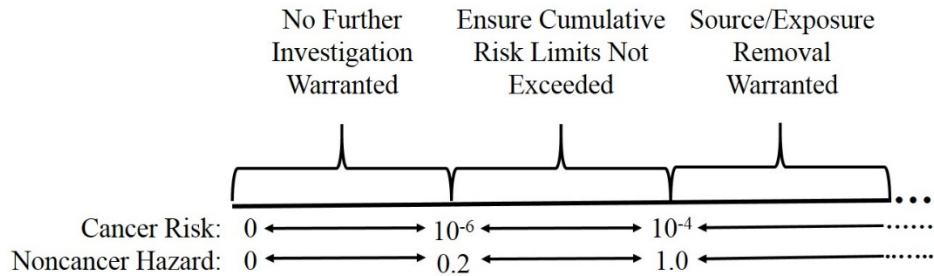
Chemicals are subdivided in terms of volatility into the following categories for use in this guidance (see Table H):

- Volatile: Henry's Constant >0.00001 (atm-m³/mole) OR Vapor Pressure (VP) >1 mm Hg AND molecular weight <200;
- Semi-volatile: Henry's Constant >0.00001 (atm-m³/mole) OR VP >1 mm Hg and molecular weight ≥200;
- Nonvolatile: Henry's Constant ≤0.00001 (atm-m³/mole) AND VP ≤1 mm Hg.

Soil and groundwater screening levels for vapor intrusion are only developed for “volatile” chemicals as defined above (Tables E-1a and E-1b), although indoor air and subslab soil vapor screening levels are also included for semi-volatile chemicals (Tables E-2 and E-3). Tapwater and soil direct exposure screening levels are calculated using the “volatile” chemical model incorporated into the USEPA RSLs for both “volatile” and “semi-volatile” chemicals (Tables F-3b and K-1 through K-3). Soil and water screening levels for nonvolatile chemicals are generated using alternative models, as discussed below.

1.4 Cumulative Risk vs Target Action Level

Calculation of a risk-based, action level for a chemical in soil, water, air or other media requires incorporation of a target cancer risk and/or noncancer Hazard Quotient into the exposure models (see Appendix 2). Three ranges of risk are used to determine the need for additional actions at a site under investigation, as summarized in the following figure:



“Cancer risk” represents a theoretical increase in cancer occurrences based on comparison of exposure to a toxicity factor intended to reflect a one-in-a-million risk (10^{-6}). A cancer risk of less than one-in-ten thousand (10^{-4}) is considered to be insignificant and not detectable in a population. A Hazard Quotient represents the ratio of the potential exposure to the substance and the level at which no adverse, systemic or “noncancer” health effects are expected. A Hazard Quotient less than or equal to “1” indicates that adverse noncancer effects are not likely to occur, and exposure can thus be considered to have negligible hazard.

The USEPA recommends that removal of the source of contamination or exposure to the contamination be carried out if a cumulative, excess cancer risk of 10^{-4} (one-in-ten-thousand) or a noncancer Hazard Index of 1.0, calculated as the sum of Hazard Quotients for individual chemicals, is exceeded (USEPA 1989a,b, 1991, 1994, 2017b). Use of these target risk levels to develop action levels is in general not appropriate, however, since the cumulative health risk posed by the presence of multiple contaminants in soil with similar health effects could be exceeded, even though the risk posed by individual chemicals is deemed acceptable.

More conservative risk targets are instead used to develop action levels for individual chemicals. This allows the action levels to be used without the need to evaluate cumulative risk in the majority of cases. For example, an excess cancer risk of 10^{-6} (one-in-a-million) is used as the default, departure point for calculation of the majority of cancer-based action levels presented in this guidance. This allows up to 100 chemicals with similar, carcinogenic effects to be present in the soil at the corresponding action levels before a cumulative, target cancer risk of 10^{-4} is exceeded. This is highly, if not excessively,

conservative, since it is rare to identify more than five potential carcinogens associated with a single source of contamination at typical release sites.

A default, noncancer target Hazard Quotient of 0.2 is utilized to develop soil, air and soil vapor action levels (see above figure). This allows up five chemicals with similar, systemic health effects to be present in the soil at the corresponding action levels before exceedance of a cumulative, Hazard Index of 1.0 is possible. A similar target Hazard Quotient was used by the Massachusetts Department of Environmental Protection (MADEP) (MADEP 1994) and Ontario Ministry of Environment and Energy (MOEE) (MOEE 1996) to develop action levels for direct-exposure concerns. Additional evaluation may be required for sites where more than five chemicals with similar noncarcinogenic health effects are present. For reference, a compilation of chronic health effects for the chemicals listed in the EALs is provided in Table J of this appendix. Note that a noncancer Hazard Quotient of 3.0 is sometimes used to develop screening levels for emergency removal actions (e.g., USEPA 2017b). This is intended to only address short-term exposure risks, however, and requires followup consideration of cumulative risk as part of a longer-term remedy.

A default Hazard Quotient of 1.0 is utilized for calculation of toxicity-based, drinking water action levels unless otherwise noted in the lookup tables (refer to Section 4.2). Consideration of potential cumulative risk is thus not directly incorporated into the resulting action levels. This is consistent with development of promulgated drinking water standards, however, and takes into consideration the likely assessment of cumulative risk in the event of actual impacts to an actively used, drinking water supply.

Less conservative, target risks that exceed the default 10^{-6} excess cancer risk or 0.2 Hazard Quotient but fall within the range for consideration of potential cumulative risk noted in the above figure are applied to some chemicals, particularly for develop of direct-exposure action levels for soil. Refer to Section 4.2.2 for discussion of specific chemicals. This was implemented to expedite the identification of impacts that could require remedial actions by upfront consideration circumstances where a single chemical typically drives cancer risk (e.g., arsenic), where there is greater confidence in toxicity factors based on noncancer studies (e.g., organochlorine pesticides), and/or widespread, natural or anthropogenic, background levels of a chemical in excess a target risk of 10^{-6} (e.g., PAHs). Additional assessment of cumulative risk could be required in rare cases where the action levels are applied to sites where complex mixtures of contaminants could cause cumulative risk targets to be exceeded.

Exposure assumptions used to develop direct-exposure and indoor-air action levels primarily reflect parameter values presented in USEPA risk assessment guidance for Superfund sites (refer to USEPA 2017a). Alternative, and in some cases less conservative, exposure assumptions are presented in the USEPA technical document *Exposure Factors Handbook* (USEPA 2011c), among other examples. For example, recommended inhalation

rates for residents are 11.3 m³/day for women and 15.2 m³/day for men, in comparison to the value of 20 m³/day used to develop the direct-exposure action levels presented in this appendix (Section 4). The average time (50th percentile) spent at one residence is also stated to be 9 years, in contrast to the more conservative exposure duration used of 30 years (revised to 26 years in the 2015 USEPA RSL guidance; USEPA 2017a). The average occupational tenure is similarly stated to be 6.6 years, in contrast to the occupational exposure duration used of 25 years. While the more conservative exposure assumptions are still generally recommended for use in site-specific risk assessments, the variance in the assumptions helps to demonstrate the overall conservative nature of the models referenced in this document.

As discussed in Volume 1, the action levels presented in this guidance are not intended to represent mandatory, cleanup levels. Exceedance of an action level does not necessarily indicate that an adverse health risk is present, but rather that additional action is warranted. Use of the action levels for final decision making will in many, if not most, instances be both time and cost beneficial, however. Consideration of alternative exposure assumptions, target risks and related factors in a more "site-specific" risk assessment could result in an increase of direct-exposure action levels while still allowing for cumulative risk targets to be met..

A Hazard Quotient of 1.0 was used for calculation of risk-based action levels for Total Petroleum Hydrocarbons (TPH, see Section 6 and Appendix 6). Nonspecific compounds collectively measured as TPH dominate soil, water and air impacted by releases of common, petroleum fuels and overwhelmingly drive noncancer health risks. A less stringent target Hazard Quotient is therefore considered justified. The need to calculate cumulative risks in more detail should be evaluated on a site-by-site basis.

The direct-exposure action levels do not address potential synergistic effects (e.g., 1+1=3). Synergistic effects are primarily of concern for exposure to multiple chemicals at concentrations significantly higher than those expressed in the direct-exposure EALs. Conservative target risk goals and exposure assumptions used to develop the action levels further reduce this concern. Methods to quantitatively assess synergistic effects have not been fully developed.

2 Background and Use of Vapor Intrusion Models

2.1 Background

This section describes the general approach used to develop vapor intrusion action levels for indoor air, subslab soil vapor, soil and groundwater, presented in Sections 3, 4 and 5 of this document. Indoor air action levels are based on a model used by USEPA to generate Regional Screening Levels (RSLs) for ambient air (USEPA 2017a). Subslab soil vapor action levels were developed based on estimations of indoor air exchange rates (IAERs) and building slab vapor entry rates for tropical settings published by Brewer et al. (2014). A copy of the paper is included in Appendix 3. Corresponding vapor intrusion action levels for soil and groundwater were generated using a computer spreadsheet model published by the U.S Environmental Protection Agency (USEPA 2004b and updates).

The USEPA vapor intrusion model incorporates a model presented in the document *Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings* (Johnson and Ettinger, 1991). These models were developed to study radon intrusion into homes but were subsequently modified for use with any volatile chemical. Development of the models included calibration with field data. They are thus based on empirical data and not purely theoretical. Excerpts of key text from the USEPA guidance document is provided in Appendix 3, as is a sensitivity evaluation of the Johnson and Ettinger model.

Refer to Section 4.5 in Volume 1 of this guidance for a basic overview of vapor intrusion. The model considers both diffusive and convective flow of subsurface vapors into buildings. Diffusive flow occurs as soil vapor migrates from areas of higher concentration to areas of lower concentration. Wind effects and indoor heating can cause a decrease in air pressure inside a building and lead to upward, advective flow of subslab vapors through cracks and gaps in the floor. Potential adverse impacts to indoor air are driven by the concentration of volatile organic chemicals (VOCs) in the intruding vapors, the vapor entry rate into the structure and the exchange rate of the building with fresh, outdoor air.

2.2 Vapor Intrusion Model Parameters

Example printouts of the model as used to calculate action levels for this document are included in Appendix 4. Input parameter values used in the models are noted in the

examples (front pages). Default parameters values presented in the spreadsheet technical document were generally selected for use.

2.2.1 Target Risks

Human exposure assumptions were set equal to assumptions used in the USEPA RSLs. Unless otherwise noted in Table E-3. Action levels were calculated using a target risk of 10^{-6} for chemicals with carcinogenic health effects and a target Hazard Quotient of 0.2 for chemicals with noncarcinogenic health effects (1.0 for TPH, see Section 6). For consistency purposes, default physio-chemical constants included in the original, USEPA vapor intrusion models were replaced with constants used in the USEPA RSL models if different (refer to Table H and Appendix 4).

2.2.2 Assumed Building Parameters

Default building characteristics presented in the USEPA spreadsheet guidance were used in the models (see Appendices 3 and 4). The thickness of the building floor slab was assumed to be 15 cm. For both unrestricted (“residential”) land use and commercial/industrial exposure scenarios, the models assume a small, one-thousand square foot (9.61m x 9.61m), one-story building (ceiling height of 2.44 meters) situated on mono-slab concrete base (total indoor air volume approximately 225m³). This may be overly conservative for commercial/industrial sites with existing, larger buildings but is considered to be protective of future redevelopment of such sites. The guidance default value of 1mm was used for the assumed perimeter crack width.

Default indoor-air exchange rates of one-time per hour for residences and two-times per hour for commercial/industrial buildings were used (see Brewer et al. 2014; directly input into the model). Based on the input building design and volume, this generates an indoor air exchange rate of 225 m³/hour or 3,750 L/min for a residential home model and 7,500 L/min for a commercial building of the same size (see Appendix 4). The IAERs are assumed to be conservative for the tropical climate of Hawai‘i, where buildings are not heated and windows at homes are often left open year round. Air exchange rates could be lower for homes and buildings that rely on heating, air conditioning and ventilation (HVAC) systems for ventilation. This would result in lower vapor entry rates, however, especially in cases where air conditioning is being used due to over pressurization of lower floors (see Brewer et al. 2014). Assumptions regarding persistent vapor entry due to wind effects and open windows are therefore considered to be conservative.

2.2.3 Assumed Vapor Entry Rate

An annual average, subslab vapor entry rate (Q_{soil}) of 2 L/min (per 100 m² floor area) was incorporated into the vapor intrusion models, based on estimations tropical climates

presented in Brewer et al. (2014). This was generated in the models by inputting “Sand” as the soil type for Layer A soil type and a default value of 20 g/cm-s² for the “Soil-Building Pressure Differential” parameter (see Appendix 4). The latter reflects the assumed, annual-average difference between indoor and outdoor air pressures and an under pressurization of the structure. This generates a default vapor flux rate through the building slab of approximately 38 cm³/second or two liters per minute. **A vapor entry rate of 2 L/min per 100m² floor space should be maintained for site-specific models where a larger building size is used unless otherwise approved by HDOH.**

The vapor entry rate and the vapor intrusion models in general are highly sensitive to the permeability of vadose-zone soil immediately beneath the floor of the building. The input soil type for Layer A is one of the most critical model parameters. This is because the permeability of this zone controls the volume of air (and soil vapor) that can be convectively pulled up through the floor and into the building. The soil beneath most buildings is engineered, silty or sandy fill with moderate to high vapor permeability. This is incorporated into the models by including a 15 cm thick layer of highly permeable sand immediately beneath the building slab (Layer A). Note that it is critical to include this subslab layer of vapor-permeable fill in all site-specific, vapor intrusion models. Use of the native soil type at the subject site (e.g., more clay rich and less permeable) is not appropriate, since this may not be the soil used for structural fill immediately beneath the slab. Modifications to this assumption must be approved by HDOH on a site-by-site basis.

The default, annual average vapor entry rates incorporated into the models are intended to reflect an overall lower vapor intrusion risk for buildings in tropical climates in comparison to colder climates, where buildings are heated for much of the year and thus more susceptible to vapor intrusion (see Brewer et al. 2014). Higher, assumed indoor-outdoor pressure differentials and correspondingly higher average vapor entry rates are typically recommended for buildings in colder climates (Brewer et al. 2014; see also USEPA 2004b, 2015a). This would be reflected by a corresponding reduction in soil vapor, soil and groundwater action levels for vapor intrusion. Example modification of HDOH action levels for use in other climate zone is included in Section 13 of the HEER Office *Technical Guidance Manual* (HDOH 2016 and updates).

2.2.4 Assumed Indoor Air:Subslab Soil Vapor Attenuation Factors

A key part of the action levels is the assumed attenuation of subsurface vapors as they intrude a building and mix with indoor air. Shallow soil vapor action levels for vapor intrusion are calculated by dividing the indoor air goal by an Indoor Air:Subslab Soil Vapor attenuation factor that reflects dilution of subsurface vapors upon mixing with indoor air:

$$\text{Soil Vapor Action Level} = \frac{\text{Indoor Air Action Level}}{\text{Subslab Attenuation Factor}}$$

The subslab soil attenuation factor (SSAF) reflects the ratio of the estimated, mean annual vapor entry rate and the mean annual IAER for tropical climates (see Brewer et al. 2014).

$$SSAF = \frac{\text{Vapor Entry Rate (L/min)}}{\text{Indoor Air Exchange Rate (L/min)}}$$

This generates a default, SSAF of approximately 0.0005 (1/2,000) for residential homes and 0.00025 (1/4,000) for commercial and industrial buildings. These attenuation factors are used in Section 3 to calculate subslab vapor intrusion action levels for subslab soil vapor. The default building pressure differential and IAERs are incorporated into the soil and groundwater vapor intrusion models to generate correlative action levels for those media.

Note that the vapor intrusion models used to develop soil and groundwater action levels are not sensitive to the “Soil-Building Pressure Differential” parameter. A reduction or increase in the input pressure differential and the calculated SSAF will not result in a significant change in the action levels. This is because the mass of a VOC entering an overlying structure during a given time period is governed by rate of upward diffusion from the source into the advective zone under the slab, not by the vapor entry rate, and remains unchanged. The mass of VOCs that diffuses into the advective zone and is ultimately drawn into the overlying building over a given time period is unaffected by the vapor entry rate. Reducing the flow rate of vapors under the slab and into the structure by half, for example from 4 L/min to 2 L/min, will result in a doubling of VOC concentrations in vapors under the slab. The volume of vapors entering the building is concurrently reduced by half during the same time period, however, effectively cancelling out the doubling of VOC concentrations in the vapor. This can be observed in the vapor intrusion models by reducing the “Soil-Building Pressure Differential” parameter from 40 to 20 g/cm-s². This results in a reduction of the calculated vapor entry rate from approximately 4 L/min to 2 L/min without causing a noticeable change in calculated screening level for a given VOC.

3 Indoor Air and Soil Vapor Action levels

3.1 Introduction

This section describes the development of risk-based action levels for indoor air and subsurface soil vapors. Indoor air action levels were developed based on models and exposure assumptions incorporated into the USEPA Regional Screening Levels (RSLs) for ambient air (USEPA 2017a). Corresponding action levels for VOCs in subsurface soil vapors were estimated based on attenuation factors published by Brewer et al. (2014). These action levels are intended to correlate with and be used in conjunction with vapor intrusion action levels for subsurface soil and groundwater presented in Chapters 4 and 5 respectively.

3.2 Indoor Air Action levels

Indoor air action levels were calculated using the following equation incorporated in the model (see USEPA RSL equations in Appendix 2):

Carcinogens:

$$C_{ia} = \left(\frac{TR \times AT_c \times 365 \text{ days/yr}}{URF \times EF \times ED \times ET} \right)$$

Noncarcinogens:

$$C_{ia} = \left(\frac{THQ \times AT_{nc} \times 365 \text{ days/yr}}{\left(\frac{1}{RfC} \right) \times EF \times ED \times ET} \right)$$

where:

C_{ia} = Target indoor air concentration;

TR = Target risk (carcinogens);

THQ = Target hazard quotient (noncarcinogens);

AT_c = Averaging time for carcinogens;

AT_{nc} = Averaging time for noncarcinogens;

URF = Unit risk factor for carcinogens (carcinogens);

RfC = Reference concentration (noncarcinogens);

EF = Exposure frequency;

ED = Exposure duration;

ET = Exposure time.

Exposure time is expressed in terms of a 24 hour day. An ET of 24hr/24hrs is assumed for residents. An ET of 8hrs/24hrs is assumed for commercial/industrial workers (see Appendix 2). A summary of the indoor-air action levels calculated is provided in Table C-3. Cancer-based action levels reflect a default, target excess cancer risk of 10^{-6} unless otherwise noted (refer to Section 2.2.1 and footnotes to Table C-3).. Exceptions, including ethylbenzene and naphthalene. Noncancer-based action levels reflect a target Hazard Quotient of 0.2 unless otherwise noted. Exceptions include TPHg and TPHmd, in which case a Hazard Quotient of 1.0 was used (refer also to Section 6). Inhalation toxicity factors for volatile chemicals are summarized in Table H.

3.3 Soil Vapor Action levels

Section 2.2.4 describes the development of default, subslab attenuation factors (SSAFs) for subsurface vapors that intrude homes and impact indoor air. A default SSAF of 0.0005 was estimated for residential homes. A default SSAF of 0.00025 was estimated for commercial/industrial structures. The latter assumes better and more consistent ventilation of businesses during normal operating hours.

Soil vapor action levels (C_{sv}) were subsequently calculated as:

$$C_{sv} = \frac{\text{Indoor Air Action Level } (\mu\text{g}/\text{m}^3)}{\text{SSAF}}$$

A summary of soil vapor action levels for volatile chemicals is provided in Tables C-2.

Note that soil vapor action levels do not take into account the actual mass of the chemical present and could be overly conservative for the evaluation of long-term impacts to indoor air. At sites where a limited amount of impacted soil or groundwater is present, the concentration of the chemical in soil vapor can be expected to decrease over time as the supply of the chemical is depleted. This would lead to steadily decreasing impacts to indoor air. Thus, while impacts to indoor air may initially exceed target goals, average, long-term impacts could conceivably fall below these goals.

This issue should be evaluated on a site-by-site basis as needed. As a conservative measure, and for the purpose of this screening levels document, it is recommended that indoor-air goals be used as "not-to-exceed" criteria and adjustment of models and soil vapor to address potential mass-balance not be carried out in the absence of strong site data. This issue is currently under reviewed. Additional information will be incorporated into the EAL document as available.

4 Soil Action levels

4.1 Introduction – Selection of Tier 1 Soil EALs

The final Tier 1 EAL for soil presented in Volume 1 of this guidance represents the lowest of a chemicals action level for direct-exposure and vapor intrusion, leaching and the chemicals maximum ceiling level (nuisance concerns etc.). The final, Tier 1 EALs presented in the Volume 1 summary tables are based on an assumption that contaminated soil is now or at some time in the future could be exposed at the ground surface *and* that no restrictions are placed on future use of the property.

Direct exposure, vapor intrusion and gross contamination action levels are compiled and presented for both unrestricted (“residential”) and commercial/industrial land use scenarios. Alternative action levels are also presented for “deep” or otherwise isolated soils that are not likely to be exposed at the ground surface in the future. Only the action levels for unrestricted (“residential”) exposure concerns were carried forward for consideration in compilation of final, Tier 1 EALs, however, (refer to Table A and B series). Alternative action levels can be incorporated into a site-specific *Environmental Hazard Evaluation* as needed (refer to Chapter 4 in Volume 1).

Consideration of published, soil action levels for terrestrial ecotoxicity in earlier editions of the EHE guidance was discontinued in 2011 due to concerns over the reliability and applicability of the screening levels to Hawai'i. This primarily applied to trace metals. A background metals study carried out in 2010 and 2011 revealed that the natural, background concentrations of several trace metals were above the published screening levels for potential ecotoxicity. This is in part due to a reliance on laboratory testing of soils with freshly applied and highly bioavailable solutions of trace metals to develop ecotoxicity action levels. The naturally occurring trace metals in the volcanic soils of Hawaii are, in contrast, generally tightly bound to iron hydroxides and other metal complexes and not significantly bioavailable to flora or fauna. As discussed in Section 4.6, a site-specific ecological evaluation is now recommended where sensitive, terrestrial habitats could be threatened by anthropogenic contaminants in soil.

4.2 Soil Action levels for Direct-Exposure Concerns

4.2.1 Direct Exposure Models and Assumptions

Direct exposure soil action (“screening”) levels for unrestricted land use (e.g., “residential”), commercial/industrial land use and construction/trench worker exposure are

presented in Tables I-1 through I-3, respectively. A summary of the models and assumptions used to develop the direct-exposure action levels for soil is provided in Appendix 2. Action levels for the Unrestricted Land Use category are based on a standard, residential exposure scenario (refer to Appendix 2). The action levels are considered to be adequate for residential housing, schools, day care and medical facilities, parks and similar sites with sensitive land use. The action levels are intended to be protective of residents and workers who may be exposed to chemicals in exposed soils on regular basis via incidental ingestion, dermal absorption, and inhalation of vapors and particulate matter.

The direct-exposure action levels closely follow the approach used to develop the USEPA RSLs, with the exceptions noted below (RSLs; USEPA 2017a). Direct-exposure soil action levels generated for the Unrestricted Land Use category are consistently more stringent (lower) than action levels developed for the commercial/industrial and construction/trench worker exposure scenarios. This is due to the longer, assumed exposure duration (years) and frequency (days per year) as well as the presence of young children in comparison to the latter two scenarios (see Appendix 2). Action levels for construction and trench workers take precedence over action levels based on residential and/or commercial/industrial exposure scenarios if lower. This is the case for several chemicals that pose an increased risk via inhalation of dust particles, including a number of trace metals as well as some volatile compounds (see Table I-2).

As a default, direct-exposure models and associated physiochemical constants, toxicity factors, exposure assumptions and target risks used to develop the USEPA Regional Screening Levels (USEPA 2017a) were referred to for development of the direct exposure action levels presented in this document (refer to Section 1.2). Use of the USEPA RSLs by state agencies is not mandatory, but the guidance serves as a very useful starting point for state-specific guidance. Staff in HDOH are in routine contact with the developers of the RSLs and exchange information and suggestions for specific chemicals to help ensure that the underlying fundamentals of the respective guidance documents are consistent.

Exposure assumptions incorporated into the USEPA RSLs were adhered to in most cases. Exceptions include an increase in the assumed, adult body weight from 70 kg to 80kg in recent updates of the RSLs. The original, default body weight of 70 kg was retained for use in the EALs, due to a lower, average body weight for women in Hawaii of 66 kg (City-Data.com 2017). This does not significantly affect the resulting action levels.

Preliminary Remediation Goals (PRGs) previously published USEPA Region IX included a hybrid, direct-exposure action level for total chromium in soil based on an assumed 1:6 ratio of Cr VI (highly toxic) to Cr III (minimally toxic) (USEPA 2004a). This is not included in more recently published, USEPA RSLs (USEPA 2017a) and likewise omitted from the HDOH EALs. The soil action level for total chromium is instead based on an assumed natural background concentration of 1,100 mg/kg, based primarily on data for

soils developed over basaltic bedrock (refer to Table K). If the reported concentration of total chromium in soil exceeds 1,100 mg/kg then an additional evaluation of background concentrations in the area should be carried out and/or chromium in the soil should be speciated into Cr III and Cr VI and data compared to action levels for these compounds. Note that background concentrations of total chromium in soils developed over caprock can be lower than 100 mg/kg. If a release of Cr VI is suspected at a site then chromium should be speciated and evaluated, even if total chromium concentrations do not exceed the default action level of 1,100 mg/kg.

4.2.2 Target Risks

Refer to Section 1.4 for a detailed discussion of default target risk levels used to generate soil action levels. Deviations from the default, target cancer risk of 10^{-6} and a target, noncancer Hazard Quotient of 0.2 noted in Section 1.4 for calculation of direct-exposure soil action levels are summarized in the following table:

| Chemical | HDOH-Specific Models |
|-----------------------|--|
| Aldrin | Target Excess Cancer Risk (ECR) of 10^{-4} applied to reflect higher confidence in noncancer toxicity factors (see also Dieldrin). |
| Arsenic | Bioaccessibility data required if natural background exceeded, with target noncancer. Target ECR of 5×10^{-5} used to calculate bioaccessible arsenic action levels in order to reflect higher confidence in noncancer toxicity studies and background, dietary exposure; HQ of 1 applied to reflect typical dominance as risk driver when present in soil. |
| Chlordane (Technical) | Target ECR of 10^{-5} applied to reflect higher confidence in noncancer toxicity studies and primary risk driver when present. |
| Dieldrin | Target ECR of 10^{-4} applied to reflect higher confidence in noncancer toxicity factors (see also Aldrin). |
| Dioxins (TEQ) | Refer to 2010 HDOH action levels for TEQ dioxins. Final action level based on noncancer Hazard Quotient of 1.0. |
| Chromium (hexavalent) | Target ECR of 10^{-4} applied to reflect higher confidence in noncancer toxicity factors and natural background. |
| Ethylbenzene | Target ECR of 10^{-5} applied to reflect higher confidence in noncancer toxicity factors. |

| Chemical | HDOH-Specific Models |
|--------------------------------|--|
| Heptachlor, Heptachlor Epoxide | Target ECR of 10^{-5} applied to reflect higher confidence in noncancer toxicity studies and primary risk driver when present. |
| Lead | Residential direct-exposure soil action level of 200 mg/kg based on consideration of both health risk and anthropogenic background in urban areas. |
| PAHs (carcinogenic) | Target ECR of 5×10^{-5} applied to benzo(a)pyrene to reflect higher confidence in noncancer toxicity factors and address anthropogenic background. Target ECR of 10^{-5} applied to other, carcinogenic PAHs to address widespread, anthropogenic background. |
| PCBs (total) | Target ECR of 10^{-5} applied to reflect increased confidence in noncancer toxicity studies and address anthropogenic background. |
| Thallium | Target HQ of 1.0 applied to consider natural background and assumed low bioavailability in soil. |
| TPH | Target HQ of 1.0 applied to reflect TPH-related compounds as dominant mass and risk driver for noncancer hazard in common petroleum mixtures. |

In most cases, use of an alternative, target cancer risk of 10^{-4} to 10^{-5} resulted in a cancer-based action level that was higher than the action level for noncancer hazard and the protection of young children. If so then the latter was selected as the final, direct-exposure action level (refer to Tables I-1 and I-2). Confidence in noncancer toxicity studies is also often higher than for cancer-based studies. When present, the chemicals noted above also tend to dominate or “drive” potential health risk with little additional risk posed by other chemicals present in the soil. The target, cumulative, excess cancer risk of 10^{-4} and noncancer Hazard Index of 1.0 is therefore unlikely to be exceeded. Additional evaluation of cumulative risk might be required on a site-specific basis, however, in rare cases where multiple chemicals in the above list are present in soil at concentrations that approach the Tier 1 action levels.

Due to the short, assumed exposure duration for **construction/trench workers**, direct-exposure action levels for nonvolatile chemicals are based on a target excess cancer risk of 10^{-5} (Table I-3; see also Appendix 2). An excess cancer risk of 10^{-6} was retained for carcinogenic VOCs, however, due to low confidence in the vapor emission model for this scenario (see Table I-3). A more conservative vapor emission factor is also incorporated into the direct-exposure models for construction and trench workers to reflect poor air flow in trench and other construction environments (see Appendix 2).

Low levels of **PAHs** in soil are ubiquitous in urban environments due to auto exhaust and the use of asphalt. Anthropogenic, background concentrations of PAHs in urban area soils due to auto exhaust and other sources can easily exceed risk-based screening levels based on a conservative, excess cancer risk of 10^{-6} . Massachusetts, for example, uses a background soil screening level of 2.0 mg/kg for benzo(a)pyrene (MADEP 2002a). A target excess cancer risk of 5×10^{-5} was used to develop the unrestricted/residential soil action level for benzo(a)pyrene in order to help identify site-specific releases anticipated to exceed anthropogenic background and express a higher confidence in newly developed toxicity factors for noncancer health risks posed by exposure to benzo(a)pyrene (refer to USEPA 2017a). A target risk of 5×10^{-5} likewise incorporates a reasonable safety margin for risk associated with the presence of multiple, potential carcinogens in the same soil to help ensure that a cumulative excess risk of 10^{-4} is not exceeded. This generates a soil action level of 5.7 mg/kg, which is greater than the noncancer-based action level of 3.6 mg/kg. The latter was therefore selected by HDOH as the final, direct-exposure soil action level for benzo(a)pyrene under an unrestricted, landuse exposure scenario (refer to Table I-1). A more conservative, target risk of 10^{-5} was applied to carcinogenic PAHs that lack noncancer-based toxicity factors, A target risk of 10^{-5} was utilized for all carcinogenic PAHs under commercial/industrial and construction worker exposure scenarios, since the resulting screening levels are above anticipated background (refer to Tables I-2 and I-3).

Note that concentrations of PAHs in coal tar and older formulations of asphalt can be orders of magnitude higher than direct-exposure action levels set at a target risk of 10^{-4} . Since asphalt is likewise ubiquitous in urban environments, cleanup of soil contaminated with small particles of asphalt that was used in its intended manner is generally not warranted. This exception would not apply to sites where asphalt, coal tar or similar materials were manufactured and disposed of as waste associated with those operations.

A similar approach was taken for **PCBs**. Use of PCBs in transformers, capacitors and other electrical equipment was widespread in the 1960s and 1970s. Although less widespread than PAHs, ambient levels in soil often fall within a target risk range of 10^{-5} and 10^{-6} . In order to again help focus attention on sites where significant releases of PCBs occurred, a target excess cancer risk of 10^{-5} was used to develop direct-exposure action levels for soil. A target Hazard Quotient of 0.2 for noncarcinogenic effects was retained. Note that noncarcinogenic effects drives human health concerns for PCBs in soils under a residential exposure scenario and is used to generate the Tier 1EAL (refer to Table I-1).

A target Hazard Quotient of 1.0 was used to develop risk-based screening levels for **TPH**. Nonspecific compounds collectively reported under “TPH” dominate the total mass of petroleum in soil, as well as water, soil vapor and indoor air (refer to Appendix 6). Use of a target HQ of 1.0 is therefore justified.

A target excess cancer risk of 10^{-5} was used for **Technical Chlordane**. This was done to reflect the cumulative inclusion of multiple chemicals (i.e., chlordane isomers, heptachlor, heptachlor epoxide) as a single concentration in the Technical Chlordane laboratory analysis, as well as the toxicity factors used in the models (see discussion in Volume 1). A target noncancer Hazard Quotient of 1.0 was used to reflect the common sole occurrence of Technical Chlordane in the absence of other contaminants (used as a termiticide around and beneath older buildings).

A target excess cancer risk of 10^{-5} was used for heptachlor and heptachlor epoxide. Heptachlor is typically the primary risk driver when present in soil. A target risk of 10^{-5} is considered to be adequate to ensure that a target, cumulate cancer risk of 10^{-4} posed by multiple carcinogenic contaminants in the soil is not exceeded.

A target excess cancer risk of 10^{-4} was used for **aldrin** and **dieldrin** to reflect low confidence in cancer slope factors and the potency of these chemicals (see update notes in Appendix 9). An updated review of cancer- and noncancer-based toxicity studies published by Hooker et al. (2013) were used to develop screening levels. A target noncancer Hazard Quotient of 0.5 was used to reflect the common co-occurrence of these two chemicals in the absence of other contaminants (aldrin used as a termiticide around and beneath older buildings, with dieldrin as a breakdown product).

A target excess cancer risk of 10^{-4} was used for **hexavalent chromium** in order to reflect natural background concentrations of this chemical in soil and groundwater (see groundwater technical memo in Appendix 8). Confidence in the cancer-based toxicity factors is also low.

Separate guidance has been prepared for **arsenic** (HDOH 2011b) and **dioxins** (HDOH 2010) in soil. Soil action levels presented in the respective technical memorandums are incorporated into the I-series tables of Appendix 1. Bioaccessibility tests are recommended for site-specific evaluation of arsenic-contaminated soil when the upper background concentration in soil is exceeded (e.g., 24 mg/kg). The World Health Organization Reference Dose used to develop the dioxin action levels incorporates an assumed bioavailability of 50%.

A target noncancer Hazard Quotient of 1.0 was used to generate soil action levels for **thallium** due to the potential for natural, background levels of thallium to exceed the unadjusted, direct-exposure action level (Tier 1 action level 0.78 mg/kg). Naturally occurring thallium in iron-rich, volcanic soils is expected to be tightly bound to the soil and not significantly bioavailable. This is not considered in the direct-exposure models. The potential for a release of highly bioavailable, thallium salts at a site should be evaluated

in cases where the Tier 1 action level is exceeded. Based on limited data, natural background levels of thallium in soil could approach 15 mg/kg (HDOH 2011a).

The direct exposure soil action level of 200 mg/kg for **lead** in residential (unrestricted) soil is based on consideration of both health risk and anthropogenic background in urban areas. The current, USEPA residential RSL of 400 mg/kg is intended to reflect a target blood-lead level in children of 10 µg/dl (USEPA 2017a). The HDOH action level in part reflects recommendations to reduce the target blood level to 5 µg/dl (USEPA 2011b; USCDC 2012a,b). The model used to calculate soil screening levels for lead is not linear, however (USEPA 2007). Any future, revised USEPA RSL based on the lower blood level is likely to be somewhat lower than the HDOH action level.

A reduction in the soil action level for lead below 200 mg/kg is not practical for heavily developed, urban areas, however. Background, anthropogenic levels of lead in urban soils from past auto exhaust and other sources is estimated to average 75-200 mg/kg and in places far exceed these values (USEPA 1994, 1998). In HDOH's experience, the use of an action level below 200 mg/kg can complicate the identification and characterization of localized contamination that could conceivably be remediated. The HEER office does, however, recommend the inclusion of soil that exceeds the natural background action level for lead of 73 mg/kg (HDOH 2011) in remediation plans when practicable and when the contamination can be attributed to a specific release. In contrast, if sample data indicate a concentration of lead above 200 mg/kg but below the USEPA RSL of 400 mg/kg a specific source cannot be identified then no further action is generally warranted. Capping or other efforts to minimization of exposure of young children should be considered where area-wide impacts above 400 mg/kg lead are identified, regardless of the suspected source.

4.2.3 Exposed or Potentially Exposed Soils

Direct-exposure soil action levels for unrestricted ("residential") land use (Table I-1) and commercial/industrial land use (Table I-2) are based on an assumption that the soil is, or at some time in the future could be, exposed at the ground surface where regular exposure of residents or workers could occur (refer to Section 2.4 and Section 4.26 in Volume 1). Equations and exposure assumptions used in each scenario are summarized in Appendix 2. For residential properties, it is assumed that soil within 3 meters (approximately 10 feet) of the ground surface could be exposed at the ground surface at some time in the future (e.g., installation of a swimming pool). For commercial/industrial properties, it is assumed that soil within one meter of the ground surface could be exposed during routine landscaping or shallow, utility work. This should be reviewed on a site-by-site basis and provisions for long-term management of deeper or otherwise isolated soil made as necessary. As discussed in the next section, risk-based soil action levels for construction/trench workers take precedence over action levels for unrestricted or commercial/industrial land use if lower (refer to next section).

4.2.4 Isolated Soils

By default, soils are assumed to be “isolated” if they are greater than three meters below ground surface in a residential setting and one meter in a commercial/industrial setting (refer to previous section and Section 2.4 of Volume 1). Direct-exposure action levels for deep or otherwise isolated soils are based on the potential exposure of construction and utility workers to contaminants in soil (Table I-3). A summary of exposure assumptions used to generate the action levels is provided in Appendix 2. The exposure assumptions are based on guidance presented in the USEPA Exposure Factor Handbook (USEPA 2011c), trench-worker risk assessment guidance developed by the Massachusetts Department of Environmental Protection (MADEP 1994), general direct-exposure assumptions included in the USEPA RSL document, and professional judgment (see Appendix 2, Table 1). As discussed above, action levels were calculated using a default, target risk of 1×10^{-5} for non-volatile, carcinogenic chemicals and 1×10^{-6} for volatile chemicals. A default, target Hazard Quotient of 0.2 was applied for chemicals with noncarcinogenic health effects except as noted in the above table. A more detailed summary of exposure assumptions and selected parameter values is included in Appendix 2.

As can be seen in Table I-2, soil action levels for construction/trench workers are lower than action levels generated for commercial/industrial exposure for Cr VI and cobalt under the construction/ trench worker scenario. Action levels for these chemicals are more stringent under the construction/trench worker exposure scenario than under the commercial/industrial exposure scenario (see Table I-2). This is due to the combined high oral and/or inhalation toxicity of these chemicals and the assumed higher soil ingestion rate and higher level of airborne dust under the construction/trench worker exposure scenario. As noted in Table I-2, commercial/industrial land use direct-exposure action levels for these chemicals are replaced with construction/trench worker action levels for use in the lookup tables if less stringent.

4.2.5 Soil Saturation Levels

For chemicals that are liquids under ambient conditions, upper limits for soil direct-exposure action levels are set at the chemicals theoretical soil saturation limit or “C_{sat}” (refer to Appendix 2, 2011). As discussed below, soil action levels for volatile chemicals are only valid if they are below the chemicals C_{sat} concentration. C_{sat} concentrations represent an upper limit to the applicability of the soil screening level Volatilization Factor (VF) model because a basic principle of the model (Henry’s Law) does not apply when contaminants are present in free phase (USEPA 1996a, 2002, 2004a, 2011). VF-based inhalation soil screening levels are reliable only if they are at or below C_{sat}. This is discussed in more detail below.

The soil saturation limit represents the point at which additional contaminant mass can no longer be sorbed to soil particles (primarily organic carbon but also clays) or dissolved into soil moisture. Above this concentration it is assumed that free product (e.g., light non-aqueous phase liquid [LNAPL]) will be present in the soil. This is critical for VOCs. Above C_{sat} , the USEPA direct-exposure model is no longer technically viable for prediction of vapor emissions to outdoor air and subsequent direct exposure risks posed by inhalation.

This is because vapor emissions are estimated based on the concentration of the contaminant in soil moisture in the absence of free product (e.g., LNAPL). The model first estimates the dissolved-phase concentration of a contaminant in soil based on the input total soil concentration and the contaminants estimated soil:water equilibrium partitioning coefficient or “ K_d ” value (i.e., ratio of sorbed mass to dissolved-phase mass, generally calculated as the contaminants sorption coefficient or “ k_{oc} ” times the known or estimated concentration of organic carbon in the soil; refer to Appendix 2). The model then estimates the concentration of the chemical in soil vapor (vapor phase) by comparison of the estimated concentration in the soil moisture to the contaminants air:water equilibrium coefficient (Henry’s Law constant). Fick’s Law is then used to estimate the vapor emission rate of the contaminant at the ground surface.

When C_{sat} is exceeded, the assumed presence of free product violates the use of only the Henry’s Law constant to estimate the concentration of the chemical in soil vapor and subsequently the vapor emission rate at the ground surface. As noted in USEPA risk assessment guidance, the direct-exposure model is no longer valid above this concentration (USEPA 1996a, 2002, 2004b, 2011). C_{sat} is used to set maximum direct-exposure action levels for volatile contaminants in the USEPA RSLs (USEPA 2017a) and in past publications of the USEPA Region IX Preliminary Remediation Goals (USEPA 2004a).

Soil vapor data can be used to estimate vapor emission from soil where C_{sat} concentrations of a volatile chemical are exceeded, although direct-exposure models that allow input of soil vapor data have not been published (in preparation by HEER office). Vapor flux at the surface in the presence of free product can also be modeled mathematically. A model to do this is presented in Appendix A of the USEPA vapor intrusion guidance (USEPA 2004b, see Appendix 4). This is incorporated into the USEPA vapor intrusion model but has yet to be included in USEPA direct exposure models for soil (e.g., USEPA 2017a; see below). As discussed above for direct-exposure models, the USEPA vapor intrusion model incorporates a chemical’s Henry’s Law constant to estimate the concentration of the chemical in soil vapor up to C_{sat} . When a residual phase is present, the vapor concentration is independent of the soil concentration but proportional to the mole fraction of the individual component of the residual phase mixture. At this point, the vapor intrusion model numerically estimates the equilibrium vapor concentration of the chemical in soil vapor for a series of time-steps. For each time-step, the mass of each constituent that is

volatilized is calculated using Raoult's Law and the appropriate mole fraction. At the end of each time-step, the total mass lost is subtracted from the initial mass and the mole fractions are recomputed for the next time-step to take into account mass balanced over time. Refer to the USEPA vapor intrusion guidance for additional information.

The 1996 and 2002 editions of USEPA's *Soil Screening Levels* guidance make an apparent error in the conclusion that the emission flux from soil to air for a chemical reaches a plateau when a chemical's C_{sat} concentration in soil has been reached (USEPA 1996a, 2002, "Soil Saturation Limit"). This error is repeated in the recently published USEPA RSLs guidance (USEPA 2017a). Each document mistakenly states that C_{sat} represents the concentration *at which soil pore air is saturated with the target contaminant*. This is not the case. As noted above, C_{sat} represents the concentration of the chemical in soil in which the *sorbed- and dissolved-phases* are saturated. Saturation of these phases in the soil does *not* necessarily indicate that the vapor phase of the chemical has reached its maximum, nor that the vapor flux rate at the surface has reached a maximum. The concentration of a chemical in soil vapor at a soil concentration of C_{sat} merely reflects equilibrium conditions with the chemical in soil moisture at the chemical's solubility limit. Saturation of the vapor phase will only occur in the presence of free product in the soil, when the gas phase reaches equilibrium with the *Nonaqueous Phase Liquid* or "NAPL." The concentration of the chemical in the vapor phase at this point is likely to be significantly higher than at the point that the soil moisture has reached the solubility limit of the chemical. This is why the Henry's Law Constant-dependent, vapor flux model incorporated into most soil action level models (including the one used in this guidance) is only valid in the absence of free product in the soil (i.e., concentration of chemical in soil $< C_{sat}$). This is also the case frequently observed in soil vapor studies, where the concentration of a volatile chemical in soil vapor increases significantly in the presence of free product.

4.3 Soil Action levels for Potential Vapor Intrusion Concerns

Soil action levels for the evaluation of potential vapor intrusion concerns are presented in Table C-1b. As discussed in Section 3.3, the use of soil vapor data and action levels to evaluate this concern is preferred (refer also to Section 7 of the HEER *Technical Guidance Manual*). Vapor intrusion action levels were calculated for both unrestricted ("residential") and commercial/industrial land-use exposure scenarios. Only the action levels for unrestricted land use were carried forward for consideration in compilation of final, Tier 1 EALs (refer to Table A and B series).

A spreadsheet included with guidance published by the U.S. Environmental Protection Agency (USEPA 2004) was used to generate soil action levels for potential vapor intrusion concerns. A summary of these action levels is provided in Table C-1b. Correlative soil vapor action levels are provided in Table C-2. Target indoor air goals are provided in Table

C-3. Target groundwater action levels for vapor intrusion hazards are presented in Table C-1a.

As discussed in Section 2, the spreadsheet is based on a model presented in the paper *Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings* (Johnson and Ettinger 1991). The model considers both diffusive and convective flow of subsurface vapors into buildings. Summary text from the guidance document accompanying the spreadsheet is provided in Appendix 3, as is a sensitivity evaluation of the Johnson and Ettinger model. Example printouts of the model as used to calculate action levels for this document are included in Appendix 4. A more detailed discussion of models is provided in Section 5.4 for correlative groundwater action levels.

Input parameter values used in the soil models are noted in the example spreadsheets in Appendix 4 (see front pages). Parameter values assumed for building characteristics and human exposure were consistent with values used in the soil vapor intrusion models. The aerial extent of impacted soil is assumed to be equal to the footprint of the building. The base of the floor was assumed to immediately overlie impacted soil (depth to top of soil equals thickness of floor). The thickness of impacted soil was assumed to be 200 cm (approximately 6 feet). The soil type was assumed to be a highly permeable sand (intrinsic permeability = $1.0E-07$ cm²). The model is not significantly sensitive to the input "Depth to Top of Contamination" for impacted soil situated within a few meters of the ground surface.

A default Soil-Building Pressure Differential of 20g/cm-s² was used. This generates a target vapor entry rate through the building slab of approximately 38 cm³/second or two liters per minute (refer to Section 2.2.3).

For nonchlorinated VOCs, field experience suggests that the vapor intrusion model typically overestimates the vapor-phase concentrations of these chemicals by an order of magnitude or more, due in part to high rates of natural biodegradation. Evaluation of this issue is ongoing. To address this in the lookup tables, soil action levels generated with the model were adjusted upwards by a factor of 10 (see Table C-1b). Collection of soil vapor data and concurrent use of soil vapor action levels for vapor intrusion concerns is strongly recommended for sites where this pathway may be of significant concern.

The USEPA spreadsheet calculates the theoretical emission rate of a chemical into an overlying building based on the properties of the chemical and the soil type. For highly volatile chemicals (e.g., vinyl chloride), however, an unrealistic mass of the chemical per unit area would have to be present at depth to maintain the theoretical emission rates over the assumed exposure duration. To compensate, the model spreadsheet calculates a second, mass-balanced emission rate by dividing the total mass of the chemical in the soil per unit

area by the input exposure duration. This conservatively assumes that the entire mass of the chemical directly beneath the building will ultimately be emitted into the building over the assumed exposure duration. For chemicals where the mass-balanced vapor emission rate is lower than the theoretical emission rate, the mass-balanced emission rate is used to generate an action level (or calculate risk).

The same action levels developed for shallow soils should be applied to deep soils for initial, screening surfaces. While conservative, the parameter for depth to impacted soil does not significantly control calculated action levels for soils within 5 to 10 meters of the ground surface. As discussed in Volume 1, the collection of soil vapor data is preferred over the use of models for more detailed evaluations of vapor intrusion hazards.

4.4 Soil Action Levels for Leaching Hazards

4.4.1 Default Soil Leaching Model

Soil action levels for leaching hazards and subsequent impacts to groundwater are summarized in Table E and included in summary lookup tables for both shallow and deep soils (refer to Tables A and B of this appendix). These action levels are intended to address potential leaching of chemicals from vadose-zone soils and subsequent impact on groundwater. The soil action levels are back calculated based on target groundwater action levels. Target groundwater action levels are summarized in the Table D series and discussed in Chapter 2.

The majority of the action levels were calculated based on an empirical equation presented in guidance published by the Massachusetts DEP (MADEP 1994):

$$C_{\text{soil}} = \text{DAF} \times C_{\text{gw}} \times 0.001 \text{ mg}/\mu\text{g}$$

$$\text{DAF} = (6207 \times H) + (0.166 \times K_{\text{oc}})$$

where: DAF = SESOIL-based dilution/attenuation factor;
H = Henry's Law Constant ($\text{atm}\cdot\text{m}^3/\text{mol}$);
K_{oc} = Organic carbon partition coefficient (cm^3/g);
C_{soil} = Leaching based soil concentration (mg/kg);
C_{gw} = Target groundwater action level ($\mu\text{g}/\text{L}$).

The term DAF is defined for the purposes of the model as the concentration of the contaminant in soil (in mg/kg) divided by the concentration of the contaminant in groundwater (in mg/L). The algorithm was originally developed by the state of Oregon (Anderson 1992), slightly modified for use by the Massachusetts DEP (MADEP 1994) and then incorporated into the Ontario MOEE lookup table guidance (MOEE 1996). The

algorithm is based on a combined use of the computer applications SESOIL and AT123D. These applications model the leaching of chemicals from the vadose zone and subsequent mixing of leachate to groundwater, respectively.

SESOIL models the generation and downward migration of leachate in the vadose zone. The AT123D application models the mixing of leachate with groundwater immediately below the impacted area. A more detailed discussion of the derivation and application of the SESOIL/AT123D algorithm as modified by the Massachusetts DEP and adopted for use by the Ontario MOEE is provided in Appendix 5. The algorithm is based on a three-meter thick vadose zone characterized by one meter of impacted soil sandwiched between two one-meter thick layers of clean soil. The lower layer immediately overlies groundwater. All vadose-zone soil is conservatively assumed to be very permeable sand that freely allows the migration of leachate to groundwater. The organic carbon content of the soil is assumed to be 0.1%. (Note that this is more conservative than the 0.6% organic carbon content assumed in the direct-exposure models.) Mixing with groundwater is modeled over a 10-meter by 10-meter area. Use of a thicker assumed sequence of impacted soil would not significantly alter the results of the model given the assumed one-meter depth to groundwater.

The model assumes an annual rainfall of 1,100 mm (approximately 43 inches). A total of 720 mm (28 inches) of the total rainfall is assumed to infiltrate the ground surface and reach groundwater (assumed to be conservative for the majority of developed areas in Hawai'i). This is assumed to also be adequate for higher rainfall areas, although a site-specific evaluation may be required for large (e.g., > one-half acre) areas of contaminated soil with persistent and highly mobile chemicals. Biodegradation during migration of leachate to groundwater is not considered. This could cause the model to be especially over conservative for non-chlorinated, petroleum compounds. The model does, however, allow for resorption and volatilization of chemicals from the leachate during migration based on the physio-chemical properties of the chemical and the assumed soil properties. Groundwater is assumed to flow at a moderate rate of approximately 73m (240 feet) per year. The concentration of a chemical in leachate is assumed to be further reduced upon mixing of the leachate with groundwater (dilution factor approximately 3).

For moderately volatile and sorptive chemicals (e.g., benzene), action levels developed using the SESOIL-derived algorithm are similar to action levels generated using the full SESOIL application under a scenario where impacted soil is within a few meters of groundwater (e.g., HDOH 1995, carried out by the principal editor of this document). Comparison to action levels developed by full but still conservative use of SESOIL suggests, however, that the simplified algorithm may be excessively conservative in the following cases:

- Leaching of highly volatile chemicals (e.g., vinyl chloride);

- Leaching of highly sorptive chemicals (e.g., PAHs);
- Leaching of highly biodegradable chemicals (e.g., common petroleum compounds);
- Sites where the depth to groundwater is greater than 10 meters below the base of the impacted soil.

The depth-to-groundwater factor is particularly important for chemicals that exhibit one or more of the above noted characteristics. As the distance between the base of impacted soil and the top of groundwater increases, there is additional time and area for chemicals to volatilize out of the leachate, resorb to soil particles, or degrade by naturally occurring biological processes. Site-specific evaluation of the potential for leaching of chemicals from soil may be warranted in such cases (including more rigorous modeling, laboratory leaching tests, groundwater monitoring, etc.).

SESOIL modeling carried out by the Hawai'i Department of Health (HDOH 1995) and site-specific, SPLP soil batch test carried out by consultants and HDOH between 2005 and 2011 (see Fall 2011 update memo in Appendix 9) suggested that chemicals with sorption coefficients greater than 30,000 cm³/g will be essentially immobile in the surface under normal soil conditions and not likely to impact groundwater. The SESOIL models were run conservatively assuming an annual rainfall of 400 cm/year (158 inches/year), an infiltration rate of 144 cm/year (57 inches/year) and very permeable soil overlying fractured bedrock.

More recent site data, including laboratory batch test leaching data, suggest that chemicals with sorption coefficients as low as 5,000 cm³/g are likewise essentially immobile in soil (see notes in Appendix 9 summary of updates). This was therefore selected as the *k_{oc}* cutoff for reference to the theoretical soil saturation level as the action level for leaching if higher than the action level generated by use of the SESOIL algorithm (refer to Table E). The equation and assumptions used to calculate the saturation levels is presented and discussed in Appendix 2. The HDOH document *Use of Laboratory Batch Tests to Evaluate Potential Leaching of Contaminants from Soil* (HDOH 2007) provides guidance for calculation of site-specific sorption coefficients and evaluation of potential leaching hazards.

The majority of PCBs releases are related to 1242 to 1260 range Aroclors or similar mixtures. The default *k_{oc}* of 33,000 cm³/g presented in Table H was considered to be adequately conservative for this range and used in the leaching model. For less chlorinated PCB mixtures, a site-specific evaluation of potential leaching concerns and even possible vapor emission concerns is required.

Leaching based action levels were generated only for chemicals considered to be significantly soluble and mobile in groundwater under normal, ambient conditions (e.g., pH 5.0 to 9.0 and normal redox conditions). Leaching-based soil action levels were not

developed for metals. Leaching of metals from soil is highly dependent on the species of the metal present and the geochemical nature of the soil. At sites where physio-chemical conditions may promote enhanced leaching of metals and other chemicals from soils or waste piles (e.g., mining related wastes), the use of laboratory-based leaching tests is recommended (refer to Section 4.2.3 in Volume 1).

Leaching based soil action levels were developed for perchlorate (ClO₄). Perchlorate, a salt, is not significantly sorptive, volatile or biodegradable under normal conditions. Use of the SESOIL/AT123D algorithm was therefore not considered appropriate. As an alternative, a simple, chemical partitioning model presented in the USEPA *Soil Screening Level Guidance* document was referred to (USEPA 2002):

$$C_{soil} = C_{water} \times \left((K_{oc} \times foc) + \left(\frac{\theta_w + (\theta_a \times H')}{\rho_b} \right) \right) \times DAF$$

where:

- C_{soil} = Soil action level for leaching concerns (mg/kg)
- C_{water} = Target dissolved-phase concentration of chemical (mg/L)
- K_{oc} = Sorption coefficient (L/Kg)
- foc = Fraction organic carbon in soil (g/g)
- θ_w = Water-filled porosity (L_{water}/L_{soil})
- θ_a = Air-filled porosity (L_{air}/L_{soil})
- H' = Dimensionless Henry's Number constant (“unitless”)
- ρ_b = Soil bulk density (Kg/L)
- DAF = Dilution/Attenuation Factor [(mg/kg)/(mg/L)]

This model can be used to back calculate the total soil concentration of a chemical based on a target dissolved-phase concentration of the chemical in the soil (i.e., concentration in leachate). For perchlorate, k_{oc} and H' are presumed to be zero and the equation reduces to:

$$C_{soil} = C_{water} \times \left(\frac{\theta_w}{\rho_b} \right) \times DAF$$

The default water-filled porosity in the models is 0.15 and the default soil bulk density is 1.5. Based on groundwater action levels for perchlorate of 3.6 µg/L for drinking water resources and 600 µg/L for non-drinking water resources (refer to Tables D-1a and D-1b), leaching based soil action levels of 0.00036 mg/kg and 0.06 mg/kg are generated, respectively. A dilution/attenuation factor of 20 was incorporated to account for mixing of leachate with groundwater (USEPA 2002). This yielded final soil action levels for leaching concerns for perchlorate of 0.007 mg/kg and 1.2 mg/kg (refer to Table E). Laboratory-

based tests are recommended for more site-specific analysis of potential leaching of perchlorate from soil (refer to Chapter 4 in Volume 1).

4.4.2 Soil Vapor Screening Levels for Groundwater Protection

Soil vapor screening levels that can be used to indirectly evaluate leachate conditions in the vadose zone and potential threats to groundwater are presented in Table E-2 (see also Section 4.3.4 of Volume 1). The screening levels focus on volatile hydrocarbons, solvents, explosives and fumigants. The evaluation of leachate associated with petroleum fuels focuses on TPHgasoline, TPHmiddle distillates, benzene, toluene, ethylbenzene and xylenes (BTEX) and naphthalene. Testing for additional, semi-volatile, PAHs in soil vapors is not necessary to evaluate potential leachate conditions (e.g., acenaphthene or methylnaphthalenes; see Section 2.6 of Volume 1 and Section 9 of the HDOH *Technical Guidance Manual*; HDOH 2009).

The ultimate focus of soil leaching models is the concentration of a targeted chemical in the soil moisture or “leachate.” The leaching threat to groundwater posed by the presence of a chemical in vadose-zone soil would ideally be evaluated by the direct measurement of the dissolved-phase concentration of the chemical in pore water. This could be compared to a target groundwater screening level times an assumed, dilution-attenuation factor. The collection of adequate volumes of pore water to evaluate potential leaching hazards using currently available investigation tools is impractical, however. As an alternative, soil screening levels are developed that represent the total concentration of a chemical in soil at equilibrium with target concentrations of the chemical in soil moisture or leachate (see the previous section; see also USEPA 2002). This allows soil data to be used to evaluate potential leaching hazards as an alternative to the direct collection and testing of soil pore water. Soil batch tests can also be used to more accurately evaluate the mobility of chemicals in soil and the potential threat to groundwater (see Section 4.3.3 in Volume 1).

Although relatively simple in concept and easy to implement in the field, this approach is highly prone to error due to assumptions that must be made regarding how a chemical partitions between sorption to organic carbon (and clay) and dissolution into soil moisture. The collection of representative soil samples from the subsurface is also very prone to error, give the small number of samples typically collected and the small mass of soil ultimately analyzed (e.g., 5 grams or less than one teaspoon of volatile chemicals). The use of multi-increment sampling (MIS) approaches and preservation of samples in methanol in the field can help, but limited coverage can still hamper the representativeness of the data (HDOH 2009). As discussed in Section 4.3.3 of Volume 1, batch tests suggest that soil leaching overestimate the concentration of a chemical in leachate based on the total concentration of the chemical in soil by orders of magnitude (i.e., greater proportion of chemical sorbed to soil particles than predicted by standard, equilibrium model).

For volatile chemicals (VOCs), direct measurement of the vapor-phase concentration of a chemical in vadose-zone soil or bedrock offers a more accurate method for estimation of the concentration of a chemical in leachate than a soil sample. The equilibrium concentration of a chemical in soil vapor to that in leachate is described by the Henry's Constant for that chemical (ratio of concentration in soil vapor over concentration dissolved in water at an assumed temperature; see Table H). Soil vapor screening levels for potential leaching (or leachate) hazards can be developed by designating a target concentration of the chemical in soil leachate, for example the target groundwater concentration (+/- attenuation factor), and then multiplying this by the chemical's Henry's Constant. (Note that a chemical's Henry's Constant varies as a function of temperature. The Henry's Constants presented in Table H are conservatively based on an assumed temperature of 25°C, as presented in the USEPA RSL guidance; USEPA 2017a.)

This approach was used to generate the soil vapor screening levels for leaching concerns presented in Table E of Volume 1 and Table E-2 of this appendix. The screening levels are based on the following, simple equation:

$$C_{soil\ gas} = C_{gw} \times H' \times DAF$$

where: $C_{soil\ vapor}$ = soil vapor screening level for leaching concerns;
 C_{gw} = Target dissolved-phase concentration of chemical in groundwater;
 H' = Dimensionless Henry's Number constant; and
DAF = Dilution-Attenuation Factor

Soil vapor screening levels focus on protection of drinking water, with the target groundwater action level set to the lowest of the toxicity-based screening level and the taste and odor threshold for the chemical (see Table D-1a). Henry's Constants for VOCs are noted in Table E-2 and Table H. A default DAF of 20 was included in the model to take into account mixing of leachate with groundwater (after USEPA 2002). For example, a concentration of 5 µg/L benzene in vadose zone leachate would in theory yield an equilibrium concentration in soil vapor of 24,000 µg/m³, taking into account the dilution-attenuation factor.

The presence of a VOC in soil vapor above its respective screening level suggests that the concentration of the VOC in soil moisture or leachate could adversely impact an unconfined, underlying drinking water aquifer. The screening levels do not consider the actual mobility of the soil moisture. Vapor concentrations would be relatively high in dry soils with little soil moisture in comparison to saturated soils with migrating leachate. Whether or not the leachate (or even the vapors) is actually mobile and poses a true threat to groundwater depends on site-specific factors, including the size of the source area and the mass of contaminant present, the rainfall infiltration rate, the rate and amount of

downward moving leachate, the distance to the water table, the rate of groundwater flow and the thickness of the leachate-groundwater mixing zone. These factors need to be evaluated in more detail on a site-specific basis if the soil vapor screening levels are exceeded.

4.5 Soil Ceiling Levels for Gross Contamination Concerns

Ceiling levels for gross contamination concerns are presented in each of the EAL summary tables for soil. These action levels are intended to be protective against odor and other nuisance and aesthetic concerns, as well as restrict the presence of potentially mobile, free product and limit the overall degradation of soil quality (i.e., "gross contamination"). The selection of soil ceiling levels was based on methods originally published by the Massachusetts DEP (MADEP 1994) and also used by the Ontario MOEE (MOEE 1996), as described in the Table F series of this appendix. Only the gross contamination action levels for shallow, exposed soils are carried forward for consideration in the Tier 1 EALs (refer to Table A and B series). Alternative action levels for isolated or deeper soils are provided for reference in site-specific Environmental Hazard Evaluations as needed.

“Odor Thresholds” presented in the Table F series are intended to represent the concentration of a chemical in air at which 50% of the population can detect a chemical odor. An "Odor Index" for a chemical is calculated by dividing the chemical's vapor pressure (in Torr, at 20 to 30°C) by its odor threshold (in ppm-volume, see Tables F-2 and F-3). This provides a relative ranking of chemicals for potential nuisance concerns. As summarized in Tables F-2 (shallow soils) and F-3 (deep soils), ceiling levels were then selected based on a comparison of a chemical's vapor pressure and odor index to a table of generic action levels (Tables F-1). For chemicals that are liquids under ambient conditions, the final ceiling level was selected as the lowest of the generic level from Table F-1 and the chemical's theoretical saturation level in soil (see Appendix 2). This was intended to prevent the presence of mobile, free product in the subsurface.

4.6 Soil Action levels for Terrestrial Ecotoxicity

Soil action levels for the protection of terrestrial flora and fauna were included in 2009 and earlier editions of the HEER Office EALs. The action levels were taken directly from guidance developed by the Ontario MOEE (MOEE 1996). Action levels were available for heavy metals and a small number of high-molecular-weight organic compounds and pesticides. Action levels for both unrestricted (“residential”) and commercial/industrial land use scenarios were presented, although only the unrestricted land use action levels are considered in the Tier 1 EALs. Alternative action levels for commercial/industrial land use were provided for reference in site-specific Environmental Hazard Evaluations as needed.

Direct inclusion of the soil ecotoxicity action levels was discontinued in the Fall 2011 edition of the EALs. This was due to low confidence for use in volcanic soils, including higher-than-normal background concentration of metals in Hawaiian soils in comparison to areas on mainland where the ecotoxicity action levels were developed. Trace metals in the volcanic soils tend to be tightly bound to iron hydroxides and other minerals and not significantly available for uptake into plants. A site specific, ecological risk assessment is now recommended at sites where significant anthropogenic contamination is identified and sensitive, terrestrial ecological habitats could be threatened (see Volume 1, Section 4.2).

5 Groundwater and Surface Water Action Levels

5.1 Introduction

Action levels for groundwater are summarized in the "D" series of tables at the end of this appendix. A discuss of individual concerns considered in the action levels is provided in this Chapter and summarized below. For the purpose of developing Tier 1 action levels, it is assumed that all groundwater could at some point in time potentially discharge to a body of surface water. Discharge could occur through natural processes (e.g., natural discharge of groundwater to a stream, river, lake, wetland, bay, etc. via springs) or through human activities (e.g., pumping and discharge of groundwater at remediation or construction dewatering projects).

A summary of environmental concerns incorporated into groundwater action levels for different site scenarios is provided in Table 2-1. The final groundwater action level for sites that threaten drinking water resources reflects the lowest of a chemicals screening level for drinking water toxicity, aquatic habitat protection (discharges to surface water), indoor-air impacts (volatile chemicals only) and a "ceiling level" for tastes and odors, or other nuisance concerns (Tables D-1a and D-1b). The final groundwater EAL for sites that do not threaten drinking water resources (Tables D-1c and D-1d) reflects the lowest of a chemical's screening level for the same set of environmental concerns with the exception of the drinking water component and use of less stringent ceiling level.

As discussed below, groundwater action levels for potential discharges to aquatic habitats consider chronic surface water quality goals for sites within 150m of a surface water body and acute goals for sites >150m from a surface water body. Although not used for groundwater action levels, HDOH standards for the potential bioaccumulation of contaminants in aquatic organisms and subsequent consumption of the organisms by humans must be used to evaluate actual impacts to a body of surface water. A summary of these standards is provided in Table D-3f for reference.

Groundwater action levels should be compared to dissolved-phase chemical concentrations unless instructed by the overseeing regulatory agency. This may require filtering of turbid samples (refer to Section 6 of the HEER Office *Technical Guidance Manual*). Filtering should not be carried out on samples to be tested for volatile chemicals.

5.2 Action levels for Drinking Water (Toxicity)

A summary of drinking water standards and guidelines used in this document is provided in Table D-2. Action levels for drinking water intended to address human toxicity were generally selected based on the following order of preference:

- HDOH Maximum Contaminant Level;
- USEPA Primary Maximum Contaminant Level;
- Risk-based goal based on USEPA Region IX Tapwater model.

HDOH and/or USEPA Primary Maximum Contaminant Level (MCLs) are available for approximately half of the chemicals listed in the lookup tables (HDOH 2002; USEPA 2006). Although numerous factors are taken into account in development of primary MCLs (toxicity, detection limits, attainability, etc.), these standards are primarily intended to address toxicity to humans in drinking water supplies and are used for this purpose in this document.

For chemicals where Primary MCLs have not been promulgated, a tapwater model presented in the USEPA RSLs (RSL) document (USEPA 2017a) was used to calculate alternative drinking water goals (Table D-4). Toxicity factors and physiochemical constants published in the 2011 USEPA RSLs were used to develop the action levels with the exceptions noted in Table H (refer to Section 1.3). The action levels are based on a target excess cancer risk of 10^{-6} and a target Hazard Quotient for noncancer concerns of 1.0. Note that the noncancer action levels in particular may not be adequate to address potential cumulative risks concerns. The need to evaluate cumulative risks should be determined on a site-by-site basis (refer to Chapter 4 of Volume 1).

For volatile chemicals, the tapwater goals take into account uptake via inhalation of vapors during showering and other activities in addition to toxicity via normal ingestion of drinking water. Goals for nonvolatile chemicals are based on ingestion only. Equations for the USEPA RSLs for tapwater are included in Appendix 2. Risk-based goals for noncarcinogenic effects take precedence over goals for carcinogenic effects if lower. Note that the more recent RSL tapwater model includes an additional and complicated component for dermal absorption of VOCs during water use. Risk posed by exposure to VOCs in drinking water is largely driven by ingestion, however, and to a lesser extent inhalation. The inclusion of a dermal absorption pathway in the model does not significantly alter the resulting screening level and was not incorporated into the EAL model.

Drinking water goals intended to address taste and odor concerns (e.g., Secondary MCLs) take precedence if lower than toxicity-based goals. For example, the USEPA Primary MCL for xylenes is 10,000 µg/L. The USEPA Secondary MCL for xylenes is only 20 µg/L, however. The latter value should be (and is) used as the groundwater action level for drinking water concerns. This is discussed under ceiling levels for groundwater (see Section 5.5).

5.3 Action Levels for Aquatic Habitat Protection

5.3.1 Basis of Action Levels

Groundwater action levels for the protection of aquatic habitats are based on the goal that concentrations of contaminants in groundwater should meet chronic surface water goals at the point that the groundwater discharges into a body of surface water. Dilution of contaminated groundwater as it mixes with surface water is not considered under a Tier 1 assessment. In accordance with this approach, chronic surface water goals are incorporated into groundwater action levels for sites (or groundwater plumes) located within 150m of a surface water body. For more inland sites, acute surface water goals are referred to. As a default under Tier 1, the lowest of freshwater versus saltwater goals are used. The prioritization and selection of these goals is described below.

5.3.2 Surface Water Aquatic Habitat Goals

A summary of aquatic habitat goals considered for use in this document is provided in Tables D-3a and D-3b. Separate goals were compiled for freshwater and saltwater habitats.

The goals reflect a compilation of standards formally promulgated in state law by HDOH and goals published by USEPA and other sources. Formal standards have not been promulgated for the majority of chemicals listed. Final goals were selected based on the following order of preference and availability, unless otherwise noted in Table D-4f:

- HDOH Surface Water Standard (HDOH 2012b);
- USEPA Region 4 (USEPA 2015c);
- USEPA Office of Pesticides (USEPA 2016);
- USGS National Water Quality Program (USGS 2012);
- U.S. Department of Energy (USDOE 1996);
- Ontario MOEE (MOEE 1996);
- USEPA AQUIRE database (USEPA 2008b);
- Toxicity-based drinking water goal.

An exception to this approach is the use of a general, acute aquatic toxicity action level of 300 µg/L published by the Canadian Council of Ministers of the Environment (CCME) for semivolatile PAHs, excluding naphthalenes (CCME 2002; refer to Table D-4e). Goals provided in each reference are generally based on dissolved-phase concentrations of the chemicals in water. Goals for arsenic, chromium III, chromium VI, lead, mercury, nickel, selenium, silver and zinc are, however, based on total concentrations (see USEPA 2015c).

The USEPA AQUIRE ECOTOX database of ecotoxicity studies was referred to for chemicals with no published aquatic habitat goals, primarily a small number of pesticides (USEPA 2008b). Emphasis was placed on 96 hour-duration aquatic animal studies (48 hours for daphnia studies). Modification factors in general followed recommendations and methods provided in the USEPA Great Lakes water quality initiative guidance (USEPA 1995). Goals provided in each reference are generally based on dissolved-phase concentrations of the chemicals in water.

Note that many if not most of the referenced aquatic ecotoxicity action levels focus on toxicity to fish and benthic organisms. Action levels based on toxicity to aquatic plants could be lower. A more site-specific evaluation of this issue should be considered where discharges of impacted groundwater might adversely affect aquatic plants.

Chronic surface water goals were compiled for all of the chemicals listed in the lookup tables (Table D-3a). Acute goals were available for approximately 75% of the chemicals listed (Table D-3b). Chronic goals were substituted as acute goals when the latter were not available and in some cases adjusted upwards. Freshwater goals were similarly substituted for saltwater ("marine") goals if the latter were not available and vice versa.

Chronic and acute surface water standards specific to Hawaii are presented in the Hawaii Administrative Rules, Title 11, Chapter 54, Section 11-54-04: Basic Water Quality Criteria (HDOH 2012b). Surface water standards for potential bioaccumulation of chemicals in aquatic organisms and subsequent human consumption of these organisms are presented in Table D-4f. Both Hawaii and Federal standards are given. Aquatic toxicity action levels presented in Table D-4e that include a component of bioaccumulation and potential impacts to predators are noted in red (see USEPA 2015c).

5.3.3 Groundwater Action levels for Aquatic Habitat Impacts

For the purposes of this document, it is assumed that groundwater could discharge into an estuary environment (tidally influenced portions of creeks, rivers, streams, etc.). Tier 1 goals for aquatic habitat protection are therefore based on the lowest of the goals for saltwater versus freshwater environments. For settings where this is not appropriate, target surface water goals and correlative groundwater goals can be adjusted on a site-specific

basis under a Tier 2 or Tier 3 assessment. The goals should be compared to dissolved-phase chemical concentrations unless otherwise instructed by HDOH.

Dilution of groundwater upon discharge to surface water was not considered in the selection of groundwater action levels for aquatic habitat protection. Benthic organisms were assumed to be exposed to the full concentration of chemicals in impacted groundwater prior to mixing of the groundwater with surface water. Potential dilution of groundwater upon discharge to surface water or in groundwater "mixing zones" adjacent to shorelines areas was therefore not appropriate for development of conservative action levels. Adjustment of the final groundwater action levels with respect to potential dilution may, however, be appropriate on a site-specific basis (e.g., no significant benthic habitat present, see Volume 1, Section 4.3).

Note that natural background concentrations of boron, copper, lead, mercury, selenium, thallium and zinc among other metals could exceed groundwater action levels presented in the lookup tables. This issue should be evaluated on a site-by-site basis and discussed with HDOH where necessary. This potential issue has been noted for shallow groundwater in caprock sediments around the islands, although data are too sparse to prepare a strong summary.

Surface water standards for potential bioaccumulation of chemicals in aquatic organisms and subsequent human consumption of these organisms were not directly considered in the selection of groundwater action levels for potential aquatic habitat impacts. Use of these standards would be excessively conservative at the large number of relatively small sites overseen by HDOH. Consideration of the standards may be appropriate for sites where the discharge of large plumes of impacted groundwater threatens long-term impacts to important aquatic habitats. This should be evaluated on a site-by-site basis.

5.4 Groundwater Action Levels for Potential Vapor Intrusion Concerns

5.4.1 Vapor Intrusion Model Parameters

Groundwater action levels intended to address the intrusion of vapors into buildings and subsequent impact on indoor-air quality are summarized in Table C-1a and included in Tables D-1a through D-1d. Correlative soil vapor action levels and indoor air action levels are presented in Tables C-2 and C-3, respectively, and discussed in Chapter 4.

All groundwater was assumed to potentially flow offsite and pass under residential areas. Final action levels are therefore based on a unrestricted ("residential") land use exposure

scenario. Groundwater action levels for commercial/industrial areas are included in Table C-1a for reference but were not carried on for use in subsequent lookup tables.

Default building parameters including anticipated IAERs and vapor entry rates are discussed in Section 2. The same building characteristic assumptions are used to develop action levels for subslab soil vapor, soil and groundwater. In particular, a default Soil-Building Pressure Differential of 20g/cm-s^2 was incorporated into the model. This generates a targeted vapor entry rate through the building slab of approximately $38\text{ cm}^3/\text{second}$ or 2 L/min (refer to Section 2.2.3). This, combined with the default, input IAERs for residential versus commercial/industrial settings, is used to generate a targeted SSAF for the intrusion and mixing of vapors into the overlying building. The SSAF subsequently plays an important role in generation of corresponding vapor intrusion action levels for VOCs in underlying groundwater.

For the purposes of this document, the vadose-zone soil profile overlying groundwater is modeled as one meter of coarse-grained, dry, sandy soil (S) overlying two meters of somewhat more moist clayey loam (CL, 1/3 sand, 1/3 silt, 1/3 clay). This is considered to be representative of fill material commonly placed beneath the slabs of new buildings. "Sand" is defined as material that is equal to or greater than 0.075 mm in diameter (i.e., will not pass through a U.S. Standard 200 mesh sieve). Silt and clay are defined as material that is less than 0.075 mm in diameter (i.e., will pass through a U.S. Standard 200 mesh sieve). These definitions are consistent with default parameter values for soil types presented in the USEPA model (USEPA 2004). The depth from the ground surface to the top of impacted groundwater in both sets of models was assumed to be 3.0m. This is just above the minimum thickness allowed for modeling of vapor transport through a low to moderate permeability vadose-zone soil profile, due to capillary fringe height constraints.

This vadose-zone profile is similar to the profile for coastal sediments in many areas of Hawai'i. *It is important to understand, however, that the profile itself is not necessarily intended to mimic the profile at a subject site.* The primary objective of the input, model profile is instead intended to approximate concentrations of VOCs observed in shallow (e.g., subslab) soil vapor over contaminated groundwater, based on comparisons of groundwater and soil vapor data in the field. The modeled soil profile is considered to reasonably replicate groundwater and soil vapor observations in the field under most site conditions, even if the input soil types and layers do not match actual field conditions.

Input soil parameter values for total porosity, water-filled porosity and fraction organic carbon for the upper portion of the soil profiles were set equal to values used by USEPA in development of the RSLs (USEPA 2017a). Soil moisture was assumed to be somewhat higher for the lower soil units than the upper units, at 0.30 (vs 0.15), consistent with the default recommended in the USEPA vapor intrusion guidance document. Default values presented in the USEPA spreadsheets were used for remaining soil properties.

Default soil vapor permeability values for the selected soil types were used in the models. For site-specific estimation of this parameter, the use of rigorous, in-situ methods intended for the design of soil vapor extraction systems is recommended. Secondary porosity and permeability in fine-grained soils can be significantly enhanced by plant roots, desiccation cracks, disturbance during redevelopment, faulting, etc. Reliance on a small number of borings or laboratory analysis could significantly underestimate the actual vapor permeability of the site and in turn underestimate the risk of potential impacts to indoor air.

Note that when using the USEPA vapor intrusion spreadsheets to back calculate a groundwater action level from an input target risk, the values appearing in the spreadsheet for "Csource" (concentration in soil vapor) and "Cbuilding" (concentration in indoor air) are based on a theoretical initial soil concentration of 1E-06 g/g or 1,000 micrograms per kilogram and are not directly related to the modeled action level. The values presented do not represent actual modeled concentrations and should be ignored.

5.4.2 Adjustment of Action levels

Field studies at sites impacted by volatile chemicals have clearly documented impacts to indoor air due to the intrusion of subsurface vapors, particularly for sites where soil or groundwater has been impacted by chlorinated volatile organic compounds. One example is the report *An Evaluation of Vapor Intrusion into Buildings Through A Study of Field Data* prepared by staff of the Massachusetts DEP (Fitzpatrick and Fitzgerald 1997). Results of the Massachusetts DEP study suggest that the vapor intrusion model may over-predict the concentration of chlorinated, volatile chemicals in soil vapor by an order of magnitude or more with respect to the measured concentration of the chemical in groundwater, although in some cases the model appeared to be slightly under conservative. More significantly, the Massachusetts DEP field study indicated that the vapor intrusion model over-predicted the soil vapor concentration of petroleum-based volatile organic compounds (e.g., benzene) in the vadose zone by up to three or more orders of magnitude. This was interpreted to reflect substantial, natural biodegradation of the vapor-phase of these chemicals in the subsurface. This in turn causes the models to over predict impacts to indoor air by several orders of magnitude and makes use of the model for this group of chemicals questionable, particularly in the absence of field-based soil vapor data.

To account for the potentially over conservative nature of the vapor intrusion model for nonchlorinated volatile chemicals, action levels generated by the model were adjusted upwards by a factor of ten (refer to Table C-1a). As discussed below, the use of soil vapor data in combination with groundwater studies may be most appropriate for evaluating sites where a more detailed evaluation of this issue is warranted. Evaluation of this issue is ongoing.

5.5 Water Ceiling Levels for Gross Contamination Concerns

Ceiling levels based on gross contamination concerns for surface water and groundwater are summarized in the Table G series. Ceiling levels for surface water and groundwater that is considered to be a current or potential source of drinking water are based on the lowest of the chemicals taste and odor threshold (e.g., Secondary MCLs), one-half the solubility and a maximum of 50,000 µg/L for any chemical based on general resource degradation concerns (Tables G-1 and G-4, after MADEP 1994). Taste and odor thresholds for drinking water were selected in the following order of preference and availability:

- HDOH Secondary MCLs (HDOH 2002);
- USEPA Secondary MCLs;
- California Department of Health Services Taste and Odor Action Levels;
- Taste and odor levels developed by Amoore and Hautala (as presented in Central Valley Regional Water Quality Control [RWQCBCV] 2007);
- Odor thresholds presented in Massachusetts DEP (MADEP 1994) and Ontario MOEE (MOEE 1996) guidance documents and other published reports (e.g., Young et al 1996).

Hawai'i drinking water regulations reference USEPA Secondary MCLs for a short list of chemicals (HDOH 2002). USEPA and California DHS secondary MCLs and taste and odor thresholds were taken from the California Environmental Protection Agency (CalEPA) document *A Compilation of Water Quality Goals* (RWQCBCV 2007).

Ceiling levels for surface water and groundwater that is NOT considered to be a current or potential source of drinking water were selected in a similar manner with the exception that the drinking water taste and odor thresholds were replaced with general nuisance thresholds and gross contamination concerns (Tables G-2 and G-4). Nuisance thresholds are intended to reflect the concentration at which a chemical in water poses unacceptable odor problems or sheens.

Thresholds presented in the Massachusetts DEP and Ontario MOEE guidance documents were used as the primary sources of data. Taste and odor levels developed by Amoore and Hautala (in RWQCBCV 2007) were referred to for chemicals that lack odor thresholds in the Ontario guidance, although conservative considerations for drinking water concerns could cause these criteria to be overly stringent. It is apparent, however, that similar sources were used to develop both the Ontario MOEE and the Amoore and Hautala databases (compare Tables G-1 and G-2). In keeping with the Ontario and Massachusetts guidance documents, a ten-fold dilution/attenuation of chemical concentrations in groundwater upon discharge to surface water was assumed (non-drinking water resources, gross contamination action levels only). The potential for an adverse buildup of contaminants in

sediment over time through long-term discharges of contaminated groundwater should be evaluated on a case-by-case basis (e.g., sorption and buildup of dissolved-phase petroleum onto organic material in sediment over time).

The nuisance threshold for methyl tertiary butyl ether (MTBE) is based on average, upper range at which most subjects in a USEPA study could smell MTBE in water (180 µg/L), as summarized in the public health goals document for MTBE prepared by Cal EPA (CalEPA 1999a). This was selected as a nuisance action level for MTBE in surface water. Assuming a dilution factor of ten yields the odor threshold of 1,800 µg/L for groundwater.

Drinking water taste and odor thresholds for TPH are discussed separately in Section 6.6. Note that consideration of the aqueous solubility for individual compounds to assess the potential presence of free product in groundwater is not appropriate for petroleum mixtures. Solubility should instead be assessed on a molar composition basis using Raoult's Law. Free product is likely to be present when the sample data equals or exceeds the estimated mixture solubility of an individual compound or the sum of the individual component solubilities. One-half of the total petroleum product solubility measured as TPH can also be considered, although data might be biased high to the presence of more soluble, degradation compounds (refer to Section 6).

5.6 Other Groundwater Action Levels

Additional action levels for groundwater provided in the California EPA technical document *A Compilation of Water Quality Goals* include USEPA and National Academy of Sciences "Suggested No-Adverse-Response (SNARL)" goals for toxicity other than cancer risk and "Agricultural Water Quality" goals developed by the United Nations (RWQCBCV 2007). The SNARL goals largely duplicate risk-based action levels for drinking water presented in Table D-3. Agricultural Water Quality goals for 12 metals are provided in Table D-5. These goals were not considered in the final lookup tables but may need to be considered on a site-specific basis. The agricultural goals are higher than action levels for both drinking water and surface water protection for 7 of the 12 metals listed. Agricultural goals for copper, cobalt, selenium and zinc are higher than goals for aquatic habitat protection but are lower than goals for drinking water (i.e., drinking water goals may not be adequately protective for irrigation use). The agricultural goal for molybdenum is lower than both the drinking water goal and the surface water goal for this metal. The development of these goals was not reviewed for preparation of the EAL document.

Table 5-1. Environmental concerns considered in groundwater action levels.

| Category | Drinking Water Toxicity | Drinking Water Taste and Odors | Vapor Emissions To Indoor Air | Discharges To Surface Water (Chronic Goals) | Discharges To Surface Water (Acute Goals) | Surface Water Impact Ceiling Levels |
|--|-------------------------|--------------------------------|-------------------------------|---|---|-------------------------------------|
| Table A-1 Source of Drinking Water; NOT Within 150m of Surface Water Body | X | X | X | | X | X |
| Table A-2 Source of Drinking Water; Within 150m of Surface Water Body | X | X | X | X | | X |
| Table B-1 NOT A Source of Drinking Water; NOT Within 150m of Surface Water Body | | | X | | X | X |
| Table B-2 NOT A Source of Drinking Water; Within 150m of Surface Water Body | | | X | X | | X |

6 Soil, Soil vapor and Groundwater Action

Levels for TPH

6.1 Introduction

Petroleum is a complex mixture of hundreds of different compounds composed of hydrogen and carbon (i.e., "hydrocarbon" compounds). The carbon range makeup of common petroleum fuels is noted in Figure 3. Non-specific, aliphatic and aromatic compounds and related degradation compounds make up the overwhelming majority of the mass in fuels and in vapors emitted from fuels (see Appendix 6). These compound and related, degradation compounds are collectively measured and assessed as "Total Petroleum Hydrocarbons" or "TPH" (refer to Volume 1, Section 2.6.1). Risk to human health and the environment posed by petroleum releases is evaluated in terms of both TPH and individual, "indicator" compounds such as benzene, toluene, ethylbenzene and xylenes (BTEX) as well as naphthalene and other targeted polyaromatic hydrocarbons (PAHs). The latter only make up a small percentage of the total mass in fuels and in vapors but can pose a significant risk due to their higher toxicity.

Testing and evaluation of the TPH component of petroleum-contaminated soil and groundwater and in associated soil vapor in addition to targeted, individual compounds is therefore important. A summary of target analytes for petroleum in soil vapor, soil and water in addition to TPH and with respect to different fuel types is provided in Table 6-1. In many cases the TPH component of the contamination will drive risk to human health and the environment over the minority fraction represented by individual BTEX and PAH compounds.

Petroleum-related, polar compounds are considered to have similar toxicities as the parent compounds and TPH action levels are applicable to both the nonpolar and polar fractions for initial screening. The use of alternative toxicity factors and physiochemical constants for metabolites can be proposed in a site-specific Environmental Hazard Evaluation. Refer to Volume 1, Section 2.6.1 and Section 9 of the HEER *Technical Guidance Manual* (HDOH 2016). This issue will be reviewed in an ITRC document entitled *TPH Risk Evaluation at Petroleum Contaminated Sites*, currently under preparation (ITRC 2017). Several HEER staff are participating in the preparation of the document, particularly in the Chemistry and Case Studies sections of the document, both of which discuss methods to address petroleum-related degradation compounds.

The development of risk-based action levels for TPH in soil, soil vapor and groundwater is described below. For the purposes of this document, petroleum mixtures are subdivided into "gasolines", "middles distillates" and "residual fuels", following the methodology used by the American Petroleum Institute (API 1994). Middle distillates include common diesel fuel, kerosene and jet fuels such as JP-8. The action levels are based on the assumed carbon range makeup of fuel types and associated vapors in conjunction with carbon range-specific toxicity factors published by USEPA and Massachusetts, among other agencies.

Several published documents were available to select a default, carbon range makeup of different fuel types (e.g., TPHCWG 1998, MADEP 1997, 2003). Published data on the carbon range makeup and toxicity of vapors associated with petroleum fuels are limited. In 2011, the HEER office carried out a soil vapor study of key, petroleum-contaminated sites in Hawai'i to help fill this data gap and updated the environmental hazard evaluation (EHE) guidance and associated TPH EALs (HDOH 2012a). The results of that study are summarized below. A paper published on the study (Brewer et al. 2013) and an overview of common questions regarding TPH are included in Appendix 6.

Not surprisingly, and as described below and in Appendix 6, vapors are strongly biased toward lighter-end aliphatic compounds in comparison to the parent fuel type. Significant vapors were identified at both gasoline and middle distillate release sites. Gasoline is routinely considered to be "volatile" and a potential vapor intrusion hazard. As is obvious by their distinctive smell, middle distillates such as diesel fuel are also volatile and can pose vapor intrusion hazards if present at high enough concentrations and mass in soil and groundwater.

Sections 7 and 9 of the HEER Office *Technical Guidance Manual* describes laboratory methods for testing of TPH in soil, water and soil vapor contaminated with petroleum fuels. Detailed carbon range analysis of the aliphatic and aromatic makeup of the TPH component of the petroleum and development of site-specific, TPH action levels can be carried out as needed as an alternative to the action levels published in this guidance (see Volume 1). This is not anticipated to be necessary or cost-beneficial at most sites, however. An exception might be the need for more detailed carbon range data for soil vapor at sites where reported concentrations of TPH exceed the Tier 1 action levels by less than a factor of three, the approximate magnitude that site-specific action levels might be increased over the default action level.

As discussed in the Volume 1, the use of EALs as final "cleanup levels" for petroleum-related compounds that are known to be highly biodegradable may be unnecessarily conservative. This is especially true for TPH and petroleum-related compounds. Final cleanup levels should be evaluated on a site-specific basis and in conjunction with guidance from the overseeing regulatory agency (e.g., refer to HDOH 2007).

6.2 TPH Carbon Range Makeup of Fuels and Fuel Vapors

A summary of the selected, default carbon range TPH makeup of fuels and fuel vapors is provided in Table 6-2. This was used in combination with carbon range toxicity factors published by USEPA and other agencies to develop risk-based action levels for TPH in indoor air, soil vapor, soil and groundwater. A copy of the paper published on the 2011 HDOH soil vapor study is provided in Appendix 6 (Brewer et al. 1013).

A detailed review of the chemistry and carbon range makeup of different petroleum fuel types is presented in guidance published by the Total Petroleum Hydrocarbon Working Group (TPHCWG 1998). Summaries have also been published by several states, including Massachusetts (MADEP 1997, 2003) and Indiana (IDEM 2010). A brief overview is provided below, with a focus on gasoline, #2 diesel fuel and residual fuels such as motor oil.

6.2.1 Gasolines

Gasolines are defined as petroleum mixtures characterized by a predominance of branched alkanes and aromatic hydrocarbons with carbon ranges of C6 to C12 and lesser amounts of straight-chain alkanes, alkenes and cycloalkanes of the same carbon range (TPHCWG 1998). Based on information published by the State of Indiana, a relative TPH carbon range makeup of gasoline fuels (not including BTEX, naphthalene and other individual, targeted compounds) of 45% C5-C8 aliphatics, 12% C9-C12 aliphatics and 43% C9-C12 aromatics was selected for development of TPHgasoline action levels for soil and groundwater (see Table 6-2a). Separately targeted, individual compounds such as BTEX and naphthalene generally do not make up more than 5% of gasoline fuels in Hawai'i. Other compounds such as MTBE are not added in significant quantities.

An assumed TPH carbon range makeup of vapors associated with gasolines of 77.3% C5-C8 aliphatics, 7.3% C9-C12 aliphatics and 15.4% C9-C10 aromatics was selected for development of TPHgasoline soil vapor screening levels. This is based on the median carbon range composition of gasoline vapors published in the USEPA Petroleum Vapor Intrusion database (see Table 6-2b; Brewer et al. 2013; see also USEPA 2012). A much greater dominance of gasoline vapors by C5-C8 aliphatics has been reported by other entities (e.g., BioVapor 2010). The higher, relative proportions of longer chain aliphatics and heavier aromatics in the USEPA database could be due to weathering, inadvertent inclusion of vapor data from middle distillate release sites and/or the incorporation of volatile metabolites in the data. The latter issue has not been studied in detail.

Vapors associated with fresh gasoline are dominated by C2-C4 aliphatics and C5-C8 aliphatics, with only a minor component (<5%) of BTEX and non-specific aromatic

compounds (see Appendix 6). Vapors associated with weathered fuel, as is the case at most gasoline-release sites, are dominated by C5-C8 aliphatics with little to no C2-C4 aliphatics remaining and again a relatively minor component of BTEX and non-specific aromatic compounds (see Appendix 6; may differ on the mainland due to local gasoline formulations). The C2-C4 aliphatics primarily pose explosion hazards. Chronic toxicity factors have not been developed for these compounds.

The ratio of TPH to benzene in soil vapor at sites contaminated with releases of older, high-benzene gasoline sites is typically less than 500:1, with the ratio lower (i.e., increased proportion of benzene) at fresh release sites and higher ratio at more weathered sites (i.e., preferential loss of benzene). The ratio of TPH to benzene can be much higher at more recent releases (post 2005) of gasoline due to an initially much lower proportion of benzene in the formulation in comparison to earlier formulations (see Brewer et al 2013).

6.2.2 Middle Distillates

Middle distillates (e.g., kerosene, diesel fuel, home heating fuel, JP-8 jet fuel, etc.) are characterized by a wider variety of straight, branched and cyclic alkanes, PAHs, especially naphthalene and methylnaphthalenes and heterocyclic compounds with carbon ranges of approximately C9 to C25. A small component of C5-C8 aliphatics and BTEX aromatics is also present.

Diesel #2 was selected as the most representative fuel for this petroleum type due to its more widespread use in comparison to other fuels. (JP-8 jet fuel is essentially diesel fuel with an increased component of lighter-end compounds.) Based on guidance published by the State of Indiana (IDEM 2010), an assumed, carbon range makeup for Diesel #2 fuel of 0.4% C5-C8 aliphatics, 35.2% C9-C12 aliphatics, 42.5% C19 and greater aliphatics, 14.2% C9-C12 aromatics and 7.7% C13 and higher aromatics was selected for development of soil and groundwater TPH action levels (see Table 6-2a). This is in line with the carbon range makeup of individual chemicals in diesel fuel published by the TPHCWG (TPHCWG 1998).

Selection of a default, carbon range makeup of vapors associated with middle distillates is less straight forward than for gasolines. Published data regarding the specific, carbon range makeup of vapors associated with diesel fuel and other middle distillates is lacking. Vapor headspace chromatograms have been published by a few private entities, however (e.g. Hayes 2007, NCFS 2011). Not surprising given the chemical makeup of middle distillate fuels, the chromatograms suggest a dominance of C12 and greater aliphatic compounds in vapors associated with these fuels, with an accompanying significant amount of C5-C8 aliphatics. The increased presence of the latter in vapor in part reflects the preferential release of lighter-end and more volatile aliphatic compounds from the fuels. Elevated C5-C8 aliphatics in the vapor could also reflect degradation of longer-chain compounds. The

U.S. Geologic Survey (USGS) has documented the latter in groundwater for a diesel release site they have been monitoring since the 1980s (Chaplain et al, 2002). Aromatic compounds, including BTEX and naphthalene make up only a small amount of the total mass of vapor-phase compounds.

Commercial laboratories are only able to reliably report up to C12 aliphatics and C10 aromatics in soil vapor samples collected in summa canisters (e.g., see Hayes 2007). This is because longer-chain vapor compounds tend to condense on the inside of the canisters stick to the sides and not be included in the sample removed for testing. This in turn means that the soil vapor samples collected in summa canisters at middle distillate release sites could significantly under report the total concentration of TPH present in the soil vapor and subsequently under represent the potential vapor intrusion hazard posed by the contamination.

In order to address this potential concern HDOH collected TO-17 sorbent tube soil vapor samples at five key petroleum sites as part of its TPH vapor study (see HDOH 2012a). The TO-17 samples allowed full capture and extraction of the full range of petroleum compounds present in the soil vapor. The samples were collected by drawing a fixed volume of soil vapor (e.g., 50ml) through a narrow tube filled with a carbon-based sorbent material (see Appendix 6). Summa canister samples were also collected at the sites for comparison. The laboratory extracts and measures the mass of targeted VOCs captured by the sorbent material. Dividing this by the volume of soil vapor (or air) drawn through the tube yields the original concentration of the individual VOC in the soil vapor..

Soil vapor data collected by HDOH at several middle distillate release sites in Hawai'i revealed wide variations in the ratio of C5-C8 and C9-C12+ aliphatic compounds between and even within sites (HDOH 2012a; Brewer et al. 2013; see Appendix 6). In some cases C9-C12+ aliphatics dominated, in agreement with published chromatograms for headspace samples over diesel fuel (e.g. Hayes 2007, NCFS 2011). In other cases C5-C8 aliphatics dominated. This may have been in part due to mixing of vapors with nearby gasoline releases and/or the breakdown of longer-chain aliphatics into shorter chain aliphatics at more weather sites. Vapor samples collected over fresh fuels were likewise mixed (see Appendix 6), although it is suspected that the fuel associated with the sample that reported a higher proportion of C5-C8 aliphatics may have been excessively warmed in the sun prior to collection of the vapor sample. The distinct presence of C9-C12+ aliphatics in the soil vapor samples, however, clearly distinguishes sites with middle distillate contamination from gasoline-release sites.

Based on the results of the HEER Office study, an assumed TPH carbon range makeup of vapors associated with middle distillate fuels of 25% C5-C8 aliphatics, 75% C9-C12+ aliphatics and 0% C9-C10 aromatics was selected for development of TPH soil vapor action levels (see Table 6-2b and Appendix 6). This reflects the worst-case sample

collected at diesel-release site and is considered to be conservative, given that the toxicity of longer-chain aliphatics is assumed to be six times greater than shorter-chain aliphatics (see Table 6-3). An assumed dominance of C9-C12+ aliphatic compounds in middle distillate vapors is consistent with published chromatograms for headspace samples over diesel fuel noted above (e.g. Hayes 2007, NCFS 2011). A high percentage of C12+ aliphatics and C10+ aromatics was not, however, identified in the middle distillate sites investigated, even this was predicted by the published chromatograms (maximum 13%, see Appendix 6). This may reflect the fact that the chromatograms reflect vapors collected over fresh fuels.

Small amounts of BTEX and naphthalene were reported in vapor samples collected over fresh fuel. Benzene, naphthalene and other aromatic compounds were present in only trace amounts in soil vapor samples collected at targeted middle distillate release sites, however (generally <0.1%). The ratio of TPH to benzene was typically greater than 1,000:1 and in some cases over 10,000:1. Non-specific aliphatics clearly drove vapor intrusion risks at these sites over individual compounds such as benzene and naphthalene. Testing for only the latter in the soil vapor samples would have significantly underestimated the vapor intrusion risk.

6.2.3 Residual Fuels Distillates

Residual fuels (e.g., Fuel Oil Nos. 4, 5, and 6, lubricating oils, “waste oils”, “oil and grease,” asphalts, etc.) are characterized by complex, polar PAHs, naphthenoaromatics, asphaltenes and other high-molecular-weight, saturated hydrocarbon compounds with carbon ranges that in general fall between C24 and C40. Published data on the specific, aliphatic and aromatic makeup of the TPH fraction of residual fuels after subtracting individual, targeted PAH compounds was not identified for use in this guidance but is expected to vary widely between different products and wastes.

For the purposes of this guidance, and as a conservative measure for risk-based action levels, a TPH carbon range composition of 75% C19+ aliphatics and 25% C17+ aromatics was assumed for estimation of a TPH reference dose for residual fuels and subsequent calculation of risk-based action levels (see Table 6-2a). This is based on the aliphatic-aromatic makeup of lubricating and motor oil presented in Table 13 of the TPHCWG guidance (TPHCWG 1998). Testing for targeted, individual PAHs in addition to TPH at residual fuel release sites is critical. Motor oil that has been heated to high temperatures can contain a significant proportion of carcinogenic, PAH compounds. Significant amounts of PAHs (e.g., naphthalene) could also be present at former gas manufacturing plants, asphalt production facilities, and other sites where PAHs made up a significant proportion of the petroleum product released.

For the purposes of this guidance the makeup of vapors associated with heavy fuels was assumed to be identical to middle distillate vapors, with 25% C5-C8 aliphatics, 75% C9-C12 aliphatics and 0% C9-C10 aromatics (see Table 6-2b). The HEER Office study did not include the review or collection of soil vapor samples at sites contaminated with heavy petroleum fuels or products (e.g., Bunker C fuel oil). Vapor-phase compounds are expected to be dominated by C9-C12+ aliphatics, with little to no BTEX. As is suspected for some middle distillates sites, C5-C8 and even C9-C12 aliphatics could be present as breakdown products of longer-chain hydrocarbon compounds. Naphthalene may be a concern at manufactured gas plant (MGP) sites. The TPH fraction of soil and groundwater contaminated with residual fuels is only likely to pose significant vapor intrusion hazards if gross contamination is situated immediately beneath building floors, especially in comparison to gasoline- and even diesel-contaminated sites (with the exception of MGP sites). Methane buildup may also be a concern at heavy fuel release sites.

Mineral oils used in electrical transformers are highly refined, fractions of crude oil with little to no chemical additives (EPRI 1998). The oils are dominated by C9-C30 aliphatics (approximately 85%) with a lesser amount of non-specific, aromatic compounds (approximately 15%) and overlap the carbon ranges discussed for middle distillates and residual fuels (see Figure 3). The volatile component of mineral oils is significantly lower than that found in middle distillates. The viscosity of the oils is also significantly greater. Carcinogenic PAHs such as benzo(a)pyrene are not present in detectable amounts. Additives including PCBs were included in older formulations of mineral oil but have been banned from new formulations in the 1970s. Releases of mineral oils from electrical transformers are relatively small in comparison to releases of diesel fuels and contamination is generally limited.

6.3 Carbon Range TPH Toxicity Factors and Physiochemical Constants

Carbon range toxicity factors published by Massachusetts (MADEP 2003) and more recently by the USEPA (USEPA 2009) were used to calculate weighted inhalation and oral toxicity factors for each of the three noted TPH categories, based on the assumed aliphatic and aromatic makeup of each category. A summary of toxicity factors selected for the each of the targeted carbon ranges is provided in Table 6.3. The following equations were used to calculate weighted Reference Concentrations and Reference Doses (see ODEQ 2003):

Weighted RfC ($\mu\text{g}/\text{m}^3$) =

$$\frac{1}{\left[\left(\frac{\text{FractionC5} \cdot 8\text{aliphatics}}{\text{C5} \cdot 8\text{aliphaticsRfC}} \right) + \left(\frac{\text{FractionC9} \cdot 12 + \text{aliphatics}}{\text{C9} \cdot 12 + \text{aliphaticsRfC}} \right) + \left(\frac{\text{FractionC9} \cdot 10 + \text{aromatics}}{\text{C9} \cdot 10\text{aromatics} + \text{RfC}} \right) \right]}$$

Weighted RfD (mg/kg-day) =

$$\frac{1}{\left[\left(\frac{\text{FractionC5} \cdot 8\text{aliphatics}}{\text{C5} \cdot 8\text{aliphaticsRfD}} \right) + \left(\frac{\text{FractionC9} \cdot 12 + \text{aliphatics}}{\text{C9} \cdot 12 + \text{aliphaticsRfD}} \right) + \left(\frac{\text{FractionC19} + \text{aliphatics}}{\text{C19} + \text{aliphaticsRfD}} \right) + \left(\frac{\text{FractionC9} \cdot 10 + \text{aromatics}}{\text{C9} \cdot 10\text{aromatics} + \text{RfD}} \right) \right]}$$

As noted in Table 6-4, weighted, oral Reference Doses of 0.03, 0.02 and 0.12 mg/kg-day were calculated for TPHgasolines, TPHmiddle distillates and TPHresidual fuels, respectively, based on the assumed carbon range makeup of the petroleum products. Weighted, inhalation Reference Concentrations of 571 $\mu\text{g}/\text{m}^3$ and 126 $\mu\text{g}/\text{m}^3$ were calculated for TPHgasolines and TPHmiddle distillates, respectively.

Default physiochemical constant values for TPHg and TPHd were revised to reflect default parameter values for C9-C10 aromatics published by Massachusetts DEP (see Table H, MADEP 1997, 2002). This is primarily a factor for the soil leaching models and reflects the anticipated, preferential dissolution of more soluble and less volatile aromatic compounds into infiltrating surface water. A cap of 5,000 mg/kg was applied to leaching based screening levels due to uncertainty regarding the utility of the model at high concentrations. Reference to C9-C10 parameter values is intended to reflect the increased mobility of TPH and TPH degradation products warranted deference to more mobile aromatic compounds, primarily with respect to the assumed sorption coefficient (k_{oc}). The increase in mobility with degradation is also reflected in application the default solubility for C9-C10 aromatics of 51 mg/L to TPHd. This is significantly higher than a solubility for fresh product of approximately 5 mg/L (USACE 1998).

As summarized below, these toxicity factors and physiochemical constants were used to develop soil vapor, soil and groundwater TPH action levels. Risk-based action levels for TPH are based on a target, noncancer Hazard Quotient of 1.0. This is based on an assumption that TPH represents the primary noncancer risk posed by petroleum-contaminated soil, soil vapor and groundwater due to the overwhelming mass of hydrocarbon compounds included in the analysis (see Section 1.4 and Appendix 6).

6.4 TPH Action Levels for Indoor Air and Soil Vapor

Preliminary, risk-based action levels for TPHgasolines and TPH middle distillates in indoor air and soil vapor as were calculated in the same manner as done for other volatile chemicals but with the use of a target, noncancer Hazard Quotient of 1.0 (see above and equations in Appendix 2). An indoor action level of 290 $\mu\text{g}/\text{m}^3$ was calculated for TPHgasolines. An indoor action level of 130 $\mu\text{g}/\text{m}^3$ was calculated for TPHmiddle

distillates. Soil vapor action levels were calculated using the default, Indoor Air:Soil vapor attenuation factors discussed in Section 2 (Residential: 1/2,000, Commercial/Industrial: 1/4,000). This generates residential soil vapor action levels of 590,000 $\mu\text{g}/\text{m}^3$ for TPHgasolines and 260,000 $\mu\text{g}/\text{m}^3$ for TPHmiddle distillates (Table 6-5; soil vapor action levels for carbon ranges also provided). Commercial/Industrial action levels are much higher-4,900,000 $\mu\text{g}/\text{m}^3$ for TPHgasolines and 2,200,000 $\mu\text{g}/\text{m}^3$ for TPHmiddle distillates. This is due to both an adult-only exposure scenario and an average, daily exposure time of 8 hours instead of 24 hours (see Appendix 2).

Petroleum release sites often contain a mix of fuels. Vapors in soil vapor could likewise be a mix of several fuel types. Applying soil vapor (and indoor air) action levels for gasolines versus middle distillate fuels is therefore not straightforward. The default, carbon range makeup assumed in the action levels can be re-evaluated on a site-specific basis as needed. Note also that the TPH indoor air action levels could be below ambient background levels for indoor and outdoor air, due to the use of petroleum-based cleaners, auto exhaust, etc.

The soil vapor action levels do not take into account an expected reduction in concentration and associated risk over time due to biodegradation. This is also true for risk-based, TPH soil action levels presented in the Table I series. This can be evaluated on a site-specific basis as needed.

The collection and evaluation of soil vapor samples at sites impacted with residual fuels is warranted where heavy contamination is to be left in place (see HDOH 2007). Soil vapor action levels for vapors associated with TPHmiddle distillates should be applied in the absence of soil vapor carbon range data. This will help to rule out potential vapor intrusion hazards and ensure that other sources of petroleum contamination were not missed.

6.5 TPH Action Levels for Soil

6.5.1 TPH (gasolines, middle distillates)

Risk-based, direct-exposure action levels for TPHgasolines and TPHmiddle distillates in soil can be calculated in the same manner as done for individual chemicals, using the toxicity factors noted above and physiochemical constants noted in Table H (see Chapter 4). The model calculated residential direct-exposure soil action levels of 450 mg/kg and 220 mg/kg using this approach, respectively. These action levels are highly conservative. This is especially true for soil exposed at the surface, where offgassing and biodegradation is likely to be significant.

As discussed in Chapter 4, maximum, direct-exposure action levels for volatile liquids in soil are normally set equal to the contaminants theoretical soil saturation level or Csat (e.g., refer to xylene action levels in Table I series). This represents the concentration above which the contaminant can no longer be sorbed to soil particles (e.g., organic carbon or clay) or dissolved into the soil moisture (e.g., solubility limits reached). Above this concentration, free product will be present in the soil. This approach was also used to establish Csat and maximum direct-exposure action levels for TPHg and TPHd. (refer to Table I series). Residual fuels are not considered to pose significant vapor emission hazards other than the potential generation of methane and related explosion hazards (refer to Volume 1).

As discussed in Section 6.3, physio-chemical constants for the C9-C10 aromatics carbon range fraction developed by Massachusetts were referred to for calculation of soil screening levels for TPHg and TPHd (MADEP 2002b, refer to Section 6.3). Ceiling levels for nuisance and other gross contamination concerns developed by Massachusetts for TPH as gasoline and diesel (latter included under "middle distillates") were modified for use in this document (MADEP 1997a,b, refer to Table F series). Based on calculated "odor indexes", a shallow soil ceiling level of 100 mg/kg was selected for unrestricted ("residential") land-use scenarios and a ceiling level of 500 mg/kg was selected for commercial/industrial land-use (both categories of TPH). For deep soils, a ceiling level of 5,000 mg/kg was retained (primarily intended to prevent the presence of potentially mobile free product in soil).

6.5.2 TPH (residual fuels)

Risk-based, direct-exposure action levels for TPH as residual fuels were calculated in the same manner as done for individual chemicals, using the toxicity factors and physiochemical constants noted earlier. The action levels developed incorporate the Particulate Emission Factor used by USEPA to calculate RSLs for nonvolatile contaminants (USEPA 2017a, refer to Appendix 2). Risk-based action levels for TPH residual fuels in drinking water and soil were then developed in the same manner as done for other chemicals (Table D-3 and Table I series, respectively). As discussed in Volume 1, testing for individual, target indicator compounds is also recommended for soil and groundwater contaminated by heavy fuels (e.g., PAHs, heavy metals, etc.).

Individual PAHs are likely to drive health risks posed by soils contaminated with residual fuels. The non-specific, TPH fraction of the petroleum may, however, pose gross contamination concerns even in the absence of significant PAHs. Following Massachusetts DEP guidance (MADEP 1997a,b), ceiling levels for gross contamination concerns of 500 mg/kg and 2,500 mg/kg were selected for exposed or potentially exposed soils in

unrestricted (“residential”) and commercial/industrial land use scenarios, respectively (see Table F series). The MADEP ceiling level of 5,000 mg/kg was selected for isolated or otherwise deep soils.

The Massachusetts DEP did not develop specific action levels for leaching of heavy hydrocarbons from soil (refer to C19-C36 carbon range summary in Appendix 6). Residual fuels are by definition characterized by a predominance hydrocarbon compounds with carbon ranges greater than C24. These compounds are considered to be substantially less mobile in the subsurface than hydrocarbon compounds that make up the lighter-weight petroleum mixtures. For TPH that is characterized by a predominance of C23-C32 carbon range compounds, the California EPA Los Angeles Regional Water Board proposed an action level of 1,000 mg/kg for protection of drinking water resources (RWQCBLA 1996). This action level was adopted for use in this document (refer to Table E). The target TPH action level for groundwater was not specifically stated but was presumably 100 µg/L, an informal action level in use at that time. The action level is likely to be highly conservative, given the relative immobility of heavier hydrocarbons in soil.

The Los Angeles Regional Water Quality Control Board did not present a similar action level for potential leaching of TPH from soil and subsequent discharge of impacted groundwater to a body of surface water. The TPHd action level of 1,500 mg/kg was adopted for reference in this guidance (see Table E, refer also to Section 4.4).

The toxicity of mineral oils and vegetable oils is low. The oils are more viscous and less volatile than fuels. Significant vapor emissions from contaminated soil and groundwater are not anticipated, although methane buildup could be a concern for very large, subsurface releases. For the purpose of this guidance and in order to address potential gross contamination concerns, a TPH action level of 5,000 mg/kg is recommended for exposed soils or soils within three feet of the ground surface that has been contaminated with mineral or vegetable oil. For deeper soils an action level of 25,000 mg/kg is recommended. Refer also to the HEER Office 2007 guidance for the long-term management of petroleum-contaminated sites (HDOH 2007). These action levels are not specifically called out in the EAL lookup tables. Soil and other media contaminated by releases of oil from electrical equipment should also be tested for PCBs unless it can be demonstrated that PCB-based oils were never used in the equipment.

6.6 TPH Action levels For Groundwater

Regulatory drinking water standards for TPH and petroleum in general have not been developed. Toxicity-based drinking water goals of 300 µg/L for gasoline, 400 µg/L for middle distillates (e.g., diesel) and 2,400 µg/L for residual fuels were developed using on the USEPA RSL Tapwater model and the above-noted toxicity factors (refer to Table F-

3). The action level for TPHgasoline considered exposure via both ingestion and inhalation of vapors, as called for in the USEPA RSL model for volatile chemicals. The action level for TPHmiddle distillates assumes that petroleum-related compounds reported in this range will be dominated by non-volatile, degradation compounds or “metabolites” of biogenic origin (Zemo et al. 2013, 2016). The resulting action level is therefore based on ingestion only and does not incorporate an inhalation pathway. Petroleum-related, degradation compounds are assumed to have a similar toxicity as the parent hydrocarbon compounds for the purpose of this document, unless otherwise demonstrated in a site-specific risk assessment (refer to Volume 1, Section 2.5.1).

Past HDOH guidance presented a taste and odor threshold for TPH in drinking water of 100 µg/L TPHgasoline. This was based on a taste and odor threshold or “Suggested No Adverse Response Level (SNARL)” for kerosene in drinking water published by the USEPA (1980). A review of the original source documents (in Polish and Russian) by Zemo and O’Reilly (2016) identified flaws in the derivation of this threshold.

A closer review of the original references reviewed to develop the SNARL suggests that this threshold could be too low for some types of petroleum (Zemo and Reilly 2016). Most of the research was carried out in the 1940s to 1960s. The representativeness of the petroleum formulations in the studies of more recent fuels is uncertain. McFee and Wolfe (1963) reference odor thresholds for drinking water that range from 10 µg/L to 2,000 µg/L for gasoline, 82 µg/L to 667 µg/L for kerosene and heating oil, and 500 µg/L to 25,000 µg/L for heavier oils. Additional screening levels of 100 µg/L to 500 µg/L are referenced for “unrefined petroleum,” with screening levels of 1,000 µg/L to 2,000 µg/L noted for “refined petroleum.” Based on the studies presented, a taste and odor threshold for refined, low- to mid-range petroleum fuels of 500 µg/L is reasonable for initial screening purposes (see Table G-1). The adequacy of this threshold should be verified if impacts to actively used sources of drinking water are identified.

This is marginally above toxicity-based action levels for TPH in drinking water and suggests that exposure to potentially significant levels of TPH in drinking water will be readily noticeable by the user (see Tables D-1a and D-1b).

For the protection of aquatic life, an action level of 500 µg/L was selected for TPH-gasoline in freshwater and 3,700 µg/L in saltwater (see Table D-4b). A single action level of 640 µg/L was selected for TPH-diesel and TPH-residual fuels in both freshwater and saltwater. The freshwater action level for TPH-gasoline is based on a summary of available ecotoxicity data compiled for use at the Presidio of San Francisco under Regional Water Board Order 96-070 (RWQCBSF 1998b, Montgomery Watson 1999). The TPH-gasoline criteria for saltwater and the TPH criteria for diesel and residual fuels in general are based on action levels developed for use at the San Francisco Airport under Regional Water Quality Control Board Order No. 99-045 (RWQCBSF 1999a).

The groundwater nuisance and odor concerns action level of 5,000 µg/L for TPH (all categories) noted in the Table G series for nondrinking water was taken directly from Massachusetts DEP risk assessment guidance (MADEP 1997a,b). MADEP lists a gross contamination, "Ceiling Value" of 50,000 µg/L for all aliphatic and aromatic carbon ranges. This includes an assumed, dilution factor of "10", however. The dilution factor was omitted for used in the action levels, since as a default groundwater should meet surface water action levels at the point of discharge, both for aquatic toxicity and potential nuisance concerns. This also corresponds with the approximate solubility of diesel fuel and light motor oil in fresh water (ATSDR 2001) and is intended to address potential nuisance issues (odors, etc.) if discharged to surface water. The TPH ceiling levels for gross contamination concerns are based on 1/2 the solubility of the respective TPH categories (refer to Table G series). The solubility of gasoline in freshwater is approximately 150,000 µg/L. The solubility of diesel range and heavier fuels is assumed to be approximately 5,000 µg/L. These action levels are intended to highlight the potential presence of free product on groundwater.

6.7 Additional Target Indicator Compounds

Laboratory measurement and assessment of each individual compound within a petroleum mixture is technically complex and generally not feasible or appropriate under most circumstances. More importantly, data regarding the physio-chemical and toxicity characteristics of the majority of petroleum compounds are lacking. Impacts to soil and water from petroleum mixtures are instead evaluated in terms of both TPH and well characterized "indicator chemicals" (e.g., benzene, toluene, ethylbenzene, xylenes and targeted PAHs). Indicator chemicals typically recommended for petroleum mixtures include (after CalEPA 1996):

Monocyclic Aromatic Compounds (primarily gasolines and middle distillates)

- benzene
- ethylbenzene
- toluene
- xylene

Fuel additives (primarily gasolines)

- MTBE
- other oxygenates as necessary

Polycyclic Aromatic Compounds (primarily middle distillates and residual fuels)

- methylnaphthalene (1- and 2-)
- acenaphthene
- acenaphthylene
- anthracene
- benzo(a)anthracene

- benzo(b)fluoranthene
- benzo(g,h,i)perylene
- benzo(a)pyrene
- benzo(k)fluoranthene
- chrysene
- dibenzo(a,h)anthracene
- fluoranthene
- fluorene
- indeno(1,2,3)pyrene
- naphthalene
- phenanthrene
- pyrene.

The TPH EALs should be used in conjunction with EALs for these chemicals. Note that volatile chemicals such as butylbenzene, isopropyl benzene, isopropyl toluene and trimethylbenzenes are often reported in analyses of gasoline and other light-end petroleum products. These chemicals are collectively addressed under action levels for “TPH” and generally do not need to be evaluated separately.

Soil and groundwater impacted by releases of waste oil may also require testing for heavy metals and chemicals such as chlorinated solvents and PCBs. Action levels for these chemicals are included in the lookup tables.

6.8 Ethanol

Gasoline formulations are anticipated to include an increasing proportion of ethanol in the near future. Soil, soil vapor, indoor air and groundwater action levels for ethanol have therefore been added to the EAL document. Human-health, chronic toxicity factors for ethanol have not been developed. Ethanol is not considered to pose chronic health risks at the low doses posed by exposure to contaminated soil and groundwater. The action levels are therefore based only on nuisance and gross contamination concerns. “Ceiling Levels” for these concerns are presented in Tables F (soil and indoor air) and I (groundwater and surface water). The final action level for each of the groundwater categories is based on an “Upper Limit” of 50 mg/L (Table G series, see also Tables D-1a and F-1b). The final soil action level presented in each of the soil categories of 45 mg/kg is based on the protection of groundwater to the noted target groundwater action level (Table E, see also Table A and B series). The leaching based action level was adjusted upwards by a factor of 10 to take into account the high, anticipated biodegradation rate of ethanol in the environment. The adequacy of this action level should be further evaluated in the field as appropriate (e.g., sites near producing water wells or bodies of surface water). The indoor air action level of 19,200 $\mu\text{g}/\text{m}^3$ (10 ppmv) is based on the published odor threshold potential for ethanol (Table F series, see also Table C-3). This concentration is well below the Occupational

Safety and Health Administration (OSHA) Permissible Exposure Limit (PEL) of 1,000 ppmv for workers.

Although highly mobile in the environment, ethanol is also highly biodegradable, not significantly toxic in low dose, and is likely to only persist in the presence of other, more toxic components of gasoline, including benzene (Ulrich 1999). An assessment and cleanup of contaminated soil and groundwater to address health threats posed by associated compounds is expected to address any potential health concerns posed by exposure to residual ethanol in soil, air or water.

Table 6-1. Target analytes for petroleum contaminated media (see also Section 9 of the HEER office *Technical Guidance Manual*; HDOH 2009).

| Petroleum Product | Media | Recommended Target Analytes |
|--|--------------|--|
| Gasolines | Soil | TPH, BTEX, naphthalene, MTBE and appropriate additives and breakdown products (e.g., DBA, TBA, lead, ethanol, etc.) |
| | Soil Vapor | Same as soil plus volatile additives and methane |
| | Groundwater | Same as soil |
| Middle Distillates (diesel, kerosene, Stoddard solvent, heating fuels, jet fuel, etc.) | Soil | TPH, BTEX, naphthalene, and methylnaphthalenes (1- and 2-) |
| | Soil Vapor | TPH, BTEX, naphthalene, and methane |
| | Groundwater | Same as soil |
| Residual Fuels (lube oils, hydraulic oils, transformer oils, Fuel Oil #6/Bunker C, waste oil, etc.) | Soil | TPH, *VOCs, naphthalene, methylnaphthalenes (1- and 2-), the remaining 16 priority pollutant PAHs, PCBs, and heavy metals unless otherwise justified |
| | Soil Vapor | TPH, BTEX, naphthalene, and methane |
| | Groundwater | same as soil |

*VOCs include BTEX and chlorinated solvent compounds

Table 6-2a. Default carbon range makeup of TPH in petroleum fuels (after IDEM 2010).

| Carbon Range | ¹ TPH _{gasoline} | ¹ TPH _{diesel} | ² TPH _{resfuels} |
|-------------------|--------------------------------------|------------------------------------|--------------------------------------|
| C5-C8 aliphatics | 45% | 0.4% | 0% |
| C9-C18 aliphatics | 12% | 35.2% | 0% |
| C19+ aliphatics | 0% | 42.6% | 75% |
| C9-C16 aromatics | 43% | 21.8% | 25% |

1. Indiana Department of Environmental management (IDEM 2010).

2. Massachusetts DEP (MADEP 1997).

Table 6-2b. Default carbon range makeup of TPH in petroleum fuel vapors.

| Carbon Range | ¹ TPH _{gasoline} | ¹ TPH _{diesel} |
|-------------------|--------------------------------------|------------------------------------|
| C5-C8 aliphatics | 77.3% | 25% |
| C9-C18 aliphatics | 7.3% | 75% |
| C9-C16 aromatics | 15.4% | 0% |

1. Median carbon range makeup of gasoline vapors in USEPA 2013 Petroleum Vapor Intrusion database (see Brewer et al. 2013; Appendix 6).

2. HDOH soil vapors study and published information (see Brewer et al. 2013; Appendix 6).

Table 6-3. Selected toxicity factors of for individual carbon range fractions.

| Carbon Range | RfD _{oral} (mg/kg-day) | RfC (µg/m ³) |
|-------------------|------------------------------------|-----------------------------|
| C5-C8 aliphatics | ^b 0.04 | ^a 600 |
| C9-C18 aliphatics | ^a 0.01 | ^a 100 |
| C19+ aliphatics | ^a 3.0 | ^c nv |
| C9+ aromatics | ^a 0.03 | ^a 100 |

a. USEPA 2009

b. MADEP 2003

c. Not significantly volatile. C17+ aromatics not considered separately.

Table 6-4. Weighted TPH toxicity factors for fuels and fuel vapors.

| Carbon Range | RfD _{oral} (mg/kg-day) | RfC (µg/m ³) |
|-----------------------------------|------------------------------------|-----------------------------|
| TPH _{gasolines} | 0.03 | 281 |
| TPH _{middle distillates} | 0.02 | 126 |
| TPH _{residual fuels} | 0.12 | - |

Table 6-5a. Indoor Air and Soil vapor Carbon Range action levels.

| Carbon Range | ¹Indoor Air | | ¹Subslab Soil vapor | |
|---------------------|--|---|--|---|
| | Residential ($\mu\text{g}/\text{m}^3$) | Commercial/ Industrial ($\mu\text{g}/\text{m}^3$) | Residential ($\mu\text{g}/\text{m}^3$) | Commercial/ Industrial ($\mu\text{g}/\text{m}^3$) |
| C5-C8 aliphatics | 630 | 2,600 | 1,300,000 | 11,700,000 |
| C9-C18 aliphatics | 100 | 440 | 210,000 | 1,800,000 |
| C19+ aliphatics | - | - | - | - |
| C9+ aromatics | 100 | 440 | 210,000 | 1,800,000 |

1. Assumed indoor air:subslab vapor attenuation factor: Residential = 0.0005; C/I = 0.00025 (see Section 3.3). Noncancer Hazard Quotient = 1.0. Calculate cumulative risk if used to evaluate site-specific carbon range data for soil vapor.

Table 6-5b Indoor Air and Soil vapor TPH action levels.

| Carbon Range | Indoor Air | | Subslab Soil vapor | |
|--|--|---|--|---|
| | Residential ($\mu\text{g}/\text{m}^3$) | Commercial/ Industrial ($\mu\text{g}/\text{m}^3$) | Residential ($\mu\text{g}/\text{m}^3$) | Commercial/ Industrial ($\mu\text{g}/\text{m}^3$) |
| TPH _{gasolines} | 290 | 1,200 | 590,000 | 4,900,000 |
| TPH _{middle distillates} | 130 | 330 | 260,000 | 2,200,000 |
| ¹ TPH _{residual fuels} | - | - | - | - |

1. Use TPH_{middle distillate} indoor air and soil vapor action levels at sites contaminated with residual fuels if vapors present.

7 Other Issues

7.1 Background Concentrations

EALs should be replaced with the natural background concentration of the chemical if the background value is higher. Table K presents a summary of natural, background metals for soils in Hawai'i based on a study and compilation of existing data carried out in 2011 (focus on volcanic soils; HDOH 2011). Naturally occurring, background concentrations of metals in soil exceed risk-based action levels in some cases. This is especially true for arsenic, but can also occur for heavy metal such as thallium, vanadium and other metals associated with soils developed over basaltic bedrock (compare direct-exposure action levels in Table I-1 to background levels in Table K). The 2011 report includes a summary of previous background metal documents published by the Air Force (USAF 2005) and Navy (USN 2006) environmental programs in Hawai'i. A summary of background concentrations of metals in various soil types on the mainland US has been published by the University of California (UCR 1996) and Lawrence Berkeley National Laboratory (LBNL 2002).

The risk-based action level for arsenic for soils in an unrestricted (“residential”) land use scenario is 0.42 mg/kg (refer to Table I-1). This purely risk-based action level is based on an assumed bioavailability of arsenic in soil of 100%. This is unrealistic for most soils and especially iron-rich, volcanic soils in Hawai'i, since arsenic will tightly bind to iron in soil and not be available for uptake if the soil is incidentally ingested (see HDOH 2011b). Background concentrations of arsenic in soils in Hawai'i typically range from 5 mg/kg to 24 mg/kg (see above references). A default, upperbound background concentration of 24 mg/kg arsenic is incorporated into the lookup tables (Table K; see also Table A and B series). Soils with total arsenic that exceed this concentration should be tested for bioaccessible arsenic (see HDOH 2011b). Upper threshold values of arsenic in soil can approach 40 to 50 mg/kg, especially in discrete samples. Concentrations of arsenic in soil tend to be higher in soils associated with silicic volcanic rocks (not present in Hawai'i) and hydrothermally altered rocks (e.g., UCR 1996, LBNL 2002).

Background concentrations of total chromium in soil developed over basaltic bedrock can exceed several hundred ppm and in some areas up to several thousand ppm (HDOH 2011a). An upperbound, total chromium concentration of 1,100 mg/kg was selected to help to screen out sites where releases of chromium used as a screening can be assumed (see Table K; applies to volcanic soils). Note that background concentrations of total chromium in soils developed over caprock can be lower than 100 mg/kg. If a release of chromium VI is suspected then chromium should be speciated and evaluated even if total chromium concentrations do not exceed this action level.

Available background soil data for thallium suggest that this metal is generally not detectable in the volcanic soils of Hawaii (<0.25 mg/kg). Data are lacking, however, with only ten samples referenced in the 2011 HEER Office study (HDOH 2011a). Thallium was reported at 12 to 15 mg/kg in two samples, however. No anthropogenic source is known at these two sample sites. Nonetheless, a default background concentration of 0.25 mg/kg was selected for consideration in the Tier 1 EALs due to the high toxicity of thallium salts and the associated low action level for potential direct exposure hazards (e.g., 0.78 mg/kg for residential exposure scenarios). The potential release of thallium salts should be evaluated at sites where the reported level of thallium in soil exceeds this concentration. It is reasonable to assume that the thallium is naturally occurring and non-toxic for reported concentrations in soil between 0.25 and 15 mg/kg when there is no reason to suspect a release of thallium salts.

7.2 Laboratory Reporting Levels

Laboratory method reporting limits and background concentrations of chemicals were not directly considered in development of the lookup tables. As discussed in Volume 1 of this document, however, reporting limits approved by the overseeing regulatory agency should be used in place of the EALs presented in this document when higher.

7.3 Reporting of Soil Data

Soil data are calculated by dividing the mass of the chemical of concern detected in the soil by the total weight of the soil. The weight of a soil sample can be measured on either a dry-weight basis (i.e., excluding the weight of water in the soil sample) or a wet-weight basis (i.e., including the weight of water in the soil sample). For a typical soil sample, the inclusion of soil moisture in calculation of chemical concentrations can effectively reduce the reported concentrations by 10-20% or greater, simply because the measured total weight of the sample is greater.

From a site-investigation and risk assessment-standpoint, a difference in the reported concentration of a chemical of 10-20% is not necessarily significant. **For consistency and for comparison to soil EALs presented in this document, however, soil data should be reported on dry-weight basis.** This is in part because soil ingestion rates assumed in direct-exposure models (see Appendices 1 and 2) are based on dry-weight studies (USEPA 2011c). Comparison of wet-weight data to direct-exposure action level would technically require adjustment of the direct-exposure action levels to reflect wet weight-based soil ingestion rates. A site-specific consideration of wet-weight soil data will be dependent on assumptions in the model(s) being used to evaluate risk or generate environmental action levels. Existing wet-weight soil data may not necessarily need to be adjusted prior to comparison to the EALs unless the introduced bias is considered to be a potentially

significant factor at the site. (Note that sediment data should also be reported on a dry-weight basis.)

7.4 Additional Soil Parameters

For surface soils, action levels are also presented for Electrical Conductivity and Sodium Absorption Ratio (after MOEE 1996). Both parameters are intended primarily for evaluation of soils impacted by brines (e.g., from former salt ponds and discharges of brackish groundwater). The Sodium Absorption Ratio reflects the amount of sodium present in the soil with respect to other major cations. An overabundance of sodium can inhibit plant uptake of nutrients, reduce soil cohesion and cause excessive erosion of topsoil. The electrical conductivity of a soil reflects the total concentration of soluble salts in the soil solution. A high concentration of salts can have a significant influence on osmotic processes involved in plant growth. (NOTE: The Electrical Conductivity action levels assumes a fixed 2:1 water:soil solution in the laboratory method. The USEPA Laboratory Method 120.1(Mod) normally calls for a 1:1 dilution ratio, i.e., extract from a saturated sample. The laboratory should be notified of the need for a 2:1 dilution ratio prior to analysis.)

7.5 Degradation to Daughter Products

Consideration of the degradation of a chemical to more toxic daughter products, such as the breakdown of PCE to vinyl chloride, is an important part of site investigations. Degradation can be significant at sites where groundwater is contaminated with both chlorinated solvents and petroleum fuels (e.g., resulting from the past use of stoddard solvent at a dry cleaning facility). Elevated levels of trichloroethylene, dichloroethylene and/or vinyl chloride at a PCE-release site generally indicate the presence of co-mingled petroleum contamination and the need to test for petroleum-related compounds refer to Figure 2-4 in Volume 1).

Tier 1 lookup tables generated by the Massachusetts Department of Environmental Protection (MADEP) and other regulatory agencies incorporate a very conservative assumption that the entire mass of a parent chemical will be eventually be transformed to the daughter product at the same initial concentration (e.g., MADEP 1994, MOEE 1996). MADEP reduces the initially derived action levels for parent compounds to reflect the action levels for the more toxic daughter product, without taking into account issues such as the lower molecular weights (and lower ultimate masses) of the daughter products.

Degradation to potentially more toxic daughter products is not directly considered in the Tier 1 EALs presented in this guidance document. While the need to monitor for degradation byproducts is well founded, HDOH feels that the MADEP approach is

excessively conservative and not reflective of the wide range of conditions at different sites. As an alternative, HDOH recommends that soil and groundwater samples be tested for both parent and daughter products. HDOH also strongly recommends the collection of soil vapor data at sites where initial soil or groundwater data suggests that volatile contaminants could pose potential vapor intrusion hazards (refer to Section 2.0 and Volume 1, Section 4.4, as well as the HEER *Technical Guidance Manual*).

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FIGURES

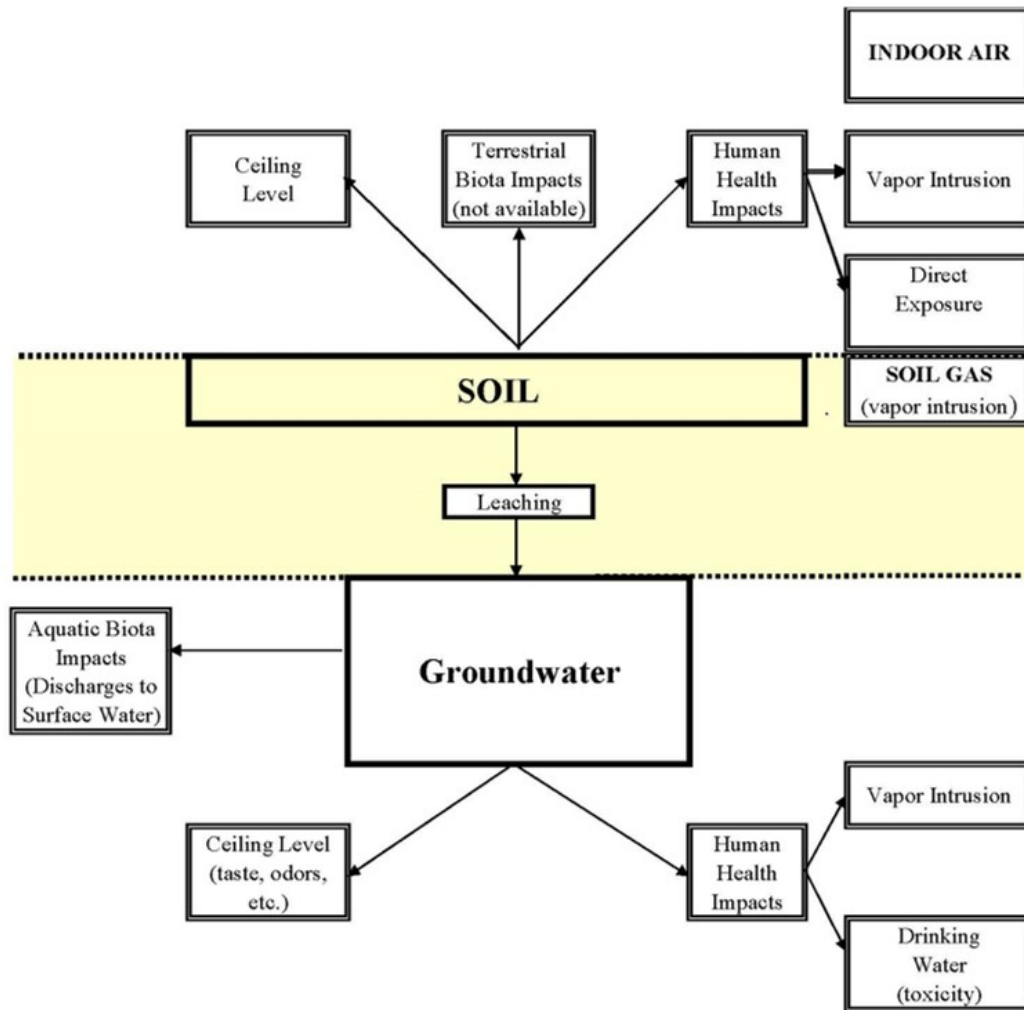


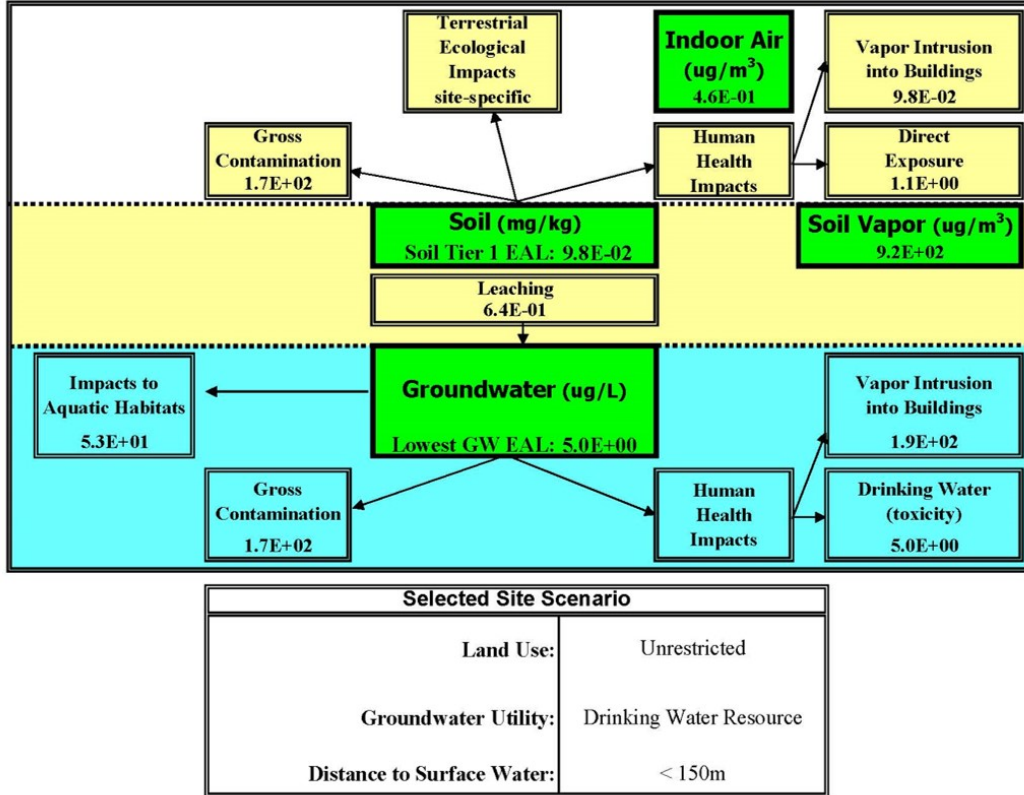
Figure 1. Summary of environmental hazards considered in action levels. Additional site-specific considerations include groundwater beneficial use, depth to impacted soil, soil type and land use. Evaluation of environmental hazards in addition to those shown should be carried out in a site-specific EHE.

**Tier 1 Environmental Action Levels Surfer
(Screening Levels For Specific Environmental Hazards)**

Hawai'i DOH (Summer 2016)



TETRACHLOROETHYLENE



3. EAL Surfer - De

Figure 2. Summary of individual action levels used to select final, Tier 1 EALs for tetrachloroethylene (PCE) in soils situated within 10 feet of the ground surface and in groundwater that is a current or potential source of drinking water; based on a residential land-use scenario. Final EALs presented in Volume 1 summary tables are the lowest of the individual action levels. Vapor intrusion concerns drive selection of the final soil Tier 1 EAL (0.098 mg/kg). For groundwater, drinking water toxicity concerns drive selection of final Tier 1 EAL (5.0 ug/L).

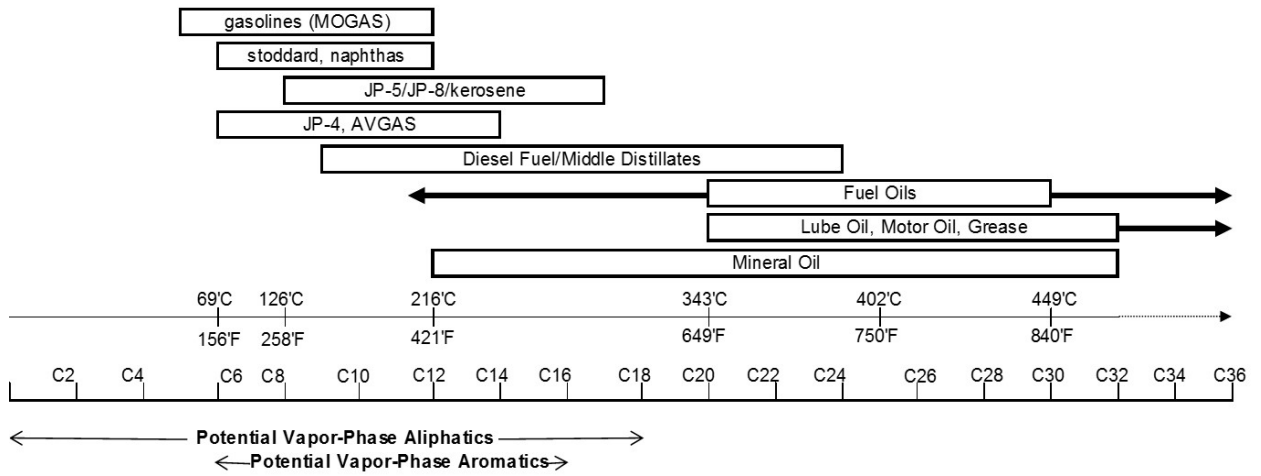


Figure 3. Fuel types versus carbon range composition.

DETAILED ACTION LEVEL TABLES

