

SECTION 9 SUPPLEMENTAL GUIDANCE FOR SELECT CONTAMINANTS OF CONCERN

Interim Final - April 2014

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SECTION 9 ACRONYMS AND ABBREVIATIONS

μm	Micrometers (micron)
2,4,5-T	2,4,5-trichlorophenoxyacetic acid
2,4,5-TP	2,4,5-trichlorophenoxypropionic acid
ΑΡΙ	American Petroleum Institute
ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	Benzene, toluene, ethylbenzene, and total xylenes
CalEPA	California Environmental Protection Agency
cm³/g	cubic centimeters per gram
D-D	A mixture of 1,2-dichloropropane; 1,3-dichloropropene; and 2,3-dichloropropene
DBCP	1,2-dibromo-3-chloropropane
DDT	dichloro-diphenyl-trichloroethane
EAL	Environmental Action Level
EDB	1,2-dibromoethane
EHE	Environmental Hazard Evaluation
GC/MS	Gas Chromatography-Mass Spectrometry
HDOA	Hawai'i Department of Agriculture
HDOH	Hawai'i Department of Health
HEER Office	Hazard Evaluation and Emergency Response Office
Кос	organic carbon sorption coefficient
m³/mol	cubic meters per mole
MADEP	Massachusetts Department of Environmental Protection
mg/kg	Milligrams per kilogram
MSMA	monosodium methane arsenate
MTBE	Methyl tertiary butyl ether
NEIWPCC	New England Interstate Water Pollution Control Commission
NOAA	National Oceanic and Atmospheric Administration
NTP	National Toxicology Program
РСВ	Polychlorinated Biphenyl
PCP	Pentachlorophenol
RSL	Regional Screening Level
SVOC	Semi-volatile organic compound
ТСР	1,2,3-trichloropropane
TEF	Toxicity Equivalence Factor
Telone	1,3-dichloropropene
TEQ	Toxic Equivalency
TGM	Technical Guidance Manual
ТРН	Total Petroleum Hydrocarbons
түн	Total Volatile Hydrocarbons
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

WHO World Health Organization



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9.0 SUPPLEMENTAL GUIDANCE FOR SELECT CONTAMINANTS OF CONCERN

This section presents guidance for select contaminants frequently encountered in Hawai'i, including target pesticides at former agricultural facilities/fields as well as non-agricultural sites, and of target petroleum-related contaminants. Additional guidance on these contaminants is provided in the fall 2011 edition (and updates) of the Hawai'i Department of Health (HDOH) document *Screening for Environmental Hazards at Sites with Contaminated Soil and Groundwater* (Environmental Hazard Evaluation [EHE] guidance [HDOH, 2016]). In the EHE guidance, refer specifically to:

- Volume 1, Chapter 2, Subsection 2.6: Contaminants of Potential Concern at Petroleum Release Sites.
- Volume 1, Chapter 2, Subsection 2.7: Contaminants of Potential Concern for Former Agricultural Lands.
- Volume 1, Chapter 4: Advanced Environmental Hazard Evaluations.

Section 9 also includes information on methane, background metals in soils, and methamphetamine laboratory cleanup.



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9.1 PESTICIDE CONTAMINATION AT FORMER AGRICULTURAL FACILITIES AND SITES

The Hazard Evaluation and Emergency Response (HEER) Office recommends that sites with known pesticide-related contamination and also those where pesticides were regularly applied be evaluated for residual contamination prior to redevelopment. "Pesticides" is a general term that includes any type of chemical mixture specifically formulated to kill "pests." Pesticides commonly used in Hawai`i include herbicides, fungicides and insecticides, the latter including termiticides and nematocides.

This section presents specific guidance regarding former sugarcane and pineapple operations because these were Hawai'i's most significant commercial agricultural crops during the 19th and 20th centuries. HDOH has created maps of former sugarcane lands in the Hawaiian islands in the early 20th century that can be accessed on the HEER Office <u>soil arsenic information</u> <u>webpage</u>. Between sugarcane and pineapple operations, these two industries cultivated as much as 250,000 acres of Hawai'i's farmlands (at the peak of production in the 1920s). However, it may be necessary to evaluate additional pesticides that could pose an unacceptable risk to human health and the environment. Large areas of former agricultural land are currently under consideration for residential and commercial development. Strategies for investigating former agricultural operations are discussed in <u>Section 3</u> and <u>Section 4</u>.

The criteria for selecting a target pesticide for a soil investigation is the potential for the pesticide to be present in soil at concentrations that pose potential direct-exposure hazards and/or leaching hazards. Factors that should be taken into account in selecting target pesticides for analysis include:

- 1. Known or suspected use
- 2. Application rate and duration of application
- 3. Environmental persistence (e.g., resistance to chemical and biological breakdown)
- 4. Nature of potential environmental hazards
- 5. Availability of toxicity and physiochemical data
- 6. Availability of commercial laboratory test methods

Investigations of former field areas should focus on pesticides and related contaminants that are persistent, toxic, and pose potential direct-exposure hazards for future residents and workers (e.g., dioxins, arsenic, organochlorine pesticides, etc.). Conditions in pesticide mixing and storage areas are much more uncertain, however. In addition to direct-exposure hazards, contamination could also pose leaching hazards and subsequent contamination of underlying groundwater resources (e.g., triazine pesticides and fumigants). This generally requires that the full range of pesticides be screened in these areas, and that all potential environmental hazards be fully evaluated in an Environmental Hazard Evaluation report (refer to <u>Sections 3</u> and <u>Section 13</u>).

Although specifically directed to former sugarcane and pineapple operations, the approaches described in this section can be modified for investigation of lands that may have been impacted by cultivation of other agricultural crops, including macadamia nuts, coffee, and vegetables, as well as commercial pest control operations.

In 2011 the HEER Office prepared a summary of pesticide data for environmental investigations carried out for fields, mixing areas, seed dipping vats and various other sugarcane operations across Hawai'i (<u>HDOH 2011d</u>). An overview of the report is provided in <u>Section 9.1.4</u>.

9.1.1 TARGETED OPERATIONS

Table 9-1 identifies specific areas of sugarcane and pineapple operations to target for investigation. Operations are divided into field areas and various non-field areas. Pesticide mixing and other areas that could contain localized but heavy contamination should be investigated separately from field areas (refer to <u>Section 3</u>). In this way, field areas may be quickly screened and, ideally, cleared of contamination concern while closer investigation of smaller areas is carried out. Bagasse pile and cane wash discharge areas should be tested for the same suite of target pesticides as field areas.

Table 9-1 Example Target Areas for Investigation of Potential Pesticide Contamination

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Sugarcane Operations ² Fields Heavy metals (arsenic only), organochlorine pesticides Pesticide mixing areas Carbamates, chlorinated herbicides, dioxins/furans, heavy metals (arsenic, lead, and total mercury), organochlorine pesticides, organophosphorus pesticides (known spill areas only), semivolatile organic compound (SVOCs), triazine pesticides, Total Petroleum Hydrocarbons (TPH) (middle distillates) Seed dipping areas Fungicides (benomyl and propiconizole [carbamates], total mercury) ³ Settling ponds Heavy metals (arsenic only), organochlorine pesticides ³ Bagasse piles Heavy metals (arsenic only), organochlorine pesticides ⁹ Bagasse piles Heavy metals (arsenic only), organochlorine pesticides Pesticide container disposal areas Carbamates, chlorinated herbicides, dioxins/furans, heavy metals (arsenic, lead, and total mercury), organochlorine pesticides, organophosphorus pesticides (known spill areas only), SVOCs, triazine pesticides, TPH (middle distillates) Pineapple Operations 2 ² Fields Heavy metals (arsenic only), organochlorine pesticides Pesticide mixing areas Carbamates, chlorinated herbicides, dioxins/furans, heavy metals (arsenic and lead), organochlorine pesticides, organophosphorus pesticides (known spill areas only), SVOCs, triazine pesticides, volatile organic compound (VOCs), TPH (middle distillates) Seed dipping areas Fungicides (benomyl and propiconizole [carbamates])
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³ Other Potential Areas of Concern
Air Strip mixing Same as for pesticide mixing areas and storage areas
Drainage ditches Site specific depending on areas drained (e.g., pesticide mixing areas, seed dipping vats, cane wash, etc.)
Plantation camp Site-specific
Maintenance Site-specific facilities
Transformer pads Polychlorinated biphenyls (PCBs); total petroleum hydrocarbons (TPH) as mineral oil
Rail lines Same as fields

Notes

1. Categorized by laboratory method used for analysis. Refer to <u>Appendix 9-B</u> and <u>Appendix 9-C</u> for specific pesticides.

2. Dioxins removed as potential contaminant of concern for former sugarcane field areas based on 2011 HEER Office review (see Section 9.1.4).

3. See <u>Tables 9-2</u> and <u>9-3</u>. Testing for full suite of pesticides listed recommended for any areas that may have been impacted by runoff or discharges from a pesticide mixing area (e.g., mill ditches, settling ponds, areas of canewash discharges, bagasse piles, etc.).

9.1.2 TARGET PESTICIDES AND RELATED CONTAMINANTS

Categories of pesticides and related contaminants associated with sugarcane and pineapple cultivation in Hawai'i are shown in <u>Tables 9-2</u> and <u>9-3</u>, respectively. These typically are grouped based on laboratory analytical methods, as follows, rather than by type of application:

- Organochlorine pesticides
- Organophosphorus pesticides

- Triazine pesticides
- Chlorinated herbicides
- Carbamates
- Fumigants
- Dioxins/furans
- Heavy metals (primarily arsenic, lead & mercury)
- Petroleum (e.g., Total Petroleum Hydrocarbons (TPH) (middle distillates), often used as a vehicle, or carrier oil, for application of pentachlorophenol, EDB, DBCP and other pesticides)
- Other (pentachlorophenol, etc.)

<u>Appendix 9-A</u> identifies pesticides (and related contaminants) known or suspected to have been used for agricultural purposes, and presents criteria for evaluating specific pesticides for further consideration. The list is based primarily on review of historical documents related to sugarcane and pineapple cultivation (e.g., <u>Hanson 1959</u>, <u>1962</u>; <u>HDOA 1969</u>, <u>1977</u>, <u>1987</u>, <u>1989</u>, <u>USDA 2000</u>). Few records exist prior to the late 1960s; therefore pesticide use prior to that time is uncertain. Rapid growth in the synthetic organic chemical industry began during the 1930s and 1940s. Prior to World War II, most pesticides were inorganic chemicals and naturally occurring plant extracts (<u>Newman 1978</u>), with the most common being arsenical compounds (<u>Sheets 1980</u>) and sulfur and mercury compounds (<u>Newman 1978</u>). In particular, arsenical compounds are known to have been used in sugarcane cultivation in Hawai`i in the 1920s through the 1940s, when up to 200,000 acres of land in Hawai`i was being used for sugarcane cultivation.

Several pesticides were banned or discontinued after the 1960s (e.g., dichloro-diphenyl-trichloroethane [DDT] in 1972). For the purposes of the target pesticide tables, it is assumed that use of these pesticides in Hawai'i ended at that time. However, it is possible that these pesticides may have continued to be used at a given site (e.g., use of existing supplies, etc.). Additional pesticides may have been used in some areas, but the appended list is considered to capture pesticides that would drive the need for remedial actions. Petroleum products, such as diesel fuel (middle distillates), were used to prepare some pesticide mixtures as carrier oils and may need to be included in the site investigation. See also <u>Section 9.2</u> for a discussion of petroleum contaminated sites.

Herbicides are the primary pesticide of potential concern for former sugarcane lands in Hawai'i (i.e., weed killers). Insect control (i.e., insecticides) on sugarcane fields historically has been primarily through biological control methods (i.e., predator species). The overall use of insecticides by the Hawai'i sugar industry historically has been very low (less than one half of one percent of total crop protection chemical usage), and it is unlikely that residues from past applications or handling/storage of insecticides would be of concern at a site used only to cultivate sugarcane. In many cases, the use of insecticides would have been counterproductive, since they could impact the desirable predator species as well as the target species.

Pesticides that are contaminants of potential concern in field and non-field areas are presented in <u>Appendix 9-B</u> and <u>Appendix 9-</u> <u>C</u>. For former field areas, the emphasis is on pesticides and related compounds that are persistent and primarily pose directexposure hazards (e.g., vs. leaching hazards).

The assumed persistence of other pesticides is based on published half lives in soil (refer to <u>Appendix 9-A</u>). A pesticide is considered to be highly persistent if the published half life exceeds one year or if the half-life exceeds 100 days and sorption coefficient is greater than 3,000 cubic centimeters per gram (cm³/g) (default cutoff for "mobile" vs. "nonmobile" contaminants; <u>HDOH, 2016</u>). All metals, as well as organochlorine pesticides and dioxins/furans fall into this category.

A pesticide is considered to be moderately persistent if the published half-life is between 30 and 100 days. A pesticide is considered to have low persistence if the expected half-life in soil is less than 30 days. Existing field data support this breakdown of anticipated pesticide persistence. The half-lives noted in <u>Appendix 9-A</u> are considered to be gross estimates only, but suitable for purposes of this guidance.

Information regarding pesticide application rates for field areas was not available for most pesticides at the time this guidance was prepared. Estimating long-term buildup of pesticides in soil was therefore not practical. Assumptions regarding likely application rates, likely persistence, and the time needed to exceed target action levels were used to screen out a small number of pesticides with relatively low toxicity from further consideration (refer to <u>Appendix 9-B</u> and <u>Appendix 9-C</u>).

Toxicity factors, physiochemical constants, and standard commercial laboratory test methods were not available for several pesticides at the time this guidance was published (refer to <u>Appendix 9-A</u>). These pesticides were excluded from further

consideration. The majority of these pesticides were developed after the 1960s, when stricter regulations on pesticide formulations were put into effect. These pesticides are assumed to be less persistent and toxic than the broader list of pesticides selected for inclusion in site investigations and noted in the appendices.

Tables 9-2 and 9-3 summarize categories of pesticides that should be tested at former sugarcane and pineapple cultivation operations. The investigation of former field areas should focus on pesticides and associated contaminants that are highly persistent, as indicated, with an emphasis on arsenic and organochlorine pesticides (see <u>Section 9.1.4</u>). For non-field areas (mixing areas, storage areas, etc.), the investigation should focus on all pesticides with moderate to high persistence that may have been used or released at the site. Testing for the full suite of pesticides listed is recommended for any areas that may have been impacted by runoff or discharges from a pesticide mixing area (e.g., mill ditches, settling ponds, areas of canewash discharges, bagasse piles, etc.). Contaminants identified in initial, screening level investigations above laboratory reporting limits (e.g., neighborhood-size decision units) should be carried forward in more detailed investigations (e.g., lot-size decision units). Refer to Section 3 and Section 4 for additional information on sampling decision units and sampling strategies.

Laboratory Analytical Group ¹	Laboratory Analytical Method	Field Areas	Non-Field Areas ²	Notes
Carbamates	8321	No	Yes	Test for benomyl and propiconazole at seed dipping operations (fungicides).
Chlorinated Herbicides	8151 or 8321	No	Yes	
Dioxins/furans	8280 or 8290	No	Yes	See footnotes.
Heavy Metals (Arsenic, Lead)	6010B/ 6020	Yes	Yes	Arsenic only in field areas.
Mercury (elemental)	7471	No	Yes	Test for total mercury at seed dipping operations (fungicides).
Organochlorine Pesticides	8081 or 8270	Yes	Yes	Field areas: heptachlor Non-Field areas: heptachlor and trifluralin.
Organo- phosphorus Pesticides	8141 or 8270	No	No	Limited use. Include as contaminant of concern in known spill areas only.
Triazine Pesticides	8141 or 619M/ 8270	No	Yes	
Volatile Organic Compounds	8260	No	No	
Semi-Volatile Organic Compounds	8270	No	Yes	
Total Petroleum Hydrocarbons	8015M	No	Yes	Petroleum (e.g., diesel fuel) used as a base for applying some pesticides.

Table 9-2 Summary	of Tar	net Pesticide	Categories	for Investi	nation of	f Former	Sugarcane (Operations
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Notes:

1. May differ from actual family of individual pesticides tested under noted laboratory method.

2. Testing for full suite of pesticides listed recommended for any areas that may have been impacted by runoff or discharges from a pesticide mixing area (e.g., mill ditches, settling ponds, areas of canewash discharges, bagasse piles, etc.).

Table 9-3 Summary of Target Pesticide Categories for Investigation of Former Pineapple Operations

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Laboratory Analytical Group ¹	Laboratory Analytical Method	Field Areas	Non-Field Areas ²	Notes
Carbamates	8321	No	Yes	Test for benomyl and propiconazole at seed dipping operations (fungicides).
Chlorinated Herbicides	8151 or 8321	No	Yes	
Dioxins/furans	8280 or 8290	No	Yes	See footnotes. PCP used to lesser extent in pineapple operations than sugarcane operations
Heavy Metals (Arsenic, Lead)	6010B/ 6020	Yes	Yes	Arsenic only in field areas.
Organochlorine Pesticides	8081 or 8270	Yes	Yes	
Organo- phosphorus Pesticides	8141 or 8270	No	No	Limited use. Include as contaminant of concern in known spill areas only.
Triazine Pesticides	8141 or 619M/ 8270	No	Yes	
Semi-Volatile Organic Compounds	8270	No	Yes	
Fumigants (Volatile Organic Compounds)	8260	No	Yes	
Total Petroleum Hydrocarbons	8015M	No	Yes	Petroleum (e.g., diesel fuel) used as a base for applying some pesticides.

Notes:

1. May differ from actual family of individual pesticides tested under noted laboratory method.

2. Testing for full suite of pesticides listed recommended for any areas that may have been impacted by runoff or discharges from a pesticide mixing area (e.g., drainage ditches, settling ponds, etc.).

Soil action levels are provided in the EHE guidance for the majority of the pesticides listed in <u>Appendix 9-C</u> (<u>HDOH, 2016</u>). Follow the methodology presented in the HDOH EHE guidance to compile action levels for pesticides not currently listed in that guidance. At a minimum, site data should be compared to action levels for both direct exposure and leaching hazards. Soil action levels for a number of additional pesticides are included in the United States Environmental Protection Agency Regional Screening Level guidance (<u>USEPA 2012b</u>).

An evaluation of potential contaminant mobility in terms of vapor-phase or dissolved-phase (i.e., leachate) mobility in soil is important (refer to <u>Appendix 9-B</u>). Detailed discussions of contaminant mobility are provided in Volume 1 and Appendix 1 of the HDOH EHE guidance (<u>HDOH, 2016</u>); refer also to HDOH technical memorandum Use of laboratory batch tests to evaluate potential leaching of contaminants from soil (<u>HDOH 2007</u>).

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Pesticides classified as "volatile" in the HDOH EHE guidance are considered to be highly mobile in the vapor phase [Henry's number >0.00001 atmosphere cubic meters per mole (m^3 /mol)] and molecular weight <200 (see <u>HDOH, 2016</u>). Pesticides with organic carbon sorption coefficients (Koc) values less than 100 cm³/g are considered highly mobile in leachate. Pesticides with Koc values >100 cm³/g but <3,000 cm³/g are considered to be moderately mobile. Pesticides with Koc values greater than 3,000 cm³/g are considered to be essentially immobile. Metals are given a default mobility ranking of low, although the need to evaluate potential leaching hazards posed by metals should be considered on a site-by-site basis (refer to <u>Sections 3</u> and <u>13</u>; see also <u>Section 9.1.4</u>).

9.1.3 DISCUSSION OF SELECT PESTICIDES

A summary of historical pesticide use for sugarcane and pineapple in Hawai'i is provided in the appendices to this section, including primary references for more detailed information. A brief discussion of select pesticides and pesticide groups is provided below. Additional information on arsenic, dioxins, and technical chlordane is provided in the HDOH EHE guidance document (HDOH, 2016, Volume 1, Chapters 2 and 4).

9.1.3.1 FUMIGANTS

Fumigants used in pineapple cultivation to control nematodes began in the 1940s (<u>HDOH 1985b</u>; see <u>Appendices 9-A</u> and <u>9-B</u>). Soil fumigants commonly used in Hawai`i include:

- 1,2-dibromo-3-chloropropane (DBCP);
- 1,2-dibromoethane (EDB);
- 1,3-dichloropropene (Telone);
- D-D (a mixture of 1,2-dichloropropane; 1,3-dichloropropene; and 2,3-dichloropropene);
- 1,2,3-trichloropropene (TCP; an impurity associated with D-D).

Fumigants were typically injected from four to fourteen inches below ground surface. DBCP and EDB have been detected in groundwater wells on Oahu and Maui and have not been used since the mid-1980s (<u>HDOH 1985</u>, <u>1985c</u>). 1,2,3-Trichloropropene (TCP) is an impurity associated with D-D and has also been detected in groundwater wells in the state (see <u>HDOH 1985</u>)

Fumigants are not likely to be persistent in field areas more than one year after use due to a propensity to volatilize into the atmosphere and degrade or be carried downward in leachate. Fumigants could, however, be a contaminant of concern in former pesticide mixing, storage or disposal areas. Soil vapor data collection is strongly recommended when investigating for these areas.

9.1.3.2 ARSENIC

<u>Appendix 9-E</u>, Update to Soil Action Levels for Inorganic Arsenic and Recommended Soil Management Practices, contains detailed information on updated soil action levels for total inorganic arsenic, bioaccessible arsenic, and recommended soil management practices. Contact the HEER Office for further assistance if needed.

Historical Use

Arsenic-based pesticides are largely associated with sugarcane cultivation in Hawai'i during the 1910s through the 1940s. Various arsenic-based compounds were used as herbicides, insecticides and rodenticides in agricultural operations. The primary use was for weed control with respect to the overall volume stored, mixed and applied. The HEER Office has a dedicated webpage, <u>Soil Arsenic Guidance and Information</u>, which houses fact sheets, arsenic assessments throughout Hawai'i, maps and technical guidance for arsenic. Monosodium methane arsenate (MSMA) and sodium arsenite were used as herbicides during various stages of sugarcane cultivation (<u>HDOA 1969</u>). Arsenic was typically applied to surface soils by "poison gangs" using backpack sprayers. In addition, Canec, a building material made from sugarcane waste (i.e., bagasse) and used extensively in Hawai'i, was treated with calcium arsenate and arsenic acid as an anti-termite agent (<u>NOAA 1990</u>). The HEER Office fact sheet, <u>Arsenic in Canec Ceilings and Wallboard in Hawai'i</u>, provides an overview of the potential public health concerns associates with Canec (<u>HDOH 2010b</u>). Other arsenic-based pesticides include lead arsenite and lead arsenate, but it is unknown if these were used in Hawai'i.

Significantly elevated levels of total arsenic have been identified in a small number of former sugarcane fields in Hawai'i. Based on a review of pesticide data for former sugarcane operations, arsenic drives human health risk posed by residual pesticides in these fields (<u>HDOH 2011d</u>, see <u>Section 9.1.4</u>). A brief discussion on public health concerns associated with arsenic is provided in HDOH's <u>Arsenic in Hawaiian Soils: Questions and Answers on Health Concerns (HDOH 2013</u>).

Arsenic Bioaccessibility Tests

Because of extensive, historic use of arsenic-based pesticides in Hawai'i, soil samples collected at former agricultural sites should always be analyzed for total arsenic. The HEER Office recommends that a laboratory bioaccessibility test be carried out when the total arsenic concentration in the <2mm fraction of soil exceeds 24 mg/kg, the default, upper limit assumed for background arsenic in soil (see <u>Appendix 9-E</u> and <u>HDOH, 2016</u>). Soil action levels and categories specific to bioaccessible arsenic are included in <u>Appendix 9-E</u>. The bioaccessibility test and the associated action levels apply to the <250µm, fines fraction of soil.

Bioaccessible tests are used to estimate the fraction of total arsenic that could be stripped or "desorbed" from the soil following ingestion and thus made available for uptake. Arsenic that remains sorbed to the soil sample is considered to be unavailable for uptake and essentially non-toxic. Bioaccessibility should be tested and evaluated based on the gastric-phase, *in vitro* Solubility Bioaccessibility Research Consortium method ("SBRC" or "Drexler method"; <u>Ruby 1996, 2001</u>; <u>Kelly 2002</u>; <u>Juhasz et al 2007</u>). Studies have demonstrated that the SBRC assay method provides the best predictive capability to swine *in vitro* bioavailability testing in comparison to other in vitro methods, such as the Physiologically Based Extract Test (PBET) method or the In-Vitro Gastrointestinal Method (IVG).(<u>Juhasz et al 2009</u>; <u>Juhasz et al 2011</u>). These studies concluded that a 1:1 relationship between swine arsenic bioavailability and bioaccessibility using the SBRC gastric-phase method could be estimated, without the need for a correction factor. A direct correlation between SBRC data and in vivo data was also observed in soil from Hawai'i that was included in a cynomolgus monkey study overseen by the University of Florida (Roberts et al 2007). In this study an average of 5.4% bioavailability was determined in the in vivo tests compared with an average SBRC-gastric phase bioaccessibility of arsenic in the same soil of 6.5%.

A higher confidence in the SBRC-gastric method over other approaches was also observed in suite of twenty arsenic contaminated soil samples from Hawai'i that were submitted to a Canadian laboratory (<u>RMC 2007</u>). Three different bioaccessibility in vitro tests were evaluated, including SBRC, PBET and In Vitro Gastro-Intestinal (IVG) methods. The results demonstrated that the SBRC assay provided the highest estimate of bioaccessible arsenic of the gastric phase testing results, and consequently provides the most "protective" estimate of bioaccessibility of the three in vitro methods.

The SBRC bioaccessibility test is carried out on the <250µm fraction of dried soil separated from the original bulk sample by the laboratory. Under this method, one gram of the <250µm soil fraction is placed in 100ml of extraction solution intended to mimic human gastro-intestinal fluids and agitated for one hour. The concentration of bioaccessible arsenic in the soil sample is calculated by dividing the mass of arsenic that moves into the batch test solution by the mass of the sample. The percent bioaccessiblity is calculated as the concentration of bioaccessible arsenic divided by the concentration of total arsenic reported for the same sample.

Both the total and bioaccessible concentrations of arsenic (mg/kg) in the $<250\mu$ m fraction of the soil should be reported, even though the former may not be required as part of the bioaccessibility test. The percent bioaccessible arsenic, calculated as the concentration of bioaccessible arsenic divided by the concentration of total arsenic in the $<250\mu$ m fraction, should also be reported. This will help confirm the test results and provide insight on possible enrichment of arsenic in the fine-grained fraction of contaminated soil.

The USEPA recommends a default bioavailability of 60% for arsenic in soil, based on a review of data for samples collected primarily on the mainland (<u>USEPA 2012c</u>). This default can be applied to the concentration of total arsenic reported for the <250µm soil fraction in lieu of a laboratory-based test if desired, provided that the total concentration of arsenic in this fraction does not exceed 160 mg/kg. This reflects the concentration of total arsenic in soil that would equate to the commercial/industrial action level for bioaccessible arsenic of 95 mg/kg and a bioaccessibility of sixty-percent. Laboratory-based bioaccessibility tests are recommended when the concentration of total arsenic in the <250µm soil fraction exceeds a concentration of 160 mg/kg.

Data compiled for Hawai'i suggest that bioaccessibility as well as bioavailability is unlikely to exceed this threshold for soils with low to moderate concentrations of total arsenic, regardless of iron content and other factors (e.g., <u>Cutler 2011</u>, <u>HDOH 2011c</u>, <u>Cutler et al 2013</u>). Note that this default value is highly conservative for iron-rich, volcanic soils, where bioaccessibility is more typically less than 30% and as low as 5%. The default factor should not be applied to total arsenic in the <2mm fraction of soil due to the potential for enrichment of metal concentrations in the fines.

9.1.3.3 TECHNICAL CHLORDANE AND OTHER ORGANOCHLORINE PESTICIDES

Technical chlordane is a mixture of chlordane isomers (50-75%) and over 100 related compounds, including heptachlor and heptachlor epoxide (<u>ATSDR 1994</u>). Technical chlordane was used in Hawai`i in large quantities by pest control operators, lawn and garden services, and homeowners for the control of termites, armyworms, and other pests. The use of technical chlordane was discontinued in the 1980s. Soil contaminated with technical chlordane is highly likely to be present around and under the foundations of buildings constructed before this time. Technical chlordane was also used as an insecticide during pineapple cultivation (HDOA 1969).

The HEER Office recommends that soil samples be analyzed for technical chlordane rather than individual chlordane isomers and related compounds generally found in technical chlordane. The concentrations of chlordane isomers, heptachlor, and heptachlor epoxide do not need to be reported unless applied as a separate chemical. Laboratories should be directed to test for technical chlordane using USEPA Method 8081A or an equivalent method (<u>USEPA 1996</u>). This must be specifically requested prior to submitting the samples for analysis and noted on the chain of custody form. Laboratories also should be instructed to report any additional organochlorine pesticides that are not typically found in technical chlordane (e.g., DDT, dieldrin, endrin, etc.). Additional information on technical chlordane is presented in <u>HDOH 2011g</u>, <u>2011h</u>.

In addition to the approach noted for technical chlordane, concentrations of the following chemicals should be summed as indicated for comparison to HDOH EALs in a screening level EHE:

- Hexachlorocyclohexane ("BHC" as Lindane) = Alpha-BHC + Beta-BHC + Gamma-BHC (Lindane) + Delta-BHC;
- Endosulfan = Endosulfan I + Endosulfan II + Endosulfan sulfate;
- Endrin = Endrin + Endrin aldehyde + Endrin ketone.

These chemicals can be evaluated individually in a site-specific risk assessment as necessary.

9.1.3.4 DIOXINS AND FURANS

<u>Appendix 9-F</u>, Update to Soil Action Levels for TEQ Dioxins and Recommended Soil Management Practices, contains detailed information on updated soil action levels for TEQ dioxins and recommended soil management practices. Contact the HEER Office for further assistance if needed.

Dioxins and furans ("dioxins") should be included as chemicals of potential concern at former pesticide mixing areas associated with both sugarcane and pineapple operations. Although significant data are not currently available for the latter, dioxin contamination in soil well above HDOH action levels have been documented at numerous former pesticide mixing and storage areas associated with past, sugarcane operations (see following section).

Dioxins were created as a manufacturing byproduct in older formulations of several commonly used pesticides, especially pentachlorophenol (PCP), 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), and 2,4,5-trichlorophenoxypropionic acid (2,4,5-TP or Silvex; <u>NTP 2005</u>). Soils in former pesticide mixing areas should be analyzed for dioxins if any the above-noted pesticides are known or suspected to have been stored, mixed or otherwise released in the area under investigation. These chemicals are not known to have been widely used in pineapple fields and dioxins are no longer considered a potential chemical of concern for these areas (see <u>Table 9-3</u>). Organochlorine pesticides such as heptachlor, used for ant control, are instead considered to drive the need for investigation of former pineapple field areas.

Dioxins and furans are evaluated in terms of Toxicity Equivalent calculations or "TEQ "dioxins. Quantification of dioxins in soil for use in human health risk assessments requires conversion of congener-specific gas chromatography/mass spectrometry (GC/MS) data to TEQ dioxin concentrations by use of Toxicity Equivalence Factors (TEFs) (WHO 2005). A summary of World Health Organization (WHO) TEFs is provided in Table 9-4. The TEQ concentrations for individual congeners are then added together to calculate a total TEQ dioxin concentration for the sample. Unless otherwise approved by HDOH, one-half of the Method Detection Limit (not the Reporting Limit) should be used for calculation of TEQ concentrations when the specific congener is reported as "Non Detect."

The HEER Office currently accepts the use of bioassay methods such as CALUX for testing of TEQ dioxins in soil provided that splits of 10% of the samples are tested using GC/MS methods such as Method 8280 or 8290, generally samples with the highest-reported concentration of TEQ dioxins (see <u>Appendix 9-F</u>). Bioassay data in studies carried out by the HEER Office consistently overestimated TEQ dioxin concentrations in soil in comparison with split samples that were tested using laboratory GC/MS methods (<u>HDOH 2007e</u>). This suggests that the bioassay tests provide a conservative estimate of TEQ dioxin concentrations. Paired GC/MS and bioassay data for split samples can be used to develop a correction factor and adjust the bioassay data for actual comparison to HEER Office EALs.

Other investigations, however, suggest that bioassay tests may *underestimate* TEQ dioxin concentrations for very-low concentrations of dioxins in soil (e.g., <100 ng/kg; e.g., see <u>TTEMI 2012</u>). While this will not affect development of a correction factor based on paired, GC/MS data, it is important to be aware of for initial screening of sites, and emphasizes the need for Method 8280 or 8290 data.

Table 9-4 Summary of Toxicity Equivalence Factors for Dioxin

Compound	WHO 2005 TEF				
chlorinated dibenzo-p-dioxins					

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2,3,7,8-TCDD	1
1,2,3,7,8-PeCDD	1
1,2,3,4,7,8-HxCDD	0.1
1,2,3,6,7,8-HxCDD	0.1
1,2,3,7,8,9-HxCDD	0.1
1,2,3,4,6,7,8-HpCDD	0.01
OCDD	0.0003
chlorinated dibenzofurans	
2,3,7,8-TCDF	0.1
1,2,3,7,8-PeCDF	0.03
op2,3,4,7,8-PeCDF	0.3
1,2,3,4,7,8-HxCDF	0.1
1,2,3,6,7,8-HxCDF	0.1
1,2,3,7,8,9-HxCDF	0.1
2,3,4,6,7,8-HxCDF	0.1
1,2,3,4,6,7,8-HpCDF	0.01
1,2,3,4,7,8,9-HpCDF	0.01
OCDF	0.0003

WHO World Health Organization

TEF Toxicity Equivalence Factor

9.1.4 REVIEW OF PESTICIDE CONTAMINATION AT FORMER SUGARCANE OPERATIONS

In 2011 the HEER Office prepared a summary of pesticides identified in fields, mixing areas, seed dipping vats and various other sugarcane operations across Hawai'i (<u>HDOH 2011d</u>). An overview is provided below. Refer to references in the 2011 report, for examples associated with different operations.

9.1.4.1 PESTICIDE MIXING AREAS

Data reviewed for the pesticide and dioxin summary report (<u>HDOH 2011d</u>) confirm that pesticide mixing areas have the highest potential for significant contamination and maintain a high priority for identification and investigation. Identification of these areas through historical records, interviews with past employees and field reconnaissance is especially important as urban growth expands into former agricultural areas.

In order of potential risk to human health and the environment and presence at former mixing sites, the pesticide categories and pesticide-related chemicals can be generally prioritized as follows (see <u>HDOH 2011d</u>):

- Arsenic and dioxins (chronic direct exposure),
- Ametryn and atrazine (leaching),
- Petroleum (vapor intrusion, gross contamination, leaching),
- Lead (chronic direct exposure),
- DDT (chronic direct exposure),
- Chlorinated herbicides (leaching),
- Carbamates (leaching),
- Organophosphates (acute direct exposure).

Arsenic, dioxins, ametryn, atrazine, and petroleum in particular drive the need for remediation at former mixing areas. Significant lead contamination is also identified at many mixing area sites, although this may in part be due to the use of lead-based paint, since lead-based pesticides are not known to have been widely used.

Although the remaining chemicals can also be present in the same soil at elevated levels, addressing potential environmental hazards posed by the former will almost always coincidentally address potential concerns posed by the latter. Organophosphates primarily pose a short-term, direct exposure risk during and immediately after application. These chemicals are not normally identified in abandoned, former mixing areas above levels of potential concern. Full testing of Decision Units within a former pesticide mixing area most suspected of heavy contamination is recommended. These observations, however, can be used to limit testing for these chemicals to areas suspected of the highest contamination in order to reduce investigation costs, if needed.

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Heavy arsenic contamination due to the past use of water-based, arsenical herbicides has been identified to depths of greater than ten feet at former pesticide mixing areas. In some cases contamination can be so significant that soils will fail Toxicity Characteristic Leaching Procedure (TCLP) tests and require management as hazardous waste. It is important to determine this as part of the site investigation in order to help design future remedial actions. Fortunately, the strong binding capacity of iron-rich, volcanic soils in Hawai'i limits this potential problem to sites with arsenic concentrations in excess of several thousand ppm or at sites where the soil is relatively iron-poor. Arsenic can expected to be much more mobile (and bioaccessible) at sites in coastal areas that are situated on low-iron, calcareous soils rather than volcanic soils.

Petroleum contamination is also present at many former pesticide mixing areas. This can be associated with the use of diesel for preparation of pesticide emulsions. Examples include the use of Concentrated Activated Diesel Emulsion or "CADE" that is "activated" with pentachlorophenol (PCP) for application as an herbicide. Long-term release of petroleum-based emulsions at mixing sites can lead to heavy contamination of underlying soils with dioxins to a depth of ten or more feet. The identification of diesel-contaminated soil at a mixing site should raise concerns about potential dioxin contamination.

Trace levels of PCP are typically identified at pesticide mixing areas operated prior to 1970, when the use of PCP for agricultural operations was banned (<u>HDOA 1969</u>, <u>1977</u>). Most non-wood preservative uses of PCP were banned in 1987 and use of PCP for wood treatment was significantly restricted by the Federal government (<u>USEPA 2008e</u>; see also <u>ATSDR 2001</u>). The reported concentration of PCP in soil is often below or only marginally above the Tier 1 soil action level of 0.82 mg/kg (<u>HDOH, 2016</u>). Pentachlorophenol degrades relatively rapidly in the environmental and is only moderately persistent (see <u>Appendix 9-A</u>). The reported level of PCP in the soil is not a reliable indicator of the presence or absence of significant dioxin contamination. Heavy dioxin contamination, well over 10,000 to 100,000+ ng/kg, associated with the past use of PCP has been identified at sites where little to no PCP remains.

This highlights that the presence or absence of PCP in soil cannot be used as a stand-alone tool to screen for potentially significant dioxin contamination. Soils that could have been significantly impacted by past releases of PCP or similar, dioxin containing chemicals (e.g., 2,4,5 TP) should always be independently tested for dioxins in addition to the suspected parent chemical.

Soils in some, but not all, pesticide mixing areas are also heavily contaminated with ametryn and atrazine. While reported levels often do not exceed action levels for potential direct-exposure concern, these chemicals can still pose leaching threats to underlying groundwater. Comparison to screening levels that do not consider leaching is therefore not appropriate (e.g., USEPA Regional Screening Levels, <u>USEPA 2012b</u>). Reference to the more comprehensive HDOH EALs or equivalent is required. It is important to indentify and remediate soils contaminated with these chemicals in order to prevent and/or cease long-term contamination of drinking water aquifers.

9.1.4.2 FORMER FIELD AREAS

With the local exception of arsenic, residual pesticides in former sugarcane fields are rarely detected above levels of potential concern (see <u>Appendix 9-E</u>). Arsenic has been identified in some fields at concentrations that are marginally above HDOH action levels for residential exposure. The distribution of former field areas with elevated arsenic is not uniform, but appears to be associated with specific sugarcane companies that operated from the 1910s through the 1940s and relied on arsenic-based herbicides for weed control in high-rainfall areas (see <u>Section 9.1.3.2</u>). Continued testing for arsenic in former sugarcane fields is recommended (see <u>Table 9-2</u>).

Data compiled over the past ten (and especially five) years indicate that dioxins in former sugarcane fields do not pose significant health risk should these areas be redeveloped for residential use in the future. Dioxins have subsequently been removed as a recommended contaminant of concern for former field areas (see <u>Table 9-2</u>). Trace levels of dioxins, reported in terms of Toxicity Equivalent or TEQ dioxins, are often below or slightly above expected, ambient background in many fields (<20 ng/kg; refer to <u>Appendix 9-F</u>). In other fields the concentration of TEQ dioxins typically ranges between 50ng/kg and 100 ng/kg, below the HDOH residential action level of 240 ng/kg (e.g., see <u>HDOH 2007e</u>). In relatively rare cases, the concentration of TEQ dioxins in soil at the scale of an individual, hypothetical, residential lot (e.g., 5,000 ft2; see <u>Section 3</u>), may slightly exceed the current action level but are still at or below past, residential action levels (e.g., 390 to 1,000 ng/kg; see Appendix 9-F; see also <u>USEPA 1998g</u>). This does not pose a significant risk to future residents when more site-specific exposure factors such as soil ingestion rates for urban areas are taken into consideration (see <u>HDOH, 2016</u>).

9.1.4.3 SEED DIPPING VATS

Heavy mercury contamination has been identified at the outfalls of seed dipping vats that operated before the mid 1970s (see <u>HDOH 2011d</u>). Contaminated sediment has also been identified in mill ditches that drain these areas, however contamination to date is primarily associated with arsenic and dioxins (see <u>HDOH 2011d</u>). Earlier reports of mercury contamination in mill ditches that drained former seed dipping vats were not verified in followup sampling. This may have been due to misreporting of units in laboratory reports or investigation summaries. Laboratories in general report metal concentrations in soil or sediment in units of mg/kg. In the case of mercury, however, laboratories sometime report concentrations in units of μ g/kg (1 mg/kg = 1000 μ g/kg).

Background levels of mercury in soil are typically less than 1.0 mg/kg (<u>HDOH 2012b</u>). It is important to review and confirm units for mercury at sites where apparent contamination is identified.

9.1.4.4 OTHER AREAS AND TARGET PESTICIDES

The review of data for former sugarcane operations did not identify a need to revise guidance for testing in other areas where pesticides may have been used or stored. Significant contamination with organochlorine pesticides (e.g., DDT, Technical Chlordane, aldrin-dieldrin) has not been identified at the majority of pesticide mixing areas or field areas (see <u>HDOH 2011d</u>). Given their high toxicity and persistence in the environment, however, and past use for mosquito, termite and other pest control around former agricultural areas (e.g., around field margins), continued testing for these chemicals in both former mixing areas and in former field areas is still recommended.

Testing for thallium and barium in an area where rat poison was formerly stored and potentially mixed is currently underway (used in cakes, versus sprayed as a liquid), and data are anticipated in the future. Elevated levels of thallium have not been reported in mixing areas or fields. Due to its potential toxicity, anticipated background levels in soil are likely to be close to risk-based action levels for direct exposure (see <u>HDOH. 2016</u>, <u>2011d</u>). Toxicity factors employed in the action levels assume that the thallium is highly soluble and bioavailable, however. Like arsenic, the actual bioavailability of both natural and pesticide-related thallium in soil is expected to be low.



TGM for the Implementation of the Hawai'i State Contingency Plan Section 9.2 PESTICIDE CONTAMINATION AT NON-AGRICULTURAL FACILITIES AND SITES

9.2 PESTICIDE CONTAMINATION AT NON-AGRICULTURAL FACILITIES AND SITES

The HEER Office recommends safe management practices to limit potential exposure to and test soil for organochlorine (OC) termiticides found in and near wooden buildings built between the 1940s to the 1980s. The recommendations in this section are described in further detail in two HEER Office website fact sheets regarding the <u>past use of OC termiticide</u>, and <u>soil testing for OC termiticides at residential sites (HDOH 2011g, 2011h</u>).

Termiticides is a general term that includes any type of chemical mixture specifically formulated to kill termites. Organochlorine termiticides are a group of persistent pesticides used for termite control in and around wooden structures from the mid-1940s to the late 1980s. Technical Chlordane and/or aldrin were applied in most instances (refer to <u>Section 9.1.3.3</u>). Dieldrin, a breakdown product of aldrin, is also commonly identified at these sites. The chemicals were used primarily by pest control operators in Hawai'i's urban areas, but also by homeowners, the military and counties to protect buildings against termite damage.

The USEPA banned all production and import of these and other OC pesticides in the 1970s (DDT) and 1980s (e.g., Technical Chlordane) due to concerns over potential long-term, ecological impacts as well as risks to human health.

Organochlorine termiticides were commonly applied directly to soil underneath foundations (e.g., around wooden piers or under slabs) and/or around the immediate perimeter of a building foundation. Application practices included pouring a liquid mixture into shallow (e.g., six inches) trenches excavated around the foundation, or by injection through holes drilled next to the foundation or in the flooring at the edge of foundation walls.

Reported concentrations of these compounds in treated soil can exceed HDOH soil action level for soil that is regularly contacted by residents or workers over many years. Typically the highest concentrations of termiticides in soil are found beneath the house or around the perimeter extending away from the building foundation up to 1 to 3 feet. The top six inches to one foot usually have the highest concentrations of OC termiticide. These chemicals were developed to be persistent and can be expected to remain in the soil for decades. Concentrations of OC termiticides under building slabs could be higher because the slab can act as a barrier or cap protecting the degradation of the termiticides in the soil over time. In some cases OC termiticides have been identified in open yard areas, apparently due to additional spraying, the existence of a former building in that area, or reuse of treated soil from former building foundations.

The HEER Office fact sheets discuss potential health concerns associated with OC termiticides in soil and recommend that contact with treated soils be minimized (<u>HDOH 2011g</u>, <u>2011h</u>). Termiticides applied more than two decades ago are not detectable by smell or sight. Soil testing is recommended to confirm the presence and level of these chemicals. Soil sampling techniques are described further in the HDOH fact sheet on soil testing for OC termiticides at residential sites in Hawai'i (<u>HDOH 2011g</u>, <u>2011h</u>). This fact sheet provides an overview of the soil sampling techniques for construction or demolition contractors, homeowners, and others. Further information on soil sampling techniques can be found in TGM Sections 4 and 5.

If OC termiticides are confirmed by testing or suspected based on the age of the building then measures to minimize contact are recommended. This can include removal of treated soil or placement of gravel or landscaping around the perimeter of a house or building. Soil treated with termiticides should not be reused for other purposes without testing (refer to Clean Fill guidance, <u>HDOH 2011e</u>).



9.3 PETROLEUM CONTAMINATED SITES

A discussion of target chemicals of potential concern and the evaluation of petroleum releases is included in Volume 1 and Appendix 1 of the EHE guidance document (<u>HDOH, 2016</u>). This guidance is summarized and expanded below.

Petroleum is a complex mixture of hundreds of different compounds composed of hydrogen and carbon or "hydrocarbon" compounds (<u>API 1994</u>). The chemistry and toxicity of petroleum releases depends in part on the type of fuel released and the media tested. The bulk of the compounds are evaluated collectively under the all-inclusive category of Total Petroleum Hydrocarbons (TPH). The concentration of TPH in soil and groundwater is typically reported in terms of "carbon ranges," or the number of carbon molecules in individual hydrocarbon compounds based on the type of fuel released: 1) C5-C12 ("gasoline range" or "TPHg"), 2) C10-C24 ("diesel range" or "TPHd") and 3) C24-C40+ ("residual fuels" or "TPHo"). A number of different terms are applied to these ranges. As discussed below, reference to these ranges is less useful for air and soil vapor data.

"Gasoline-range" TPH is defined as a mixture of petroleum compounds 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 (see also <u>NEIWPCC 2003</u>). Vapors from these fuels tend to be dominated by lighterrange, more volatile, C5-C8 aliphatics (<u>HDOH, 2016, 2012</u>). Although not studied in detail, dissolved-phase gasoline in groundwater is also likely to be biased towards more soluble, lighter-range compounds.

Petroleum compounds characterized by a wider variety of straight, branched, and cyclic alkanes, polynuclear aromatic hydrocarbons (PAHs, especially naphthalenes and methylnaphthalenes), and heterocyclic compounds with carbon ranges of approximately C9 to C25 are referred to as "Diesel Range" TPH. These compounds dominate the makeup of diesel and other middle distillates fuels (e.g., kerosene, diesel fuel, home heating fuel, JP-8, etc.). These fuels also contain a small but important amount of lighter, aliphatic compounds. Vapors from the fuels can somewhat counterintuitively be dominated by these "gasoline range," C5-C12, aliphatic compounds (<u>HDOH 2012</u>). As discussed in <u>Section 9.3.1.2</u> below and in <u>Section 7</u>, it is important that these compounds be included in the analysis of TPH in air and soil vapor samples associated with releases of middle distillate fuels. Dissolved-phase, middle-distillate fuel in groundwater could also be biased towards more soluble, "gasoline-range" compounds. A dominance of "TPHg" in groundwater samples does not in itself indicate that the source of the contamination is associated with gasoline. A more detailed review of the chromatograph pattern and site history will be necessary to make this determination.

Residual fuels (e.g., Fuel Oil Nos. 4, 5, and 6, lubricating oils, mineral oil, used oils, and asphalts) 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. Compounds associated with these fuels and related products are not considered to be volatile, although methane generated by degradation of the fuels could pose potential hazards at some sites.

Note that the breakdown of heavy petroleum can lead to an increase in volatile petroleum compounds (<u>Chaplin 2002</u>). This necessitates the collection of soil vapor samples at sites contaminated by heavier fuels, as well as gasolines and middle distillates.

Due to the number of sites with residual petroleum contamination, HDOH prepared a guidance document that outlines procedures for long-term management of residual petroleum contamination where full cleanup is not practicable. This guidance, Long-Term Management of Petroleum-Contaminated Soils and Groundwater (<u>HDOH, 2007c</u>) is included in TGM Section 19 as <u>Appendix 19-A</u>. The document includes three, supporting decision trees for determining the need for continued, HDOH oversight. Self-implemented, long-term management by the property owner and closure of the case in the HDOH database is possible in scenarios where the area and volume of contaminated soil and/or groundwater is minimal.

Table 9-5 Target Analytes for Releases of Petroleum Products

Petroleum Product	Media	¹ Recommended Target Analytes				
Gasolinos	Soil	TPH, BTEX, naphthalene, MTBE and appropriate additives and breakdown products (e.g., TBA, lead, ethanol, etc.)				
Gasonies	Soil Vapor	TPH, BTEX, naphthalene and MTBE plus other volatile additives and methane				

	Groundwater	Same as soil
Middle Distillates	Soil	TPH, BTEX, naphthalene, and methylnaphthalenes (1- and 2-)
(diesel, kerosene, Stoddard solvent,	Soil Vapor	TPH, BTEX, naphthalene, and methane
heating fuels, jet fuel, etc.)	Groundwater	Same as soil
Residual Fuels (lube oils, hydraulic oils, mineral oils,	Soil	TPH, ² VOCs, naphthalene, methylnaphthalenes (1- and 2-), the remaining 16 priority pollutant PAHs, PCBs, and heavy metals unless otherwise justified
transformer olls, Fuel Oll #6/Bunker C, waste oil_etc.)	Soil Vapor	TPH, VOCs, naphthalene, and methane
	Groundwater	same as soil

1. Include any additional volatile additives in soil vapor samples if suspected to be present.

2. VOCs includes BTEX and chlorinated solvent compounds.

9.3.1 RECOMMENDED TARGET ANALYTES

Recommended target analytes for petroleum contaminated soil and groundwater are provided in Table 9-5.

Petroleum contamination in soil, water or air/soil vapors should be evaluated in terms of both TPH and a short list of target "indicator chemicals" that are specific to the type of petroleum product released. As discussed in the previous section, non-specific compounds collectively reported as TPH typically comprise the bulk of petroleum fuels. Target indicator chemicals typically make up only a small fraction of the total petroleum present but are also important players in the assessment of environmental hazards posed to human health and the environment. The toxicity and fate and transport of these chemicals in the environment has been studied in detail.

9.3.1.1 TARGET INDICATOR COMPOUNDS

Target, indicator compounds for petroleum fuels include benzene, toluene, ethylbenzene, xylenes (total), methyl-tert butyl ether (MTBE), naphthalene and number of individual, polyaromatic hydrocarbon compounds (see Table 9-5). Separate evaluation of these chemicals is based on the availability of adequate toxicity data and the potential for the chemicals to drive risk and the need for remedial actions at contaminated properties in conjunction with TPH. Separate environmental action levels for these compounds are presented in the HEER Office EHE guidance (HDOH, 2016).

All other petroleum compounds are collectively reported and evaluated under "TPH," as described above. Volatile components of petroleum that are not specifically identified as target indicator compounds in Table 9-5 but reported as separate compounds by the laboratory using EPA Method 8260 or similar methods do not need to be separately evaluated. Examples include trimethylbenzenes and other aliphatics and aromatics not specifically identified as target indicator compounds are included under the analysis and evaluation of the TPH component of petroleum.

Seventeen, semi-volatile PAHs are recommended as target, indicator compounds for releases of heavier petroleum fuels or waste oils:

- 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
- fluorine
- indeno(1,2,3)pyrene,
- methylnaphthalenes (1 & 2)
- naphthalene
- phenanthrene
- pyrene

In practice, the need for remedial actions at sites impacted with PAHs is typically driven by benzo(a)pyrene. Naphthalene can be reported with either semi-volatile or volatile compounds (see <u>Section 7</u>). Separate Environmental Action Levels (EALs) for 1- and 2- methylnaphthalenes are presented in the EHE guidance document (<u>HDOH, 2016</u>).

The suite of PAHs that should be tested at a given site depends on the type of the petroleum product released (after <u>MADEP</u> <u>2002</u>). As indicated in the Table 9-5, naphthalene is the only PAH that requires reporting for gasoline release sites. Both methylnaphthalenes and naphthalene should be reported at sites with releases of middle distillates (diesel, jet fuel, etc.). The full suite of PAHs should be considered at sites with releases of heavier petroleum fuels and waste oil, unless site-specific information on the product released justifies eliminating specific PAHs.

Methylnaphthalenes do not need to be reported for soil vapor samples as a default. Based on data reviewed by HDOH, these compounds are unlikely to drive potential vapor intrusion hazards at petroleum release sites over TPH or benzene due to their relatively low volatility and concentration in most middle distillates and residual fuels. Testing for these compounds in soil vapor also requires different sample collection and analytical methods (e.g., sorbent tubes and TO-1 analysis; see <u>Section 7.8.2</u>). Reporting of these compounds in soil vapor samples may, however, be required at sites impacted by Manufactured Gas Plant waste.

9.3.1.2 TOTAL PETROLEUM HYDROCARBONS

Soil, groundwater, and soil vapor samples must <u>always</u> be tested for TPH (or equivalent) in addition to targeted, individual chemicals. Laboratory analysis for TPH as gasolines and middle distillates is generally carried out using gas chromatography, modified for "gasoline-range" organics ("Volatile Fuel Hydrocarbons") and "diesel-range" organics ("Extractable Fuel Hydrocarbons"), respectively (e.g., EPA Method 8015). Analysis for TPH as residual fuels up to the C40 carbon range can be carried out by gas chromatography, infrared absorption, or gravimetric methods. The latter methods are rarely used, however, due to their inability to discriminate the type of the petroleum present and interference with organic material in the soil.

The concentration of TPH (or equivalent) in soil vapor should always be reported as the sum of C5-C12 compounds for whole air samples and C5-C18 for sorbent tube samples, regardless of the type of petroleum fuel involved. Refer to Appendix 1 of the HDOH EHE guidance for a detailed discussion on total volatile petroleum hydrocarbons (see also <u>Brewer et al 2013</u>). As discussed above and in <u>Section 7.8.2</u>, results from a petroleum vapor study carried out by HDOH study indicate that C5-C8 aliphatic compounds can make up a significant if not dominant fraction of the total TPH present in vapors associated with diesel and other middle distillate fuels (<u>HDOH 2012</u>, <u>2012c</u>). This is important, since current laboratory protocols typically require that they report "TPHdiesel" in any media as the sum of C10 to approximately C24 hydrocarbon compounds. Excluding the contribution of C5-C8 aliphatics to the total concentration of TPH reported in air or soil vapor samples associated with middle distillate fuels would be inappropriate, however.

To help address this issue, laboratories should be instructed to report TPH (or equivalent) in air or vapor samples as: 1) The sum of C5-C12 compounds for whole-air samples (e.g., summa canister samples and TO-15 lab methods, with the understanding that aromatics can only be confidently summed to C10) or 2) The sum of C5-C18 for samples collected using a sorbent media (e.g., sorbent tubes and TO-17 lab methods, with the understanding that aromatics can only be confidently summed to C10). This should be done regardless of whether the samples are associated with gasolines or middle distillates.

Laboratory methods for reporting of TPH in indoor air and soil gas are discussed in Section 7.13. A combination of both TO-15 (Summa canister samples) and TO-17 (sorbent tube samples) is currently recommended for initial investigation of petroleumcontaminated sites (see <u>HDOH 2012c</u>). The collection of concurrent, sorbent tube samples can be discontinued if initial data indicate that C12+ compounds make up less than 10% of the total TPH present in vapors.

Designation of chromatogram patterns as "gasoline range" (e.g., C5-C12) or "diesel range" (e.g., C10-C24) with respect to traditional, laboratory methods for TPH in soil or water is not applicable to air and vapor samples and can be misleading. The reported concentration of TPH can then be compared to HDOH soil gas action levels. The sum of concentrations of individual, target analytes such as BTEX and naphthalene that will be evaluated separate can be subtracted from the reported concentration of TPH in order to avoid double counting, although this is not likely to make a significant difference in the final concentration.

As discussed in TGM <u>Section 7.8</u>, the initial collection of both Summa canister samples and sorbent tube samples is recommended for soil vapor investigations at diesel and middle distillate sites. This is due to limitations on the ability to extract >C12 compounds from Summa canisters (see <u>Section 7.13.1.1</u>). A minimum Summa canister size of one-liter is recommended, in order to help collect a representative sample (tested for both TPH and target, indicator compounds such as BTEX and naphthalene). A maximum, 50ml vapor draw might be required for sorbent tube samples due to limitations of the sorbent material (tested only for TPH). Sorbent tube data are used to evaluate the relative proportion of >C12 compounds associated with TPH.

If the relative fraction of >C12 is less than 10% of the TPH then the concentration of TPH reported for the Summa canister can be used for comparison to action levels and Summa canisters can be relied upon for the collection of future samples. If >10% of the vapor-phase TPH is associated with >C12 compounds then a combined use of Summa data and sorbent tube data should be used to evaluate the site. For example, request that the laboratory report TPH for the sorbent tube sample as the sum of >C12 compounds. Add this to the concentration of TPH reported for the Summa sample (i.e., TPH as sum of C5-C12). The resulting, total TPH concentration can then be compared to soil gas action levels. This approach excludes the concentration of aromatic compounds greater than C10 but less than C12. Based on published information and data collected by the HEER Office, however, these compounds make up an insignificant (i.e., <10%) proportion of TPH vapors at typical, petroleum-release site.

Reported concentrations of unidentified hydrocarbons as gasoline, diesel or oil indicate that the chromatogram generated for the sample does not match standards used to quantify TPH. Reported concentrations of TPH should be considered approximate, but adequate for comparison to HDOH action levels. A more detailed evaluation through petroleum carbon range analysis can be carried out on a site-specific basis as warranted.

Silica gel cleanup of samples, in particular for surface water and groundwater, should not be carried out without consultation with HDOH. Two options are recommended: (1) Directly compare TPH data to HDOH EALs in the absence of silica gel cleanup, and/or (2) Report data both with and without silica gel cleanup. For the second option, compare the nonpolar, TPH fraction to HDOH EALs and evaluate potential hazards posed by TPH-derived, polar breakdown products to drinking water and aquatic habitats in a site-specific EHE (see <u>HDOH, 2016</u>).

Dissolved-phase TPH in water is composed of unaltered, nonpolar compounds originally in the parent fuel and polar compounds associated with the oxidation and biodegradation of the former (e.g., <u>Zemo 1995</u>, <u>2008</u>, <u>Lang et al 2009</u>, <u>Mohler et al. 2013</u>). Polar compounds can be removed by passing the sample through silica gel prior to analysis, referred to as "silica gel cleanup (SGC)." A column SGC lab method should be used rather than a shake or funnel method (e.g., Method 3630C, <u>USEPA 1996k</u>). If polar compounds are removed, both non-SGC and SGC data should be reported.

In many cases silica gel cleanup will significantly reduce the concentration of TPH reported for the sample. The polar compounds, which can dominate the overall mass of TPH in groundwater at aged-release sites, are primarily organic acids/esters and alcohols with variable amounts of ketones, phenols and aldehydes. These compounds must be taken into account as part of a site investigation. From an environmental hazard standpoint, the sum of the polar compounds and nonpolar compounds (i.e., the concentration of TPH reported in the absence of a silica gel cleanup) represents the concentration of TPH that should be directly compared to HDOH Environmental Action Levels (refer to HDOH EHE guidance; <u>HDOH, 2016</u>).

Methods for development of separate EALs for TPH-related, polar compounds or evaluation of these compounds in a sitespecific EHE or human-health risk assessment have not been fully developed. The toxicity of the polar fraction of the TPH to both humans and aquatic organisms has only recently begun to be studied (e.g., <u>Zemo et al. 2013</u>). As a default, and for the purposes of this guidance, the health risk and other potential environmental concerns associated with these compounds (e.g., toxicity to aquatic organisms, taste and odors in drinking water, etc.) is assumed at an initial screening level to be identical to the parent, nonpolar TPH compounds.

If silica gel cleanup of samples for a site is still desired (e.g., evaluation of degradation, fingerprinting of fuel releases, sitespecific risk assessment, etc.), then the objectives and methodology to be implemented should be presented to HDOH for review and approval. A quantitative evaluation of potential threats to human health and the environment should be carried out in accordance with the HDOH EHE guidance document for a site-specific EHE. This includes addressing potential aquatic ecotoxicity concerns as well as gross contamination concerns (e.g., drinking water taste and odors). Alternative action levels for each environmental hazard should be presented and supported for comparison to data. In most cases, it is anticipated that longterm management of groundwater contaminated primarily with polar, TPH breakdown compounds above HDOH action levels will still be required due to potential nuisance and aquatic toxicity hazards, even in the absence of apparent risk to human health (e.g., via impacts to drinking water resources).

Comparison of data for groundwater samples tested with and without silica gel cleanup could be useful for assessing the state of natural biodegradation within a plume of petroleum-contaminated groundwater and optimizing remedial and monitoring actions. For example, no further active remediation may be appropriate for areas of the plume where the majority of dissolved-phase hydrocarbons have degraded into polar compounds (i.e., significant reduction of reported TPH concentration in samples processed with silica gel cleanup). Active remediation could focus on areas of the plume where a comparison of data indicates that significant, natural degradation is not occurring. Data can also be used as one line of evidence to support a recommendation for no further monitoring and site closure following the HEER office guidance for long-term monitoring of petroleum-contaminated sites (HDOH 2007c; see TGM Section 19, Appendix 19-A).

9.3.2 PETROLEUM CONTAMINATION ENCOUNTERED DURING SUBSURFACE SOIL EXCAVATION

Unanticipated petroleum (free product) or petroleum-contaminated soil is sometimes encountered during construction work where subsurface soil is being excavated. The HEER Office has a Guidance Fact Sheet, consistent with the Hawai`i Environmental Response Law (HRS 128D; <u>HDOH 1990</u>), to assist project managers, contract workers, safety and health personnel or anyone involved in construction and excavation of soils when petroleum is encountered on a site. This document, "Guidance Fact Sheet for Use When Petroleum Contamination is Encountered During Subsurface Soil Excavation", is provided in <u>Appendix 9-D</u>.

In rare cases the reported concentration of TPH in soil with strong petroleum odors could fall below HEER Office EALs for gross contamination (refer to <u>HDOH, 2016</u>). This could be due to sampling error in the field, laboratory sample processing error, or the inability of the laboratory method to accurately quantify the amount of TPH in the soil. Even so, soil with an obvious petroleum odor should be considered grossly contaminated and managed appropriately. Removal and/or treatment of vadose-zone soil that exceeds the HEER Office EAL for subsurface gross contamination (e.g. 5,000 mg/kg) is typically recommended at a minimum when complete cleanup cannot be achieved. The HEER Office should be contacted regarding the on-site management or re-use of additional, petroleum contaminated soil. Refer also to the HEER Office Clean Fill Guidance for additional information (<u>HDOH 2011e</u>).

9.3.3 PAHS IN ASPHALT, TAR AND WASTE OIL

Understanding the potential source of polyaromatic hydrocarbon compounds (PAHs) in soil is important for decision making. Benzo(a)pyrene, the most potent of the PAHs, is almost always the risk driver in soils contaminated with PAHs. With the possible exception of naphthalene and methylnaphthalenes, these compounds are not present in significant amounts in gasolines and middle distillate fuels or soils impacted by these fuels (<u>API 1994</u>, <u>TPHCWG 1998</u>). They are present, however, in asphalt, waste oil and coal tar.

Samples of soil impacted with waste oil can have concentrations of benzo(a)pyrene and related PAHs in the tens of parts-permillion, well above Tier 1 EALs for potential direct-exposure concerns. Correlative concentrations of TPH up to approximately C40 are usually in the thousands of parts-per-million range (e.g., see <u>API 1994</u>). The concentration of PAHs in Bunker C and similar, residual fuels can also contain similar levels of BaP and other PAHs. Investigation and remediation of these soils is necessary for the protection of human health and the environment.

Soils impacted with asphalt can express similar concentrations of PAHs (e.g., see <u>API 1994</u>). An asphalt source of the PAHs is usually readily identifiable by relatively low concentrations of TPH, usually in the low hundreds of parts-per-million range. The bioavailability of PAHs in asphalt is relatively low and the presence at these levels does not pose a significant health risk. Asphalt is also regulated as an "inert waste" under Hawaii Revised Statutes 342H-1 and does not fall under HEER Office oversight, even if BaP concentrations exceed EALs. If the source of PAHs identified in soil can reasonably be attributed to asphalt, then no further action is required. The inclusion of small particles of asphalt in soil from heavily developed areas or previously paved areas may be unavoidable. The reuse or import of asphalt as fill material is not recommended at remediation sites overseen by the HEER Office (<u>HDOH 2011e</u>).

Relatively low concentrations of <C40 TPH are also often reported for soils impacted with coal tar, including manufactured as plant waste, older clay pigeons used at skeet ranges and petroleum-based patching material for roads or roofing (<u>API, 1994;</u> <u>EPRI, 1993</u>). The concentration of PAHs associated with these materials is often in the hundreds of parts-per-million range, however, highlighting coal tar or similar material as the likely source of the PAHs. Concentrations of PAHs in soil at these levels could pose potential direct-exposure concerns, even if the bioavailability of the PAHs is relatively low. Investigation and remediation of sites impacted with coal tar and similar material is essential.

In addition to asphalt, parts-per-billion to low, parts-per-million range concentrations of PAHs in soil in urban environments in combination with relatively low concentrations of TPH can also be associated with exhaust from vehicles, ash from fires and other source of combustion (<u>Mauro et al., 2006</u>). Recognition of anthropogenic background as part of a site investigation is necessary in order to correctly define the extent of contamination associated with releases of waste oil, manufactured gas plant waste or other sources that might require remediation.



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9.4 METHANE

Figure 9.1 Methane Mitigation Decision Matrix

Distance to		Methane Co	ncentration in Soil Gas	
structure <1000 ppm (<0.1%, <2% LEL) 1000 - 5000 ppm (0.1% - 0.5% 2% LEL - 10% LEL			5000 - 12,500 ppm (0.5% - 1.25% 10% LEL - 25% LEL)	> 12,500 ppm (> 1.25% > 25% LEL)
0 ft (beneath structure)	No Controls Recommended	Methane Monitoring Conduit Seals and Utility Trench Dams	Methane Monitoring Conduit Seals and Utility Trench Dams Vapor Mitigation	Methane Monitoring Conduit Seals and Utility Trench Dams Vapor Mitigation
0 - 100ft	No Controls Recommended	Methane Monitoring	Methane Monitoring Conduit Seals and Utility Trench Dams	Methane Monitoring Conduit Seals and Utility Trench Dams Vapor Mitigation
100 - 300ft	No Controls Recommended	No Controls Recommended	Methane Monitoring	Methane Monitoring Conduit Seals and Utility Trench Dams
>300ft	No Controls Recommended	No Controls Recommended	No Controls Recommended	Methane Monitoring

1. Decision matrix modeled after Geonsyntec 2011.

2. Actions listed in this decision matrix assume soil gas pressure is < 2 in-H2O. If soil gas pressure is greater than 2 in-H2O, then the need for enhanced mitigation measures should be evaluated.

This mitigation matrix does not preclude site-specific evaluation of engineering controls. Engineering control requirements can be reduced if additional indoor/sub-slab monitoring is conducted following construction of building or if site conditions are in the more conservative end of the listed criteria (i.e., lower end of methane concentration and upper end of distance criteria). If reduced controls are utilized, a mitigation decision matrix for soil gas and indoor air data should be developed.
 Methane Monitoring can include testing of exterior soil gas, sub-slab, and/or indoor air. A specific monitoring program

should be proposed prior to building construction.

Methane is a colorless, odorless and highly flammable gas generated by the anaerobic biodegradation of organic material, including petroleum. Methane can pose explosion and fire hazards under some conditions. In order for methane to create hazardous conditions, three conditions must be met: 1) A sufficient concentration of methane; 2) A sufficient concentration of oxygen and 3) An ignition source. Potential safety risks should be assessed by considering concentrations of methane and oxygen in soil gas, significance of advective (i.e., under pressure) transport, and potential for methane attenuation between the soil gas and structure or enclosed space.

Advective flow of methane under pressure from a source area is primarily a concern at landfills. This creates a high risk for significant, offsite migration and potential intrusion into the lower floors of buildings or subsurface utility corridors. Methane can be present at high concentrations in vadose-zone soil at petroleum-contaminated sites but is rarely under significant pressure and typically migrates by diffusion rather than advection. While significant offsite migration is less likely, diffusion into subsurface utility corridors could pose localized flash explosion or fire concerns if the methane mixes with oxygenated air and is encountered during subsurface construction or utility work. Accumulation of methane in poorly ventilated rooms of buildings with cracked floors, gaps around utility penetrations in the floor or other vapor entry routes could also pose potential hazards.

Figure 9-1 presents a summary of recommended monitoring and mitigation actions for site where high levels of methane are detected in soil vapors (<u>Geosyntec 2011</u>).

Final monitoring and mitigation actions for potential methane hazards will necessarily be site specific, and depend in part on the estimated area and volume of the source area, planned remedial actions to address the source, the presence and use of existing buildings and the planned use or redevelopment of the site. Coordination with HDOH and submittal of a site-specific

workplan for review is recommended. Additional methane guidance can be found in the following document: Advisory on Methane Assessment and Common Remedies at Schools Sites (<u>CalEPA 2005b</u>).

Be aware that high levels of light-end (C5-C12), petroleum vapors can cause false, elevated readings of methane in vapor samples using a standard, landfill gas analyzer. The use of a carbon trap is recommended when evaluating for methane when using field instruments at sites where high levels of petroleum may be present in soil gas. A carbon trap will remove the majority of petroleum aliphatic and aromatic compounds from the soil gas and allow for a more accurate reading of methane.



9.5 BACKGROUND METALS IN SOIL

Table 9-6 ¹Background Metals in Hawai'i Soils

Metal	Range (mg/kg)	² Upperbound Concentration (mg/kg)
Antimony	0.004-2.4	2.4
Arsenic	0.3-50	24
Barium	4.5-926	690
Beryllium	0.05-3.8	3
Cadmium	0.02-17	2.3
Chromium (Total)	8.52-3,180	1145
Cobalt	0.69-113	80
Copper	2.4-450	252
Lead	0.76-73	73
Mercury	<0.017-1.4	0.72
Molybdenum	0.06-4.0	4.0
Nickel	2.1-767	410
Selenium	0.24-12	7.1
Silver	0.02-1.5	1.5
Thallium	<0.25-15	0.25
Vanadium	0.25-1,090	770
Zinc	3.6-1,200	349

Reference: HDOH 2012b

Notes:

1. Excludes samples with known or suspected anthropogenic contamination.

2. Upper Bound concentration selected based on evaluation of univariate sample data plots.

3. Background Threshold Value set to maximum-reported concentration, excluding samples with suspected anthropogenic contamination.

4. Background action level based on Upper Bound concentration unless otherwise noted.

A review of background metals in soil is included in the HEER Office document Hawaiian Islands Soil Metal Background Evaluation (<u>HDOH 2012b</u>). The results of this study were incorporated into the EHE guidance document and associated EALs. As discussed in the EHE guidance document, naturally occurring background concentrations of some metals in soil exceed risk-based action levels for these metals (see <u>HDOH, 2016</u>). This is especially true for arsenic, but can also occur for heavy metals such as thallium, vanadium and other metals associated with soils developed over basaltic bedrock. These metals in soils are tightly bound to iron hydroxide and other complexes and do not pose a health risk, however.

The upper bound concentration of the metal was selected for background screening purposes in the EALs. A summary of selected background concentrations is provided in Table 9-6. Risk-based action levels were replaced with the natural background concentration of the chemical if the background value was higher.

As discussed in the HEER EHE guidance, the risk-based action level for arsenic for soils in an unrestricted ("residential") land use scenario is 0.42 mg/kg based on a 10-6 excess cancer risk (see <u>HDOH, 2016</u>). 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 (e.g., <u>Cutler et al 2013</u>). Background concentrations of arsenic in soils in Hawai'i typically range from 5 mg/kg to 24 mg/kg (see above references). A default, upper bound background concentration of 24 mg/kg arsenic is incorporated into the EAL lookup tables. Soils with total arsenic that exceed this concentration should be tested for bioaccessible arsenic (see <u>Section 9.1.3.2</u>). Upper threshold background values of arsenic in soil can approach 40 to 50 mg/kg, especially in discrete samples.

Note that background concentrations of naturally occurring metals in soil should not be included in calculation of cumulative risk as part of a site-specific risk assessment. Additional guidance on site-specific risk assessments is included in the HEER Office EHE guidance document (HDOH, 2016).

Direct comparison of background metals concentrations to sediment samples should be done with caution. Although data are limited, concentrations and relative ratios of metals in sediment derived primarily from volcanic soils and rocks should be similar to those noted in the table. Separation and concentration of heavy metals during sediment transport is possible, however. This could lead to either elevated or decreased concentrations of heavy metals in sediment in comparison to the parent material. A high concentration of organic matter in sediment (e.g., >10%) will also "dilute" the reported concentrations of heavy metals in comparison to the parent material. This can be accounted for by adjusting reported metal concentrations with respect to the concentration of Total Organic Carbon (TOC) in the sample (i.e., Adjusted Concentration = Reported Concentration/(1-Fraction TOC). As discussed in the report, the background data also focus on volcanic soils are not directly applicable to either soils or sediments derived primarily from coral and limestone. Concentrations of heavy metals in these cases are likely to be considerable lower than those noted in the above table.

Further information on background metals in Hawaiian island soils can be found on the <u>HEER Office website</u>. This website also has a link to the HEER Office document *Hawaiian Islands Soil Metal Background Evaluation* (<u>HDOH 2012b</u>).



9.6 METHAMPHETAMINE LABORATORY CLEANUP

9.6.1 BACKGROUND

Methamphetamine, also known as "meth," "speed," "crank," "crystal" and "ice," is a very powerful man-made drug that affects the central nervous system. Manufacture of methamphetamine is illegal. The product is often made in makeshift laboratories set up in rented property, including houses, apartments and hotel rooms. The majority of current operations in Hawai'i are believed to be small scale.

Many of the chemicals used to produce methamphetamine are highly volatile and toxic. These chemicals can cause death or injury to the lab operators and other occupants, law enforcement officials and first responders to lab explosions.

The number of properties contaminated by illegal methamphetamine laboratories has been increasing through the years. After the operations move or are shut down, property owners are often left with unknown and not necessarily obvious levels of contamination. Carpeting, wall board, ceiling tile, wood and fabric and other materials in a building can absorb the chemicals used in meth labs. Furniture or draperies also can be contaminated. Contamination can spread to other areas of the building if residues enter the heating, ventilation and air-conditioning system. Soil or groundwater may become contaminated if chemicals are disposed of in a septic system or dumped outside.

Detailed information and guidance on methamphetamine laboratory cleanup can be found at the <u>HEER Office meth labs</u> <u>webpage</u>. The webpage contains fact sheets, policies, and useful links outside of the website. A brief overview is provided below.

9.6.2 HDOH GUIDANCE

In 2006, Act 170 was signed into law in response to concern over the potential health effects associated with residual methamphetamine and related contaminants at these operations. The Act required HDOH to establish administrative rules for the cleanup of these sites. These rules became effective in November 2007. Guidance was prepared and <u>published in July 2010</u> (<u>HDOH 2010c</u>).

The guidance discusses methamphetamine manufacturing in Hawai'i, safety considerations during inspection and testing of former operations, hazardous materials disposal, decontamination procedures, reporting, and criteria that must be met before a No Further Action determination can be made by HDOH.

9.6.3 INVESTIGATION PROCESS

The HDOH HEER Office provides general oversight for the decontamination of methamphetamine manufacturing sites upon referral by the chief investigating law enforcement officer and coordination with the property owner. Testing is carried out prior to commencement of remediation activities.

The HEER Office reviews and approves the field sampling plan, quality assurance project plan, hazard assessment and recognition plan and health and safety plan submitted by the cleanup contractor(s). The contractor in most cases is hired by the property owner, unless a separate responsible party can be located to conduct sampling and decontamination. HDOH itself does not carry out sampling or decontamination activities.

Chemicals of potential concern to test for at former methamphetamine operations are necessarily site-specific. A number of methods are used to synthesize methamphetamine. The active ingredient is derived from one of three chemicals, ephedrine, pseudoephedrine, or phenylpropanolamine. Other chemicals used in the synthesizing process include iodine, red phosphorous, hydrochloric acid, ether, kerosene (e.g., Coleman fuel), paint thinner, acetone, drain cleaner, battery acid, lithium batteries, hydriodic acid, and anhydrous ammonia.

Table 9-7 includes a summary of chemicals that typically need to be included for testing for former methamphetamine labs and their associated hazards.

Table 9-7 Chemical Hazards Associated with Illegal Methamphetamine Labs

Typical Chemicals Found in Lab Sites	Common Legitimate Uses	Poison	Flammable	Toxic Vapors	Explosive	Corrosive	Skin Absorption	Common Health Hazards
Acetone	Fingernail polish remover, solvents	х	х	Х			X	Reproductive disorders
Methanol	Brake cleaner fluid, fuel	х	x	х			Х	Blindness, eye damage
Ammonia	Disinfectants	х		х		Х	x	Blistering, lung damage
Benzene	Dye, varnishes, lacquers	х	х		х	Х	х	Carcinogen, leukemia
Ether	Starter fluid, anesthetic	x	x		x			Respiratory failure
Freon	Refrigerant, propellants	х		x		Х		Frostbite, lung damage
Hydriodic Acid	Driveway cleaner	х		x		X	x	Burns, thyroid damage
Hydrochloric Acid (HCL Gas)	Iron ore processing, mining	Х		x		Х	x	Respiratory, liver damage
lodine Crystals	Antiseptic, catalyst	x	x		x	Х		Birth defects, kidney failure
Lithium Metal	Lithium batteries	Х				Х	x	Burns, pulmonary edema
Muriatic Acid	Swimming pool cleaners	х		x		Х		Burns, toxic vapors
Phosphine Gas	Pesticides	Х		Х			Х	Respiratory failure
Pseudoephedrine	Cold medicines	х						Abuse: Heart damage
Red Phosphorus	Matches, fireworks	Х	Х	Х	Х			Unstable, flammable
Sodium Hydroxide	Drain cleaners, lye	Х		Х		Х	X	Burns, skin ulcers
Sulfuric Acid	Battery acid	x		x		Х	х	Burns, thyroid damage
Toluene	Paint, thinners, solvents	X	X	Х	X		X	Fetal damage, pneumonia
Liquid Lab Waste	None	X	X	X	X	X	X	Unknown long term effects

Reference: HDOH 2010c

Prior to issuance of a No Further Action determination, the HEER Office confirms that each remediation process has been completed according to the approved work plan, and that the property has been decontaminated to below state-approved levels of concern. Refer to the full guidance for additional details (<u>HDOH 2010c</u>).



SECTION 9 REFERENCES

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SECTION 9 APPENDICES

- 9-A General Pesticide Information
- 9-B Initial Shortlist of Pesticides Used in Sugarcane and Pineapple Operations and Selection for Further Consideration
- 9-C Summary of Pesticides Used in Sugarcane and Pineapple Operations and Selection for Further Consideration
- 9-D Guidance Fact Sheet for Use When Petroleum Contamination is Encountered During Subsurface Soil Excavation
- 9-E Update to Soil Action Levels for Inorganic Arsenic and Recommended Soil Management Practices
- 9-F Update to Soil Action Levels for TEQ Dioxins and Recommended Soil Management Practices



APPENDIX 9-A GENERAL PESTICIDE INFORMATION

Chemical	Laboratory Analytical Group*	Standard Laboratory Method*	Availability of Toxicity Factors**	KoC (cm³/g)	Half- Life in Soil (days)	Half- Life Refer- ence***	Notes
Ametryn	Triazine Pesticides	8141 or 619M	Yes	4.5E+02	1.8E+02	5	Moderately persistent herbicide. Used since the 1960s (possibly earlier).
Arsenic	Heavy Metals	6010B/ 6020	Yes	?	na	-	Highly persistent herbicide component.
Atrazine	Triazine Pesticides	8141 or 619M	Yes	2.3E+02	1.0E+02	3	Moderately persistent herbicide. Used since the 1960s (possibly earlier).
Benomyl	Carbamates	8321	Yes	5.2E+02	3.6E+02	6	Moderately persistent fungicide used for seed dipping. Used since the 1970s.
Bromodichloromethane	VOCs	8260	Yes	3.5E+01	1.5E+00	3	Fumigant with low persistence.
Bromomethane	VOCs	8260	Yes	1.4E+01	2.8E+01	2	Fumigant with low persistence.
Captafol	Organochlorine Pesticides	8081 or 8270	Yes	2.7E+03	7.0E+00	8	Fumigant with low persistence.
Captan	SVOCs	8270	Yes	8.6E+02	2.5E+00	8	Fumigant with low persistence.
Chlordane (Technical)	Organochlorine Pesticides	8081	Yes	8.7E+04	1.0E+02	8	Moderately persistent insecticide. Cancelled in 1988.
Chlorpyrifos	Organo- phosphorus Pesticides	8141	Yes	6.8E+03	8.4E+01	1	Moderately persistent insecticide used since the 1970s.
Dalapon	Chlorinated Herbicides	8151 or 8321	Yes	2.7E+00	3.0E+01	8	Low to moderately persistent herbicide used since the 1950s.
Diazinon	Organo- phosphorus Pesticides	8141	Yes	1.3E+03	4.0E+01	8	Moderately persistent insecticide broadly used since the 1960s (possibly earlier).
Dibromo-3-Chloropropane, 1,2-	VOCs	8260 or 8081	Yes	1.3E+02	1.8E+02	1	Moderately persistent (although volatile) fumigant broadly used from the 1940s through 1980s.
Dibromochloromethane	VOCs	8260	Yes	3.5E+01	1.8E+02	2	Moderately persistent pesticide; unknown if used in cultivation.

Table 9-A (continued)

Chemical	Laboratory Analytical Group*	Standard Laboratory Method*	Availability of Toxicity Factors**	KoC (cm³/g)	Half- Life in Soil (days)	Half- Life Refer- ence***	Notes
Dibromoethane, 1,2-	VOCs	8260	Yes	4.4E+01	1.0E+02	8	Moderately persistent (although volatile) fumigant broadly used from the 1940s through 1980s.
Dicamba	Chlorinated Herbicides	8151 or 8321	Yes	2.9E+01	3.1E+01	7	Herbicide with low to moderate persistence.
Dichlorodiphenyl- dichloroethane (DDD)	Organochlorine Pesticides	8081 or 8270	Yes	1.5E+05	1.0E+03	8	Highly persistent impurity of DDT insecticide.
Dichlorodiphenyl- dichloroethylene (DDE)	Organochlorine Pesticides	8081 or 8270	Yes	1.5E+05	1.0E+03	8	Highly persistent impurity of DDT insecticide.
Dichlorodiphenyl- trichloroethane (DDT)	Organochlorine Pesticides	8081 or 8270	Yes	2.2E+05	1.2E+02	8	Moderately persistent insecticide. Used by State for mosquito control until banned in 1972.
Dichlorophenol, 2,4-	SVOCs	8270	Yes	7.2E+02	2.6E+00	1	Intermediate product of 2,4-D and other herbicides with low persistence.
Dichlorophenoxyacetic Acid (2,4 D)	Chlorinated Herbicides	8151 or 8321	Yes	7.2E+02	1.0E+01	8	Herbicide with low persistence.
Dichloropropane, 1,2-	Chlorinated Herbicides	8151	Yes	6.8E+01	3.6E+02	8	Moderately persistent (although volatile) fumigant used from the 1940s to 1974.
Dichloropropene, 1,3-	Chlorinated Herbicides	8151	Yes	8.1E+01	1.0E+01	8	Fumigant with low persistence.
Dioxins/Furans	Dioxins/furans	8280/8290	Yes	2.6E+05	3.7E+04	1	Highly persistent impurity of chlorinated phenol pesticides (pentachlorophenol; 2,4,5-T; 2,4,5-TP).
Diuron	Carbamates	8321	Yes	1.4E+02	9.0E+01	8	Moderately persistent herbicide. Used since the 1960s (possibly earlier).
Endosulfan	Organochlorine Pesticides	8081 or 8270	Yes	2.2E+04	1.5E+02	15	Pesticide with moderate persistence.

Chemical	Laboratory Analytical Group*	Standard Laboratory Method*	Availability of Toxicity Factors**	KoC (cm³/g)	Half- Life in Soil (days)	Half- Life Refer- ence***	Notes
Ethephon	SVOC	8270	Yes	3.6E+00	8.0E+00	7	Growth regulator with low persistence.
Glyphosate	Other	547	Yes	1.9E+01	4.7E+01	-	Herbicide with low to moderate persistence (beaks down in water).
Heptachlor	Organochlorine Pesticides	8081 or 8270	Yes	5.2E+04	2.5E+02	8	Moderately persistent insecticide and component of technical chlordane. Cancelled in 1988. Potentially used in fields with drip irrigation between 1979 & 1985.
Heptachlor Epoxide	Organochlorine Pesticides	8081 or 8270	Yes	5.3E+03	3.7E+02	-	Highly persistent component of technical chlordane.
Hexachlorocyclohexane, Gamma	Organochlorine Pesticides	8081 or 8270	Yes	3.4E+03	2.4E+02	12	Moderately persistent insecticide.
Hexazinone	Triazine Pesticides	8141	Yes	6.1E+02	2.2E+02	7	Moderately persistent herbicide used since the 1970s.
Lead	Heavy Metals	6010B/ 6020	Yes	?	na	-	Unknown if lead-based insecticides, herbicides, & rodenticides used in cultivation. Highly persistent.
Malathion	Organo- phosphorus Pesticides	8141 or 8270	Yes	3.1E+01	1.0E+00	7	Insecticide with low persistence. Used since the 1960s (possibly earlier).
Mercury	Heavy Metals	7471	Yes	1.7E+02	?	-	Highly persistent fungicide (seed dipping). All food uses cancelled in 1969.
Methyl Mercury	Heavy Metals	7471	Yes	?	?	-	Methylated form of mercury generated in reducing environments; potential byproduct.
Methyl Sulfanilcarbamate	Carbamates	8321A	Yes	1.2E+03	3.1E+01	-	Herbicide used since the 1970s. Low to moderate persistence.
Metribuzin	Triazine Pesticides	8141	Yes	1.2E+03	4.4E+02	7	Highly persistent herbicide used since the 1970s.

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Chemical	Laboratory Analytical Group*	Standard Laboratory Method*	Availability of Toxicity Factors**	KoC (cm³/g)	Half- Life in Soil (days)	Half- Life Refer- ence***	Notes	
Mirex	Organochlorine Pesticides	8081 or 8270	Yes	4.7E+05	3.7E+02	-	Highly persistent insecticide. Very limited use in Hawai'i. Not sold in US since 1978.	
Oxamyl	Carbamates	8321	Yes	1.0E+01	2.7E+01	7	Insecticide with low persistence.	
Parathion	Organo- phosphorus Pesticides	8141 or 8270	Yes	1.7E+03	7.3E+02	13	Highly persistent insecticide. Registration cancelled in 1992.	
Pentachlorophenol	SVOCs or Chlorinated Herbicides	8270 or 8151	Yes	3.4E+03	3.0E+01	15	Herbicide used from 1960s (possibly earlier) until 1970. Low to moderate persistence.	
Picloram	Chlorinated Herbicides	8151	Yes	1.8E+01	3.0E+02	7	Moderately persistent sugarcane herbicide used since the 1960s (possibly earlier).	
Propiconazole	Carbamates	8321	Yes	5.6E+03	8.4E+01	7	Moderately persistent fungicide. Used since the 1980s.	
Simazine	Triazine Pesticides	8141 or 619M	Yes	1.5E+02	2.5E+02	8	Moderately persistent herbicide. Used since the 1960s (possibly earlier).	
Terbacil	Organonitrogen	633	Yes	7.8E+01	5.2E+02	7	Highly persistent herbicide. Limited used since the 1970s; not significantly toxic.	
Tetrachlorophenol, 2,3,4,6-	SVOCs	8270	Yes	2.0E+03	3.0E+01	-	Component of pentachlorophenol with low to moderate persistence.	
Trichlorophenoxyacetic Acid, 2,4,5- (2,4,5 T)	Chlorinated Herbicides	8151 or 8321	Yes	1.2E+03	3.0E+02	10	Moderately persistent herbicide. Limited possible use with sugarcane in 1960s. Suspended in 1985.	
Trichlorophenoxypropionic Acid, 2,4,5- (2,4,5 Tp)	Chlorinated Herbicides	8151 or 8321	Yes	4.9E+01	1.7E+01	11	Herbicide with low persistence. Limited possible use with sugarcane in 1960s. Suspended in 1985.	
Trichloropropene, 1,2,3- (TCP)	VOCs	8260	Yes	1.3E+02	3.1E+01	-	Impurity in 1,3 dichloropropene with low to moderate persistence.	
Trifluralin	Organochlorine Pesticides	8081 or 8270	Yes	9.7E+03	6.0E+01	8	Moderately persistent herbicide. Used since the 1980s.	

Chemical	Laboratory Analytical Group*	Standard Laboratory Method*	Availability of Toxicity Factors**	KoC (cm³/g)	Half- Life in Soil (days)	Half- Life Refer- ence***	Notes
Used But No Toxicity Data	And/Or No Star	dard Labora	tory Method	3			
Amitrole	Other	?	No	2.0E+01	2.6E+01	4	Herbicide used pre-1971 with low persistence.
Ammonium Sulfamate	Other	?	Yes	?	?	-	Herbicide used in the 1960s until possibly the 1980s; assumed low persistence.
Bromacil	Carbamates	8321	No	9.3E+00	2.4E+02	3	Moderately persistent herbicide. Used since the 1960s.
Chloropicrin	Other		No	5.1E+01	1.0E+00	8	Fumigant with low persistence.
Dichloropropene, 2,3-	Chlorinated Herbicides	8151	No	8.1E+01	1.6E+01	8	Fumigant with low persistence.
Diphacinone	Other	?	No	5.0E+03	3.7E+02	?	Rodenticide with moderate to high persistence.
Diquat	Other	?	Yes	1.9E+03	1.0E+03	8	Highly persistent growth regulator.
Endrin Aldehyde	Organochlorine Pesticides	8081 or 8270	No	1.1E+04	3.7E+02	8	Highly persistent impurity of Endrin.
Fenaminosulf	Other	?	Yes	1.0E+00	1.5E+01	8	Fungicide with low persistence.
Fenamiphos	Organo- phosphorus Pesticides	8141	No	2.3E+02	5.0E+00	8	Nematicide with low persistence.
Fenthion	Organo- phosphorus Pesticides	8141 or 8270	No	1.1E+02	3.4E+01	8	Moderately persistent insecticide used since the 1960s.
Fosetyl-Aluminum	Other	?	Yes	5.3E+03	1.0E-01	8	Fungicide with low persistence.
Hydramethylnon	Other	?	No	6.3E+08	?	-	Insecticide (ant control) with unknown persistence.
Mancozeb	Other	?	Yes	1.0E+01	2.0E+00	7	Fungicide with low persistence.
Monuron	Carbamates	8321	No	?	1.0E+02	-	Herbicide with moderate persistence. Registration cancelled in 1977.
Paraquat	Other	?	Yes	1.4E+03	7.3E+02	14	Highly persistent herbicide. Used since the 1960s.

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Chemical	Laboratory Analytical Group*	Standard Laboratory Method*	Availability of Toxicity Factors**	KoC (cm³/g)	Half- Life in Soil (days)	Half- Life Refer- ence***	Notes
Pindone	Other	?	No	2.8E+01	?	-	Rodenticide with unknown persistence.
Quizalofop-P-Ethyl	Other	?	No	5.4E+02	6.0E+01	3	Moderately persistent herbicide. Used from the 1980s until present.
Sodium Chlorate	Other	?	No	1.0E+00	?	-	Herbicide with unknown persistence.
Sodium Monofluoracetate	Other	?	Yes	1.2E+00	?	-	Rodenticide with unknown persistence. Used in 1960s until unknown time.
Sodium Trichloroacetate	Other	?	No	1.0E+00	?	-	Herbicide with unknown persistence. Used in the 1960s until unknown time.
Sulfometuron-Methyl	Carbamates (modified)	8321Mod	No	7.8E+01	2.8E+01	7	Herbicide with low persistence.
Temephos	Other	?	Yes	1.6E+06	?	-	Insecticide with unknown persistence. Used in the 1960s until unknown time.

Notes:

*

*	Laboratory	y analytical method used to categorize pesticides may not match actual pesticide chemical category.
**	Toxicity va (USEPA, 2	alue availability noted as "Yes" if listed in May 2008 USEPA Regional Screening Levels guidance 2008). KoC values from same reference.
***	Half-Life F	References. The number in the column above corresponds to the references shown below.
	1	Montgomery, J.H. 2000. Groundwater Chemicals. Desk Reference (3rd Ed).
	2	Mackay, Shiu, Ma. 1992. Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals.
	3	Extonet. Available online at: http://extoxnet.orst.edu/
	4	USEPA. Reregistration Eligibility Decision - Amitrole. List A. Case 0095. (http://www.epa.gov/oppsrrd1/REDs/0095red.pdf)
	5	Spectrum. Chemical fact Sheet - Ametryn (http://www.speclab.com/compound/c834128.htm)
	6	Benomyl fact Sheet. Pesticides News No.35, March 1997, p20-21 (http://www.pan- uk.org/pestnews/actives/benomyl.htm)
	7	ARS Pesticide Properties Database (http://www.ars.usda.gov/Services/docs.htm?docid=14199)
	8	Knisel & Davis. 2000. Groundwater Loading Effects of Agricultural Management Systems.
	9	Toxicological Profile for Pentachlorophenol. ATSDR 1991. http://www.atsdr.cdc.gov/toxprofiles/tp51.html
	10	Spectrum Chemical fact Sheet - 2,4,5-Trichlorophenoxyacetic Acid. http://www.speclab.com/compound/c93765.htm
	11	Spectrum Chemical fact Sheet - 2,4,5-Trichlorophenoxypropionic Acid. http://www.speclab.com/compound/c93721.htm
	12	Extoxnet - Lindane (BHC). Available online at http://extonet.orst.edu/
	13	Extoxnet - Parathion. Available online at http://extoxnet.orst.edu/
	14	Extoxnet - Paraquat. Available online at http://extoxnet.orst.edu/
	15	Toxnet HSDB. Available online at http://toxnet.nlm.nih.gov/cgi-bin/sis/htmlgen?HSDB



APPENDIX 9-B

Initial Shortlist of Pesticides Used in Sugarcane and Pineapple Operations and Selection for Further Consideration

Chemical ¹	Synonyms	Laboratory Analytical Grouping ²	Period Used in Hawaii ³	Persistence⁴	Mobility⁵	Known Use in Sugar Cane Production?	Known Use in Pineapple Production?
Benomyl	Benlate	8321 (Carbamates)	1970s to present?	Moderate	Moderate	Yes	Yes
Diuron	Karmex	8321 (Carbamates)	1960s- present	Moderate	Moderate	Yes	Yes
Methyl Sulfanilcarbamate	Asulam	8321 (Carbamates)	1970s- present	Moderate	Moderate	Yes	Yes
Oxamyl	Vydate	8321 (Carbamates)	1980s- present?	Low	High	No	Yes
Propiconazole	Tilt	8321 (Carbamates)	1980s- present?	Moderate	Low	Yes	Yes
Dalapon		8151 or 8321 (Chlorinated Herbicides)	1953 - present?	Moderate	High	Yes	Yes
Dicamba		8151 or 8321 (Chlorinated Herbicides)	? to present	Moderate	High	Yes	No
Dichlorophenoxyacetic Acid (2,4 D)	2,4-D	8151 or 8321 (Chlorinated Herbicides)	1960s- present	Low	Moderate	Yes	No
Dichloropropane, 1,2-		8151 or 8321 (Chlorinated Herbicides)	1940s- 1974	Moderate	High	No	Yes
Dichloropropene, 1,3-	Telone, D-D 92	8151 or 8321 (Chlorinated Herbicides)	1940s- present?	Low	High	No	Yes
Picloram	Tordon	8151 or 8321 (Chlorinated Herbicides)	1960s- present?	Moderate	High	Yes	No
Trichlorophenoxyacetic Acid, 2,4,5- (2,4,5 T)	2,4,5-T	8151 or 8321 (Chlorinated Herbicides)	1960s?	Moderate	Moderate	Yes	No
Trichlorophenoxypropionic Acid, 2,4,5- (2,4,5 Tp)	2,4,5-TP, Silvex	8151 or 8321 (Chlorinated Herbicides)	1960s?	Low	High	Yes	No

Table 9-B (continued)

Chemical ¹	Synonyms	Laboratory Analytical Grouping ²	Period Used in Hawaii ³	Persistence⁴	Mobility⁵	Known Use in Sugar Cane Production?	Known Use in Pineapple Production?
Arsenic		6010B or 6020 (Heavy Metals)	1913 to 1960s	High	Site- specific	Yes	?
Lead		6010B or 6020 (Heavy Metals)	Unknown	High	Site- specific	Yes	No
Mercury	Phenylmercuric acetate	7471 (Mercury)	?-1969	High	Moderate	Yes	No
Methyl Mercury		7471 (Mercury)	?-1969	High?	High?	Yes	No
Captafol	Difolatan	8081 or 8270 (Organochlorine Pesticides)	1970s to ?	Low	Moderate	Yes	Yes
Chlordane (Technical)	Technical Chlordane	8081 or 8270 (Organochlorine Pesticides)	1960s to 1988	Moderate	Moderate	No	Yes
Endosulfan		8081 or 8270 (Organochlorine Pesticides)	1960s- 1980s?	Moderate	Moderate	No	Yes
Heptachlor		8081 or 8270 (Organochlorine Pesticides)	1960s- 1988	Moderate	Moderate	Yes	Yes
Heptachlor Epoxide		8081 or 8270 (Organochlorine Pesticides)	1960s- 1988	High	Low	No	Yes
Hexachlorocyclohexane, Gamma	Lindane, BHC	8081 or 8270 (Organochlorine Pesticides)	1960s- present?	Moderate	Moderate	No	Yes
Trifluralin	Treflan	8081 or 8270 (Organochlorine Pesticides)	1980s- present	Moderate	Moderate	Yes	No
Chlorpyrifos	Dursban	8141 or 8270 (Organophosphorus Pesticides)	1970s to present?	Moderate	Low	Yes	Yes

Chemical ¹	Synonyms	Laboratory Analytical Grouping ²	Period Used in Hawaii ³	Persistence ⁴	Mobility⁵	Known Use in Sugar Cane Production?	Known Use in Pineapple Production?
Diazinon		8141 or 8270 (Organophosphorus Pesticides)	1960s - present	Moderate	Moderate	Yes	Yes
Malathion		8141 or 8270 (Organophosphorus Pesticides)	1960s- present?	Low	High	Yes	Yes
Parathion		8141 or 8270 (Organophosphorus Pesticides)	1960s- 1992	High	Moderate	No	Yes
Ethephon	Ethrel	8270 (SVOCs)	1980s- present?	Low	High	Yes	Yes
Captan	Ethyl Mercapton	8270 (SVOCs)	1960s to ?	Low	Moderate	No	Yes
Dichlorophenol, 2,4-		8270 (SVOCs)	1960s- present	Low	Moderate	Yes	No
Tetrachlorophenol, 2,3,4,6-		8270 (SVOCs)	1960s- 1984?	Moderate	Moderate	Yes	Yes
Pentachlorophenol		8270 or 8151 (SVOCs or Chlorinated Herbicides)	1960s- 1970	Moderate	Low	Yes	Yes
Ametryn	Evik	8141 or 8270 (Triazine Pesticides)	1960s to present	Moderate	Moderate	Yes	Yes
Atrazine	Astrex	8141 or 8270 (Triazine Pesticides)	1960s to present	Moderate	Moderate	Yes	Yes
Hexazinone	Velpar	8141 or 8270 (Triazine Pesticides)	1970s- present	Moderate	Moderate	Yes	Yes
Metribuzin		8141 or 8270 (Triazine Pesticides)	1970s- present	High	Moderate	Yes	No
Simazine		8141 or 8270 (Triazine Pesticides)	1960s- present	Moderate	Moderate	Yes	Yes

Chemical ¹	Synonyms	Laboratory Analytical Grouping ²	Period Used in Hawaii ³	Persistence⁴	Mobility⁵	Known Use in Sugar Cane Production?	Known Use in Pineapple Production?
Bromodichloromethane		8260 (VOCs)	1960s to ?	Low	High	No	Yes
Bromomethane	Methyl Bromide	8260 (VOCs)	1960s to present	Low	High	No	Yes
Dibromo-3- Chloropropane, 1,2-	DBCP	8260 (VOCs)	1940s- 1985	0s- 35 Moderate Moder		No	Yes
Dibromochloromethane		8260 (VOCs)	Unknown	Moderate	High	No	Yes
Dibromoethane, 1,2-	EDB	8260 (VOCs)	1940s- 1983	Moderate	High	No	Yes
Trichloropropene, 1,2,3-	TCP	8260 (VOCs)	1940s- 1978	Moderate	Moderate	No	Yes
Dioxins/Furans		8280/8290 (Dioxins/furans)	1960s- 1985?	High	Low	Yes	Yes
Glyphosate	Roundup, Rodeo, Polado	547		Low	High	Yes	Yes
Terbacil	Sinbar	633 (Organonitrogen Pesticides)	1970s- present	High	High	Yes	No

Notes:

- 1 Refer to Appendix 9-A. Pesticide retained for consideration if toxicity data and standard laboratory analytical method available. Includes pesticide likely to drive environmental hazards at former agricultural sites.
- 2 Laboratory analytical method used to categorize pesticides may not match actual pesticide chemical category.
- 3 For sugarcane and pineapple agricultural purposes, reported or estimated dates of use in Hawai'i.
- 4 Persistence ranking based on chemical and biological degradation potential.
 - Metals all given persistence of "high"
 - Scale for persistence for chemicals with half-life data: High = >1 year Moderate = one month to one year Low = <one month
 - Where multiple values reported, highest value used to make determination. Soil degradation rates used are used preferentially.
 - Data for one isomer used to estimate persistence of other isomers, as necessary.

5 Mobility ranking based on sorption coefficient, solubility and volatility.

- Sorption coefficient (Koc): High = KoC<100 Moderate = 100<Koc<3,000 Low KoC>3,000
- KoC values from USEPA May 2008 RSL guidance when available; otherwise as complied as noted in Appendix 9-A.
- If no KoC was available, but water solubility was high, pesticide was assumed to have high mobility.
- All volatiles given a mobility of High. Volatiles = Henry's law constant (unitless) >1E-4 and molecular weight <200
- All metals given a mobility of Low
- VOC Volatile Organic Compounds
- SVOC Semi-Volatile Organic Compounds

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APPENDIX 9-C Summary of Pesticides Used in Sugarcane and Pineapple Operations and Selection for Further Consideration

Chemical	Synonyms	Laboratory Analytical Grouping ¹	Retained as COPC for Sugar Cane? (Field Areas) ²	Retained as COPC for Sugar Cane? (Non-Field areas) ²	Retained as COPC for Pineapple? (Field Areas) ²	Retained as COPC for Pineapple? (Non-Field areas) ²	Notes
Benomyl	Benlate	8321 (Carbamates)	No	Yes	No	Yes	Fungicide used in seed dipping operations.
Diuron	Karmex	8321 (Carbamates)	No	Yes	No	Yes	
Methyl Sulfanilcarbamate	Asulam	8321 (Carbamates)	No	No	No	No	Limited use and not significantly toxic.
Oxamyl	Vydate	8321 (Carbamates)	No	No	No	No	
Propiconazole	Tilt	8321 (Carbamates)	No	Yes	No	Yes	Fungicide used in seed dipping operations.
Dalapon		8151 or 8321 (Chlorinated Herbicides)	No	Yes	No	Yes	
Dicamba		8151 or 8321 (Chlorinated Herbicides)	No	Yes	No	No	
Dichlorophenoxyacetic Acid (2,4 D)	2,4-D	8151 or 8321 (Chlorinated Herbicides)	No	No	No	No	
Dichloropropane, 1,2-		8151 or 8321 (Chlorinated Herbicides)	No	No	No	Yes	
Dichloropropene, 1,3-	Telone	8151 or 8321 (Chlorinated Herbicides)	No	No	No	No	
Picloram	Tordon	8151 or 8321 (Chlorinated Herbicides)	No	No	No	No	Limited use and not significantly toxic.

Chemical	Synonyms	Laboratory Analytical Grouping ¹	Retained as COPC for Sugar Cane? (Field Areas) ²	Retained as COPC for Sugar Cane? (Non-Field areas) ²	Retained as COPC for Pineapple? (Field Areas) ²	Retained as COPC for Pineapple? (Non-Field areas) ²	Notes
Trichlorophenoxyacetic Acid, 2,4,5- (2,4,5 T)	2,4,5-T	8151 or 8321 (Chlorinated Herbicides)	No	Yes	No	No	
Trichloro- Phenoxypropionic Acid, 2,4,5- (2,4,5 Tp)	2,4,5-TP, Silvex	8151 or 8321 (Chlorinated Herbicides)	No	No	No	No	
Arsenic		6010B or 6020 (Heavy Metals)	Yes	Yes	Yes	Yes	Include arsenic for pineapple operations.
Lead		6010B or 6020 (Heavy Metals)	No	Yes	No	Yes	Lead-based pesticides not used in sugarcane field areas.
Mercury	Phenyl- mercuric acetate	7471 (Mercury)	No	Yes	No	No	
Methyl Mercury		7471 (Mercury)	No	Yes	No	No	Investigate only if total Hg contamination identified.
Captafol	Difolatan	8081 or 8270 (Organochlorine Pesticides)	No	No	No	No	
Chlordane (Technical)	Technical Chlordane	8081 or 8270 (Organochlorine Pesticides)	No	No	No	Yes	
Endosulfan		8081 or 8270 (Organochlorine Pesticides)	No	No	Yes	Yes	

Chemical	Synonyms	Laboratory Analytical Grouping ¹	Retained as COPC for Sugar Cane? (Field Areas) ²	Retained as COPC for Sugar Cane? (Non-Field areas) ²	Retained as COPC for Pineapple? (Field Areas) ²	Retained as COPC for Pineapple? (Non-Field areas) ²	Notes
Heptachlor		8081 or 8270 (Organochlorine Pesticides)	Yes	Yes	Yes	Yes	Only used in fields with drip irrigation between 1979 & 1985. Cancelled in 1988.
Heptachlor Epoxide		8081 or 8270 (Organochlorine Pesticides)	No	No	Yes	Yes	
Hexachlorocyclohexane, Gamma	Lindane, BHC	8081 or 8270 (Organochlorine Pesticides)	No	No	Yes	Yes	
Trifluralin	Treflan	8081 or 8270 (Organochlorine Pesticides)	No	Yes	No	No	
Chlorpyrifos	Dursban	8141 or 8270 (Organophosphorus Pesticides)	No	No	No	No	Limited use in small amounts.
Diazinon		8141 or 8270 (Organophosphorus Pesticides)	No	No	No	No	Limited use in small amounts.
Malathion		8141 or 8270 (Organophosphorus Pesticides)	No	No	No	No	Limited use in small amounts.
Parathion		8141 or 8270 (Organophosphorus Pesticides)	No	No	No	No	Limited use in small amounts.

Chemical	Synonyms	Laboratory Analytical Grouping ¹	Retained as COPC for Sugar Cane? (Field Areas) ²	Retained as COPC for Sugar Cane? (Non-Field areas) ²	Retained as COPC for Pineapple? (Field Areas) ²	Retained as COPC for Pineapple? (Non-Field areas) ²	Notes
Ethephon	Ethrel	8270 (SVOCs)	No	No	No	No	
Captan	Ethyl Mercapton	8270 (SVOCs)	No	No	No	No	
Dichlorophenol, 2,4-		8270 (SVOCs)	No	No	No	No	
Tetrachlorophenol, 2,3,4,6-		8270 (SVOCs)	No	Yes	No	Yes	
Pentachlorophenol		8270 or 8151 (SVOCs or Chlorinated Herbicides)	No	Yes	No	Yes	Banned for use in agricultural fields in 1970
Ametryn	Evik	8141 or 8270 (Triazine Pesticides)	No	Yes	No	Yes	
Atrazine	Astrex	8141 or 8270 (Triazine Pesticides)	No	Yes	No	Yes	
Hexazinone	Velpar	8141 or 8270 (Triazine Pesticides)	No	No	No	No	Limited use in small quantities
Metribuzin		8141 or 8270 (Triazine Pesticides)	No	No	No	No	Limited use in small quantities
Simazine		8141 or 8270 (Triazine Pesticides)	No	Yes	No	Yes	
Bromodichloromethane		8260 (VOCs)	No	No	No	No	
Bromomethane	Methyl Bromide	8260 (VOCs)	No	No	No	No	
Dibromo-3- Chloropropane, 1,2-	DBCP	8260 (VOCs)	No	No	No	Yes	
Dibromochloromethane		8260 (VOCs)	No	No	No	Yes	
Dibromoethane, 1,2-	EDB	8260 (VOCs)	No	No	No	Yes	
Trichloropropene, 1,2,3-	TCP	8260 (VOCs)	No	No	No	Yes	

Chemical	Synonyms	Laboratory Analytical Grouping ¹	Retained as COPC for Sugar Cane? (Field Areas) ²	Retained as COPC for Sugar Cane? (Non-Field areas) ²	Retained as COPC for Pineapple? (Field Areas) ²	Retained as COPC for Pineapple? (Non-Field areas) ²	Notes
Dioxins/Furans		8280/8290 (Dioxins/furans)	No	Yes	No	Yes	
Glyphosate	Roundup, Rodeo, Polado	547	No	No	No	No	
Terbacil	Sinbar	633 (Organonitrogen Pesticides)	No	No	No	No	Limited use and toxicity.

<u>Notes:</u> 1

2

Laboratory analytical method used to categorize pesticides may not match actual pesticide chemical category.

Retained as chemical of potential concern (COPC) if: any of the following:

• Known past use.

• Commercial lab method available.

• Toxicity factors & physiochemical constants available.

• Non-field areas are moderately or highly persistent or field areas are highly persistent (see text for details).



APPENDIX 9-D Guidance Fact Sheet for Use When Petroleum Contamination is Encountered during Subsurface Soil Excavation

PURPOSE: The purpose of this Guidance Fact Sheet is to provide guidance for construction projects when petroleum or petroleum contaminated soil (PCS) is encountered. These guidelines apply to construction projects that involve soil excavation, except associated with underground storage tank (UST) removal. These guidelines are consistent with Hawaii Revises Statutes Chapter 128D, Hawaii Environmental Response Law. Administrative procedures must be in place within your organization, so that project managers, contract workers, field workers, health and safety personnel, and essentially anyone who might be involved in construction and the excavation of soils follow these basic guidelines:

When must notification to the HEER Office be made?

The reportable quantity for petroleum is one of the following:

- a. Any amount of oil which when released into the environment causes a sheen to appear on surface water, or any navigable water of the State.
- b. Any free product that appears on groundwater.
- c. Any amount of oil released to the environment greater than 25 gallons.
- d. Any amount of oil released to the environment, which is not contained and remediated within 72 hours. Note: The HEER Office interprets this criteria to require petroleum-stained soil encountered during excavation work to be reported.

Who must notify?

Any person who has any knowledge of a release of a reportable quantity must immediately notify the HEER Office. Failure to notify the HEER Office of a release is subject to a civil penalty not to exceed \$10,000 for each day of failure to report.

What is the number to call?

Hawaii State Department of Health, Hazard Evaluation and Emergency Response Office (HEER Office):

(808) 586-4249 during working hours, Monday – Friday, 7:45 a.m. – 4:30 p.m.

or

(808) 247-2191 during non-working hours including holidays.

What information is required to be provided to the HEER Office?

The information gathered should be sufficient to answer the following, but notification shall not be delayed due to incomplete notification:

- 1. Name of the observed chemical released
- 2. Approximate quantity observed
- 3. The location and an address of the release. The location may be determined by either surveying by a licensed surveyor or the use of a Global Positioning System (GPS) unit, which provides latitude and longitude. The latitude and longitude of the contaminated area should be accurate to within 25 feet of the actual position. A detailed map should be submitted to the HEER Office at a later date
- 4. The name, address, and telephone number of the caller
- 5. The name, address, and telephone number of the owner/operator of the site where the release has occurred
- 6. The name, address, and telephone number of the contact person at the site where the release has occurred
- 7. Measures taken or proposed to be taken in response to the release at the time of the notification

8. Any other information, including but not limited to, potential on-site worker and public or environmental impacts

Who else should be notified?

If a party other than the landowner is conducting the project, then a separate notification needs to be made to the landowner to allow them to determine their liability and the next course of action.

What additional steps must be taken?

1. When petroleum or PCS is discovered during construction activities, an immediate determination is needed as to whether it may be a threat to the health and welfare of on-site workers or the nearby public.

If a combustible hazard is identified, an Emergency Response Plan should be put into effect. No work may continue until the area is determined to be safe.

[Note: A Combustible Gas Indicator may be used to determine if there is a flammable or explosive potential. Each combustible gas has its own Lower Explosive Level (LEL) and its Upper Explosive Level (UEL). For example, methane gas has a LEL of 5 percent (%) by volume and an UEL of 15% by volume. Between 5 to 15% by volume, a spark could cause an explosion. If the atmosphere has less than 5% methane, an explosion cannot occur even if a source of ignition is present. Likewise, if the atmosphere has greater than 15% methane, the air-fuel mixture is too rich to burn. Gasoline has a LEL of 1.4% by volume and an UEL of 7.4% by volume.

- 2. The project may continue with implementation of a Health and Safety Plan in accordance with applicable occupational safety and health regulations. This plan should address exposure issues and include appropriate air monitoring.
- 3. If free-floating petroleum product is encountered during the project, the product is to be recovered and either re-used or disposed of appropriately.
- 4. Petroleum-contaminated water encountered during dewatering projects must be tested and treated as necessary prior to discharge into a storm drain or other pathway that leads to surface water bodies. At a minimum, this will usually require that the water be passed through an oil/water separator. The water should also be tested for dissolved-phase petroleum contaminants prior to discharge (at least initially). The water should be treated to meet HDOH Environmental Action Levels for discharges to surface waters or a more site-specific assessment of potential impacts to aquatic habitats carried out. The HEER Office Environmental Hazard Evaluation (EHE) guidance can be consulted for applicable surface water environmental action levels, or call the HEER Office (808) 586-4249 during business hours for assistance.

Groundwater Management:

Groundwater that contains free product or a sheen can assumed to be contaminated with dissolved analytes. Reinfiltration, reinjection, treatment, disposal, or discharge are all acceptable options for the disposition of groundwater generated during subsurface excavation that encounters contaminated groundwater. Of these choices, re-infiltration within the Work Area where the water was extracted is the least expensive and easiest way to manage contaminated groundwater; however this option may not be feasible at all project locations.

- A. Groundwater should be reused within the Work Area and within the same aquifer where it was removed. Reuse in other areas could spread unidentified contamination or cause existing plumes in those areas to migrate.
- B. Removal and reuse must meet existing Federal and State permit requirements.
- C. If discharged to storm sewers or surface water bodies:
 - 1. National Pollution Discharge Elimination System and State permit requirements also apply. Prior to dewatering, clearance and/or permits from the CWB are required.
 - Removal of floating product via an oil water separator and/or passage of the water through settling ponds or sand filters may not be adequate to reduce dissolved-phase contaminant concentrations to below action levels. Therefore, in addition to analytical screening required in applicable Federal and State permits, the HEER Office recommends:
 - a. At a minimum, all groundwater discharged to storm sewers must be analyzed for constituents related to petroleum and solvents.
 - b. Additional analytical data may be required based on knowledge of contamination within the vicinity of the work area.
 - c. The groundwater must be analyzed for known or suspected contaminants and the results must be screened against the Estuarine EALs for Surface Water Bodies, in Table D of Volume

1 of Screening for Environmental Hazards at Sites with Contaminated Soil and Groundwater, Fall 2011 Updates, Revised January 2012 (and updates)

- d. For some site-specific locations, the HEER Office analytical requirements may be adjusted with advance approval. Permit requirements will not be adjusted.
- D. If discharged to sanitary sewers, contractors must follow the requirements of all permits.
- E. If discharged to a re-infiltration trench:
 - 1. The trench must be within the Work Area, especially if the groundwater is extracted from a Work Area in the vicinity of known or observed contamination.
 - The trench must not be an underground injection control (UIC) well by SDWB definitions. If some part
 of the trench system is deemed to be a UIC well, then the whole system is considered an injection
 well.
 - 3. Advance clearance from SDWB is required if a re-infiltration trench is deeper than 10 feet.
- F. UIC wells may be used, but advance planning and approval are required. SDWB permit requirements must be met for well construction, placement, use, and closure.
- G. In instances where "oily water" is disposed, the receiving facility must be permitted for that type of waste.
- 5. Petroleum contaminated soil is to be excavated and segregated from clean soils. Excavated contaminated soil must be placed under a liner and covered. Contaminated soil must be treated or disposed of in accordance with all applicable local, state and federal requirements.

On-Site Management of Contaminated Soils:

When deciding whether to re-deposit contaminated soil, the time saved by proceeding with the project immediately should be weighed against the possible increase in cost caused by deferring remedial action to a later date. If re-deposition is chosen, be advised that this does not absolve any party from liability should the actions taken exacerbate potential health and environmental impacts. If the option of re-depositing is chosen, excavated soils should be stored under cover before re-deposit into the excavation. Excavated soil that is contaminated should not be placed into an excavation that is clean, i.e., an excavation other than that from which the soil was removed, otherwise the soil should be treated as in No. 5 above. Excavated soil with petroleum contamination that is re-deposited into the excavation should be provided with a cover of clean soil or cap of asphalt/concrete once the work has been completed.

- 6. Detailed records of the investigation, any re-deposited contaminated soils, and any other clean-up activities are to be maintained and submitted to the HEER Office.
- In cases where a site assessment and evaluation is to be conducted, the HEER Office Technical Guidance Manual, Environmental Hazard Evaluation (EHE) Guidance, and the State Contingency Plan are accessible through the HEER Office website:

http://hawaii.gov/doh/heer

If uncertain of the action to take, call the HEER Office at 808-586-4249



TGM for the Implementation of the Hawai'i State Contingency Plan Appendix 9-E Update to Soil Action Levels for Inorganic Arsenic and Recommended Soil Management Practices

APPENDIX 9-E Update to Soil Action Levels for Inorganic Arsenic and Recommended Soil Management Practices

(see PDF file)



TGM for the Implementation of the Hawai'i State Contingency Plan Appendix 9-F Update to Soil Action Levels for TEQ Dioxins and Recommended Soil Management Practices

APPENDIX 9-F Update to Soil Action Levels for TEQ Dioxins and Recommended Soil Management Practices

(see PDF file)

