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SUBJECT: Use of laboratory batch tests to evaluate potential leaching of
contaminants from soil

Executive Summary

This technical memorandum presents the Batch Test Leaching Model (BTLM), a simple, Tier 3 approach for assessing the potential impact to groundwater posed by leaching of contaminants from vadose-zone soils. The BTLM uses site-specific soil data to evaluate contaminant mobility and estimate contaminant concentrations in soil leachate. If the contaminant is deemed sufficiently mobile, the model predicts future impacts to groundwater based on simple leachate dilution assumption. This can then be compared to target groundwater action levels appropriate for the site. An Excel spreadsheet is included to facilitate use of the model. Use of the spreadsheet model only requires input of the concentration of the contaminant in soil (in mg/kg) and the result of the batch test analysis (in µg/L). The BTLM can also be used to develop more realistic, site-specific soil action levels in lieu of the conservative, Tier 1 action levels for this concern published by HDOH. This guidance will be updated periodically as additional information and improved approaches are identified.

The guidance is most pertinent to vadose zone soils. Direct monitoring of groundwater should be carried out to evaluate leaching of contaminants in soils situated below the water table. Guidance presented in this memo does not apply to the evaluation of waste being placed in regulated landfills or to hazardous waste determinations. Evaluation of waste to be placed in landfills must be carried out under direction of the HDOH Solid and Hazardous Waste Branch.

Introduction

At a screening level, leaching of contaminants from soil is the primary environmental concern for the majority of the organic contaminants presented in the Hawai'i Department of Health (HDOH) document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater* (i.e., Tier 1 soil action levels for leaching concerns are lower than action levels for direct exposure, vapor intrusion, ecotoxicity and gross contamination concerns (HDOH 2017). Site-specific evaluation is recommended when soil action levels for leaching concerns are exceeded. In addition, action levels for metals are not provided in the document and leaching concerns must again be evaluated on a site-by-site basis. However, easy-to-use and technically sound soil leaching models that can be applied to both organic and inorganic contaminants have been lacking. The guidance presented below is intended to help address this issue.

The guidance focuses on the use of laboratory batch tests to quantify the mobility of the contaminant in soil and estimate the initial concentration of the contaminant in soil leachate. Batch tests involve placing a small amount of the soil in buffered, de-ionized water, agitating the mixture for a set period of time and measuring the fraction of the contaminant that desorbs from the soil and goes into solution. The ratio of the mass of a contaminant that remains sorbed to the mass that goes into solution, adjusted to the test method, is referred to the contaminant's "desorption coefficient" or "Kd" value.

A contaminant's Kd value is a key parameter in soil leaching models. The lower the Kd value, the greater the mobility of the contaminant in soil and the greater the leaching threat. Contaminants with Kd values less than 1.0 are considered to be highly mobile and pose a significant threat to groundwater resources. Contaminants with Kd values greater than 20 are considered to be so tightly bound to the soil that they are essentially immobile and do not pose a significant leaching concern. The strength of binding can vary among different soil types, as well as contaminant concentration and the age of the release.

Batch test data can be input into an Excel spreadsheet model ("Batch Test Leaching Model (April 2007)) that accompanies this technical memorandum to calculate Kd values for target contaminants. Use of the model only requires input of the concentration of the contaminant in soil (in mg/kg) and the results of batch test analysis (in µg/L). Additional, default parameter values in the model can be adjusted if needed but this is generally not recommended. The concentration of the contaminant in leachate hypothetically derived from the soil tested is calculated based on the Kd value determined for the contaminant. The spreadsheet then estimates the ultimate concentration of the contaminant in groundwater based on a simple groundwater/leachate mixing model. The inclusion of a more refined approach for estimating contaminant concentrations in groundwater is anticipated for future updates to this guidance.

The remainder of this guidance provides a detailed discussion of contaminant partitioning in soil, key questions to be asked in site-specific leaching models, batch test methodologies for estimation of site-specific Kd values and calculation of contaminant concentrations in soil leachate and groundwater. Equations used in the Batch Test Leaching Model are presented in Appendix 1. The use of soil gas data to estimate concentrations of volatile contaminants in leachate is also briefly introduced. A detailed understanding of these topics is not necessarily needed to use the accompanying spreadsheets and carry out a simple, site-specific evaluation of potential soil leaching concerns using batch test data. A basic understanding of contaminant fate

and transport in the subsurface is very useful, however, in determining how confident one can be in applying the results of the models to actual field conditions.

This memo updates a previous November 2006 version of the guidance and replaces text regarding use of the SPLP test presented in the May 2005 edition of the HDOH document *Screening For Environmental Concerns at Sites With Contaminated Soil and Groundwater*” (Volume 1, Section 3.3.3; HDOH 2017). The approach described should be considered guidance only. Alternative approaches can be proposed for specific sites. This guidance will be updated as needed in the future. Comments and suggestions are welcome at any time and should be directed to Roger Brewer of HDOH at roger.brewer@doh.hawaii.gov.

Partitioning of Contaminants in Soil

Contaminants released into soil will partition into up to four different phases in the soil matrix (Figure 1). Some of the contaminant will dissolve into the soil moisture to form leachate. Another portion will chemically bind (“sorb”) to soil particles, primarily organic carbon and clay particles. If the contaminant is volatile, a portion will also partition into air-filled pore space as a vapor phase. If the total mass of the contaminant is great enough, the soil particles, soil moisture and soil vapor will become saturated and free-phase product will also be present.

In theory, the various phases of a contaminant will eventually come into equilibrium with each other. The nature of this equilibrium is controlled by the chemical properties of the contaminant, the chemistry and physical properties of the soil and the presence of other contaminants. Contaminants that readily bind to soil particles will be present primarily in the sorbed phase (e.g., PAHs, PCBs, etc.). Contaminants that are not very sorptive will accumulate in the soil moisture or soil vapor (e.g., perchlorate, chlorinated herbicides, BTEX, MTBE, solvents, etc.). Contaminants that are by nature gases will persist mainly as vapors in the air-filled pore space, especially if the soil is very dry (e.g., vinyl chloride).

In the absence of free product, the relationship between sorbed, dissolved and vapor phases of a contaminant in soil is relatively straightforward and can be described by simple partition coefficients (USEPA 2001). A contaminant’s “Henry’s Law Constant” is the ratio of the vapor-phase concentration of a contaminant to the dissolved-phase concentration, at equilibrium. The Henry’s Law Constant is relatively constant between sites, although it may vary slightly due to differences in soil temperature and the presence of other contaminants.

A contaminants sorption coefficient, or “Kd” value, is the ratio of the sorbed-phase concentration to the dissolved-phase concentration, at equilibrium (see Figure 1). For initial screening purposes and calculation of Tier 1 soil Action Levels, Kd values for organic chemicals are estimated using published *sorption* coefficients (“koc” values) and assumptions about the organic carbon content of the soil ($K_d = \text{published koc value} \times \text{assumed fraction organic carbon in soil}$, typically 0.1%). Generic Kd values have also been published for a limited number of metals and other inorganic contaminants, although they are considered to much less reliable than for organic compounds. In the field, however, contaminant sorption (or more specifically “desorption”) coefficients can vary significantly between sites, due to differences in soil properties, the mixture of contaminants present and even the age of the release. The variability of contaminant Kd values in the field implies that this parameter should be included in site- specific evaluations of potential leaching concerns. In practice, this is rarely done.

A contaminant's Henry's Law Constant and assumed (or site-specific) K_d value can be used in conjunction with assumed or known soil properties to determine how the contaminant is actually distributed in the soil. Table 1 summarizes the distribution of several common contaminants in soil as assumed in the leaching models used to generate Tier 1 action levels published by HDOH (HDOH 2017). The percent mass in each phase is calculated based on rearrangement of a simple equilibrium partitioning equation presented in USEPA's *Soil Screening Guidance* (USEPA 2001, refer also to Appendix 1). Similar assumptions about contaminant partitioning in soil are made in the models used to generate the USEPA Regional Screening Levels, although this cannot be readily discerned from the equations presented in the accompanying guidance document (USEPA 2017).

As expected, contaminants such as benzo(a)pyrene and PCBs are almost entirely absorbed to soil particles (refer to Table 1). Perhaps surprising, however, is the tendency for the main mass of moderately volatile contaminants such as benzene, PCE and MTBE to be sorbed to soil particles or dissolved in soil moisture, versus being present as vapors in the soil air space. Confusion about this issue has led to over estimation (and probably over concern) of contaminant loss during sampling of soil for this group of chemicals. Compare this to contaminants that are gases and truly volatile by nature, such as vinyl chloride (see Table 1). Testing soil samples for the presence of vinyl chloride and estimating leaching concerns is probably not a worthwhile effort. The use of soil gas samples to estimate concentrations of highly volatile contaminants in soil leachate and even monitor the downward migrating vapor plumes is much more preferable. A brief introduction to this approach is provided later in this guidance and also included in the BTLM spreadsheet.

Site-Specific Evaluation of Soil Leaching Concerns

Four basic questions need to be posed when evaluating the potential for contaminants to leach from soil and impact groundwater (Figure 2):

1. "Is the contaminant potentially mobile?"
2. "What is the concentration of the contaminant in leachate in the primary source area?"
3. "What is the concentration of the contaminant in leachate at the point that the leachate reaches the top of the water table?" and
4. "What is the concentration of the contaminant in groundwater after the leachate has impacted the groundwater?"

Each of these relatively common sense and straight forward questions should be answered in a site-specific evaluation of potential soil leaching concerns. In practice, they rarely are, due in part to the "black box" nature of most soil leaching models. The guidance presented in this technical memorandum focuses on the first two of these questions, contaminant mobility and the initial concentration of the contaminant in leachate.

Mobility in Soil

Contaminant mobility in soil is evaluated in terms of how tightly bound the contaminant is to soil particles. From a modeling perspective, this is again described in terms of the contaminant's desorption coefficient or Kd value. Increasing Kd values reflect decreasing mobility in soil.

Figure 3 presents default, Tier 1 Kd values for several common contaminants and subdivides them in terms of relative mobility or leachability in soil (after Fetter 1988). Assuming a 0.1% fraction organic carbon in soil, contaminants with a generic Kd value of less than 1.0 are considered to be highly mobile, a fact that correlates well with field data and a list of common groundwater contaminants. Contaminants with a Kd value of greater than 20 in soil are considered to be essentially immobile. Not surprisingly, contaminants such as MTBE, PCE, BTEX, perchlorate and chlorinated pesticides like atrazine are predicted to be highly mobile in soil, at least at a screening level, whereas PAHs, PCBs and similar contaminants are considered to be essentially immobile. (Note that trace levels of strongly sorptive contaminants like chlordane in groundwater indicate that these contaminants can be mobile under some circumstances, especially if the leachate is migrating through unweathered bed rock.)

The ability of a contaminant to bind to soil is very much tied to the nature and concentration of the contaminant, the presence of other contaminants that may compete for prime sorption spots, the soil mineralogy and chemistry (including organic carbon and clay content) and the time elapsed since the release of the contaminant. Use of generic Kd values could in theory *under* predict how strongly bound a contaminant is to soil, especially in the presence of other contaminants or in soils with extreme pH, redox or other soil conditions. Based on (admittedly limited) data collected to date, however, generic Kd values typically used for organic contaminants tend to significantly *over* predict the potential mobility of contaminants in soils. This is especially true for organic contaminants. This makes the use of laboratory batch tests very important when Tier 1 action levels or screening levels for potential leaching concerns (based on generic Kd values) suggest that leaching concerns need to be further evaluated.

Initial Concentration in Leachate

A contaminant's Kd value is used in conjunction with its Henry's Law Constant and assumptions about soil properties to estimate the initial concentration of a contaminant in leachate. The relatively simple equation used to perform this calculation is presented in Appendix 1 and incorporated into the accompanying spreadsheet. The proportion of the contaminant that will move into soil leachate is again mainly controlled or reflected by the contaminant's Kd value. A Kd value less than 1.0 indicates that most of the contaminant will move into soil leachate in comparison to the fraction of the contaminant that will remain sorbed to soil particles.

Concentration in Leachate at Groundwater Interface

As the leachate migrates downward, contaminant concentrations can be progressively reduced due to resorption of the contaminant to soil particles, chemical or biological degradation or volatilization into the soil air space. Estimates of contaminant concentrations in leachate at the point that the leachate reaches the groundwater interface can be made using a vadose-zone fate and transport model. This important step is not included into the BTLM at this time. The BTLM model instead very conservatively assumes that the concentration of the contaminant in leachate at the groundwater interface is equal to that in the initial source area. A more detailed evaluation of contaminant fate and transport in soil leachate (e.g., using SESOIL, VLEACH or other

vadose-zone leaching models) may be particularly useful at sites where the depth to groundwater from the base of the contaminated soil is greater than approximately ten meters and target contaminants that have default K_d values greater than $1,000 \text{ cm}^3/\text{g}$ (e.g., naphthalene), are highly degradable (e.g., TPH and BTEX), and/or are moderately or highly volatile (e.g., PCE and vinyl chloride).

Concentration in Groundwater

The concentration of a contaminant in groundwater after mixing of the leachate with the groundwater can be estimated by either dividing the concentration of the contaminant in leachate by simple dilution factor or again by use of a more rigorous fate and transport model (refer to equations in Appendix 1). The BTLM model presented relies on the former, although a more refined approach may be added in the future.

The HDOH Environmental Action Levels document (or EAL Surfer) should be referred to for target groundwater goals (HDOH 2017). Target groundwater goals will in general be the lowest of the drinking water goal (i.e., lowest of Primary and Secondary MCLs or equivalents), surface water goal (assuming potential discharge to a body of surface water, acute or chronic aquatic toxicity goal based on site location) and any other applicable goals (vapor intrusion, gross contamination, etc.).

Use of Batch Test Data to Estimate Contaminant K_d Values

Relatively simple batch test methods have been in use for decades to evaluate leaching of metals from mine tailings and estimate the mobility of pesticides sprayed on agricultural lands (USEPA 1992, 1999). The tests collectively account for a host of factors that may control binding to (sorption) and leaching of (desorption) contaminants from soil. The tests do not identify exactly how the contaminant is bound to the soil, although a review of soil properties and chemistry can shed light on this issue if needed. The most commonly used batch test method to evaluate potential leaching of contaminants from soil is the *Synthetic Precipitation Leaching Procedure* or “SPLP” test (USEPA 1994, similar to the California “WET” test). The SPLP test is carried out as follows:

Step 1. Analyze soil sample for concentrations of target contaminants (e.g., in mg/kg)

Step 2. Run SPLP test on split sample:

- Place 100 grams soil in two liters of a de-ionized water solution (use SPLP Extraction Fluid #2 for Hawai'i; pH 5.0, 25° C; USEPA 1994),
- Remove airspace (especially for VOCs),
- Agitate 18 hours.

Step 3. Analyze extract for contaminants of concern.

Step 4. Estimate K_d by comparison of the mass of contaminant that remained sorbed to the soil to the mass of the contaminant that went into solution.

The equations used to calculate a contaminant's K_d value in soil based on batch test data are provided in Appendix 1 and incorporated into the accompanying BTLM spreadsheet. The calculated K_d value is then used to evaluate the potential mobility of the contaminant in the soil

and estimate the initial concentration of the contaminant in soil leachate and groundwater, as described in the previous section.

For batch test results that are below standard, commercial lab Method reporting Limits (MRL), Kd can be estimated using 1/2 the MRL. If the estimated Kd is less than 20, a worst-case concentration of the contaminant in groundwater can be calculated as described above.

Contaminant Kd values estimated through use of batch tests apply only to the soil tested and only for the reported concentration of the contaminant in the soil. Kd values could vary with respect to contaminant concentration in the same soil type. This may need to be evaluated on a site-specific basis in cases where soil contamination is widespread and very heterogeneous.

For large areas where contaminant concentrations vary significantly and individual spill areas cannot be easily identified, it may be useful to conduct a series of batch tests and evaluate the variation in Kd with respect to contaminant concentrations in soil (keeping in mind the need to separate different soil types). Soil cleanup levels can then be developed by plotting contaminant concentration in soil versus estimated concentration in leachate, generating a regression line through the data (USEPA 1992, 1999). Soil cleanup levels can be calculated or read directly off of the graph by setting a target concentration of the contaminant in the leachate (e.g., target groundwater concentration times assumed groundwater/leachate dilution factor). An example of this approach based on perchlorate soil and SPLP data collected at a site in California is given in Figure 4. (Note that final cleanup standards varied slightly from that noted in the figure due to assumptions about representative contaminant distribution and Kd values in soil across the site.) In Hawai'i, this approach may be especially useful in the evaluation of large, pesticide mixing areas associated with former agricultural lands.

It is important to understand that batch tests were not designed to directly estimate the concentration of a contaminant in soil leachate. Batch tests were instead designed to calculate Kd sorption or desorption coefficients, which can then be used to estimate contaminant concentrations in leachate if desired. The volume of solution used in batch test can be used to illustrate this point. A solution volume of two liters was selected primarily to help ensure that laboratory detection limits could be met, not to mimic the supposed concentration of the contaminant in actual soil leachate – as is commonly misinterpreted (USEPA 1992). If the same mass of soil (generally 100 grams) were placed in a swimming pool-size volume of solution then the resulting concentrations of target contaminants in the batch test would of course be very different. Assuming that the contaminant is not completely stripped from the soil, however, the ratio of the mass that remains sorbed to the mass that moves into solution (i.e., the Kd value) should be constant. For highly sorptive contaminants (e.g., PCBs and PAHs) and for many metals, the difference between batch test results and calculated concentration of the contaminant in leachate may indeed be very small. For less sorptive contaminants like BTEX, MTBE, perchlorate and moderately mobile pesticides, however, estimated concentrations in leachate may be an order of magnitude or more greater than the concentration reported in the batch test data. This is especially true for contaminants with Kd values less than 20 in the soil tested, where a significant fraction of the contaminant partitions into the batch test solute (e.g., >25%).

Soil Sampling Strategies

A minimum of three soil samples is generally needed to validate batch test data for each area investigated. Multi Increment sampling methods should be utilized (HDOH 2016). Data based on discrete sampling methodologies will not be reliable. Recording the soil type and testing for the total organic carbon content and percent clay content of the soil is also recommended. Although not directly incorporated into the BTLM, this information may prove useful in understanding the nature of contaminant binding in the soil and help direct soil cleanup actions, if needed.

For large sites with varying soil types, contaminant mixtures or release histories, it may be necessary to define multiple “decision units” and evaluate each area separately. For example, the binding capacity of sandy soils is likely to be much lower than clayey or organic-rich soils. If both soil types are present at a contaminated site, it would be prudent to treat each soil type area as a separate decision unit.

The collection and analysis of multi-increment samples (essentially very good “composite” samples) is preferred for easily identifiable spill areas or “hot spots,” especially where the primary contaminants are non-volatile. Collection and field-based extraction of multi-increment samples for volatile contaminants may also be feasible, although this subject is beyond the current scope of this memo. Guidance on the collection and evaluation of multi-increment samples is currently being prepared by HDOH. In the interim, and especially for cases under the formal oversight of HDOH, it is recommended that potential users of the BTLM guidance review sampling plans with the HDOH project manager prior to collection and submittal of the samples for analysis.

Use of Soil Gas Data to Evaluate Groundwater Protection Concerns

Batch tests can be used to evaluate both nonvolatile and volatile contaminants, although special care must be taken during sampling and testing of the latter (refer to USEPA 1994 SPLP method guidance). The concurrent use of soil gas data to estimate the concentration of volatile contaminants in soil leachate may also be prudent. Reasonably accurate estimations of the contaminant concentrations in soil moisture or leachate can be made by dividing the concentration of the contaminant in soil gas (converted to $\mu\text{g/L}$) by the chemical’s dimensionless Henry’s Law Constant (see equation in Appendix 1). A simple model based on this approach and incorporating a groundwater:leachate dilution factor is presented in Appendix 1 and included in the BTLM spreadsheet.

Cases where soil gas data may prove beneficial for evaluation of potential impacts to groundwater include: 1) sites with releases of relatively persistent, volatile chemicals that remain very dry throughout much of the year (i.e., non-irrigated areas with very low precipitation, or paved areas that overlie shallow groundwater), 2) sites known to be impacted by volatile contaminants but where specific source areas have not been identified, 3) sites where the threat to groundwater is primarily posed by downward releases of vapors from underground tanks, pipelines, etc., and 4) sites where the vulnerability and sensitivity of the first-encountered groundwater resource is very high (e.g., unconfined aquifer that is currently used as a source of

drinking water). In very wet or heavily irrigated areas (e.g., groundwater recharge greater than ten inches or 25cm per year), mass loading of the contaminant to groundwater via vapor-phase plumes is likely to be insignificant in comparison to contaminant migration via leachate. In very dry areas, however, the amount of moisture in the soils may not be sufficient to initiate the downward migration of leachate by the force of gravity. If this is the case then the model discussed above will overstate the potential threat to groundwater posed by dissolved-phase contaminants in the soil moisture.

A focus on the potential for vapor plumes to impact groundwater will be more appropriate for dry areas. Easy-to-use models that specifically evaluate the downward migration of vapor plumes to groundwater are not currently available. An evaluation of potential groundwater impact concerns may instead have to rely on long-term monitoring of soil gas in the vadose zone. Soil gas “action levels” for protection of groundwater can be developed by rearranging the Henry’s Law Constant equation to solve for the concentration of the contaminant in soil vapor and setting the dissolved-phase concentration of the contaminant equal to a target groundwater or leachate goal (refer to equations in Appendix 1).

Soil gas data will be less useful for estimation of semi-volatile contaminant concentrations in leachate. This is due to the very low Henry’s Law Constants for these contaminants and associated limitations on soil gas method reporting limits. As noted in Table 1 for PAHs, the overwhelming majority of the contaminant mass will also be sorbed to the soil, rather than in the soil vapor. Batch tests on representative soil samples therefore offer a better approach for the evaluation of leaching concerns related to these contaminants.

Leaching of Heavily Contaminated Soils

Soils that contain significant amounts of pure-phase or “free” product” may not be amenable to use of the Batch Test Leaching Model as described above (i.e., contaminant that is not sorbed to the soil, dissolved into the soil moisture or present as vapors in air-filled pore space). This is particularly true for soils that are heavily contaminated with petroleum. Contaminant K_d values can only be calculated if any free product present completely dissolves into the batch test solution. If free product forms in the batch test solution then analysis of solution for dissolved-phase constituents will not accurately reflect the total mass of contaminants that were stripped from the soil during the test. This will cause the model to over predict the mass of the contaminant that remained sorbed to the soil and in turn over predict the contaminants K_d value.

If the reported concentration of a contaminant in a batch test analysis exceeds 75% of the assumed solubility then it should be assumed that pure-phase contaminant product may be present in the batch test solution. In such cases, the spreadsheet model will generate a caution message and a K_d value will not be calculated. The potential mobility of the contaminant with respect to its K_d value therefore cannot be accurately evaluated. In the spreadsheet model, the estimated concentration of contaminant in soil leachate is set to the highest of the contaminant’s solubility and the reported concentration of the contaminant in the batch test analysis. Potential impacts to groundwater are estimated by dividing the assumed concentration of the contaminant in leachate by the input groundwater:leachate dilution factor. The potential downward mobility of liquid-phase free product in the soil should also be further evaluated.

Special Considerations for Petroleum-Contaminated Soils

Soils impacted by petroleum should be tested for both Total Petroleum Hydrocarbons (TPH) and target indicator compounds, including BTEX, MTBE and related fuel oxygenates and the PAHs naphthalene and methylnaphthalene (refer to Volume 1, Section 2.2.2 in HDOH EAL document, HDOH 2017). Testing for other PAHs is not necessary, due to their relative immobility in soil and low concentration in most petroleum products.

Problems related to the presence of free product in the batch test solution as discussed above could be especially pronounced for soils heavily impacted with middle distillates (diesel, jet fuel, etc.) and heavier residual fuels (waste oil, hydraulic fluid, etc.). The low solubility of these fuels in comparison to gasoline can lead to the presence of droplets of free product in soil at concentrations above only a few hundred parts-per-million (mg/kg) TPH. At high enough concentrations, this could lead to the presence of free product in the batch test solution. This will negate use of the BTLM model to calculate a K_d value for the sample tested and evaluate the potential mobility of the contaminant, as discussed in the previous section.

If the batch test results for Total Petroleum Hydrocarbons (TPH) suggest the potential presence of free product in the solution then the concentration of TPH in soil leachate should be assumed to be equal to the higher of the reported result and the assumed solubility of the targeted petroleum product. In the absence of a more site-specific review, the potential concentration of the contaminant in groundwater should be estimated by dividing the concentration in leachate but the groundwater:leachate dilution factor selected for the site. This is automatically carried out in the accompanying BTLM spreadsheet.

The presence of potentially mobile free product in the soil should also be evaluated. This can be done by comparison of TPH data for vadose-zone soil to HDOH action levels for gross contamination concerns in subsurface soils (HDOH 2017, Appendix 1). An action level of 2,000 mg/kg for gasoline contaminated soils. A somewhat higher action level 5,000 mg/kg is used for soils contaminated with either middle range petroleum distillates (e.g., diesel fuel and jet fuel) or residual fuels (motor oil, waste oil, etc.). These action levels are intended to minimize the presence of mobile free product in soil and are based on field observations and published studies (e.g, API 2000). Minimum conditions for use of the action levels in other areas include: 1) the source of the release has been eliminated, 2) grossly contaminated soil has been removed to the extent practicable (e.g., within 15 feet of the ground surface and/or to the top of bedrock) and 3) remaining contamination does not threaten nearby water supply wells or aquatic habitat (refer also to Volume 1, Section 2.2 of the HDOH 2017 EAL document).

Residual petroleum contamination in soil can be expected to naturally degrade over time. Note that impacted soil that is disturbed during future subsurface activities must also be properly managed. Continued groundwater monitoring may also be required for highly sensitive sites. Additional guidance for the long-term management of petroleum-contaminated soil (and groundwater) is currently being prepared by HDOH.

Other Limitations

Evaluation of Past Impacts to Groundwater

The approach described in this technical memorandum can only be used to predict *future* leaching of contaminants from soil and subsequent impacts to groundwater. Batch tests on residual contaminants in soil cannot necessarily be used to predict if *past* impacts to groundwater may have occurred. In part this is because the contaminants may be much more strongly bound to soil particles under current conditions than during the initial release. The possibility of past impacts to groundwater must be evaluated on a site-by-site basis, based on the nature of the contaminant released, the subsurface geology and the depth to groundwater among other factors.

Placement of Soil Below Water Table

The batch test method may not accurately mimic the placement of contaminated soil or other media below the water table for long periods of time and should not be used to predict these conditions. Long-term immersion could significantly enhance desorption of contaminants, especially if rate-limited processes such as desorption, organic carbon decay or mineral dissolution affect contaminant partitioning. Long-term immersion of the soil could increase impacts to groundwater that significantly exceed levels predicted by short-term batch tests. In the absence of a more detailed groundwater impact study, placement of contaminated soil below the water table or at a depth that is subject to future inundation by a rise in groundwater should be avoided (e.g., areas where the water table has dropped significantly due a prolonged dry period but is expected to rise again in the future). If this cannot be avoided and nearby water supply wells or aquatic habitats could be threatened, then long-term monitoring of the groundwater to verify that the contaminants are not significantly mobile is probably warranted.

Long-Term Groundwater Monitoring

Although the batch test method is believed to be very accurate, long-term groundwater monitoring may be prudent in some cases to verify the results of the evaluation. Monitoring may be especially warranted at sites where batch test data suggest that relatively high concentrations of chlorinated solvents, pesticides or other persistent contaminants can be left in place (e.g., in comparison to Tier 1 action levels for leaching concerns) but important drinking water resources are potentially threatened. Monitoring may also be needed at site where subsurface conditions could change over time and allow for increased leaching of contaminants (e.g., rising water table).

Use of Kd Values in Fate & Transport Models

Contaminant Kd values derived from batch tests cannot necessarily be incorporated into vadose-zone fate and transport models for deeper soils, even if the soil types are very similar. This is because the Kd value most likely reflects an increased difficulty in desorbing or leaching of *aged* contaminants from the tested soil. Use of the Kd value to evaluate migration of the contaminant in leachate through deeper soils not yet impacted by the initial release could over predict *resorption* to soil particles thus *under* predict potential impacts to groundwater. The use of batch tests to estimate site-specific *sorption* coefficients for contaminants in deeper soils may be practical but is beyond the current scope of this technical memorandum.

Evaluation of Solid or Hazardous Waste

Guidance presented in this memo does not apply to the evaluation of waste being placed in regulated landfills or to hazardous waste determinations. Evaluation of waste to be placed in landfills must be carried out under direction of the HDOH Solid and Hazardous Waste Branch.

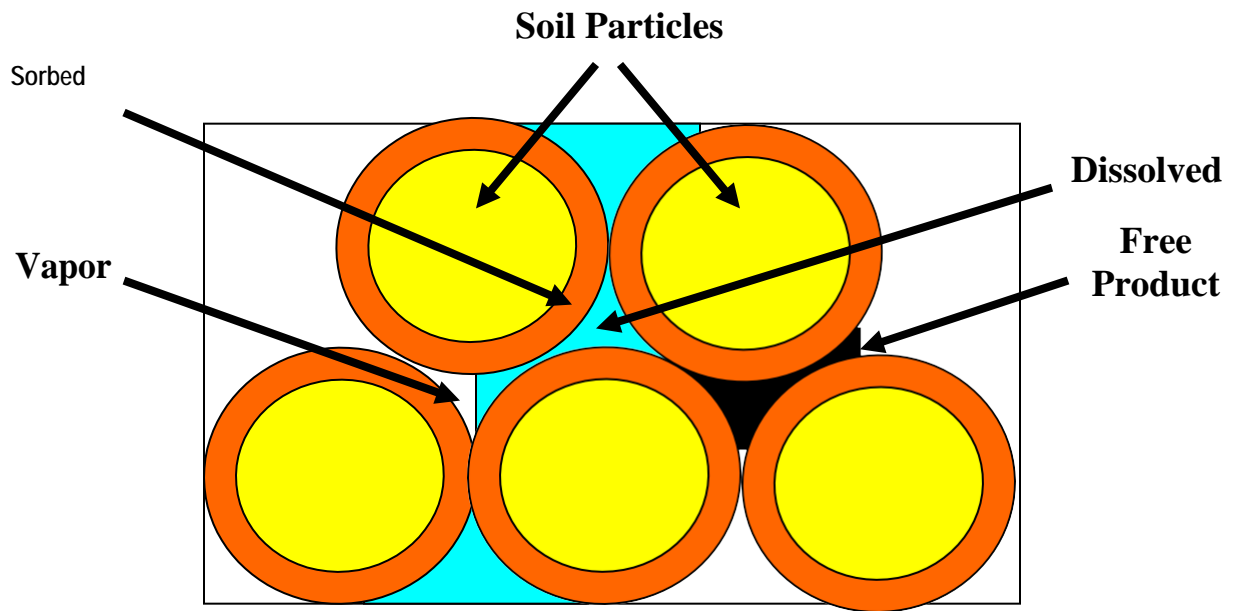
References:

- API, 2000, *Non-Aqueous Phase Liquid (NAPL) Mobility Limits in Soil*: American Petroleum Institute (June 2000), Soil and Groundwater Research Bulletin, No.9.
- Fetter, C. W., 1988, *Applied Hydrology*: Merrill Publishing Company, Columbus, Ohio, ISBN 0-0-675-20887-4.
- HIDOH, 1995, *Environmental Corrective Action and Decision Making at Sites with Contaminated Soil and Groundwater*: State of Hawai'i, Department of Health, December, 1995 (revised June, 1996).
- HIDOH, 2016, *Technical Guidance Manual*: Hawai'i Department of Health, Office of Hazard Evaluation and Emergency Response, <http://www.hawaiidoh.org/>
- HIDOH, 2017, *Screening for Environmental Concerns at Sites with Contaminated Soil and Groundwater* (Fall 2017 and updates): Hawai'i Department of Health, Hazard Evaluation and Emergency Response Office.
- McLean, J.E. and B.E. Bledsoe, 1992, *Behavior of Metals in Soil*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, EPA/540/S-92/018.
- Roy, W.R; Krapac, I.G.; Chou, S.F.J.; and R.A. Griffin, 1992, *Batch Type Leaching Procedures For Estimating Soil Absorption of Chemicals*, U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, EPA/530/SW-87/006-F.
- USEPA, 1994, *Synthetic Precipitation Leaching Procedure*: U.S. Environmental Protection Agency, Office of Solid Waste, SW-846 Method 1312, September 1994.
- USEPA, 1999, *Understanding Variation in Partition Coefficient, K_d, Values*: Office of Air and Radiation, August 1999, EPA/402/R/99/004A, <http://www.epa.gov/radiation/docs/kdreport/>
- USEPA, 2001, *Supplemental Guidance For Developing Soil Screening Levels For Superfund Sites* (Peer Review Draft, May 2001): U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response, Publication 9355.4-24.
- USEPA, 2017, *Screening Levels for Chemical Contaminants*: U.S. Environmental Protection Agency, (June 2017 and updates), prepared by Oak Ridge National Laboratories, <https://www.epa.gov/risk/regional-screening-levels-rsls>

Table 1. Distribution of contaminants in soil based on contaminant properties and soil characteristics assumed in Tier 1 leaching models. Note how the fraction of the contaminant in the dissolved-phase is strongly tied to the assumed sorption coefficient or “Kd” value.

Chemical	Default Sorption Coefficient (Kd)	*Contaminant Phase Versus Percent Total Mass in Soil		
		Sorbed	Dissolved	Vapor
Benzo(a)pyrene	5,500	99.9+%	0.002%	0%
PCBs	33	99.7%	0.3%	0.01%
TPH	5.0	98%	1.9%	0.1%
Atrazine	0.23	70%	30%	0%
PCE	0.16	39%	25%	35%
Benzene	0.059	29%	50%	21%
MTBE	0.006	5%	91%	4%
Vinyl Chloride	0.0	5%	31%	64%

*For example only. Based on soil equilibrium partitioning equation presented in USEPA *Soil Screening Guidance* (USEPA 2001). Leachate is represented by the dissolved-phase mass of the contaminant. For organic contaminants, Tier 1 Kd value = published sorption coefficient (koc) x assumed total organic carbon content in soil of 0.1% (refer to HDOH 2017, Appendix 1, Table H). Assumes and soil moisture content of 0.10. Arsenic default Kd from USEPA *Soil Screening Guidance*.



Partition Coefficients

$K_d = \text{Sorbed Concentration} / \text{Dissolved Concentration}$

Henry's Law constant = $\text{Vapor Concentration} / \text{Dissolved Concentration}$

Figure 1. Partitioning of contaminants in soil between sorbed, dissolved and vapor phases.

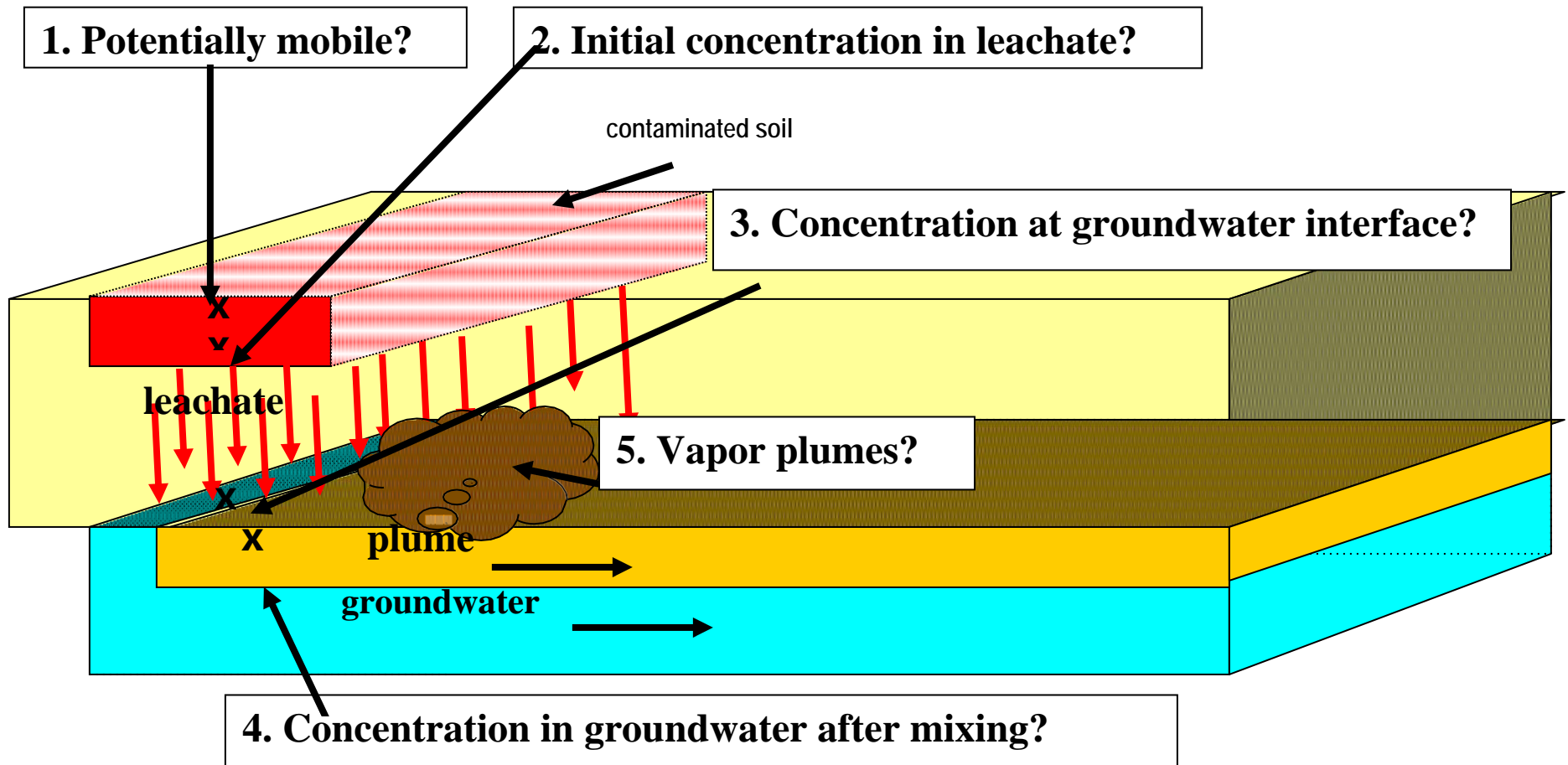


Figure 2. Basic questions that should be answered in all site-specific evaluations of soil leaching concerns. The guidance focuses on site-specific approaches to answering Questions 1 and 2, although approaches for answering the remaining questions are also provided.

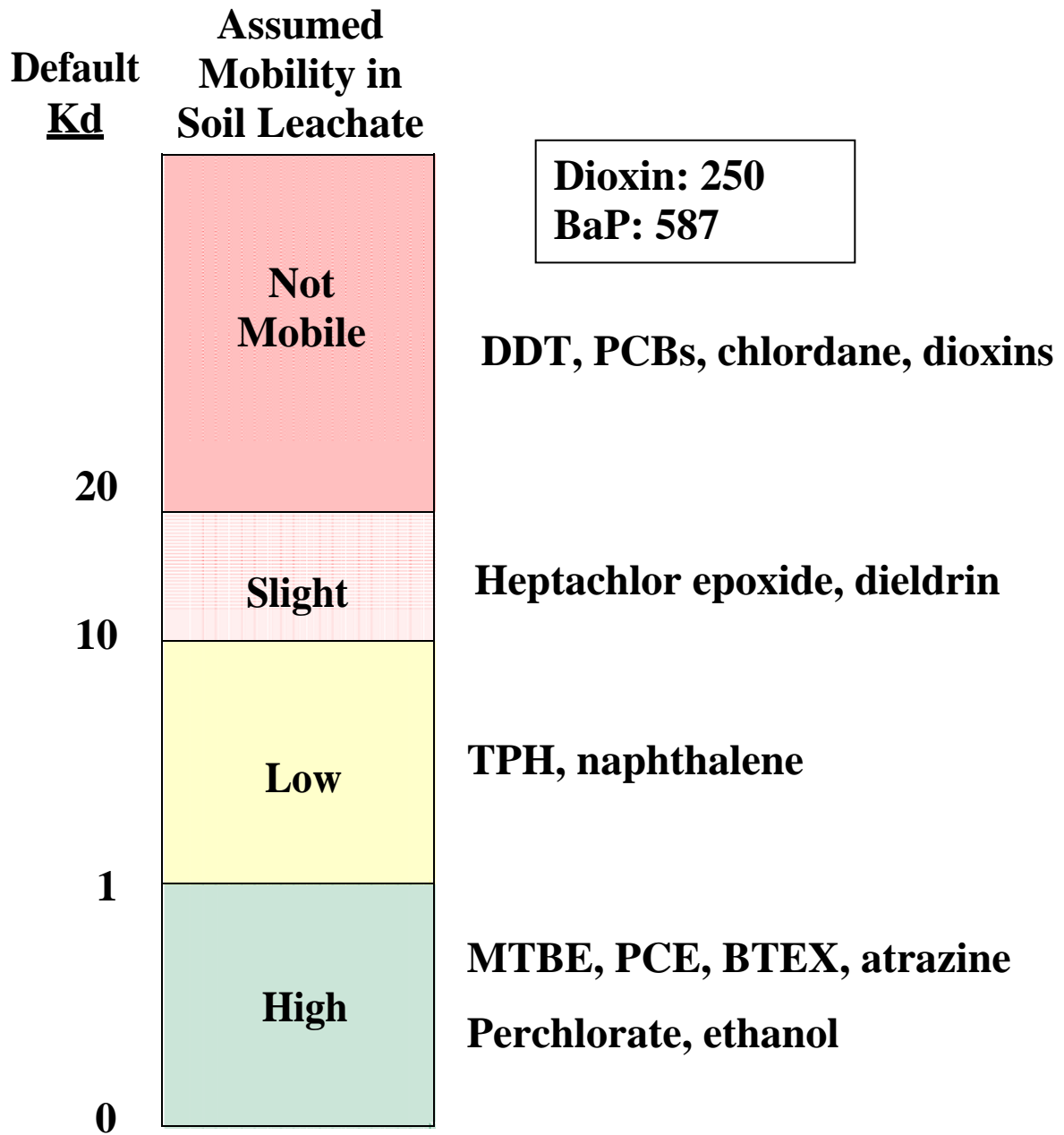


Figure 3. For example only. Assumed mobility of contaminants in soil leachate with respect to default Kd values used to develop HDOH Tier 1 soil action levels for leaching concerns. For organic contaminants, Kd values based on published koc sorption coefficients and total organic carbon content in soil of 0.1% (refer to Appendix 1 in HDOH EAL document, HDOH 2017). For arsenic, default Kd value of 29 from USEPA *Soil Screening Guidance* (USEPA 2001).

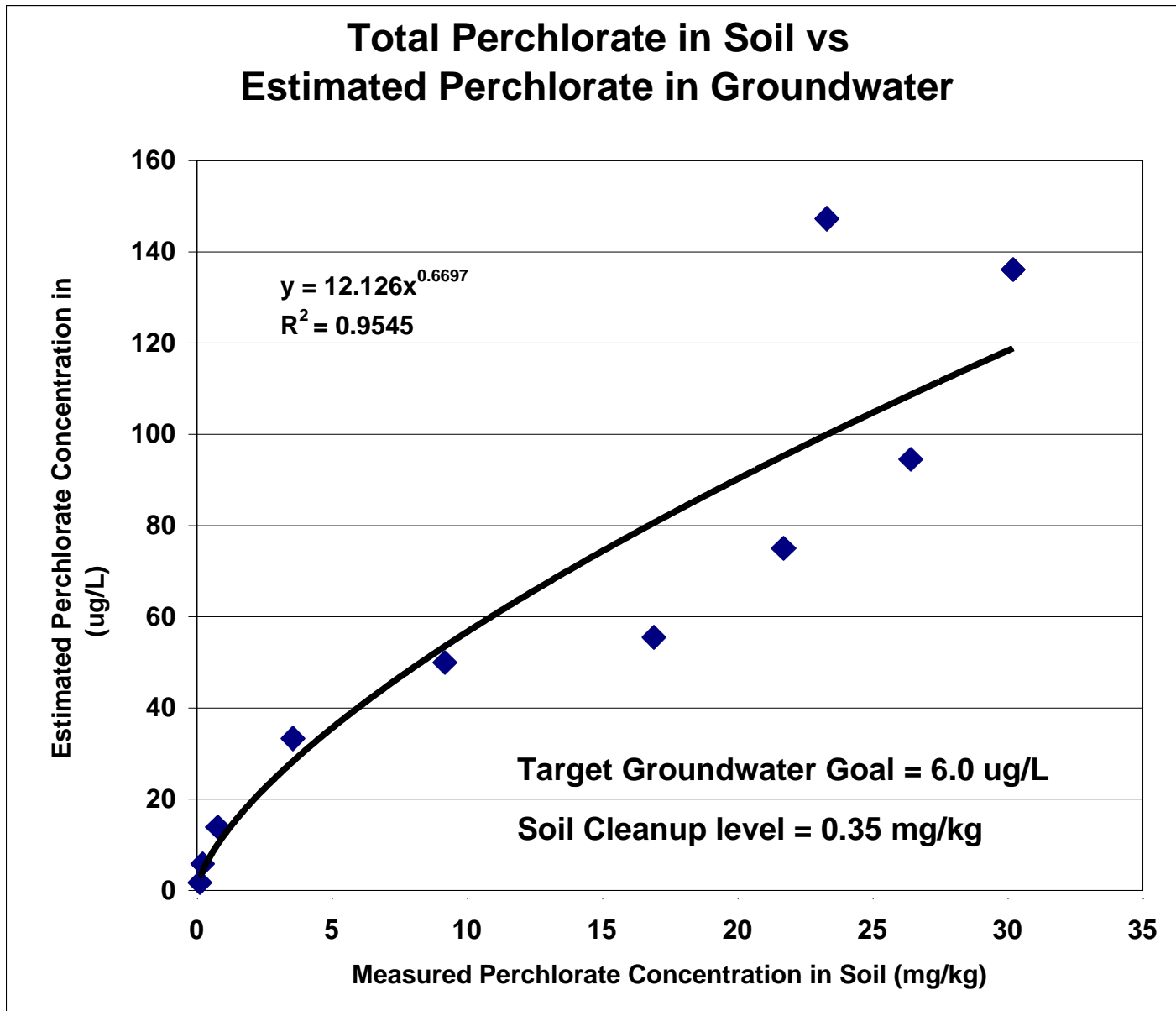


Figure 4. Example graphical calculation of soil cleanup levels based on use of multiple batch tests to estimated perchlorate desorption coefficients and correlative concentrations of perchlorate in soil leachate and groundwater at varying soil concentrations of perchlorate in soil. (For example only.)

Batch Test Leaching Model

Version: April 2007

Hawai'i Department of Health

Hazard Evaluation and Emergency Response Office

Contact: Roger Brewer (roger.brewer@doh.hawaii.gov)

- Refer to accompanying technical memorandum for background and use of this spreadsheet (HDOH 2007).
- Spreadsheet calculates Kd desorption coefficient based on input contaminant concentration in soil and Batch Test data.
- Correlative concentration of contaminant in leachate calculated based on estimated Kd value (may differ from batch test data).
- Future impacts to groundwater estimated using simple groundwater/leachate dilution factor.
- Alternative model based on soil gas data provided in accompanying worksheet.
- Possibility of past impacts to groundwater not considered and must be evaluated separately.
- Check to ensure that this is an up-to-date version of the spreadsheet.
- Password to unprotect worksheet is "EAL" (under Tools menu).**

STEPS:

1. Select chemical from pulldown list (unlisted chemicals - unprotect spreadsheet and input chemical name and chemical constants).
2. Input total contaminant concentration and SPLP (or other applicable batch test) concentration.
3. Input sample properties. Use default values if sample-specific data are not available.
4. Input Batch Test method information. Default SPLP method parameter values noted.
5. Input groundwater:leachate dilution factor (DF of 1.0 = no dilution; USEPA default = 20, USEPA 2001).
6. Input target groundwater action level for comparison to model calculation of groundwater impacts (optional).
7. Spreadsheet calculates sample-specific Kd value and dissolved-phase concentration of contaminant in saturated sample.
8. Spreadsheet calculates concentration of contaminant in groundwater following impact by leachate.

Step 1: Select Contaminant (use pulldown list)		PERCHLORATE	
Step 2: Input Sample Data		DEFAULT	INPUT
¹ Concentration in soil sample (mg/kg)	N/A	9.2E+00	
¹ Concentration in Batch Test solution (ug/L)	N/A	3.7E+02	
Step 3: Input Sample Properties (⁹USEPA soil defaults noted)			
Sample density (g/cm ³)	1.50	1.50	
Particle density (g/cm ³)	2.65	2.65	
Fraction air-filled porosity (assume saturated soil)	0.00	0.00	
Step 4: Batch Test Method Data (SPLP defaults noted)			
² Batch Test Solution Volume (ml):	2,000	2,000	
² Batch Test Solution Density (g/cm ³):	1.0	1.0	
² Batch Test Sample Weight (grams)	100	100	
Step 5: Input Groundwater/Leachate Dilution Factor		DEFAULT	INPUT
		20	20
Step 6 (optional): Input Target Groundwater Concentration (ug/L)			5.0E+00
Model Results			
⁵ Kd partition Coefficient (cm ³ /g):			4.8E+00
⁶ Estimated Concentration in Source Area Leachate (ug/L):			1.8E+03
⁷ Estimated Concentration in Groundwater (ug/L):			9.0E+01

Chemical Constants (selected from Constants worksheet)	
Kh (atm m ³ /mole)	0.00E+00
Kh (dimensionless)	0.00E+00
Solubility (ug/L)	2.00E+08

Calculations:	
Sample porosity - total	0.43
Sample porosity - air-filled	0.00
Sample porosity - water-filled	0.43
Batch Test Solution Mass (grams)	2.0E+03
Batch Test Sample Mass (grams)	1.0E+02
Sample Mass:Solution Mass Ratio (gm/gm)	5.0E-02
Total Mass of Contaminant (ug)	9.2E+02
Mass Contaminant in Batch Test Solution (ug)	7.4E+02
Mass Contaminant Sorbed to Soil (ug)	1.8E+02
Concentration Sorbed (ug/kg)	1.8E+03
Batch Test Percent Solid Phase	19.3%
Batch Test Percent Dissolved Phase	80.7%
Batch Test Solid-Phase Contaminant Conc. (mg/kg)	1.8E+00
Batch Test Solution Contaminant Conc. (ug/L)	3.7E+02

Kd <20. Contaminant potentially mobile in leachate for concentration and soil type tested. Soil leaching and groundwater impact concerns must be addressed if target groundwater action level is exceeded.

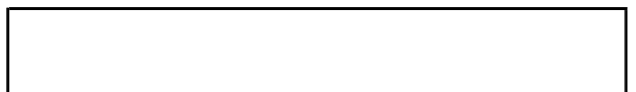
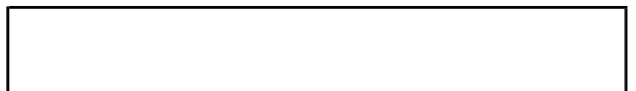
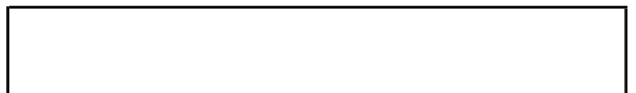


Figure 5. Original HDOH Batch Test Leaching Model that accompanies the technical memorandum (April 2007).

Appendix 1
Batch Test and Soil Gas Leaching Model Equations

Batch Test Leaching Model Equations

The equations discussed below are incorporated into the Excel-based Batch Test Leaching Model that accompanies this technical memorandum. Figure 5 in the main text depicts the first page of the model (April 2007 version). The model will be updated as needed in the future.

Step 1. Calculate a partition coefficient for each chemical of potential concern.

The results of the SPLP test can be used to develop a sample-specific partition coefficient (Kd) for each chemical of potential of concern. The partition coefficient is calculated as follows (after Roy et. al, 1992; see also McClean and Bledsoe, 1992, and USEPA 1999):

$$Kd \left(\frac{L}{Kg} \right) = \frac{\text{Concentration}_{\text{sorbed}} \left(\frac{\mu g}{Kg} \right)}{\text{Concentration}_{\text{solution}} \left(\frac{\mu g}{L} \right)} \quad (1)$$

where $\text{Concentration}_{\text{sorbed}}$ is the concentration of the contaminant that remained sorbed to the soil following the batch test and $\text{Concentration}_{\text{solution}}$ is the resulting concentration of the contaminant in the batch test solution. The term Kd is commonly reported in equivalent units of $(\mu g/g)/(\mu g/cm^3)$ or cm^3/g , based on an assumed batch test solution density of $1.0 g/cm^3$.

The sorbed concentration of the contaminant is calculated as follows:

$$\text{Concentration}_{\text{sorbed}} = \frac{\text{Mass}_{\text{sorbed}} (\mu g)}{\text{Sample Mass} (kg)} \quad (2)$$

where $\text{Mass}_{\text{sorbed}}$ is the mass of the contaminant still sorbed to the soil following the batch test. The mass of the sample called for in the SPLP batch test is 100 grams or 0.1 Kg (USEPA 1994).

The mass of the contaminant sorbed to the soil is calculated by subtracting the mass of the contaminant that went into the batch test solution from the initial, total mass of the contaminant in the soil sample:

$$\text{Mass}_{\text{sorbed}} (\mu g) = \text{Mass}_{\text{total}} (\mu g) - \text{Mass}_{\text{solution}} (\mu g) \quad (3)$$

where $\text{Mass}_{\text{total}}$ is original, total mass of the contaminant in the soil sample and $\text{Mass}_{\text{solution}}$ is the mass of the contaminant in the batch test solution. The total mass of the contaminant in the soil sample is calculated as:

$$\text{Mass}_{\text{sorbed}} (\mu g) = \text{Conc.}_{\text{total}} \left(\frac{mg}{kg} \right) \times \frac{1,000 \mu g}{1 mg} \times \text{Sample Mass} (kg) \quad (4)$$

where $\text{Concentration}_{\text{total}}$ is the reported total concentration of the contaminant in the soil sample that used in the batch test (tested on a split sample). The mass of the contaminant in the batch test solution is calculated as:

$$\text{Mass}_{\text{solution}} (\mu g) = \text{Conc.}_{\text{solution}} \left(\frac{\mu g}{L} \right) \times \text{Solution Volume} (L) \quad (5)$$

The default volume of solution used in SPLP batch tests is two liters (USEPA 1994).

Note that use of the batch test method to estimate Kd values is no longer valid if the solubility limit of the contaminant is exceeded in the batch test solution (refer to section on Leaching of Heavily Contaminated Soils in the main text). Exceeding the contaminants solubility suggests that free product is present in the soil (either liquid or dry). As a precautionary measure, a cutoff of 75% the assumed contaminant solubility is used in the Batch Test Leaching Model spreadsheet to identify if free product may be present in the batch test solution. The free product acts as a second reservoir of contaminant mass that will bias the true equilibrium concentration of the contaminant in the dissolved and sorbed phases. To accurately calculate desorption coefficients, batch test analyses must be run samples with lower concentrations of the contaminant in soil.

Step 2. Estimate the concentration of the contaminant in source-area leachate.

Once the soil-specific Kd value for a target contaminant has been determined, it is relatively simple to estimate the concentration of the contaminant in the soil moisture or “leachate” within the main body of contaminated soil or the leachate “source area”). This is done by incorporating the calculated Kd into a simple equilibrium partitioning equation and assuming default (or site-specific) soil properties (after USEPA 2001):

$$Conc_{total} = Conc_{leachate} \times \left(Kd + \left(\frac{\theta_w + (\theta_a \times H')}{\rho_b} \right) \right) \times \left(\frac{1mg}{1,000\mu g} \right) \quad (6)$$

where:

- C_{total} = Total concentration of chemical in sample (mg/kg);
- C_{leachate} = Dissolved-phase concentration of chemical (µg/L);
- Kd = Estimated or measured partition coefficient L/kg;
- Theta_w = water-filled porosity (L_{water}/L_{soil});
- Theta_a = air-filled porosity (L_{air}/L_{soil});
- H' = Henry’s Law Constant at 25°C ((µg/L-vapor)/(µg/L-water)); and
- ρ_b = Soil bulk density (Kg/L).

Table H in Appendix 1 of the HDOH EAL document provides a summary of “dimensionless” Henry’s Law Constants (H’) for common volatile contaminants (HDOH 2005). For the purpose of calculating Tier 1 action levels, Kd is calculated as the chemical’s published organic carbon partition coefficient (koc) times the fraction organic carbon in the soil (foc). This is discussed in Appendix 1 of the HDOH Environmental Action Levels document (HDOH 2005). Note that in this equation Kd and ρ_b are expressed in units of L/Kg and Kg/L, respectively, rather than in equivalent units of cm³/g and g/cm³. A default soil density of 1.5 Kg/L and soil porosity of 43% (0.43) are typically used in Tier 1 risk assessment models (e.g., USEPA 2001, 2004).

Equation 6 can be rearranged to solve for C_{leachate} as follows:

$$Conc_{leachate} = Conc_{solution} \div \left(\left(Kd + \left(\frac{\theta_w + (\theta_a \times H')}{\rho_b} \right) \right) \times \left(\frac{1mg}{1,000\mu g} \right) \right) \quad (7)$$

This equation is incorporated into the “Batch Test Leaching Model” worksheet of the Excel file that accompanies this technical memo. The sorption coefficient should be used to estimate the dissolved-phase concentration of the contaminant in a hypothetical, saturated sample of soil at equilibrium and at the same contaminant concentration as the SPLP test. Since the soil is assumed to be fully saturated with water, the vapor-phase term of the equation “ $\theta_a \times H$ ” goes to zero.

Step 3. Tier 3 calculation of ultimate contaminant concentration in groundwater.

A conservative estimate of the contaminant concentration in groundwater that could be impacted by the leachate is made by dividing the calculated concentration of the contaminant in leachate by an assumed groundwater:leachate dilution factor (DF):

$$Conc_{groundwater} = \frac{Conc_{solution}}{DF} \quad (8)$$

where: $C_{groundwater}$ = Concentration of chemical in groundwater ($\mu\text{g/L}$);
 $C_{leachate}$ = Concentration of chemical in leachate ($\mu\text{g/L}$); and
 DF = Groundwater/Leachate dilution factor (m^3/m^3).

$$DF = \frac{Volume\ Impacted\ Groundwater}{Volume\ Leachate} \quad (9)$$

This equation is incorporated into the Batch Test Leaching Model spreadsheet that accompanies this technical memo. A default DF of 20 is considered appropriate for sites less than or equal to 0.5 acres in size (USEPA 2001). A more site-specific DF factor can be calculated if needed, based on the following equation (USEPA 2001):

$$Dilution\ Factor = 1 + \left(\frac{K \times i \times d}{I \times L} \right) \quad (10)$$

where “K” is the aquifer hydraulic conductivity (m/year), “i” is the regional hydraulic gradient, “d” is the assuming mixing zone depth (default is two meters), “I” is the surface water infiltration rate (m/year) and “L” is the length of the contaminated soil area that is parallel to groundwater flow (m).

Note that this equation does not consider an expected reduction in contaminant concentrations as the leachate migrates downward. This component of the evaluation can be included in more site-specific evaluations as needed.

Soil Gas Leaching Model

For volatile contaminants, soil gas data offer an alternative approach for estimation of contaminant concentrations in leachate as well as a method to evaluate the threat posed to

groundwater by downward migrating vapor plumes. The relationship between vapor-phase and dissolved-phase volatile chemicals under equilibrium conditions is relatively straightforward:

$$H' = \frac{C_{\text{vapor}} (\text{ug} / \text{L})}{C_{\text{leachate}} (\text{ug} / \text{L})} \quad (11)$$

where: H' = Henry's Law Constant at 25°C;
 C_{vapor} = Vapor-phase concentration in soil gas;
 C_{leachate} = Dissolved-phase concentration in soil pore waters.

Table H in Appendix 1 of the HDOH EAL document provides a summary of "dimensionless" Henry's Law Constants (H') for common volatile contaminants (HDOH 2005). To calculate the concentration of the contaminant in the soil moisture the equation is rearranged to solve for " C_{leachate} ." The C_{vapor} term is also adjusted to units of ug/m³ to correspond with the units typically reported in site data:

$$C_{\text{leachate}} (\text{ug} / \text{L}) = \frac{C_{\text{vapor}} (\text{ug} / \text{m}^3) \times \frac{1 \text{ m}^3}{1,000 \text{ L}}}{H'} \quad (12)$$

Equation 8 above can be used to estimate potential impacts to groundwater with respect to soil gas-based estimates of contaminant concentrations of the in leachate.

Soil gas "action levels" for protection of groundwater can be developed by rearranging the equation to solve for C_{vapor} and setting C_{leachate} equal to a target leachate goal (e.g., groundwater action level times appropriate groundwater:leachate dilution factor):

$$C_{\text{vapor}} (\text{ug} / \text{m}^3) = C_{\text{leachate}} (\text{ug} / \text{L}) \times H' \times \frac{1,000 \text{ L}}{1 \text{ m}^3} \times \text{AF} \quad (13)$$

The term "AF" is an attenuation factor that describes the anticipated decrease in contaminant concentrations over time as the vapor migrates to and eventually impacts groundwater (e.g., via natural degradation, resorption to soil particles or migration into soil moisture). Approaches for calculation of site-specific, vapor attenuation factors are not well established and beyond the scope of this technical memorandum.