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POLLUTION CONTROL HEARINGS BOARD
FOR THE STATE OF WASHINGTON

AIRPORT COMMUNITIES COALITION,
Appellant,

v.

STATE OF WASHINGTON
DEPARTMENT OF ECOLOGY, and THE
PORT OF SEATTLE,
Respondents.

PCHB No. 01-133

SECOND DECLARATION OF C. LINN
GOULD OPPOSING ACC'S MOTION
FOR STAY

C. Linn Gould declares as follows:

1. I am over the age of 18, am competent to testify, and have personal knowledge of the facts stated herein.

2. I am a Risk Assessor and soil scientist by training, having received my BA in geology and an MS in soil science. A description of my expertise and qualifications is included in my prior declaration supporting the Port of Seattle's Motion Opposing ACC's Motion for Stay and in Exhibit A to that declaration.

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3. In its reply memorandum, ACC alleges that the Port has made a number of "errors" in deriving or setting its fill criteria. Neither ACC's brief nor the declarations supporting it, however, link these alleged "errors" to any evidence, scientific or otherwise, that would tend to show that the

ORIGINAL

1 criteria and other requirements are not protective of aquatic life and water quality. Moreover, the
2 ACC's allegations either miss the point or are simply wrong, as discussed herein.

3 4. First, despite ACC's implications to the contrary, both the numeric and the narrative
4 requirements of the 401 Certification are protective of water quality. The narrative criteria prohibit
5 acceptance of fill from contaminated sources and fill that was previously contaminated but has been
6 remediated. *See* 401 Certification, Condition E(1)(b). The numeric criteria are more stringent than is
7 necessary to ensure that water quality standards are not violated. *See* Declaration of L. Gould in
8 Support of the Port of Seattle's Response Opposing ACC's Motion for Stay. A detailed description
9 of how these criteria were derived is set out in my prior declaration at paragraphs 9-15. *Id.*

10 5. Second, ACC misses the point when it attempts to "correct" the Port's statement that
11 seven and not four numeric criteria are set based upon MTCA Method A criteria. The point is that
12 all of the criteria, including four metals constituents (arsenic, cadmium, mercury, and lead) and Total
13 Petroleum Hydrocarbons ("TPH") have been derived in a manner assured to be protective of aquatic
14 receptors. The arsenic number may be a Method A cleanup level but it also represents "natural
15 background" as described in WAC 173-340-900 at Table 740-1 (footnote b). Both arsenic and lead
16 criteria have been adjusted *downward* to Method A even though the three-phase back calculation
17 showed that higher numbers would protect water quality. Mercury is set at MTCA Method A back
18 calculation for drinking water because the fresh water back calculation was below the PQL. Cadmium
19 was adjusted to the PQL as its back calculation was below the PQL. Finally, TPH soil criteria have
20 been derived first using a conservative back calculation model protective of water quality and then
21 adjusted *downward* to residual saturation for diesel and heavy oils.

22 6. Third, ACC is simply incorrect when it states that "none of the contaminants are set at
23 the Practical Quantitation Limits ("PQL") identified in DOE Technical Memorandum #3 PQLS as
24 Cleanup Standards." *See* ACC Reply Memo, at 33-4 (Exh. B to ACC's Lucia Decl.). In fact, the
25 numeric criteria levels for selenium, silver, and antimony are set at PQLs clearly identified in the same
26 DOE Technical Memorandum #3 referenced and provided by ACC. *Id.*

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1 7. Fourth, ACC implies that the Synthetic Precipitation Leaching Procedure ("SPLP")
2 protocol is somehow less protective than the numeric fill criteria. *See* ACC Reply Memo, at 30.
3 This is simply not the case, as described below.

4 8. Fill soil satisfying the source analysis requirements and numeric criteria set out in the
5 401 Certification may be acceptable for use in the Third Runway embankment. *See* 401 Certification,
6 Condition E(1)(b). By definition, for each constituent tested, native Puget Sound soils will be at
7 levels in excess of Puget Sound background numeric fill criteria 10 percent of the time. *Id.* Thus, in
8 cases where soil from uncontaminated sites exceed numeric fill criteria, the 401 Certification provides
9 that fill acceptability may be demonstrated by using the Synthetic Precipitation Leaching Procedure
10 ("SPLP") protocol. *See* 401 Certification, Condition E(1)(b); SPLP Work Plan.

11 9. Generally, the 401 Certification's SPLP protocol directly measures the potential for
12 constituents to move from the soil into water moving through the soil in order to determine if these
13 constituents in the proposed fill are even capable of leaching at a rate that would threaten surface
14 water quality. The SPLP test, EPA SW-846 Method 1312, is an accepted laboratory leaching test, as
15 discussed in WAC 173-340-747(7). *See* Exhibit A (WAC 173-340-747). It was designed to simulate
16 the leaching of chemicals from soils by acid rain in various parts of the country and thereby to
17 determine the mobility of both organic and inorganic constituents present in soil, waste material, and
18 waste water. *See* Exhibit B (EPA SW-846 Method 1312). The SPLP test takes site-specific
19 information (fill from the specified sources) and tests its potential to leach in a laboratory setting. In
20 short, the SPLP test relies on direct observation to not only confirm the conservatism of the existing
21 criteria but also show that higher concentrations are protective of aquatic receptors.

22 10. Under the SPLP Work Plan, fluids representing acid rain are passed through the soil
23 sample and the liquid is collected and analyzed for the constituent that exceeded the numeric fill
24 criteria. *See* Exhibit B (EPA SW-846 Method 1312). These SPLP results are then compared to the
25 applicable fresh water surface water criteria, assuming a conservative dilution/attenuation factor
26 which, under the SPLP Work Plan, is set at 20.

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1 11. Based on this analysis, if the adjusted SPLP results for a specific fill sample exceed
2 freshwater ambient water quality criteria, the fill will be rejected for use in the embankment. *See*
3 SPLP Work Plan. However, if the adjusted SPLP for a fill sample meets freshwater ambient water
4 quality criteria, that fill may be acceptable for use in the embankment. *Id.* This is appropriate
5 because, despite the fact that a particular fill source may not meet the 401 Certification's numeric fill
6 criteria, use of the fill for the embankment remains protective of surface waters as the constituent(s)
7 at issue cannot leach from that fill soil at a rate sufficient to cause or even threaten to cause violation
8 of applicable water quality standards.

9 12. All SPLP test results must be submitted to Ecology and, even where a fill constituent
10 has satisfied the SPLP test, Ecology has reserved the right to disapprove of the use of fill analyzed
11 under the SPLP method. *See* 401 Certification, Condition E(1)(b).

12 13. Fifth, contrary to ACC's allegations, the Port fully intends—and in fact is required
13 —to comply with the U.S. Fish and Wildlife Service's Biological Opinion (May 22, 2001) provisions
14 that require constituent fill criteria to account for the protection of terrestrial ecological receptors in
15 the top three feet of the embankment for eight metals. With the exception of chromium, lead, and
16 barium (a metal that is not in the 401 Certification), the Biological Opinion criteria for the top three
17 feet of the embankment are similar to the existing Ecology criteria in the 401 Certification.
18 Presumably, the 401 Certification did not mention the Biological Opinion's criteria for the upper three
19 feet because the top three feet of the embankment are not determinative of water quality and
20 protection of aquatic life which is the purpose of the 401 Certification. The ACC's concerns in this
21 regard are unfounded.

22 14. Sixth, ACC has seriously misunderstood the design of the embankment and
23 specifically the purpose and impact of the drainage layer. Beneath the embankment fill, generally at
24 the original ground surface, a bottom drainage layer consisting of an approximate 3-foot thickness of
25 free-draining sand and gravel, has been included in the fill embankment design. This drainage layer will
26 prevent groundwater pressures from building up within the embankment and direct groundwater flow
27 away from the embankment fill.

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1 15. Contrary to ACC's representations, the drainage layer will not act like a "pipe" or
2 "conduit" that will discharge to surface waters as a point source. In reality, water may enter the
3 drainage layer from above, due to infiltration through the embankment fill, or from below as
4 groundwater inflow in the form of seepage from the existing slope or existing shallow groundwater
5 discharge zones that will be buried beneath the embankment. Before reaching surface water receptors,
6 water that flows through the drainage layer will be subject to substantial dilution and attenuation
7 processes within the embankment, in groundwater, and/or in soil beyond the embankment. There is
8 no "point source" discharge running from the embankment directly into the surface water, as ACC
9 would have the Board believe.

10 16. Finally, ACC suggests that the 401 Certification's sampling procedure is inadequate,
11 and should instead be modeled after the Toxics Cleanup Program's sampling protocol. *See* ACC's
12 Reply Memo at 36. On the contrary, the sampling procedures required in the 401 Certification are
13 appropriate for fill that will be pre-screened and evaluated for the potential presence of contamination
14 under the required Phase I and Phase II investigations. The Toxics Cleanup Program's more extensive
15 area-wide sampling program is an approach designed to search for a distribution of soils at known
16 contaminated sites which may require remediation, not soils from sources previously determined not
17 to be contaminated. Investigating the extent of contamination and determining compliance with
18 cleanup levels at a source known to be contaminated requires a greater number of samples than
19 confirmatory sampling at a source where prior studies have found no contamination. Use of MTCA
20 sampling protocols is therefore not warranted.

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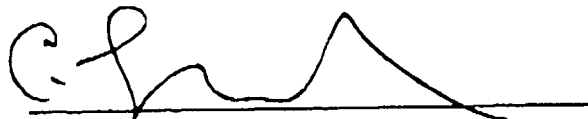
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I declare under penalty of perjury under the laws of the State of Washington that the foregoing

is true and correct.

DATED this 9^m day of October, 2001 at Seattle, Washington.



C. Linn Gould

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DECLARATION OF C. LINN GOULD

MARTEN BROWN INC
1191 SECOND AVENUE, SUITE 2200
SEATTLE, WASHINGTON 98101

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AR 006622

WAC 173-340-747

Wash. Admin. Code 173-340-747

WASHINGTON ADMINISTRATIVE CODE
TITLE 173. ECOLOGY, DEPARTMENT OF
CHAPTER 173-340. MODEL TOXICS CONTROL ACT--CLEANUP--CLEANUP
PART VII--CLEANUP STANDARDS
Current with amendments adopted through 07-18-2001.

173-340-747. Deriving soil concentrations for ground water protection. (Effective August 15, 2001)

(1) Purpose. The purpose of this section is to establish soil concentrations that will not cause contamination of ground water at levels that exceed the ground water cleanup levels established under WAC 173-340-720. Soil concentrations established under this section are used to establish either Method B soil cleanup levels (see WAC 173-340-740 (3)(b)(iii)(A) or Method C soil cleanup levels (see WAC 173-340-745 (5)(b)(iii)(A).

For the purposes of this section, 'soil concentration' means the concentration in the soil that will not cause an exceedance of the ground water cleanup level established under WAC 173-340-720.

(2) General requirements. The soil concentration established under this section for each hazardous substance shall meet the following two criteria:

(a) The soil concentration shall not cause an exceedance of the ground water cleanup level established under WAC 173-340-720. To determine if this criterion is met, one of the methodologies specified in subsections (4) through (9) of this section shall be used; and

(b) To ensure that the criterion in (a) of this subsection is met, the soil concentration shall not result in the accumulation of nonaqueous phase liquid on or in ground water. To determine if this criterion is met, one of the methodologies specified in subsection (10) of this section shall be used.

(3) Overview of methods. This subsection provides an overview of the methods specified in subsections (4) through (10) of this section for deriving soil concentrations that meet the criteria specified in subsection (2) of this section. Certain methods are tailored for particular types of hazardous substances or sites. Certain methods are more complex than others and certain methods require the use of site-specific data. The specific requirements for deriving a soil concentration under a particular method may also depend on the hazardous substance.

(a) Fixed parameter three-phase partitioning model. The three-phase partitioning model with fixed input parameters may be used to establish a soil concentration for any hazardous substance. Site-specific data are not required for use of this model. See subsection (4) of this section.

(b) Variable parameter three-phase partitioning model. The three-phase partitioning model with variable input parameters may be used to establish a soil concentration for any hazardous substance. Site-specific data are required for use of this model. See subsection (5) of this section.

(c) Four-phase partitioning model. The four-phase partitioning model may be used to derive soil concentrations for any site where hazardous substances are present in the soil as a nonaqueous phase liquid (NAPL). The department expects that this model will be used at sites contaminated with petroleum hydrocarbons. Site-specific data are required for use of this model. See subsection (6) of this section.

(d) Leaching tests. Leaching tests may be used to establish soil concentrations for certain metals. Leaching tests may also be used to establish soil concentrations for other hazardous substances, including petroleum hydrocarbons, provided sufficient information is available to demonstrate that the leaching test can accurately predict ground water impacts. Testing of soil samples from the site is required for use of this method. See subsection (7) of this section.

(e) Alternative fate and transport models. Fate and transport models other than those specified in

subsections (4) through (6) of this section may be used to establish a soil concentration for any hazardous substance. Site-specific data are required for use of such models. See subsection (8) of this section.

(f) Empirical demonstration. An empirical demonstration may be used to show that measured soil concentrations will not cause an exceedance of the applicable ground water cleanup levels established under WAC 173-340-720. This empirical demonstration may be used for any hazardous substance. Site-specific data (e.g., ground water samples and soil samples) are required under this method. If the required demonstrations cannot be made, then a protective soil concentration shall be established under one of the methods specified in subsections (4) through (8) of this section. See subsection (9) of this section.

(g) Residual saturation. To ensure that the soil concentration established under one of the methods specified in subsections (4) through (9) of this section will not cause an exceedance of the ground water cleanup level established under WAC 173-340-720, the soil concentration must not result in the accumulation of nonaqueous phase liquid (NAPL) on or in ground water. The methodologies and procedures specified in subsection (10) of this section shall be used to determine if this criterion is met.

(4) Fixed parameter three-phase partitioning model.

(a) Overview. This subsection specifies the procedures and requirements for establishing soil concentrations through the use of the fixed parameter three-phase partitioning model. The model may be used to establish soil concentrations for any hazardous substance. The model may be used to calculate both unsaturated and saturated zone soil concentrations.

This method provides default or fixed input parameters for the three-phase partitioning model that are intended to be protective under most circumstances and conditions; site-specific measurements are not required. In some cases it may be appropriate to use site-specific measurements for the input parameters. Subsection (5) of this section specifies the procedures and requirements to establish site-specific input parameters for use in the three-phase partitioning model.

(b) Description of the model. The three-phase partitioning model is described by the following equation:

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Where:

C sub s = Soil concentration (mg/kg)
C sub w = Ground water cleanup level established under WAC 173-340-720 (ug/l)
UCF = Unit conversion factor (1mg/1,000 ug)
DF = Dilution factor (dimensionless: 20 for unsaturated zone soil; see (e) of this subsection for saturated zone soil)
K sub d = Distribution coefficient (L/kg; see (c) of this subsection)
&thgr; sub w = Water-filled soil porosity (ml water/ml soil: 0.3 for unsaturated zone soil; see (e) of this subsection for saturated zone soil)
&thgr; sub a = Air-filled soil porosity (ml air/ml soil: 0.13 for unsaturated zone soil; see (e) of this subsection for saturated zone soil)
H sub cc = Henry's law constant (dimensionless; see (d) of this subsection)
&rgr; sub b = Dry soil bulk density (1.5 kg/L)
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(c) Distribution coefficient (K sub d). The default K sub d values for organics and metals used in Equation 747-1 are as follows:

(i) Organics. For organic hazardous substances, the K sub d value shall be derived using Equation 747-2. The K sub oc (soil organic carbon-water partition coefficient) parameter specified in Equation 747-2 shall be derived as follows:

(A) Nonionic organics. For individual nonionic hydrophobic organic hazardous substances (e.g., benzene and naphthalene), the K sub oc values in Table 747-1 shall be used. For hazardous substances not listed in

Table 747-1, K subd values may be developed as provided in subsection (5) of this section (variable three-phase partitioning model).

(B) Ionizing organics. For ionizing organic hazardous substances (e.g., pentachlorophenol and benzoic acid), the K suboc values in Table 747-2 shall be used. Table 747-2 provides K suboc values for three different pHs. To select the appropriate K suboc value, the soil pH must be measured. The K suboc value for the corresponding soil pH shall be used. If the soil pH falls between the pH values provided, an appropriate K suboc value shall be selected by interpolation between the listed K suboc values.

Equation 747-2

$K_{subd} = K_{suboc} \times f_{suboc}$

Where:

K_{subd} = Distribution coefficient (L/kg)

K_{suboc} = Soil organic carbon-water partitioning coefficient (ml/g). See (c)(i) of this subsection.

f_{suboc} = Soil fraction of organic carbon (0.1% or 0.001 g/g)

(ii) Metals. For metals, the K subd values in Table 747-3 shall be used. For metals not listed in Table 747-3, K subd values may be developed as provided in subsection (5) of this section (variable three-phase partitioning model).

(d) Henry's law constant. For petroleum fractions, the values for Henry's law constant in Table 747-4 shall be used in Equation 747-1. For individual organic hazardous substances, the value shall be based on values in the scientific literature. For all metals present as inorganic compounds except mercury, zero shall be used. For mercury, either 0.47 or a value derived from the scientific literature shall be used. Derivation of Henry's law constant from the scientific literature shall comply with WAC 173-340-702 (14), (15) and (16).

(e) Saturated zone soil concentrations. Equation 747-1 may also be used to derive concentrations for soil that is located at or below the ground water table (the saturated zone). The following input parameters shall be changed if Equation 747-1 is used to derive saturated zone soil concentrations:

(i) The dilution factor shall be changed from 20 to 1;

(ii) The water-filled soil porosity value shall be changed from 0.3 ml water/ml soil to 0.43 ml water/ml soil; and

(iii) The air-filled soil porosity value shall be changed from 0.13 ml air/ml soil to zero.

(5) Variable parameter three-phase partitioning model.

(a) Overview. This section specifies the procedures and requirements to derive site-specific input parameters for use in the three-phase partitioning model. This method may be used to establish soil concentrations for any hazardous substance. This method may be used to calculate both unsaturated and saturated zone soil concentrations.

This method allows for the substitution of site-specific values for the default values in Equation 747-1 for one or more of the following five input parameters: Distribution coefficient, soil bulk density, soil volumetric water content, soil air content, and dilution factor. The methods that may be used and the requirements that shall be met to derive site-specific values for each of the five input parameters are specified in (b) through (f) of this subsection.

(b) Methods for deriving a distribution coefficient (K_{subd}). To derive a site-specific distribution coefficient, one of the following methods shall be used:

(i) Deriving K_{subd} from soil fraction of organic carbon (f_{oc}) measurements. Site-specific measurements of soil organic carbon may be used to derive distribution coefficients for nonionic hydrophobic organics using Equation 747-2. Soil organic carbon measurements shall be based on uncontaminated soil below the root zone (i.e., soil greater than one meter in depth) that is representative of site conditions or in areas through which contaminants are likely to migrate.

The laboratory protocols for measuring soil organic carbon in the Puget Sound Estuary Program (March, 1986) may be used. Other methods may also be used if approved by the department. All laboratory measurements of soil organic carbon shall be based on methods that do not include inorganic carbon in the measurements.

(ii) Deriving K_{subd} from site data. Site-specific measurements of the hazardous substance concentrations in the soil and the soil pore water or ground water may be used, subject to department approval, to derive a distribution coefficient. Distribution coefficients that have been derived from site data shall be based on measurements of soil and ground water hazardous substance concentrations from the same depth and location. Soil and ground water samples that have hazardous substances present as a nonaqueous phase liquid (NAPL) shall not be used to derive a distribution coefficient and measures shall be taken to minimize biodegradation and volatilization during sampling, transport and analysis of these samples.

(iii) Deriving K_{subd} from batch tests. A site-specific distribution coefficient may be derived by using batch equilibrium tests, subject to department approval, to measure hazardous substance adsorption and desorption. The results from the batch test may be used to derive K_{subd} from the sorption/desorption relationship between hazardous substance concentrations in the soil and water. Samples that have hazardous substances present as a nonaqueous phase liquid (NAPL) shall not be used to derive a distribution coefficient and measures shall be taken to minimize biodegradation and volatilization during testing.

(iv) Deriving K_{subd} from the scientific literature. The scientific literature may be used to derive a site-specific distribution coefficient (K_{subd}) for any hazardous substance, provided the requirements in WAC 173-340-702 (14), (15) and (16) are met.

(c) Deriving soil bulk density. ASTM Method 2049 or other methods approved by the department may be used to derive soil bulk density values.

(d) Deriving soil volumetric water content using laboratory methods. ASTM Method 2216 or other methods approved by the department may be used to derive soil volumetric water content values.

(e) Estimating soil air content. An estimate of soil air content may be determined by calculating soil porosity and subtracting the volumetric water content.

(f) Deriving a dilution factor from site-specific estimates of infiltration and ground water flow volume. Site-specific estimates of infiltration and ground water flow volume may be used in the following equation to derive a site-specific dilution factor:

Equation 747-3

$$DF = (Q_{subp} + Q_{suba}) / Q_{subp}$$

Where:

DF = Dilution factor (dimensionless)

Q_{subp} = Volume of water infiltrating (m^3 / yr)

Q_{suba} = Ground water flow (m^3 / yr)

(i) Calculating ground water flow volume. The following equation shall be used under this method to calculate the volume of ground water flow (Q_{suba}):

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$$Q_{suba} = K \times A \times I$$

Where:

Q_{suba} = Ground water flow volume ($m^3 / year$)

K = Hydraulic conductivity ($m/year$). Site-specific measurements shall be used to derive this parameter.

A = Aquifer mixing zone (m^2). The aquifer mixing zone thickness shall not exceed 5 meters in depth and be equal to a unit width of

1 meter, unless it can be demonstrated empirically that the mixing zone thickness exceeds 5 meters.

I = Gradient (m/m). Site-specific measurements shall be used to derive this parameter.

(A) Equation 747-4 assumes the ground water concentrations of hazardous substances of concern upgradient of the site are not detectable. If this assumption is not true, the dilution factor may need to be adjusted downward in proportion to the upgradient concentration.

(B) Direct measurement of the flow velocity of ground water using methods approved by the department may be used as a substitute for measuring the ground water hydraulic conductivity and gradient.

(ii) Calculating or estimating infiltration. The following equation shall be used under this method to calculate the volume of water infiltrating (Q_{subp}):

Equation 747-5

$$Q_{subp} = L \times W \times Inf$$

Where:

Q_{subp} = Volume of water infiltrating (m³/year)

L = Estimated length of contaminant source area parallel to ground water flow (m)

W = Unit width of contaminant source area (1 meter)

Inf = Infiltration (m/year)

(A) If a default annual infiltration value (Inf) is used, the value shall meet the following requirements. For sites west of the Cascade Mountains, the default annual infiltration value shall be 70 percent of the average annual precipitation amount. For sites east of the Cascade Mountains, the default annual infiltration value shall be 25 percent of the average annual precipitation amount.

(B) If a site-specific measurement or estimate of infiltration (Inf) is made, it shall be based on site conditions without surface caps (e.g., pavement) or other structures that would control or impede infiltration. The presence of a cover or cap may be considered when evaluating the protectiveness of a remedy under WAC 173-340-350 through 173-340-360. If a site-specific measurement or estimate of infiltration is made, then it must comply with WAC 173-340-702 (14), (15) and (16).

(6) Four-phase partitioning model.

(a) Overview. This subsection specifies the procedures and requirements for establishing soil concentrations through the use of the four-phase partitioning model. This model may be used to derive soil concentrations for any site where hazardous substances are present in the soil as a nonaqueous phase liquid (NAPL). The model is described in (c) of this subsection. Instructions on how to use the model to establish protective soil concentrations are provided in (d) of this subsection.

(b) Restrictions on use of the model for alcohol enhanced fuels. The four-phase partitioning model may be used on a case-by-case basis for soil containing fuels (e.g., gasoline) that have been enhanced with alcohol. If the model is used for alcohol enhanced fuels, then it shall be demonstrated that the effects of cosolvency have been adequately considered and, where necessary, taken into account when applying the model. Use of the model for alcohol enhanced fuels without considering the effects of cosolvency and increased ground water contamination is prohibited.

(c) Description of the model. The four-phase partitioning model is based on the following three equations:

(i) Conservation of volume equation.

Equation
747-6

$$n = \text{&thgr; }_{subw} + \text{&thgr; }_{suba} + \text{&thgr; }_{subNAPL}$$

Where:

- n = Total soil porosity (ml total pore space/ml total soil volume). Use a default value of 0.43 ml/ml or use a value determined from site-specific measurements.
- θ_w ; subw = Volumetric water content (ml water/ml soil). For unsaturated soil use a default value of 0.3 or a value determined from site-specific measurements. For saturated soil this value is unknown and must be solved for. Volumetric water content equals the total soil porosity minus volume occupied by the NAPL.
- θ_a ; suba = Volumetric air content (ml air volume/ml total soil volume). For unsaturated soil this value is unknown and must be solved for. Volumetric air content equals the total soil porosity minus the volume occupied by the water and NAPL. For saturated soil this value is zero.
- θ_{NAPL} ; subNAPL = Volumetric NAPL content (ml NAPL volume/ml total soil volume). For both unsaturated and saturated soil this value is unknown and must be solved for.

(ii) Four-phase partitioning equation.

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Where:

- M_{subT} = Total mass of each component in the system (mg). This value is derived from site-specific measurements.
- m_{subsoil} = Total soil mass (kg).
- x_{subi} = Mole fraction (at equilibrium) of each component (dimensionless). This value is unknown and must be solved for.
- S_{subi} = Solubility of each component (mg/l). See Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
- P_{subb} = Dry soil bulk density (1.5 kg/l).
- K_{suboc} = Soil organic carbon-water partitioning coefficient for each component (l/kg). See Table 747-4 for petroleum hydrocarbons; see subsection (4)(b) of this section for other hazardous substances.
- f_{suboc} = Mass fraction of soil natural organic carbon (0.001 g soil organic/g soil).
- H_{subcc} = Henry's law constant for each component (dimensionless). See Table 747-4 for petroleum hydrocarbons; see subsection (4)(c) of this section for other hazardous substances.
- GFW_{subi} = Gram formula weight, or molecular weight of each component (mg/mol). See Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
- ρ_{NAPL} = Molar density of the mixture (mol/l). See Equation 747-8.
- Component = For petroleum mixtures, this means the petroleum fractions, and organic hazardous substances with a reference dose; for other hazardous substances, this means each organic hazardous substance that is found in the NAPL.

(iii) Molar density equation.

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Where:

- GFW_{subi} = Gram formula weight, or molecular weight of each component (mg/mol). See Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
- x_{subi} = Mole fraction (at equilibrium) of each component (dimensionless). This value is unknown and must be solved for.
- ρ_{subi} = Density of each component (mg/l). See Table 747-4 for petroleum hydrocarbons; see the scientific literature for other hazardous substances.
- Component = For petroleum mixtures, this means the petroleum fractions plus organic hazardous substances with a reference dose; for other hazardous substances, this means each organic hazardous substance that is found in the NAPL.

(d) Instructions for using the model. This subsection provides instructions for using the four-phase partitioning model to predict ground water concentrations and to establish protective soil concentrations. The model uses an iterative process to simultaneously solve multiple equations for several unknowns (see step 4 for the number of equations). To predict a ground water concentration, the mole fraction of each component (at equilibrium) must be known. The predicted ground water concentration is obtained by multiplying the water solubility of each component by the equilibrated mole fraction (Equation 747-7).

(i) Step 1: Measure hazardous substance soil concentrations. Collect and analyze soil samples and, if appropriate, samples of the product released, for each component. For petroleum hydrocarbons, see Table 830-1 for a description of what to analyze for.

(ii) Step 2: Derive physical/chemical data. For each of the components, determine the Henry's law constant, water solubility, soil organic carbon-water partitioning coefficient, density and molecular weight values. For petroleum hydrocarbons, see Table 747-4.

(iii) Step 3: Derive soil parameters. Derive a value for each of the following soil parameters as follows:

(A) Soil organic carbon content. Use the default value (0.001 g soil organic/g soil) or a site-specific value derived under subsection (5)(b)(i) of this section.

(B) Soil volumetric water content. Use the default value (0.43 minus the volume of NAPL and air) or a site-specific value derived under subsection (5)(d) of this section.

(C) Soil volumetric air content. Use the default value (0.13 ml/ml for unsaturated zone soil; zero for saturated zone soil) or a site-specific value derived under subsection (5)(e) of this section.

(D) Soil bulk density and porosity. Use the default values of 1.5 kg/l for soil bulk density and 0.43 for soil porosity or use site-specific values. If a site-specific value for bulk density is used, the method specified in subsection (5)(c) of this subsection shall be used. If a site-specific bulk density value is used, a site-specific porosity value shall also be used. The site-specific soil porosity value may be calculated using a default soil specific gravity of 2.65 g/ml or measuring the soil specific gravity using ASTM Method D 854.

(iv) Step 4: Predict a soil pore water concentration. Equation 747-7 shall be used to predict the soil pore water concentration for each component. To do this, multiple versions of Equation 747-7 shall be constructed, one for each of the components using the associated parameter inputs for K_{suboc} , H_{subcc} , GFW, and S. These equations shall then be combined with Equations 747-6 and 747-8 and the condition that $\sum x_{subi} = 1$ and solved simultaneously for the unknowns in the equations (mole fraction of each component (X_{subi}), volumetric NAPL content ($\theta_{subNAPL}$), and either the volumetric water content (θ_{subw}) or the volumetric air content (θ_{suba})).

(v) Step 5: Derive a dilution factor. Derive a dilution factor using one of the following two methods:

(A) Use the default value of 20 for unsaturated soils and 1 for saturated soils); or

(B) Derive a site-specific value using site-specific estimates of infiltration and ground water flow volume under subsection (5)(f) of this section.

(vi) Step 6: Calculate a predicted ground water concentration. Calculate a predicted ground water concentration for each component by dividing the predicted soil pore water concentration for each component by a dilution factor to account for the dilution that occurs once the component enters ground water.

(vii) Step 7: Establishing protective soil concentrations.

(A) Petroleum mixtures. For petroleum mixtures, compare the predicted ground water concentration for each component and for the total petroleum hydrocarbon mixture (sum of the petroleum components in the NAPL) with the applicable ground water cleanup level established under WAC 173-340-720.

(I) If the predicted ground water concentration for each of the components and for the total petroleum hydrocarbon mixture is less than or equal to the applicable ground water cleanup level, then the soil concentrations measured at the site are protective.

(II) If the condition in (d)(vii)(A)(I) of this subsection is not met, then the soil concentrations measured at the site are not protective. In this situation, the four-phase partitioning model can be used in an iterative process to calculate protective soil concentrations.

(B) Other mixtures. For mixtures that do not include petroleum hydrocarbons, compare the predicted ground water concentration for each hazardous substance in the mixture with the applicable ground water cleanup level established under WAC 173-340-720.

(I) If the predicted ground water concentration for each of the hazardous substances in the mixture is less than or equal to the applicable ground water cleanup level, then the soil concentrations measured at the site are protective.

(II) If the condition in (d)(vii)(B)(I) of this subsection is not met, then the soil concentrations measured at the site are not protective. In this situation, the four-phase partitioning model can be used in an iterative process to calculate protective soil concentrations.

(7) Leaching tests.

(a) Overview. This subsection specifies the procedures and requirements for deriving soil concentrations through the use of leaching tests. Leaching tests may be used to establish soil concentrations for the following specified metals: Arsenic, cadmium, total chromium, hexavalent chromium, copper, lead, mercury, nickel, selenium, and zinc (see (b) and (c) of this subsection). Leaching tests may also be used to establish soil concentrations for other hazardous substances, including petroleum hydrocarbons, provided sufficient information is available to correlate leaching test results with ground water impacts (see (d) of this subsection). Testing of soil samples from the site is required for use of this method.

(b) Leaching tests for specified metals. If leaching tests are used to establish soil concentrations for the specified metals, the following two leaching tests may be used:

(i) EPA Method 1312, Synthetic Precipitation Leaching Procedure (SPLP). Fluid #3 (pH = 5.0), representing acid rain in the western United States, shall be used when conducting this test. This test may underestimate ground water impacts when acidic conditions exist due to significant biological degradation or for other reasons. Underestimation of ground water impacts may occur, for example, when soils contaminated with metals are located in wood waste, in municipal solid waste landfills, in high sulfur content mining wastes, or in other situations with a pH <6. Consequently, this test shall not be used in these situations and the TCLP test should be used instead.

(ii) EPA Method 1311, Toxicity Characteristic Leaching Procedure (TCLP). Fluid #1 (pH = 4.93), representing organic acids generated by biological degradation processes, shall be used when conducting this test. This test is intended to represent situations where acidic conditions are present due to biological degradation such as in municipal solid waste landfills. Thus, it may underestimate ground water impacts where this is not the case and the metals of interest are more soluble under alkaline conditions. An example

of this would be arsenic occurring in alkaline (pH >8) waste or soils. Consequently, this test shall not be used in these situations and the SPLP test should be used instead.

(c) Criteria for specified metals. When using either EPA Method 1312 or 1311, the analytical methods used for analysis of the leaching test effluent shall be sufficiently sensitive to quantify hazardous substances at concentrations at the ground water cleanup level established under WAC 173-340-720. For a soil metals concentration derived under (b) of this subsection to be considered protective of ground water, the leaching test effluent concentration shall meet the following criteria:

(i) For cadmium, lead and zinc, the leaching test effluent concentration shall be less than or equal to ten (10) times the applicable ground water cleanup level established under WAC 173-340-720.

(ii) For arsenic, total chromium, hexavalent chromium, copper, mercury, nickel and selenium, the leaching test effluent concentration shall be less than or equal to the applicable ground water cleanup level established under WAC 173-340-720.

(d) Leaching tests for other hazardous substances. Leaching tests using the methods specified in this subsection may also be used for hazardous substances other than the metals specifically identified in this subsection, including petroleum hydrocarbons. Alternative leaching test methods may also be used for any hazardous substance, including the metals specifically identified in this subsection. Use of the leaching tests specified in (b) and (c) of this subsection for other hazardous substances or in a manner not specified in (b) and (c) of this subsection, or use of alternative leaching tests for any hazardous substance, is subject to department approval and the user must demonstrate with site-specific field or laboratory data or other empirical data that the leaching test can accurately predict ground water impacts. The department will use the criteria in WAC 173-340-702 (14), (15) and (16) to evaluate the appropriateness of these alternative methods under WAC 173-340-702 (14), (15) and (16).

(8) Alternative fate and transport models.

(a) Overview. This subsection specifies the procedures and requirements for establishing soil concentrations through the use of fate and transport models other than those specified in subsections (4) through (6) of this section. These alternative models may be used to establish a soil concentration for any hazardous substance. Site-specific data are required for use of these models.

(b) Assumptions. When using alternative models, chemical partitioning and advective flow may be coupled with other processes to predict contaminant fate and transport, provided the following conditions are met:

(i) Sorption. Sorption values shall be derived in accordance with either subsection (4)(c) of this section or the methods specified in subsection (5)(b) of this section.

(ii) Vapor phase partitioning. If Henry's law constant is used to establish vapor phase partitioning, then the constant shall be derived in accordance with subsection (4)(d) of this section.

(iii) Natural biodegradation. Rates of natural biodegradation shall be derived from site-specific measurements.

(iv) Dispersion. Estimates of dispersion shall be derived from either site-specific measurements or literature values.

(v) Decaying source. Fate and transport algorithms may be used that account for decay over time.

(vi) Dilution. Dilution shall be based on site-specific measurements or estimated using a model incorporating site-specific characteristics. If detectable concentrations of hazardous substances are present in upgradient ground water, then the dilution factor may need to be adjusted downward in proportion to the background (upgradient) concentration.

(vii) Infiltration. Infiltration shall be derived in accordance with subsection (5)(f)(ii)(A) or (B) of this section.

(c) Evaluation criteria. Proposed fate and transport models, input parameters, and assumptions shall comply with WAC 173-340-702 (14), (15) and (16).

(9) Empirical demonstration.

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(a) Overview. This subsection specifies the procedures and requirements for demonstrating empirically that soil concentrations measured at the site will not cause an exceedance of the applicable ground water cleanup levels established under WAC 173-340-720. This empirical demonstration may be used for any hazardous substance. Site-specific data (e.g., ground water and soil samples) are required under this method. If the demonstrations required under (b) of this subsection cannot be made, then a protective soil concentration shall be established under one of the methods specified in subsections (4) through (8) of this section.

(b) Requirements. To demonstrate empirically that measured soil concentrations will not cause an exceedance of the applicable ground water cleanup levels established under WAC 173-340-720, the following shall be demonstrated:

(i) The measured ground water concentration is less than or equal to the applicable ground water cleanup level established under WAC 173-340-720; and

(ii) The measured soil concentration will not cause an exceedance of the applicable ground water cleanup level established under WAC 173-340-720 at any time in the future. Specifically, it must be demonstrated that a sufficient amount of time has elapsed for migration of hazardous substances from soil into ground water to occur and that the characteristics of the site (e.g., depth to ground water and infiltration) are representative of future site conditions. This demonstration may also include a measurement or calculation of the attenuating capacity of soil between the source of the hazardous substance and the ground water table using site-specific data.

(c) Evaluation criteria. Empirical demonstrations shall be based on methods approved by the department. Those methods shall comply with WAC 173-340-702 (14), (15) and (16).

(10) Residual saturation.

(a) Overview. To ensure the soil concentrations established under one of the methods specified in subsections (4) through (9) of this section will not cause an exceedance of the ground water cleanup level established under WAC 173-340-720, the soil concentrations must not result in the accumulation of nonaqueous phase liquid on or in ground water (see subsection (2)(b) of this section). To determine if this criterion is met, either an empirical demonstration must be made (see (c) of this subsection) or residual saturation screening levels must be established and compared with the soil concentrations established under one of the methods specified in subsections (4) through (9) of this section (see (d) and (e) of this subsection). This subsection applies to any site where hazardous substances are present as a nonaqueous phase liquid (NAPL), including sites contaminated with petroleum hydrocarbons.

(b) Definition of residual saturation. When a nonaqueous phase liquid (NAPL) is released to the soil, some of the NAPL will be held in the soil pores or void spaces by capillary force. For the purpose of this subsection, the concentration of hazardous substances in the soil at equilibrium conditions is called residual saturation. At concentrations above residual saturation, the NAPL will continue to migrate due to gravimetric and capillary forces and may eventually reach the ground water, provided a sufficient volume of NAPL is released.

(c) Empirical demonstration. An empirical demonstration may be used to show that soil concentrations measured at the site will not result in the accumulation of nonaqueous phase liquid on or in ground water. An empirical demonstration may be used for any hazardous substance. Site-specific data (e.g., ground water and soil samples) are required under this method. If the demonstrations required under (c)(i) of this subsection cannot be made, then a protective soil concentration shall be established under (d) and (e) of this subsection.

(i) Requirements. To demonstrate empirically that measured soil concentrations will not result in the accumulation of nonaqueous phase liquid on or in ground water, the following shall be demonstrated:

(A) Nonaqueous phase liquid has not accumulated on or in ground water; and

(B) The measured soil concentration will not result in nonaqueous phase liquid accumulating on or in ground water at any time in the future. Specifically, it must be demonstrated that a sufficient amount of time

has elapsed for migration of hazardous substances from soil into ground water to occur and that the characteristics of the site (e.g., depth to ground water and infiltration) are representative of future site conditions. This demonstration may also include a measurement or calculation of the attenuating capacity of soil between the source of the hazardous substance and the ground water table using site-specific data.

(iii) Evaluation criteria. Empirical demonstrations shall be based on methods approved by the department. Those methods shall comply with WAC 173-340-702 (14), (15) and (16).

(d) Deriving residual saturation screening levels. Unless an empirical demonstration is made under (c) of this subsection, residual saturation screening levels shall be derived and compared with the soil concentrations derived under the methods specified in subsections (4) through (9) of this subsection to ensure that those soil concentrations will not result in the accumulation of nonaqueous phase liquid on or in ground water. Residual saturation screening levels shall be derived using one of the following methods.

(i) Default screening levels for petroleum hydrocarbons. Residual saturation screening levels for petroleum hydrocarbons may be obtained from the values specified in Table 747-5.

(ii) Site-specific screening levels. Residual saturation screening levels for petroleum hydrocarbons and other hazardous substances may be derived from site-specific measurements. Site-specific measurements of residual saturation shall be based on methods approved by the department. Laboratory measurements or theoretical estimates (i.e., those that are not based on site-specific measurements) of residual saturation shall be supported and verified by site data. This may include an assessment of ground water monitoring data and soil concentration data with depth and an analysis of the soil's texture (grain size), porosity and volumetric water content.

(e) Adjustment to the derived soil concentrations. After residual saturation screening levels have been derived under (d) of this subsection, the screening levels shall be compared with the soil concentrations derived under one of the methods specified in subsections (4) through (9) of this subsection. If the residual saturation screening level is greater than or equal to the soil concentration derived using these methods, then no adjustment for residual saturation is necessary. If the residual saturation screening level is less than the soil concentration derived using these methods, then the soil concentration shall be adjusted downward to the residual saturation screening level.

(11) Ground water monitoring requirements. The department may, on a case-by-case basis, require ground water monitoring to confirm that hazardous substance soil concentrations derived under this section meet the criterion specified in subsection (2) of this section.

Statutory Authority: Chapter 70.105D RCW. 01-05-024 (Order 97-09A), S 173- 340-747, filed 2/12/01, effective 8/15/01.

<General Materials (GM) - References, Annotations, or Tables>

Revisor's note:

WA ADC 173-340-747
END OF DOCUMENT

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METHOD 1312

SYNTHETIC PRECIPITATION LEACHING PROCEDURE

1.0 SCOPE AND APPLICATION

1.1 Method 1312 is designed to determine the mobility of both organic and inorganic analytes present in samples of soils, wastes, and wastewaters.

1.2 If a total analysis of the soil, waste, or wastewater demonstrates that individual analytes are not present, or that they are present but at such low concentrations that the appropriate regulatory levels could not possibly be exceeded, Method 1312 need not be run.

1.3 If an analysis of any one of the liquid fractions of the 1312 extract indicates that a regulated compound is present at such high concentrations that, even after accounting for dilution from the other fractions of the extract, the concentration would be above the regulatory level for that compound, then the waste is hazardous and it is not necessary to analyze the remaining fractions of the extract.

1.4 If an analysis of extract obtained using a bottle extractor shows that the concentration of any regulated volatile analyte exceeds the regulatory level for that compound, then the waste is hazardous and extraction using the ZHE is not necessary. However, extract from a bottle extractor cannot be used to demonstrate that the concentration of volatile compounds is below the regulatory level.

2.0 SUMMARY OF METHOD

2.1 For liquid samples (*i.e.*, those containing less than 0.5 percent dry solid material), the sample, after filtration through a 0.6 to 0.8 μm glass fiber filter, is defined as the 1312 extract.

2.2 For samples containing greater than 0.5 percent solids, the liquid phase, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid employed is a function of the region of the country where the sample site is located if the sample is a soil. If the sample is a waste or wastewater, the extraction fluid employed is a pH 4.2 solution. A special extractor vessel is used when testing for volatile analytes (see Table 1 for a list of volatile compounds). Following extraction, the liquid extract is separated from the sample by 0.6 to 0.8 μm glass fiber filter.

2.3 If compatible (*i.e.*, multiple phases will not form on combination), the initial liquid phase of the waste is added to the liquid extract, and these are analyzed together. If incompatible, the liquids are analyzed separately and the results are mathematically combined to yield a volume-weighted average concentration.

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3.0 INTERFERENCES

3.1 Potential interferences that may be encountered during analysis are discussed in the individual analytical methods.

4.0 APPARATUS AND MATERIALS

4.1 Agitation apparatus: The agitation apparatus must be capable of rotating the extraction vessel in an end-over-end fashion (see Figure 1) at 30 ± 2 rpm. Suitable devices known to EPA are identified in Table 2.

4.2 Extraction Vessels

4.2.1 Zero Headspace Extraction Vessel (ZHE). This device is for use only when the sample is being tested for the mobility of volatile analytes (i.e., those listed in Table 1). The ZHE (depicted in Figure 2) allows for liquid/solid separation within the device and effectively precludes headspace. This type of vessel allows for initial liquid/solid separation, extraction, and final extract filtration without opening the vessel (see Step 4.3.1). These vessels shall have an internal volume of 500-600 mL and be equipped to accommodate a 90-110 mm filter. The devices contain VITON[®] O-rings which should be replaced frequently. Suitable ZHE devices known to EPA are identified in Table 3.

For the ZHE to be acceptable for use, the piston within the ZHE should be able to be moved with approximately 15 psi or less. If it takes more pressure to move the piston, the O-rings in the device should be replaced. If this does not solve the problem, the ZHE is unacceptable for 1312 analyses and the manufacturer should be contacted.

The ZHE should be checked for leaks after every extraction. If the device contains a built-in pressure gauge, pressurize the device to 50 psi, allow it to stand unattended for 1 hour, and recheck the pressure. If the device does not have a built-in pressure gauge, pressurize the device to 50 psi, submerge it in water, and check for the presence of air bubbles escaping from any of the fittings. If pressure is lost, check all fittings and inspect and replace O-rings, if necessary. Retest the device. If leakage problems cannot be solved, the manufacturer should be contacted.

Some ZHEs use gas pressure to actuate the ZHE piston, while others use mechanical pressure (see Table 3). Whereas the volatiles procedure (see Step 7.3) refers to pounds-per-square-inch (psi), for the mechanically actuated piston, the pressure applied is measured in torque-inch-pounds. Refer to the manufacturer's instructions as to the proper conversion.

4.2.2 Bottle Extraction Vessel. When the sample is being evaluated using the nonvolatile extraction, a jar with sufficient capacity to hold the sample and the extraction fluid is needed. Headspace is allowed in this vessel.

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The extraction bottles may be constructed from various materials, depending on the analytes to be analyzed and the nature of the waste (see Step 4.3.3). It is recommended that borosilicate glass bottles be used instead of other types of glass, especially when inorganics are of concern. Plastic bottles, other than polytetrafluoroethylene, shall not be used if organics are to be investigated. Bottles are available from a number of laboratory suppliers. When this type of extraction vessel is used, the filtration device discussed in Step 4.3.2 is used for initial liquid/solid separation and final extract filtration.

4.3 Filtration Devices: It is recommended that all filtrations be performed in a hood.

4.3.1 Zero-Headspace Extraction Vessel (ZHE): When the sample is evaluated for volatiles, the zero-headspace extraction vessel described in Step 4.2.1 is used for filtration. The device shall be capable of supporting and keeping in place the glass fiber filter and be able to withstand the pressure needed to accomplish separation (50 psi).

NOTE: When it is suspected that the glass fiber filter has been ruptured, an in-line glass fiber filter may be used to filter the material within the ZHE.

4.3.2 Filter Holder: When the sample is evaluated for other than volatile analytes, a filter holder capable of supporting a glass fiber filter and able to withstand the pressure needed to accomplish separation may be used. Suitable filter holders range from simple vacuum units to relatively complex systems capable of exerting pressures of up to 50 psi or more. The type of filter holder used depends on the properties of the material to be filtered (see Step 4.3.3). These devices shall have a minimum internal volume of 300 mL and be equipped to accommodate a minimum filter size of 47 mm (filter holders having an internal capacity of 1.5 L or greater, and equipped to accommodate a 142 mm diameter filter, are recommended). Vacuum filtration can only be used for wastes with low solids content (<10 percent) and for highly granular, liquid-containing wastes. All other types of wastes should be filtered using positive pressure filtration. Suitable filter holders known to EPA are shown in Table 4.

4.3.3 Materials of Construction: Extraction vessels and filtration devices shall be made of inert materials which will not leach or absorb sample components. Glass, polytetrafluoroethylene (PTFE), or type 316 stainless steel equipment may be used when evaluating the mobility of both organic and inorganic components. Devices made of high-density polyethylene (HDPE), polypropylene (PP), or polyvinyl chloride (PVC) may be used only when evaluating the mobility of metals. Borosilicate glass bottles are recommended for use over other types of glass bottles, especially when inorganics are analytes of concern.

4.4 Filters: Filters shall be made of borosilicate glass fiber, shall contain no binder materials, and shall have an effective pore size of 0.6 to 0.8- μ m or equivalent. Filters known to EPA which meet these specifications are identified in Table 5. Pre-filters must not be used. When evaluating the mobility of metals, filters shall be acid-washed prior to use by rinsing with 1N

nitric acid followed by three consecutive rinses with deionized distilled water (a minimum of 1-L per rinse is recommended). Glass fiber filters are fragile and should be handled with care.

4.5 pH Meters: The meter should be accurate to ± 0.05 units at 25°C.

4.6 ZHE Extract Collection Devices: TEDLAR^{®2} bags or glass, stainless steel or PTFE gas-tight syringes are used to collect the initial liquid phase and the final extract when using the ZHE device. These devices listed are recommended for use under the following conditions:

4.6.1 If a waste contains an aqueous liquid phase or if a waste does not contain a significant amount of nonaqueous liquid (*i.e.*, <1 percent of total waste), the TEDLAR[®] bag or a 600 mL syringe should be used to collect and combine the initial liquid and solid extract.

4.6.2 If a waste contains a significant amount of nonaqueous liquid in the initial liquid phase (*i.e.*, >1 percent of total waste), the syringe or the TEDLAR[®] bag may be used for both the initial solid/liquid separation and the final extract filtration. However, analysts should use one or the other, not both.

4.6.3 If the waste contains no initial liquid phase (is 100 percent solid) or has no significant solid phase (is 100 percent liquid), either the TEDLAR[®] bag or the syringe may be used. If the syringe is used, discard the first 5 mL of liquid expressed from the device. The remaining aliquots are used for analysis.

4.7 ZHE Extraction Fluid Transfer Devices: Any device capable of transferring the extraction fluid into the ZHE without changing the nature of the extraction fluid is acceptable (*e.g.*, a positive displacement or peristaltic pump, a gas-tight syringe, pressure filtration unit (see Step 4.3.2), or other ZHE device).

4.8 Laboratory Balance: Any laboratory balance accurate to within ± 0.01 grams may be used (all weight measurements are to be within ± 0.1 grams).

4.9 Beaker or Erlenmeyer flask, glass, 500 mL.

4.10 Watchglass, appropriate diameter to cover beaker or Erlenmeyer flask.

4.11 Magnetic stirrer.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used,

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provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to reagent water in this method refer to one of the following, as appropriate.

5.2.1 Inorganic Analytes: Water which is generated by any method which would achieve the performance standards for ASTM Type II water. The analyte(s) of concern must be no higher than the highest of either (1) the detection limit, or (2) five percent of the regulatory level for that analyte, or (3) five percent of the measured concentration in the sample.

5.2.2 Volatile Analytes: Water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free water can be generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. A water purification system may be used to generate organic-free deionized water. Organic-free water may also be prepared by boiling water for 15 minutes. Subsequently, while maintaining the temperature at 90°C, bubble a contaminant-free inert gas through the water for 1 hour. The analyte(s) of concern must be no higher than the highest of either (1) the detection limit, or (2) five percent of the regulatory level for that analyte, or (3) five percent of the measured concentration in the sample.

5.2.3 Semivolatile Analytes: Water in which an interferant is not observed at the method detection limit of the compounds of interest. Organic-free water can be generated by passing tap water through a carbon filter bed containing about 1 lb. of activated carbon. A water purification system may be used to generate organic-free deionized water. The analyte(s) of concern must be no higher than the highest of either (1) the detection limit, or (2) five percent of the regulatory level for that analyte, or (3) five percent of the measured concentration in the sample.

5.3 Sulfuric acid/nitric acid (60/40 weight percent mixture) H_2SO_4/HNO_3 . Cautiously mix 60 g of concentrated sulfuric acid with 40 g of concentrated nitric acid.

5.4 Extraction fluids.

5.4.1 Extraction fluid #1: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water (Step 5.2) until the pH is 4.20 ± 0.05 . The fluid is used to determine the leachability of soil from a site that is east of the Mississippi River, and the leachability of wastes and wastewaters.

NOTE: Solutions are unbuffered and exact pH may not be attained.

5.4.2 Extraction fluid #2: This fluid is made by adding the 60/40 weight percent mixture of sulfuric and nitric acids to reagent water (Step 5.2) until the pH is 5.00 ± 0.05 . The fluid is used to determine the leachability of soil from a site that is west of the Mississippi River.

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5.4.3 Extraction fluid #3: This fluid is reagent water (Step 5.2) and is used to determine cyanide and volatiles leachability. F

NOTE: These extraction fluids should be monitored frequently for impurities. The pH should be checked prior to use to ensure that these fluids are made up accurately. If impurities are found or the pH is not within the above specifications, the fluid shall be discarded and fresh extraction fluid prepared.

5.5 Analytical standards shall be prepared according to the appropriate analytical method.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples shall be collected using an appropriate sampling plan.

6.2 There may be requirements on the minimal size of the field sample depending upon the physical state or states of the waste and the analytes of concern. An aliquot is needed for the preliminary evaluations of the percent solids and the particle size. An aliquot may be needed to conduct the nonvolatile analyte extraction procedure (see Step 1.4 concerning the use of this extract for volatile organics). If volatile organics are of concern, another aliquot may be needed. Quality control measures may require additional aliquots. Further, it is always wise to collect more sample just in case something goes wrong with the initial attempt to conduct the test.

6.3 Preservatives shall not be added to samples before extraction.

6.4 Samples may be refrigerated unless refrigeration results in irreversible physical change to the waste. If precipitation occurs, the entire sample (including precipitate) should be extracted.

6.5 When the sample is to be evaluated for volatile analytes, care shall be taken to minimize the loss of volatiles. Samples shall be collected and stored in a manner intended to prevent the loss of volatile analytes (e.g., samples should be collected in Teflon-lined septum capped vials and stored at 4°C. Samples should be opened only immediately prior to extraction).

6.6 1312 extracts should be prepared for analysis and analyzed as soon as possible following extraction. Extracts or portions of extracts for metallic analyte determinations must be acidified with nitric acid to a pH < 2, unless precipitation occurs (see Step 7.2.14 if precipitation occurs). Extracts should be preserved for other analytes according to the guidance given in the individual analysis methods. Extracts or portions of extracts for organic analyte determinations shall not be allowed to come into contact with the atmosphere (i.e., no headspace) to prevent losses. See Section 8.0 (Quality Control) for acceptable sample and extract holding times.

7.0 PROCEDURE

7.1 Preliminary Evaluations

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Perform preliminary 1312 evaluations on a minimum 100 gram aliquot of sample. This aliquot may not actually undergo 1312 extraction. These preliminary evaluations include: (1) determination of the percent solids (Step 7.1.1); (2) determination of whether the waste contains insignificant solids and is, therefore, its own extract after filtration (Step 7.1.2); and (3) determination of whether the solid portion of the waste requires particle size reduction (Section 7.1.3).

7.1.1 Preliminary determination of percent solids: Percent solids is defined as that fraction of a waste sample (as a percentage of the total sample) from which no liquid may be forced out by an applied pressure, as described below.

7.1.1.1 If the sample will obviously yield no free liquid when subjected to pressure filtration (i.e., is 100% solids), weigh out a representative subsample (100 g minimum) and proceed to Step 7.1.3.

7.1.1.2 If the sample is liquid or multiphasic, liquid/solid separation to make a preliminary determination of percent solids is required. This involves the filtration device discussed in Step 4.3.2, and is outlined in Steps 7.1.1.3 through 7.1.1.9.

7.1.1.3 Pre-weigh the filter and the container that will receive the filtrate.

7.1.1.4 Assemble filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure.

7.1.1.5 Weigh out a subsample of the waste (100 gram minimum) and record the weight.

7.1.1.6 Allow slurries to stand to permit the solid phase to settle. Samples that settle slowly may be centrifuged prior to filtration. Centrifugation is to be used only as an aid to filtration. If used, the liquid should be decanted and filtered followed by filtration of the solid portion of the waste through the same filtration system.

7.1.1.7 Quantitatively transfer the sample to the filter holder (liquid and solid phases). Spread the sample evenly over the surface of the filter. If filtration of the waste at 4°C reduces the amount of expressed liquid over what would be expressed at room temperature, then allow the sample to warm up to room temperature in the device before filtering.

NOTE: If sample material (>1 percent of original sample weight) has obviously adhered to the container used to transfer the sample to the filtration apparatus, determine the weight of this residue and subtract it from the sample weight determined in Step 7.1.1.5 to determine the weight of the sample that will be filtered.

Gradually apply vacuum or gentle pressure of 1-10 psi, until air or pressurizing gas moves through the filter. If this point is not reached under 10 psi, and if no additional liquid has passed through the filter in any 2-minute interval, slowly increase the pressure in 10 psi increments to a maximum of 50 psi. After each incremental increase of 10 psi, if the pressurizing gas has not moved through the filter, and if no additional liquid has passed through the filter in any 2-minute interval, proceed to the next 10-psi increment. When the pressurizing gas begins to move through the filter, or when liquid flow has ceased at 50 psi (*i.e.*, filtration does not result in any additional filtrate within any 2-minute period), stop the filtration.

NOTE: Instantaneous application of high pressure can degrade the glass fiber filter and may cause premature plugging.

7.1.1.8 The material in the filter holder is defined as the solid phase of the sample, and the filtrate is defined as the liquid phase.

NOTE: Some samples, such as oily wastes and some paint wastes, will obviously contain some material that appears to be a liquid, but even after applying vacuum or pressure filtration, as outlined in Step 7.1.1.7, this material may not filter. If this is the case, the material within the filtration device is defined as a solid. Do not replace the original filter with a fresh filter under any circumstances. Use only one filter.

7.1.1.9 Determine the weight of the liquid phase by subtracting the weight of the filtrate container (see Step 7.1.1.3) from the total weight of the filtrate-filled container. Determine the weight of the solid phase of the sample by subtracting the weight of the liquid phase from the weight of the total sample, as determined in Step 7.1.1.5 or 7.1.1.7.

Record the weight of the liquid and solid phases. Calculate the percent solids as follows:

$$\text{Percent solids} = \frac{\text{Weight of solid (Step 7.1.1.9)}}{\text{Total weight of waste (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2 If the percent solids determined in Step 7.1.1.9 is equal to or greater than 0.5%, then proceed either to Step 7.1.3 to determine whether the solid material requires particle size reduction or to Step 7.1.2.1 if it is noticed that a small amount of the filtrate is entrained in wetting of the filter. If the percent solids determined in Step 7.1.1.9 is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Section 7.3 with a fresh portion of the waste if the volatile 1312 analysis is to be performed.

7.1.2.1 Remove the solid phase and filter from the filtration apparatus.

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7.1.2.2 Dry the filter and solid phase at $100 \pm 20^\circ\text{C}$ until two successive weighings yield the same value within ± 1 percent. Record the final weight.

Note: Caution should be taken to ensure that the subject solid will not flash upon heating. It is recommended that the drying oven be vented to a hood or other appropriate device.

7.1.2.3 Calculate the percent dry solids as follows:

$$\text{Percent dry solids} = \frac{(\text{Weight of dry sample + filter}) - \text{tared weight of filter}}{\text{Initial weight of sample (Step 7.1.1.5 or 7.1.1.7)}} \times 100$$

7.1.2.4 If the percent dry solids is less than 0.5%, then proceed to Step 7.2.9 if the nonvolatile 1312 analysis is to be performed, and to Step 7.3 if the volatile 1312 analysis is to be performed. If the percent dry solids is greater than or equal to 0.5%, and if the nonvolatile 1312 analysis is to be performed, return to the beginning of this Section (7.1) and, with a fresh portion of sample, determine whether particle size reduction is necessary (Step 7.1.3).

7.1.3 Determination of whether the sample requires particle-size reduction (particle-size is reduced during this step): Using the solid portion of the sample, evaluate the solid for particle size. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2 , or is smaller than 1 cm in its narrowest dimension (*i.e.*, is capable of passing through a 9.5 mm (0.375 inch) standard sieve). If the surface area is smaller or the particle size larger than described above, prepare the solid portion of the sample for extraction by crushing, cutting, or grinding the waste to a surface area or particle size as described above. If the solids are prepared for organic volatiles extraction, special precautions must be taken (see Step 7.3.6).

Note: Surface area criteria are meant for filamentous (*e.g.*, paper, cloth, and similar) waste materials. Actual measurement of surface area is not required, nor is it recommended. For materials that do not obviously meet the criteria, sample-specific methods would need to be developed and employed to measure the surface area. Such methodology is currently not available.

7.1.4 Determination of appropriate extraction fluid:

7.1.4.1 For soils, if the sample is from a site that is east of the Mississippi River, extraction fluid #1 should be used. If the sample is from a site that is west of the Mississippi River, extraction fluid #2 should be used.

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7.1.4.2 For wastes and wastewater, extraction fluid #1 should be used.

7.1.4.3 For cyanide-containing wastes and/or soils, extraction fluid #3 (reagent water) must be used because leaching of cyanide-containing samples under acidic conditions may result in the formation of hydrogen cyanide gas.

7.1.5 If the aliquot of the sample used for the preliminary evaluation (Steps 7.1.1 - 7.1.4) was determined to be 100% solid at Step 7.1.1.1, then it can be used for the Section 7.2 extraction (assuming at least 100 grams remain), and the Section 7.3 extraction (assuming at least 25 grams remain). If the aliquot was subjected to the procedure in Step 7.1.1.7, then another aliquot shall be used for the volatile extraction procedure in Section 7.3. The aliquot of the waste subjected to the procedure in Step 7.1.1.7 might be appropriate for use for the Section 7.2 extraction if an adequate amount of solid (as determined by Step 7.1.1.9) was obtained. The amount of solid necessary is dependent upon whether a sufficient amount of extract will be produced to support the analyses. If an adequate amount of solid remains, proceed to Step 7.2.10 of the nonvolatile 1312 extraction.

7.2 Procedure when Volatiles are not Involved

A minimum sample size of 100 grams (solid and liquid phases) is recommended. In some cases, a larger sample size may be appropriate, depending on the solids content of the waste sample (percent solids, See Step 7.1.1), whether the initial liquid phase of the waste will be miscible with the aqueous extract of the solid, and whether inorganics, semivolatile organics, pesticides, and herbicides are all analytes of concern. Enough solids should be generated for extraction such that the volume of 1312 extract will be sufficient to support all of the analyses required. If the amount of extract generated by a single 1312 extraction will not be sufficient to perform all of the analyses, more than one extraction may be performed and the extracts from each combined and aliquoted for analysis.

7.2.1 If the sample will obviously yield no liquid when subjected to pressure filtration (i.e., is 100 percent solid, see Step 7.1.1), weigh out a subsample of the sample (100 gram minimum) and proceed to Step 7.2.9.

7.2.2 If the sample is liquid or multiphasic, liquid/solid separation is required. This involves the filtration device described in Step 4.3.2 and is outlined in Steps 7.2.3 to 7.2.8.

7.2.3 Pre-weigh the container that will receive the filtrate.

7.2.4 Assemble the filter holder and filter following the manufacturer's instructions. Place the filter on the support screen and secure. Acid wash the filter if evaluating the mobility of metals (see Step 4.4).

Note: Acid washed filters may be used for all nonvolatile extractions even when metals are not of concern.