HTRW Center of Expertise
Environmental Regulatory
Fact Sheet 97-06

DOT and RCRA, the issue of Poisons

Purpose of this Fact Sheet

There are certain situations where the relationship between a Department of Transportation (DOT) poison and an Environmental Protection Agency (EPA) hazardous waste may be unclear. In order to clarify this issue, the following is presented to help with the task of classifying environmental media contaminated with hazardous waste that are also recognized DOT poisons. The goal is to correctly classify these materials for transportation under the DOT hazardous materials regulations.

Background

Poisons are defined by dose (i.e. the dose makes the poison). Toxicity is a measurement of the relative effect of a dose. A subject organism may also show extreme sensitivity based on some species specific genetics (i.e. guinea pigs and dioxins).

Determining the relative toxicity of environmental media contaminated with a DOT poison (oral, inhalation (dust and mist) and dermal contact) is fairly straight forward in that the contaminated media is both the chemical being tested and the diluent.

A type of toxicity (lethal toxicity) is typically expressed as a lethal dose (LD) or a lethal concentration (LC). The typical threshold used in these studies is 50%. An LD_{50} indicates the dose required to kill $\geq$ 50% of the test population. Different agencies use different test animals. The DOT poison classifications are based on white albino rats.

If the $oral_{(rat)}$ LD_{50} for chemical "X" is 50 mg/kg, this equates to 50 mg of poison/ kg of body weight of the rat. Assuming the rat weighed 250 grams, it would take 12.5 mg of chemical "X" to kill the rat. Since rat weights are variable, units are reported in mg of chemical per kg body weight (mg/kg).

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$$\frac{50 \text{ mg poison}}{1 \text{ kg body wt}} \times 0.25 \text{ kg body wt.} = 12.5 \text{ mg poison}$$

If we assume we have two 1 kg rats and we can get both to eat a 50 mg pellet of pure chemical "X", if one rat dies and one lives then our experiment would meet the criteria for an LD_{50} test and the oral $LD_{50(rat)}$ for this test would be reported as 50 mg/kg (technically, for DOT, you need a "statistically valid number" of young adult male and female rats).

DOT Hazard Class 6.1 Analysis

DOT defines poisons by three routes of exposure, ingestion, dermal contact, and inhalation (of dusts, mists, and vapors). Within these subdivisions are "relative risk" categories based on the toxicity of the material. These are identified by packing group designations PGI, PGII, and PGIII listed for severely toxic to minimally toxic (49 CFR 173.132). Tables 1 and 2 are reproduced from the regulation and define the relationship between route of exposure, toxicity, and Packing Group for DOT Class 6 Division 6.1 hazardous materials.

TABLE 1

Packing Group	Oral Toxicity LD_{50} (mg/kg)	Dermal Toxicity LD_{50} (mg/kg)	Inhalation Toxicity by dusts mists LC_{50} (mg/l)
I	≤ 5	≤ 40	≤ 0.5
II	$>5, \leq 50$	$>40, \leq 200$	$>0.5, \leq 2$
III	solids: $>50, \leq 200$ liquids: $>50, \leq 500$	$>200, \leq 1000$	$>2, \leq 10$

TABLE 2

Packing Group	Vapor Concentration and Toxicity
I (Hazard Zone A)	$V \geq 500\ LC_{50}$ and $LC_{50} \leq 200$ ml/m^3
I (Hazard Zone B)	$V \geq 10\ LC_{50}$; $LC_{50} \leq 1000$ ml/m^3 and the criteria for Packing Group I Hazard Zone A are not met
II	$V \geq LC_{50}$; $LC_{50} \leq 3000$ ml/m^3 and the criteria for Packing Group I are not met.
III	$V \geq 0.2\ LC_{50}$; $LC_{50} \leq 5000$ ml/m^3 and the criteria for Packing Groups I and II are not met.

Note 1: V is the saturated vapor concentration in air of the material in ml/m^3 at 20 °C and standard atmospheric pressure. Note 2: A liquid in Division 6.1 meeting criteria for Packing Group I, Hazard Zones A or B in Table 2 is a material poisonous by inhalation subject to the

additional hazard communication requirements in 172.203(m)(3), 172.313 and Table 1 of 172.504(e) of this subchapter.

EPA Toxicity Listing Criteria

EPA has also used toxicity to identify hazardous waste, specifically listed wastes, such as the P and U wastes. In 40 CFR 261.11(a)(2) EPA identifies criteria used in the development of listed wastes. These parameters include:

- found to be fatal to humans in low doses
- oral (rat) $LD_{50} < 50$ mg/kg
- inhalation (rat) < 2 mg/L
- dermal (rabbit) < 200 mg/kg
- or otherwise capable of causing or significantly contributing to an increase in serious irreversible or incapacitating reversible illness (**Waste listed in accordance with these criteria are designated acute hazardous waste.**)

40 CFR 262.11(a)(3) further states:

- The waste contains any of the toxic constituents listed in appendix VIII and meets certain identified criteria

Example 1

Now, assume we had a spill of pure chemical "X." After the resulting clean up we tested our soil and found that the concentration was 250,000 mg/kg. We wanted to determine what the appropriate DOT shipping classification would be for transportation and disposal. By looking at Table 1 above and reviewing our first example we know that the commercial product was considered a PGII poison (i.e. an oral LD_{50} of 50 mg/kg meets the >5, ≤ 50 mg/kg PGII criteria) by an oral route of administration, and the stuff we are talking about is pure (i.e. 1,000,000 mg/kg). For a relative comparison we need to look at how much of chemical "X" is in 50 mg of soil because that is going to be the administered media for OUR 1 kg rats and 50 $mg/kg_{(rat)}$ also happens to be a break point for PGII threshold. So,

$$\frac{250{,}000 \text{ mg of "X"}}{(1 \text{ kg of soil})} \quad \frac{(1 \text{ kg soil})}{(1{,}000{,}000 \text{ mg soil})} = 0.25 \text{ mg of "X" per mg of soil}$$

$$\frac{(0.25 \text{ mg "X"})}{\text{mg of soil}} \quad \frac{50 \text{ mg of soil}}{} = 12.5 \text{ mg of "X" per 50 mg of soil}$$

So, if we feed the 1 kg rats 50 mg of contaminated soil, does either rat die?

(No: The dose is only 25% of the commercial chemical product experimental dose.)

Another way of looking at this would be, what is the equivalent dose of soil contaminated with "X" necessary to equal the LD_{50} of the pure product? We know the LD_{50} for chemical "X" is 50 $mg/kg_{(rat)}$, and we know that 50 mg of contaminated soil has 12.5 mg of chemical "X". We need 50 mg of chemical "X" so we divide:

(50 mg) ÷ (12.5 mg) = 4 4 x 50 mg = 200 mg of soil to get 50 mg of "X"

or since we need 50 mg of chemical "X" and there is 0.25 mg/mg soil (50 mg X) ÷ (0.25 mg X/mg soil) = 200 mg soil.

By looking at Table 1 we now see we no longer meet the criteria for a PGII poison, however, we still meet the criteria for a PGIII poison (>50, ≤ 200).

Now if we look up chemical "X" in the 49 CFR 172.101 table and it is found only as a PGII, you could not use the PSN for the soil/chemical mixture of chemical "X" as it appears in the table. However, you still have the option to use the n.o.s. shipping name:

"**Waste toxic solids, n.o.s. (contains X), 6.1, UN2811, PGIII**"

The same scenario can be outlined for dermal toxicity and inhalation of dusts and mists but NOT vapors.

With vapors (liquids), the scenario changes somewhat because the categorization of poisons by inhalation is based on the LC_{50} *and* the saturated vapor concentration in relation to the LC_{50}. The following text taken from a preamble rule making outlines a technical issue directly impacting this discussion.

58 FR 50224 9/24/93

Cyanogen bromide (UN1889) is assigned to Hazard Zone A. However, a commenter provided data that shows that cyanogen bromide is a solid at 20 °C (68 °F) with a melting point of 52 °C (126 °F) and a vapor pressure of 100 mm Hg at 23 °C (73 °F). Therefore, cyanogen bromide is a solid, as defined in § 171.8. **Only liquids and gases may be designated as materials poisonous by inhalation.** Therefore, cyanogen bromide is not a material poisonous by inhalation, and the entry in the Table for cyanogen bromide is revised accordingly.
A scenario is in order.

Example 2

Allyl alcohol as a commercial chemical product declared a waste is defined by EPA as an acute

hazardous waste (P005). DOT references allyl alcohol as a Packing Group I Poison by Inhalation, Hazard Zone B in the 49 CFR 172.101 Hazardous Materials Table (HMT).

Both agencies are in agreement that the chemical is a relatively toxic material as a commercial chemical product or as a waste.

If we had a 1 gallon jug of waste allyl alcohol we would ship the material as:

Waste allyl alcohol, 6.1, UN1098, PGI, "Inhalation Hazard - Zone B"

Any one know why we can't lab pack this with other poisons and ship as:
Waste toxic liquid, flammable, organic, n.o.s.....? Hint: 173.12(b)(3)

By doing a quick review of the attached Non-Human Toxicity values for allyl alcohol, we see that the LC_{50}(vapors) for rats is 76 ppm for 1 hour test as defined by DOT in 173.132(b)(3) (temperature difference is ignored for this example). So it is clear that one of the two criteria identified in Table 2 above is met, specifically the LC_{50} of a Packing Group I (Hazard Zone A or B) is $\leq$ both 200 mL/m^3 or 1000 mL/m^3 (ppm). From Table 2 we have:

PGI (Hazard Zone A) = $V \geq 500\ LC_{50}$ and $LC_{50} \leq 200\ ml/m^3$

PGI (Hazard Zone B) B = $V \geq 10\ LC_{50}$; $LC_{50} \leq 1000\ ml/m^3$ and the criteria for Packing Group I Hazard Zone A are not met

We now need the saturation value of allyl alcohol in air, so we consult the attachment and find a value of 3.13% which equates to 31,300 ppm. This is the value (V) for chemical "X" and it is clearly greater than 10 times the LC50:

(31,300 > (10)(76) or 760) and

< 500 times the LC_{50} ((76)(500) = 38,000)

Therefore, the published data does support the DOT defined hazard class PGI Zone B for allyl alcohol but not Hazard Zone A because of vapor concentration (volatility) criteria. It is interesting to note, however, if the oral reference dose is reviewed, the LD_{50} of 64 mg/kg *would indicate a PGIII designation.* It is important to note that when evaluating a chemical as a poison not specifically defined in the 172.101 table, it is important to evaluate *all routes of administration* for the purpose of defining a packing group for a poison. DOT requires that the more stringent packing group be applied (49 CFR 173.133(a)(3)).

If we use a similar spill scenario for allyl alcohol, as previously used for chemical "X" , we can develop some strategies for determining the proper hazard class and associated packing group for environmental media contaminated with inhalation hazard poisons. First, since we will be

dealing with vapors, we need a relationship to compare ppm vapors with weights.

A useful formula to keep in mind is the conversion of ppm to mg/m^3.
In general, 1 ppm = 1 mL/m^3 (mL = 1 mL of saturated air) and for a specific chemical the relationship between concentration in ppm verse mg/m^3 is:

$$ppm = \frac{mg/m^3}{M.W.} \times 24.5$$

Where M.W. is the molecular weight of a chemical, and 24.5 is the molar volume in liters at 25 °C and 1 atmosphere.

The following facts are presented:

- Table 2 above is <u>only</u> for LIQUIDS that are poisons by inhalation.
- If the resulting concentration of the spill does not result in a saturated soil (i.e. no free liquids by paint filter test) then the LD_{50}, NOT the LC_{50} would need to be evaluated.
- If the resulting concentration of the spill is less than a saturated (soil) concentration, but greater that the LD_{50} concentration then the soil needs to be evaluated for (packing group) the appropriate poison category or other hazard class as appropriate (i.e. class 9).

For example, we know that the saturation **<u>vapor</u>** concentration of allyl alcohol, as a liquid, is 31,300 ppm (see attachment) or

$$31{,}300 \text{ ppm} = \frac{\text{“?” } mg/m^3}{58.08 \text{ (g/mol)}} \quad 24.5 \qquad \text{“?”} = 74,\ 181 \ mg/m^3$$

and we further know that the relationship between volatility (V) and LC_{50} is 411.8 (31,300 ppm saturation/76 ppm (LC_{50})) which meets the PGI Zone B category criteria.

Now let us assume that the resulting concentration of a spill of allyl alcohol is 74,000 mg/kg. If the density of allyl alcohol is given as 0.8540 g/mL, then we have 854 mg/ml. Therefore we have 86.65 mL (74,000/854) of allyl alcohol in our kg of soil. If we placed this kg of soil into a 1 cubic meter chamber and assumed all the allyl alcohol would volatilize we would have approximately 86.65 mL of *liquid* in a vapor phase in 1,000,000 mLs.

Mathematically this should yield the 74,000 mg/m^3 (i.e. very near the saturation concentration). *However, the soil does not meet the definition of a liquid (free liquids would have to be present)*

therefore, we can not identify the material as a "Poison Inhalation Hazard-Zone B" material.

But, we must still evaluate the 6.1 hazard class for other administered routes of exposure. Since the oral LD_{50} (rat) from the attachment is reported as 64 mg/kg for allyl alcohol (remember DOT uses rats not mice or rabbits) the packing group designation needs to be evaluated.

$$\frac{74{,}000 \text{ mg allyl alcohol}}{\text{kg of soil}} \quad \frac{1\text{kg soil}}{1{,}000{,}000 \text{ mg soil}} = \frac{0.074 \text{ mg allyl alcohol}}{\text{mg of soil}}$$

We know that the packing group designation cut offs for LD_{50} (oral) are $\leq$ 5, 50, and 200 $mg/kg_{(rat)}$ respectively.

So, to be considered a PGIII poison by oral toxicity, a dose of 64 mg (for a 1 kg rat) would have to be received by administering 200 mg of chemical and diluent.

$$\frac{0.074 \text{ mg allyl alcohol}}{\text{mg of soil}} \quad \frac{200 \text{ mg of soil}}{200 \text{ mg of soil}} = \frac{14.8 \text{ mg of allyl alcohol}}{200 \text{ mg of soil}}$$

The dose is short of the LD_{50} by 64 mg - 14.8 mg = 49.2 mg. Therefore we can conclude that the environmental media contaminated with allyl alcohol does not meet the minimum definition of a poison based on DOT criteria. Even though we have an environmental media contaminated with a material that was listed by EPA as an acute hazardous waste and identified by DOT as a poison by inhalation, the following PSN would be appropriate:

Hazardous waste solid, n.o.s. (contains allyl alcohol, P005), 9, NA3077, PGIII

Example 3

An additional example will help to solidify this concept.

If chemical "Y", in pure form, has a oral LD_{50} of 5 mg/kg but, due to its toxicity, the chemical is blended with an inert filler and is sold with a 1% active ingredient, the LD_{50} for that material as marketed is 1/100 as toxic; therefore the LD_{50} for the marketed material is 500 mg/kg. So, even though the manufactured grade of the material would meet the PGI designation of a poison by oral toxicity, the marketed blend would not meet the definition of a poison at any PG designation as defined by DOT.

As previously discussed there are several routes of exposure that DOT acknowledges when

defining poisons. We have evaluated poisons by ingestion ($LD_{50(oral,rat)}$). We will now look at inhalation of *dusts and mists*. Although this route of exposure is the same as that of vapor inhalation, remember that DOT makes a distinction between poisons by inhalation (PIH, vapors) and other poisons (Table 1 vs. Table 2). PIHs are subject to additional hazard communication requirements (40 CFR 172.203(m)).

By reviewing Table 1 we note that inhalation toxicity by dusts and mists (LC_{50}) are reported in units of mg/l. This equates to mg of poison in one (1) liter of air. Since we do not typically think in these units, a mg/m^3 conversion is helpful.

$1\ m^3 = (100\ cm)^3$ or $1{,}000{,}000\ cm^3$
1 liter = 1000 ml; and 1ml = $1\ cm^3$
1 liter = $1000\ cm^3$

$$1m^3 = \frac{(1{,}000{,}000\ cm^3)}{(1\ m^3)} \quad \frac{(1\ liter)}{(1000\ cm^3)} = 1000\ liters$$

So 1000 liters = $1\ m^3$

Now, looking back at Table 1 for the PGI dust and mist inhalation criteria we see that the value must be ≤ 0.5 mg/l or $\leq 500\ mg/m^3$.

49 CFR 173.132(b)(3) states :

"If the material is administered to the animals as a dust or mist, more that 90 percent of the particles available for inhalation in the test must have a diameter of 10 microns or less if it is reasonably foreseeable that such concentrations could be encountered by a human during transport."

To put this in perspective, the nuisance dust standard for respirable particulates (≤ 10 microns) is $3\ mg/m^3$ and for inhalable (≤ 100 microns) is $10\ mg/m^3$.

Only in very nontypical situations would it be anticipated that the inhalation route of exposure for dusts and mists be evaluated.

However, the evaluation procedure is very similar to the oral route of exposure. The criteria used would be assumed particle size (≤ 10 microns), a $1\ m^3$ test volume, and the test material.

Example 4

As an example, say we have chemical "Z" with a PGI dust inhalation LC_{50} of .25 mg/l or 250 mg/m^3 and we will assume a spill concentration of 35% (350,000 mg/kg).
Similar to our previous example we need to find out how much contaminant there is per mg of soil. A quick calculation yields .35 mg "Z" per mg of soil. Now dividing 250 mg by .35 mg = 714 mg of soil to have 250 mg of "Z". We have exceeded the PGI threshold (714 vs 250) however, by looking at the PGII entry we see the range is 500 mg - 2000 mg. Therefore, we know that this material is still considered a poison (6.1) for the PGII category.

It is worth reiterating here that 49 CFR 173.133(a)(3) states:

"When the packing group determination by applying these criteria is different for two or more (oral, dermal or inhalation) routes of administration, the packing group assigned to the material shall be that indicated for the highest degree of toxicity for any of the routes of administration."

Therefore, when evaluating the PG designation of a poison, DOT states that you must use the route of administration that subjects the material to the most stringent packaging criteria.

Summary

In closing, to screen and evaluate a solid enviromental media contaminated with liquids poisonous by inhalation or poisons by other routes of exposure, two criteria need to be known - an LD_{50} or LC_{50} of the chemical and the concentration of the contaminant in the soil (unsaturated).

1. Remember if the waste has no free liquids, it can not by definition be a poison by inhalation.
2. Compare LD_{50} to identified criteria per PG (i.e. oral ≤ 5; > 5, ≤ 50; >50, ≤ 200 mg/kg) to see if the pure chemical meets the poison definitions. If yes then
3. Divide the LD_{50} by the soil concentration (expressed in mg contaminant/mg soil) to see how much soil you need to reach the LD_{50}.
4. Compare to the PG designation table

≤ 5 = PGI
$>5, \leq 50$ = PGII
$>50, \leq 200$ = PGIII

5. If soil/chemical mixture falls within the one of the above criteria, that is the packing group assignment.

In summary, for poisons evaluated by oral, dermal or inhalation toxicity, the environmental media can be considered a diluent and the toxicity is decreased proportionally with the decrease in concentration.

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HSDB

Topic: ALLYL ALCOHOL

Vapor Pressure:

1. **23.8 MM HG @ 25 DEG C** **PEER REVIEWED** [Sunshine, I. (ed.). CRC Handbook of Analytical Toxicology. Cleveland: The Chemical Rubber Co., 1969. 602

Other Chemical/Physical Properties:

2. 1 MG/L= 422 PPM; **1 PPM= 2.37 MG/CU M @ 25 DEG C, 760 MM HG; DENSITY OF SATURATED AIR: 1.031 @ 25 DEG C (AIR= 1); PERCENT IN SATURATED AIR: 3.13% @ 25 DEG C** **PEER REVIEWED** [Clayton, G. D. and F. E. Clayton (eds.). Patty's Industrial Hygiene and Toxicology: Volume 2A, 2B, 2C: Toxicology. 3rd ed. New York: John Wiley Sons, 1981-1982. 4663

Toxicity Values

Non-Human Toxicity Values:

1. LD50 Rabbit percutaneous 89 mg/kg **PEER REVIEWED** [Farm Chemicals Handbook 1989. Willoughby, OH: Meister Publishing Co., 1989.,p. C-16
2. LD50 Mouse oral 85 mg/kg **PEER REVIEWED** [Worthing, C. R. (ed.). Pesticide Manual. 6th ed. Worcestershire, England: British Crop Protection Council, 1979. 9
3. **LD50 Rat oral 64 mg/kg** **PEER REVIEWED** [The Merck Index. 10th ed. Rahway, New Jersey: Merck Co., Inc., 1983. 44
4. **LC50 Rat inhalation 165 ppm/4 hr** **PEER REVIEWED** [USEPA; Health and Environmental Effects Profile for Allyl alcohol p.36 (1985) ECAO-CIN-P121
5. **LC50 Rat inhalation 76 ppm/1 hr** **PEER REVIEWED** [USEPA; Health and Environmental Effects Profile for Allyl alcohol p.36 (1985) ECAO-CIN-P121
6. LD50 Mouse intraperitoneal 60 mg/kg. **PEER REVIEWED** [Dunlap MK et al; AMA Arch Ind Health 18: 303-11 (1958) as cited in USEPA; Health and Environmental Effects Profile for Allyl alcohol p.36 (1985) ECAO-CIN-P121

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