**PEER REVIEW OF EPA'S HAZARDOUS WASTE
IDENTIFICATION RULE RISK ASSESSMENT MODEL**

Source Models for Tanks and Surface Impoundments, and Watershed Module

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NOTE

This report was compiled by Eastern Research Group, Inc. (ERG), an EPA contractor, under Contract Number 68-W-99-001. The report presents comments provided by peer reviewers on the *Source Models for Tanks and Surface Impoundments*, and the *Watershed Module* documents that are part of EPA's Hazardous Waste Identification Rule risk assessments. The actual review was performed in 1998 under Contract Number 68-W5-0057.

The comments presented in this report have been compiled by topic and by individual peer reviewer. As EPA requested, this report provides the peer review comments exactly as they were submitted to ERG. Also attached are the original comments submitted by each individual reviewer.

Surface Impoundment and Aerated Tank Source Modules

Background/History

Both the tank and surface impoundment (SI) modules employ a mass balance approach to simulate the competing removal mechanisms of volatilization, biodegradation, hydrolysis, and adsorption. The surface impoundment module also considers leachate losses.

There are several differences in the current (HWIR99) tank and SI source models from the previous (HWIR95) models. One primary change is in the treatment of sediment. The HWIR95 tank model did not consider influent total suspended solids (TSS) and the SI model assumed a fixed effluent TSS concentration. The latter assumption implied some sediment removal across the waste management unit (WMU), but the model included no effect of this accumulating sediment on the hydraulic residence time, etc., of the WMU over time. In effect, this sediment was instantaneously removed from the WMU. In the HWIR98/HWIR99 model, the TSS removal efficiency is calculated based both on WMU flow and dimensions and on TSS particle density and size distribution. Inclusion of sediment consideration required a two compartment model (liquid and sediment) and a psuedo steady state solution (to account for changes in the depth of sediment) compared to the one compartment steady state solution used in HWIR95. The inclusion of the sediment compartment also allowed other comments to be addressed, such as the impact of sediment on infiltration and the facultative nature of many SI (having both aerobic and anaerobic biodegradation zones).

The second major enhancement, which is specific to the SI model, was the inclusion of a rigorous calculation for infiltration. In the HWIR95 model, infiltration losses to groundwater were calculated separately from the source module. The HWIR98/HWIR99 SI model included infiltration simply by assuming the leachate concentration was the same as the effluent (well-mixed assumption). However, with the inclusion of a sediment compartment, an internal estimate of the infiltration rate was needed in case the accumulating sediment impacts the infiltration rate. Additionally, the leachate concentration may now be different than the effluent concentration due to constituent losses within the sediment layer.

The third major enhancement of the tank and SI was inclusion of biodegradation rate losses. In HWIR95, no biodegradation was assumed as a conservative estimate for air emission. Many comments were received suggesting that biodegradation is an important removal mechanism in these units and should be added to the models.

Additionally, several comments were received suggesting that the HWIR95 models did not adequately model the effects of temperature variations on the emission estimates. Therefore, the HWIR98/HWIR99 model contains a more detailed algorithm for estimating temperature dependent chemical and physical properties.

The mas transfer coefficients used to estimate volatile emissions are identical to those used in HWIR95. These equations are used for several EPA air emissions models (e.g., Chemdat8, and Water8).

Charge to Reviewers

Sediment Removal Efficiency

Enhanced model capability includes simulation of the model is the prediction of sediment removal efficiency by means of sedimentation and resuspension velocity parameters. We invite comments on the appropriateness of this algorithm with respect to:

- the general algorithm for calculating removal efficiency based on "upflow" and terminal velocities;
- the specific methodology for calculating removal efficiency as a function of the fraction aerated; and
- the specific methodology fo adjusting removal efficiency as a function of increasing sediment layer thickness.

Average TSS Concentration Within the WMU

We invite comments on the use of a log-mean average TSS concentration in the liquid compartment to account for variations in stratification of TSS within the impoundment due to TSS removal along the flow path. (This is a device used to mitigate the completely mixed assumption so that average TSS within the tank can be greater than TSS in the tank's effluent.) Note that it is assumed that the dissolved phase liquid compartment chemical concentration is equal to the dissolved phase chemical concentration in the effluent. Also note that the biodegradation rate within the impoundment is directly proportional to the average TSS concentration. The average TSS concentration may also indirectly impact the volatilization rate and the leachate concentration. With this in mind, consider the following questions.

- Should an average TSS concentration be used where $[TSS]_{out} \neq [TSS]_1$?

- If so, is a log-mean average the most appropriate averaging methodology to represent the effective TSS concentration in the liquid compartment?

Biodegradation Rate Models

As wastewater treatment units may operate over a wide range of biomass concentrations, a biodegradation rate model was selected for the liquid compartment that was sensitive to this parameter. A Monod-type model was originally considered for the liquid compartment, but there were inadequate data to determine the constituent-specific rate constants. Because the biologically active fraction of biomass in the sediment compartment over time was believed to be a level of complexity that was incongruous with the screening level objective of the overall model, simple first order degradation was included in the sediment and digestion of biomass solids only in the temporary sediment accumulation (or burial) compartment. Comments are invited on the following:

- Is the liquid compartment biodegradation rate model appropriate (which includes biomass growth based on influent BOD)?
- Is the sediment compartment biodegradation rate model appropriate?
- Is the methodology used to estimate sediment decay appear to be appropriate?

Diffusive Transport Between the Liquid and Sediment Compartments

The equation used to estimate diffusive transport between the liquid and sediment compartments also represent enhanced functionality, although of minor importance in its impact o model outputs. It has been suggested that this diffusive transport term be estimated based on the liquid diffusivity and a boundary layer thickness within the sediment compartment. As the boundary between the liquid and sediment compartment is anticipated to be less distinct and the sediment at this interface more fluid than a boundary between soil and air, for example, a liquid mass transfer coefficient based on the mixing of liquid within the impoundment was selected. This also eliminated the need to arbitrarily select a boundary layer thickness. Comments are invited on the following:

- Is the inclusion of a diffusive transport term an unnecessary model complexity?
- Does the current methodology for estimating the diffusive mass transfer rate appear to be appropriate?
- If not, what methodology is recommended and, if a boundary layer model is suggested, how would the boundary layer thickness be determined?

Temperature Effects

There are several equations in the temperature effects section that are relatively novel and comments are sough regarding these.

- Does the method of estimating the average temperature in the WMU and ice formation appear to be appropriate for the scope of this model?
- Acclimation of biomass for estimating biodegradation is assumed to occur over a wide range of temperatures. Does the temperature correction factor for biodegradation rates appear to be appropriate?
- If not, what methodology is recommended?

Volatile Emission Estimation Methodology

This model employs widely used and accepted mass transfer coefficients for estimating air emissions, and predict the emissions rate based on the dissolved liquid phase concentration. There is not much new here, but comments are welcome.

Comments on the Source Models for Tanks and Surface Impoundments

Dr. Culligan: *General Comments*

The processes that this model is trying to simulate are very complex, and also extremely variable. Therefore, before use of the model for WMU applications, I strongly recommend the following:

1.   An analysis is carried out to determine which parameters the model is most sensitive to under an expected range of operating conditions. From here, it might be possible to simplify the model to either exclude processes that the model predictions are insensitive to and/or reduce complexity in the calculation of some of the model "constants"/ parameters. As a reviewer, it was difficult to know which of the model assumptions were the most critical, and therefore merited the most focus for investigation and discussion, without prior knowledge of the model's sensitivity. As a user, the same problem is likely to arise.

2.   That the most uncertain parameters are identified, and some representation of uncertainty is incorporated into the modeling procedure. Many of the model input parameters (e.g., hydrolysis rate; biodegradation rates and soil hydraulic conductivities) can vary by orders of magnitude in the field. This uncertainty somehow needs to be reflected in the model output.

3.   That the model is tested with physical data, either obtained from the field or from a simulated laboratory experiment. Without model validation, it is hard to be confident about whether or not the enhanced model is performing with satisfaction. Many of the new assumptions embedded in the model. e.g., the averaging methodology to estimate the TSS concentration in the liquid compartment of a WMU, could be validated, or otherwise, with appropriate physical data.

Model Assumptions and Governing Equations

The general construction of the model seems adequate. Two processes that the model does not consider within the WMU are:

(i) The growth of algae on the non-aerated surface of a WMU, which could have a significant effect on the transfer coefficients describing atmospheric emissions from the liquid compartment, as well as the degradation coefficients within the compartment itself.

(ii) Sediment consolidation in the accumulating solids compartment, which will impact WMU behavior in two ways . First, sediment consolidation will introduce a temporal, upward flux of contaminated pore fluid across the boundary between the accumulating solids/ sediment compartment, and, in the case of an SI, a temporal, downward flux of contaminated pore fluid into the base liner. Second, consolidation will effect the net accumulation of sediment over one time step, and therefore influence the time step calculations for d2 and d1. Neglecting contaminant flux due to sediment consolidation is unlikely to introduce large errors into the model. Neglecting sediment compression may introduce errors, depending on the compressibility of the solid waste, and the dredging frequency for the WMU.

The assumption of first order kinetics for the fate and transport processes is practical. However, the use of a single rate/ transfer coefficient to capture the behavior of each process is very unrealistic. For example, the hydrolysis rate for acid esters (one functional organic compound group that can hydrolyze under environmental conditions), varies over several orders of magnitude - even under constant temperature and pH conditions (see, e.g., Hemond & Fechner, Chemical Fate and Transport in the Environment, Academic Press, 1994, pp 103 - 132). The same argument can be made for biodegradation rates. Unless

the system within the WMU is well understood, and can therefore be averaged over the range of expected operating conditions (e.g, range of expected pH, temperature, nutrient loading, etc.) a single coefficient is unlikely to capture the different rates of contaminant removal or production within the WMU.

Figure 1 needs to be amended to illustrate the transfer of leachate, with entrained soilds, between the liquid and sediment compartments. In addition, clarification on this figure that only "filtered" leachate is assumed to be transferred from the sediment compartment to the groundwater would be beneficial. Note, that the validity of this latter assumption will depend on the particle size distribution (PDS) of the TSS in the leachate. It is entirely possible that colloidal size (< 0.075 mm in diameter) particles will pass through the sediment compartment and be arrested by the liner at the base of the WMU. This might cause some decrease in the hydraulic conductivity of the soil liner. However, this would not invalidate the assumption that only clarified leachate exits the WMU at its base.

There are some typing errors in the nomenclature for Equation 1. For example, $C_{tot,1}$ is incorrectly identified as the total contaminant concentration in both the liquid compartment and the effluent, and $[TSS]_1$ is also incorrectly identified as the concentration of TSS in both the liquid compartment and effluent. I assume that these constraints represent the conditions of the original model, as they infer instantaneous removal of sediment from the WMU.

Derivation of Equation Solution

Again the assumption of a uniform k_{ds} is unrealistic. Through the use of k_{ba} , the model actually presumes a partitioning between biologically active and inert solids in the WMU. Therefore, a two-region adsorption model should, ideally, be used to perform a mass balance on organic contaminant concentration within the system. However, an alternative to this more complex approach might be to weight k_{ds} according to an estimated decimal fraction of organic solids (f_{os}) in the compartment. Hence, k_{ds} could be expressed as (e.g., Hass & Vamos, Hazardous and Industrial Waste Treatment, Prentice Hall, 1995, pp 30)

$$k_{ds} = f_{os} \, k_{oc} \qquad\qquad\qquad (1)$$

where k_{oc} is the average partition coefficient of the organic contaminants onto the organic carbon of the solid phase, and f_{os} might be related to k_{ba}.

It is clear that the TSS concentration will vary with depth (and most probably horizontal location) in the liquid compartment. Therefore, an average TSS should be used where $[TSS]_{out}$ is not equivalent to $[TSS]_1$. Whether or not it is appropriate to use a log-mean average will depend on the nature of TSS variability with depth. If the TSS concentration varies over an order of magnitude with depth, and a log-linear relationship between TSS concentration and depth has been observed in practice, then this averaging is appropriate. Otherwise, another weighting function might be more appropriate. Without physical data on TSS variability in a "typical" WMU, it is hard to specify the correct methodology for prediction of TSS concentration in the liquid compartment.

There is a misplaced sentence between Equations 16 and 17, which should be located between Equations 19 and 20.

Mass Transfer Rate Equations

Rate of Volatilization

The use of the two-film theory, which assumes a low contaminant mass concentration in the atmosphere, is an acceptable means of estimating reaction rates due to volatilization. Equation 24 assumes that the overall rate of mass transfer is characterized by a liquid resistance and a gas resistance in series. Although this simplification is typical in gas transfer analyses, it would make better physical sense to use an average coefficient that is based on continuity of emission across the different boundaries (as is done in Section 4, which employs an average soil hydraulic conductivity based on continuity of infiltration across model boundaries).

Again, the assumption of singular transfer coefficients is not realistic. Gas and liquid transport coefficients will vary not only between organic compounds, but also, for a singular compound, with temperature, the concentration of the contaminant and the surface tension of the aqueous/gas boundary layer. Work published in the literature (e.g., Genereux & Hemond, 1992, Water Resources Res., 28 (9), pp 2365 - 2374) supports the fact that accurate estimates of air-water transfer coefficients generally demand experimental determination.

There is a typing error in the definition of Scg for Equation 27. $D_{i,g}$ should read $D_{i,a}$.

Effective Diffusion Velocity

It is my opinion that the inclusion of a diffusive transport term is an unnecessary model complexity if the model output is insensitive to this parameter. Nevertheless, I offer the following comment on the calculation presented for the effective diffusion velocity:

It is acceptable practice to estimate the effective liquid mass transfer coefficient in a porous medium by amending the free diffusion coefficient through multiplication by a tortuosity factor that accounts for the increase in diffusion pathlength caused by the presence of a solid phase (Equation 35). The logistics used to derive Equation 36 are also reasonable. However, given the uncertainty in $k_{l,q}$, $D_{i,l}$ and $q_{liq, 2}$ I cannot see the necessity for such complexity in this calculation. A simpler, and equally defensible, calculation would be to assume that:

$$k_{eff,2} = t\ k_{l,q} \qquad (2)$$

giving

$$v_{eff} = k_{l,q}\ (t\ /\ 1{+}t) \qquad (3)$$

where t is a tortuosity factor that accounts for the increased transport distance across a liquid-liquid film caused by the presence of a solid phase. The same Millington-Quirk tortuosity model could be used to estimate t, leading to

$$v_{diff} = k_{l,q}\ (q_{liq,2}1.33)/\ (1 + q_{liq,2}1.33) \qquad (4)$$

At high values of $q_{liq,2}$, the above equation yields similar output to Equation 37. However, the additional assumption giving rise to Equation 36 is not required in the above derivation.

Hydrolysis Rate

There are no calculations given for estimating the hydrolysis rate. Neither is k_{hyd} listed as a model input in Section 7.

Estimation of Leachate and Effluent Flow Rates

Estimating Leachate Flow Rate

The general leachate construct model is fine. Note that the leachate model assumes hydrostatic fluid conditions within the liquid compartment, which is incongruous with the upflow and, sometimes turbulent, mixing that is taking place within this compartment. However, the added complexity of considering non-hydrostatic conditions within the liquid compartment is most likely not worth the effort, unless the model proves to be very sensitive to Qleach (which I imagine to be unlikely, given that the flux through a well constructed WMU lining system will be very low).

I was not able to obtain the reference for the soil class parameters in time to comment on the applicability of Equation 39b. However, I presume that the soil retention model parameters, a and b, are either measured independently in the laboratory or are average values tabulated for given soil types. Although I am not familiar, specifically, with Equation 39b, the estimation of krw using parameters derived from soil moisture retention curves is acceptable practice in soil science/ contaminant hydrology (see, e.g., Tindall & Kunkel, Unsaturated Zone Hydrology for Scientists and Engineers, Prentice Hall, 1999, pp 191).

Note that the right hand square bracket is missing in the denominator of Equation 39b.

I have several comments/ concerns to voice with respect to the leachate flow rate model.

1.   The model demands fairly detailed information regarding the vadose zone beneath the SI (e.g., number of underlying soil layers, thickness of each layer and the layer soil retention parameters themselves). How often is this information readily available? If it is rarely available, and the WMU model is fairly insensitive to Qleach, the leachate model construct seems unnecessarily complex; in which case, the use of a single sub-surface layer with a reduced form of Equation 39b (e.g., krw = exp (ajn) ,where a is an empirical constant; Mualem, 1996, Water Resources Res., 12, pp 1248 - 1254) would probably be adequate.

2.   I am unclear on whether or not one purpose of the model is to estimate contaminant loading at the groundwater table due to leachate transport from the WMU. If this is, indeed, an intent of the model, then a constituent mass balance equation for leachate behavior in the subsurface needs to be incorporated. At present, the mass flux of leachate to the groundwater table is represented simply by Qleach Cliq,2. This form of representation neglects contaminant loss through aerobic degradation and volatilization, and contaminant spreading by the mechanisms of diffusion and dispersion. Therefore, it is generally conservative.

3.   If fairly detailed information regarding the subsurface stratigraphy beneath an SI is available, and an estimation of contaminant loading at the groundwater table is a required output of the WMU model, then the leachate model should consider the possibility of gravity fingering in the vadose zone (see, e.g., Tindall & Kunkel, Unsaturated Zone Hydrology for Scientists and Engineers, Prentice Hall, 1999, pp 312 - 314). During one-dimensional infiltration into soils where the hydraulic conductivity increases downward, wetting fronts infiltrating unsaturated media can become unstable and break into fingers. These fingers can move vertically, and very rapidly, to the water table without contacting (i.e., wetting) a large proportion of the vadose zone. Fluid transport under these circumstances is extremely non-uniform. As a result, contaminant loading at the water table will be quite different than it would be if transport is assumed to be

uniform. Because the liner material for the WMU will, most likely, have a lower hydraulic conductivity than the underlying soil, gravity fingering of leachate is a possibility and should therefore be properly investigated.

4.	Are seasonal fluctuations in the groundwater table level considered by the model? Again, the importance of considering these will depend on the sensitivity of the model to Qleach , and the purpose of the model with respect to estimating contaminant loading at the water table.

Estimating Effluent Flow Rate

	The effluent flow rate calculation requires a knowledge of Prain and Pevap. I assume that these parameters are required model input. However, they are not listed in Section 7.

Sediment Deposition, Resuspension and Burial

	Sediment deposition, resuspension and burial are all estimated from the removal efficiency for the WMU. The removal efficiency is calculated from a model that assumes an upward flow velocity in the WMU (vupflow) and a distribution of downward settling velocities (vpart), which is based on the particle size distribution (PDS) function for the TSS. Although not stated, the effects of flocculation are neglected, which is probably reasonable in the majority of cases.

	The upward flow velocity in the WMU's liquid compartment, vupflow, is calculated from the influent flow rate and the quiescent surface area. To determine if vupflow can reasonably be approximated from Qinfl / Aq for a typical WMU, requires knowledge of the physical layout of a typical WMU, which has not been given. Certainly, many surface impoundments and primary settlement tanks have a large component of flow in the horizontal direction, which would require an alternative approach based on the projected trajectory of particles entering the WMU. However, for WMUs where vupflow ~ Qinfl/ Aq, the steps followed from Equations 49 to 55 appear reasonable.

	Note that Equation 54 is simply the volume of a sphere, and must be divided by dpart to provide a mass to diameter weighting factor for the particles.

	I am uncertain as to why the removal efficiency is assumed to be constant at liquid depths of 1.2 meters or more. Is there some evidence that suggests that the majority of particles in a typical WMU influent will have mobilized their full resistance to fluid upflow (i.e., will have reached a "terminal" velocity) in 1.2 meters of water? If this is the case, and the use of first order kinetics for solids settling (Equation 56) is based on physical observation that suggests this form of relationship, then Equations 56 to 60 are defensible. Note, that Equation 58 assumes that the biomass yielded has the same PDS and dry bulk density as the influent TSS. This is unlikely to be true in many systems. Therefore, the removal efficiency for the biomass should probably be calculated separately. However, given that the prediction of sediment transport in any dynamic system is extremely complex, and requires an analysis that considers, rigorously, the boundary conditions of the system, the added complexity of considering biomass PDS and specific gravity is probably an unnecessary complexity in this model.

Sediment consolidation is ignored in the time step calculations for d2. If it hasn't already been done, I recommend that the addition total vertical stress acting on the accumulating solids compartment due to an increment of Dd2 is calculated, and the associated strain then estimated (for approaches to estimating sediment strain under load, see, e.g., Mitchell, Fundamentals of Soil Behavior, 1993, John Wiley & Sons). If the magnitude of this strain is comparable to the sediment burial and/ or decomposition increment for the time step, then sediment consolidation should be taken into account in the model.

Temperature Effects

From Equation 49, the residence time for liquid in the tank is h1Aq/Qinfl. Therefore, Qinfl on the right hand side of Equation 62 should be multiplied by a factor A/Aq. Note, that Equation 62 does not include an energy term due to heat dissipation by the impellers, which might be important in the case of aerated WMUs.

Given that the reported range of heat transfer coefficients varies over four orders of magnitude (10 to 10,000 W/m2 - oC), the assumption of an average value for h based on faer and a coefficient derived from thermal resistance theory will only ever provide a (very) rough estimate of likely conditions in the WMU. I assume that Tinfl and Tair are required model input parameters, although they are not listed in Section 7. If Tinfl can be monitored at a WMU, why is it not possible to directly monitor Tl?. Alternatively, Tl could be taken as the average value of Tinfl and Tout .Only if Tinfl is an easy parameter to approximate/ assume for most WMUs, can I can see the merit of estimating Tl using Equations 62 and 63.

I appreciate the assumptions from which Equation 64 was derived. However, I am concerned that Equation 64 is inaccurate. Ice formation is a kinematic process, which is affected by the chemical composition of the fluid forming the ice. Therefore, I would be surprised to learn that the heat lost in lowering a WMU liquid temperature from 0 to T1, can be directly translated into ice formation. However, I have little experience in cold-region studies, and therefore recommend that some-one with such experience is consulted regarding the appropriateness of this equation.

Equations 65 to 70 are standard temperature corrections reported in the literature.

The form of figure 3 will vary with bacterial type. However, for many bacteria, the relationship given in Figure 3 is reasonable.

The effect of temperature on biomass yield has not been considered.

Model Inputs

As noted in the above sections, khyd, Prain, Pevap, Tinf and Tair are all missing from the list of model inputs.

Dr. Hawthorn: *Understanding of Approach*

The main objective is to establish a set of tools for estimating pollutant mass release via infiltration and volatilization from a tank or surface impoundment. The tools used include mass balances and various transport relations within a multi-compartment conceptual model.

General Comment on Text

In general, I found the approach in principle to be acceptable. I did, however, find the specific methods used to account for the various routes/pathways to be inconsistent in the level of applied detailed. For example, in some cases very general, basic assumptions were made to simplify the calculations in terms of one or two parameters, while in others there are detailed empirical relations with as many as a dozen or more unknowns. In the end, the approach is pretty unwieldy in some parts with respect to model parameterization.

Responding to the Charge to Reviewers

That said, in addressing the Charge to Reviewers, I have made comments on each item requested, as appropriate.

1. Sediment Removal Efficiency: The definition of an upflow velocity is an interesting time. I'm not sure, however, that Eq. (49) is correct. It is assumed that Q/A, as shown, actually represents some vertical component of velocity or "driving force' for mass flux (suspension) in the liquid compartment. Notwithstanding, the Q/A shown is actually an overflow rate, which if interpreted as a velocity represents nothing more than the depth of the tank divided by the mean residence time of the fluid within a control volume. I don't see the physical link between the overflow rate and the mathematical product of the resuspension velocity and the ratio of the TSS in the sediment and liquid compartments. Equation (49) may not portray traditional theories of discrete settling very well.

Moreover, it is assumed in Eq. (55) that only those particles with settling velocities in excess of the upflow velocity (i.e. overflow rate) will actually be removed. This notion would again be in conflict with traditional design approaches to discrete particle (Type I) settling calculations. Wouldn't it be possible, even likely, that particles with settling velocities less than the upflow velocity would settle, depending on their initial location (depth) within the tank. How do you resolve Eq. (55) and the basic ideas presented in light of traditional settling removal analysis?

If Eq. (49) and the upflow velocity is being interpreted as true vertical velocity component, then I would contend it is incorrect. The traditional theories behind a resuspension velocity are based in fundamental tractive forces and shear stresses which actually lead to the uplifting of a sediment particle within a water column. By contrast, the Q/A shown in Eq. (49) is not related in any way to the same ideas. I would suggest that you use an approach based on traditional Type I settling theory. In this case, one must account for complete removal of particles with settling velocities in excess of Q/A plus a fraction whose velocities are less but reside in the system at such a location as to permit removal within the mean residence time defined by L/(Q/A), where L is the average depth of the tank. An assumption regarding the distribution of particles as specified in Eq. (53) could still be utilized. Moreover, you can still use the basic assumption that the TSS is liquid compartment is completely mixed.

2. Average TSS within the WMU: the use of the log-mean average (i.e., geometric mean) of the TSS in the liquid compartment to account for spatial variation seems reasonable. I know of no direct particular precedence for such use; however, the use of the geometric mean to represent the effective properties of a soil does have a prior history. In fact, the geometric mean is often used to represent the effective hydraulic conductivity for a spatially random soil. Accordingly, I support its use in this context, as well.

3. Biodegradation Rate Models: Proper comment on this item is out of my area of expertise. Of course, the use of first-order rate kinetics has a great deal of history in biodegradation modeling. Such as a highly dependent on the proper selection of a rate constant.

4. Diffusive Transport Between Liquid and Sediment Compartments: I believe the inclusion of a diffusive flux term is not warranted, especially under the assumed conditions of steady-state. One must contend that, in fact, the rate)or time) in which this mass transfer occurs if far quicker than changes in the larger system and that a substantial concentration gradient will exist between the two compartments. Hence, my first instinct is to believe that this would only be a very minor process and could be ignored. Moreover, its inclusion as important item presumes potentially that one is able to accurately quantify all other terms, as well. If the process tends not be dominate and it is not well defined (like may of the other process included), then it seems to only add to the confusion or uncertainty of the overall model.

5. Temperature Effects: The only problem I have with the manner in which temperature effects are developed is the inconsistent way in which accuracy is mixed with empirical models. For example, at one point it is noted that a heat transfer coefficient is estimated from driving parameters that range over several orders of magnitude (i.e. offering a great deal of uncertainty). A few pages later it is noted that a certain correction terms is only good for temperatures between 0 and 30 and another for over 31. My comment is why 31? Be careful here in mixing accuracy of this type with the various highly empirical relations shown in this section. I have no problem using them. Let's just be consistent in the manner for which both the assumptions and relations are applied. Moreover, if you apply the temperature corrections to the relations shown for the mass transfer coefficients, you've to a pretty unwieldy mess. In this case, you have created relations (with so many independent parameters) that little sense may be made in the end.

6. Volatile Emissions - No. Comments.

Specific Comments

1. Page 3 - Reference to Eq. (1). The term Q(leach) x C(tot,1) seems in error? I do not see why the leaching (infiltrating) flux (flow rate) carries mass under the total concentration. This mass rate should include only the dissolved aqueous phase - otherwise you've got a leaching component which is sorbed (partitioned) on the solids in the liquid compartment. Are you saying the solids in the liquid compartment are moving along with leaching volume? This may be true for an attached contaminant on particulate (or dissolved) organic matter.

2. Page - Reference to Eq. (4). Again, the idea of a component of the solids being transported with the leaching volume is foreign to me. Remove Q(leach)? Of course, if you did this you'd have to carry the correction through to all other equations.

3. Page 15 - Reference to Section 4. All of this section seems a little mis-directed. Let me first explain that if you have a pond (with infiltration) you generally must have a layer near the bottom of the pond (either as a sediment bed, liner or underlying soil) whose saturated hydraulic conductivity is limiting - that is to say a layer whose saturated hydraulic conductivity is less than the rate of water which is applied to the pond; otherwise the pond would never contain water - it would all infiltrate. Thus, either the sediment in the pond, the pond's liner, or the soil directly beneath the pond is limiting - in which case they are all saturated. Beneath these layers, the soil must be unsaturated - otherwise you've lost so much water out of the pond you've created your own perched water table.

Thus, just use a single soil layer (e.g. a foot or two) below the pond as the point where you break from saturated to unsaturated conditions (i.e., at this point you approximately now the pore water pressure to be atmospheric). Hence, use Eq. (40) as shown for this three layer system (i.e. Eq.(41) and call it good.

For reference, note that Eq. (41) is in error for the example stated. If the liner is limiting, then the bottom of the liner would mark the point of transition from saturated to unsaturated conditions. Hence, there is no need for the third term in the denominator of this equation. The infiltration capacity (i.e. the saturated hydraulic conductivity) of the underlying soil layer would exceed the infiltration rate established by the limiting liner - thus, leaving the underlying soil layer in an unsaturated state.

Dr. Overcash: The validity of models depends on two major factors:
>   1) the mathematical representation of some physical system, and
>   2) the parameters or constants used to fit the model to the physical system.

Since the current HWIR99 document only covers the first factor, then no peer review can be considered to verify that such models or modules are valid representations of the actual systems. As an example, the early CFR 503b regulatory models on municipal biosolids applied to land utilized a module for migration of metals in soils. This mechanistic description was adequate, but the parameters used predicted extensive migration of heavy metals and was thus profoundly wrong. Thus the model was wrong even though the mechanism was adequate.

It is unclear how to resolve this situation of major missing information needed for review. The review provided herein is of the mathematical description of physical phenomena and thus represents a peer review. However, the conclusions or critiques should in no way be taken as a review of the modules presented since without the constants or other information, the validity cannot be judged. Thus an algorithm may reflect a mode of behavior (such as sedimentation loss), but in actuality this behavior is negligible compared to biodegradation. However, if the wrong physical parameters are put in the model, the sedimentation might appear to be the major fate. The model would thus not be a realistic representation and could not be peer reviewed as valid.

The following review comments refer to specific pages, but without line numbers, the actual location of comments can be hard to specify. Most, but not all symbols used in the module are defined. Someone needs to carefully verify that all symbols are defined.

1) page 1, paragraph 1: States tanks and SI use the same volatile contaminant loss. Because of surface size, degree of surface agitation, etc., this assumption is only true if gas phase mass transfer is not limiting. The authors have not provided any data to support such a conclusion.

2) page 1, paragraph 1: States the influent SS primarily pass through the system. This is not true if there is a greater unit depth than the aeration zone or if aeration is inadequate for complete mixing.

3) page 1, paragraph 1: States no leaching from a tank. This is also true for lined SI and also from certain unlined SI with compacted or sealed bottoms

4)page 1, 1-1: The first assumption. The sediment compartment is not well-mixed in the same terminology used in the upper zone of an agitated tank. In the sediment, we find that with a low water content and small layers, that diffusion is the mechanism for apparently uniform concentrations of certain species. However, it is also found that among layers in the settled solids that distinct differences occur. Thus different strata reflect the different long term inputs to such a SI or tank. Thus it is unclear that a universal assumption of well-mixed (chemically) can be used on all sediment compartments.

5) page 2 Figure 1: Authors have not provided a clear difference between mechanically aerated SI and quiescent SI. For the former, there is an aeration, mixing zone that scours any sediment layer adjacent to the mixing zone. When the mixing zone is narrower than the tank depth, then a quiescent zone that may be only liquid (depending on the design of the aeration mixing), and then the sludge or sediment. In a quiescent system, the Figure appears as Figure 1.

6) page 3 equation 1: The symbol for solid settling velocity in the equation is a Greek letter, but is Roman letter v in the list of definitions. These look similar, but are not the same.

7) page 3: $C_{tot,l}$ assumes that the sediment column does not alter the concentration of the liquid that is leaching. This is not realistic, given the mineralized compacted nature of this sediment layer.

8) page 3: K_{OL} is not specified as different for quiescent versus aeration.

9) page 4: V_2 appears to be missing from the definitions

10) page 4: the volumetric liquid content should be volumetric liquid fraction

11) page 5 equation 2: k_{hyd} This hydrolysis rate need not be restricted to the liquid phase as hydrolysis reactions might also occur for adsorbed species

12) page 5 equation 2: v_{diff} This mass transfer coefficient should probably have a different symbol (v) than the other v's that are mostly velocities. Possibly use D

13) page 5: ë should be /g-BOD reacted. As a matter of clarity, the authors have not defined whether BOD is 5-day, 20-day, or ultimate.

14) page 6 equation 4: Authors should state that the assumption is that biomass yields are low for anaerobic systems and so formation is neglected. Probably this is not a good assumption since the sediment is essentially stabilized anaerobic organic byproducts.

15) page 6 equation 6: For a number of chemical species this simple partitioning applies, but for others this is much less reversible. Until the species is specified and the magnitude of this process is estimated it is not possible to comment.

16) page 8 near bottom: It appears that the line "Using these...." should not be here, but on page 9 between equations 19 and 18.

17) page 9 section 3: The differentiation of surface volatilization from quiescent versus aerated for a system with aeration may be too complex. Generally the measurements or estimates for aeration systems is some lumped average of areas with varying degrees of agitation and surface turbulence and thus already includes both quiescent and agitated features.

18) page 14 equation 34: The liquid mass transfer coefficient is very case dependent since this liquid zone may be all quiescent, all agitated or any combination when one looks at the sediment/liquid interface.

19) page 15 section 4.1: The leachate flow rate does not reflect field practice. In animal waste lagoons, research has found quite variable migration, because of soil sealing. This can not be clear from the discussion on this page. In addition no influence of lateral movement is included.

20) page 16 Figure 2: This schematic is inadequate for the case of a real liner in a SI since the losses are at small individual point leaks and not uniform over the entire bottom area. In addition, a liner collection system would not be well represented by this schematic.

21) page 20 top paragraph: This model is way too complex when good rule-of-thumb TSS removal efficiencies are widely available. Then the model could just partition the influent TSS

22) page 20 equation 49: This upflow resuspension model is extremely unclear. First on Figure 1 the influent arrives at a point on the surface (a pipe) and so treating the entire cross sectional area of the SI or tank as a pipe with some flow is inaccurate. The resuspension is much more determined by buoyancy of particles, cells, etc than any measurable upward volumetric flow rate. This effort seems very contrived.

23) page 22 equation 55: To estimate solid removal efficiency in tanks and SI this approach with such a large number of measurable constants is way too complex.

24) page 24 equation 61: In the sediment t is very long and decomposition is complete. What is not represented is the humus or stabilized biomass formation that would be found in sediment material. This now is only a loss term with no generation.

25) page 25 equation 62: The authors have neglected heat loss to the soil or vertical surfaces of tank which are significant. It is convention to simplify and assume the average monthly air temperature to represent the annual cycle of liquid temperature in an SI or exposed tank. Again this would simplify the model and still give an monthly variation.

26) page 27 section 6.2: Probably the biological reaction rate is the most significant input property that varies with temperature. The gas properties may vary, but are probably not significant in removal or fate effects.

27) page 28 equation 68: The flows occurring in the SI or tank are so slow that a viscosity correction is more computation but no more improvement.

28) page 30 Figure 3: The representation of a temperature correction factor for biological rates is confusing. From 5C-45C the biological rate is increasing significantly (not constant at 1.0) and then drops off in the thermophilic and psychrophilic ranges. With the present explanation it is hard to deduce this behavior from Figure 3.

LAU/WP/LF Source Modules and Watershed Module

Background/History

Source term modules were developed for waste piles (WPs), land application units (LAUs), and landfills (LFs), i.e., non-wastewater waste management units (WMUs), to provide estimates of annual average surface soil constituent concentrations and constituent mass emission rates to air and groundwater. These estimates are then used in an integrated, multi-pathway model linking source term modules with environmental fate and transport and exposure/risk modules. Additionally, LAU and WP source emission models have been combined with a local watershed model (a "local" watershed is a sheet-flow-only watershed containing the WP or LAU) to provide estimates of constituent mass flux rates from runoff and erosion to a downslope waterbody, as well as surface soil constituent concentrations in downslope buffer areas.

A soil column model was developed to describe the dynamics of constituent mass fate and transport within non-wastewater WMUs and, optionally, in the unsaturated soil below. Because it is applied in all the WMU source emission models described here, it is referred to as the Generic Soil Column Model (GSCM). Governing equations for the GSCM are similar to those used by Jury et al. (1983, 1990) and Shan and Stevens (1995). However, the analytical solution techniques used by these authors were not applicable to the source emission models developed here because of the need to consider the periodic addition of constituent mass and enhanced constituent mass loss rates in the surface soil (e.g., due to runoff, erosion, wind and mechanical processes). A new solution technique has been developed for use in the HWIR that is computationally efficient and sufficiently flexible to allow consideration of the unique design and operational aspects of each WMU under consideration.

The Watershed Module simulates the effects of indirect chemical contamination – from airborne emissions from the source and subsequent deposition – on surficial soils throughout the (approximately 2 km) area surrounding the WMU, and runoff, eroded soils, and chemical loadings to waterbodies throughout this area. Once atmospheric deposition has occurred on any particular watershed, the fate and transport processes occurring both within the soil column of that watershed and at its surface are fundamentally similar to those same processes simulated for the LAU and WP in the context of their "local watersheds." Thus, the GSCM and its coupling to the watershed hydrology and surface fate and transport model are also used to simulate each watershed within the area surrounding the WMU.

Charge to Reviewers

We invite comments on any and all portions of the modules. We have made a considerable effort within the documentation itself to identify and describe all significant assumptions and limitations. Accordingly, we will not repeat those discussions here, but rather refer the reviewer to the appropriate sections. Those sections are:

- GSCM-specific – Section 2.
- Source-specific operational aspects – Section 3.7.2 (WP), Section 3.8.2 (LAU), and Section 4.2 (LF).
- Hydrological model – Section 3.2.1, page 19.
- Spatial implementation of the soil erosion model with respect to the sheet-flow assumption and flow length – Section 3.3, page 28.
- Fixed modeling domain of the GSCM and burial/erosion processes – Section 3.4.2, page 38.
- Steady-state assumption of the runoff compartment model – Section 3.4.1, page 30.

Finally, we specifically invite comments on the conceptual model and implementation of the coupling of the surface fate and transport model with the GSCM. The particular spatial scale ("local watershed") associated with some of the HWIR exposure and risk issues have, to our knowledge, not been previously addressed by extant models. For example, PRZM deals with field-scale simulations (e.g., our WMU subarea in the local watershed), while HSPF deals with much larger, regional watersheds. Indeed, EPA has reviewed extant models with respect to their applicability to the HWIR spatial scale(s) of interest and found them lacking, or at least too computationally intensive. The combined GSCM/surface fate and transport model represents EPA's effort to fill this technological gap and we welcome comments. (A specific parameterization issue within this overall construct that we are currently attempting to resolve is how to assign values to the eroded solids' settling velocity, vs, and/or the resuspension velocity, vr. Comments/suggestions on this parameterization issue are also invited.)

Comments on the Watershed Module

Dr. Culligan: I did not receive any of documentation specified in the Charge to Reviewers. Specifically, I have not seen copies of;

The Generic Soil Column Model (GSCM)
The Source term modules for: waste piles (WP),
                                                        land application units (LAU)
                                                        landfills (LF)

        The only documentation that I did receive was a draft report of the Watershed Module (October 27, 1998, pp10).

        Without the appropriate documentation, it was not possible to address any of the issues raised in the charge. In addition, a thorough review of the Watershed Module document itself was not possible.

        Given these circumstances, I can only offer the following comments on the material presented in the Watershed Module (WM) document itself.

        Although the WM considers volatilization, leaching, runoff, erosion and biological and chemical degradation, chemical sorption/ desorption and the plant uptake of chemicals are not considered. These mechanisms may be important in some surficial soils.

        How do the 30Q2 values for each of the 18 USGS Hydrological Units compare to the 7Q10 and average annual base flows (i.e., Is the 30Q2 a good compromise between 7Q10 and the average annual base flow, as was being sought)?

        Although I can understand the advantage of a power function model for estimating baseflow, the regression analysis results for HUC Region 3 and 19 to 18 indicate very poor correlation with the data. Therefore, I recommend than an alternative model is investigated.

        I would like to be able to comment on the Fate and Transport equations upon which the WM is based. For example, is evapo-transpiration and soil vegetative cover considered in the precipitation/ infiltration/ runoff modules of the model? How does the model cope with flooding; groundfreezing; snowfall? How is the average annual infiltration rate actually estimated? However, without the documents referenced in the WM draft report, I am unable to address some of these issues, and therefore cannot reasonable asses the actual merit/ appropriateness of the WM model.

Dr. Hawthorn: *Understanding of Approach*

The main objective is to establish a set of tools for estimating (or simulating) pollutant mass release via runoff from a watershed derived from the atmospheric deposition of a contaminant from an adjacent WMU. The tools used include the (modified) Universal Soil Loss Equation (MUSLE) to determine soil loss rate from the area of interest (AOI), coupled with the surficial transport equation (2.1-1) as the descriptor of source strength in the soil. Additionally, mass (pollutant or soil) may be transported via stream in the streamflow component.

General Comment on Text

I found the text to be inadequately brief. After reading the document, I was unable to state that I fully understood the methodology used in producing the estimates of chemical mass release from the "watershed." In fact, the use of the term watershed was vague - extending from a single hillside to larger areas encompassing a regional stream network. If this is true, the methods outlined seem neither appropriate or useful in either sense. Such an approach is not generally applicable to areas of such differing size.

Moreover, the use of the assumptions of a "...single, homogeneous area with respect to soil characteristics, runoff and erosion characteristics, and chemical characteristics in soil." Would preclude one from "simulating" (as indicated) any actual processes within a real system. At best, the methodology outlined would provide a crude estimate of the actual mass loading rates for either soil or pollutant. For example, the complex process of the atmospheric deposition of mass is accounted for in the model by a single, average annual deposition rate. Furthermore, "loss" attributed to potential hydrolysis, degradation, and/or other mechanisms is included in a simple first-order decay term. That said, I fail to see how the use of Eq. 2.1-1 adequately established the proper "source term" in the model for later transport via the indicated runoff component.

I would reiterate my earlier point that, as such, the approach does not "simulate" anything that may be real. The tools shown are nothing more than a very basic, crude estimate of what are typically very complex processes. The lack of accounting for the spatial distribution within the source and of the erosional process may lead to errors in the estimate of mass loading in excess of an order of magnitude or more - not to mention the effects derived by the simple treatment of the depositional process or the overall terms. Less concern may have been raised if it were not for the poor manner in which a watershed itself were described. There is no doubt in my mind that the use of such tools over a large area that included several stream networks would have a great many flaws - more than could be justified by the approach taken.

Specific Comments

1. Page 1 - Reference to the simulation of chemical concentrations in the top 1 cm of surficial soil. The use of an equation like the one shown as 2.1-1 is inappropriate at this scale for real soils. Transport in the upper 1 cm of a native soil in an actual watershed is not controlled by classic advection-dispersion type processes. The reality is that you would have to account for macroporous flow, non-equilibrium partitioning, sorption onto natural organic matter, non-equibibrium invasion of the infiltration wetting front, and many other processes to come anywhere near getting it correct. Granted you specifically did not intend to include these processes for obvious reasos of complexity. Why then include many of the processes you now show? For example, do you think in the first 1 cm of transport that first-order decay should be included? Why? Moreover, dispersion at this scale is practically indefinable. Can you achieve a reasonable numerical solution to equation 2.1-1 over this 1 cm element without entering an artificially high effective dispersion coefficient? Why not simply drop dispersion term and solve the transport under a kinematic wave framework?

2. Page 2 - Reference to homogeneous site characteristics. Use of such assumptions over relatively large sites will invalidate any predictions which are derived under the simple tools shown. Actual spatial heterogeneity at real sites will be a source of great error and uncertainty, leaving the resulting predictions without any substantial value with respect to scientific justification.

Page 3 - Reference to Equation 3.4.1-9. No such equation is shown anywhere in the material I was provided. It is difficult to evaluate the adequacy of the coupling between surficial soil water concentrations and those in the runoff.

3. Page 3 - Reference to total concentration. As defined, refers to particulate plus dissolved. If so, how does this apply in the soil column? What do you mean by particulate concentration in this latter case? Could mass not also become a gas phase (i.e. volatilize) in the case of an unsaturated soil? There is an inadequate definition of partitioning provided here.

4. Page 3 - Reference to Equation 2.1-1. There are no boundary or initial conditions provided for this equation. As such, the so-called model is ill-posed. Moreover, do you expect users to properly provide numerical values for the parameters for the model? If so, what might be a valid range of numbers? Where would one find useful half-lives in soil? Furthermore, the effects of partitioning or retardation are not included, why?

5. Page 4 - Reference to the use of the terms convection and diffusion. Actually, in soil transport settings, these terms are referred to as advection and dispersion. It is important to note the difference is not semantics. There are very specific definitions given for advection and dispersion and the related process for which they normally define in a soil column setting and they are not the classic mechanisms defined by convection and diffusion. In particular, convection and advection are similar (i.e. related to the bulk movement of the transporting fluid). However, diffusion and dispersion are not the same. In fact, diffusion is a sub-component of dispersion. Dispersion incudes the so-called spreading of mass due to a randomness in advection. At the scales presented, dispersion may collapse to diffusion (i.e., mechanical mixing is small), however, I'm not sure this distinction is being made here properly.

6. Page 4 - Reference to hydrology submodel. There is no Section 3.2 included in the material sent to me. Very difficult to evaluate the Streamflow component.

7. Page 8 - Omission of mass rate equation. In the presentation of the MUSLE, there is no representation (i.e. equation) given for the mass rate of soil loss.

8. With respect to the Charge to Reviewers, the various section, page numbers and other references simply do not exist in the material sent to me.

Dr. Overcash: The authors state that several risk and watershed models were found not to be applicable for the current HWIR99. However, the CFR 503b risk pathway model was not cited and it seems to be a major duplication and policy error to reject such a comprehensive model as 503b. Certainly there is no larger database of actual field conditions greater that those used in 503b. It is hoped that this is not an inter-office issue.

1) page 2 paragraph 1: While the mechanism of aerial deposition occurs, the magnitude compared to other pathways can not be peer reviewed with this current document. No values or fluxes are stated nor provided in literature citations. It is unlikely that this is a large pathway.

2) page 2 second reason (bullet): The time step for transport is only limited to the rain event and immediately thereafter. Thus the authors need greater specificity on what time scales and what interaction is to be used for rain events versus the intervening time.

3) page 3 equation 2.1-1: During a rain event, the last two terms are effectively unchanged since the time constants are different from the convective flows. Simplified approaches use separate transport models from models for fate via decomposition, hydrolysis, adsorption, etc.

CONCLUSIONS

At this stage in the HWIR99 modeling review, only the mathematical form of terms influencing the behavior of waste constituents can be critiqued. That is included herein. The validity of the model is however far different from these mathematical expressions and rests on the physical constants and the computing efficiencies that are as yet undefined.

A second conclusion is that the purpose and likely outcome of this modeling effort are not well stated. In general, if constants were put in this model, it may be beyond any reasonable effort to review because of the level of complexity used. If this effort has any credibility, the behavior of each fate pathway has to be separately probed and the relative magnitude of contributions to the overall environmental fate must be determined. At this stage this is an overly complex effort for which there may be far too few data to independently verify actual behavior.