Modifications to Gleams-Driver Version 1: Augmentation of Chemical Database

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ABSTRACT

The initial release of Gleams-Driver Version 1.0 included only two chemicals in **Chemicals.mdb**: 2,4-D and hexazinone. These were arbitrarily selected and intended only to serve as a demonstration of the program's capabilities. This report documents the release of an expanded version of **Chemicals.mdb** that includes 16 chemicals on which USDA Forest Service risk assessments have been prepared and in which GLEAMS modeling was conducted. This report details the sources of information that were used and provides some guidance on the use of the values in the expanded database.

In the preparation of the expanded version of **Chemicals.mdb**, no changes were made to the Gleams-Driver code. To activate the expanded **Chemicals.mdb**, simply copy the new version of **Chemicals.mdb** to the **SupportFiles** subdirectory where the Gleams-Driver program is installed. If you do not want to over-write the existing version of **Chemicals.mdb**, just move it to a different location before copying the new version of **Chemicals.mdb** to the **SupportFiles** subdirectory.

1. INTRODUCTION

Under USDA Order No. AG-43ZP-P-05-0037, Region 8 of the USDA Forest Service has developed Gleams-Driver Version 1.0. GLEAMS is a root zone model developed by USDA/ARS that can be used to examine the fate of chemicals in various types of soils under different meteorological and hydrogeological conditions. GLEAMS is a DOS program written in Fortran. While it can and has been used by some USDA personnel to perform exposure assessments in support of USDA program activities, it is not widely used by Forest Service personnel because of the difficulties in both running the model and manipulating the output.

Gleams-Driver is a user-friendly Windows program that serves as a pre-processor and post-processor for GLEAMS. It prepares input files for GLEAMS, runs the GLEAMS program, and then reads and processes the output from GLEAMS to make estimates of concentrations of pesticides in soil (target and nontarget fields) as well as surface water (streams and ponds).

Gleams-Driver accesses information on chemicals in the Access database, **Chemicals.mdb**. This database is in the **SupportFiles** subdirectory where the Gleams-Driver program is installed. The initial release of Gleams-Driver Version 1.0 included only two chemicals in **Chemicals.mdb**: 2,4-D and hexazinone. These were arbitrarily selected and intended only to serve as a demonstration of the program's capabilities.

The Gleams-Driver program includes a simple utility for adding to the chemical library through the import of a formatted text file. This import utility may be useful for individuals who may want to take advantage of the site-specific and Monte Carlo capabilities of Gleams-Driver. For the convenience of others who may want to limit the use of Gleams-Driver to the Quick-Run facility, the current task has involved expanding the chemical library to include all chemicals on which Forest Service risk assessments have been prepared that have involved the use of GLEAMS.

2. MATERIALS AND METHODS

The chemicals that are included in the new release of **Chemicals.mdb** are listed in Table 1. Table 1 gives the common name of the chemical, the SERA report number from which the information was abstracted, the date of the SERA report, and the specific table in each SERA report where the information can be found. All documents listed in Table 1 were prepared under USDA Forest Service BPA WO-01-3187-0150 between 2001 and 2005. Additional risk assessments (e.g., some biological agents such as *B.t.k.* and Gypchek as well as some additional chemical agents such as Disparlure and DDVP) were prepared under this contract but the chemicals included in Table 1 are the only chemicals for which GLEAMS runs were conducted. Additional risk assessments were conducted on previous Forest Service contracts but all of the chemicals on which GLEAMS runs were conducted were also updated under BPA WO-01-3187-

0150 and are included in Table 1. Except as otherwise noted in the table of chemical properties (Table 3), all of the information listed in the table of chemical properties is taken from these SERA risk assessments.

The chemical information in **Chemicals.mdb** is contained in a data table named **Chemicals**. The structure of this table is extremely simple, containing only four fields: **ItemCode**, **ValueCode**, **Value**, and **Note**. All four fields are textual rather than numeric. The **ItemCode** field contains an identifier that is unique to the chemical on which the information is stored. The **ValueCode** field contains a fixed set of symbols representing the types of information that must be entered for each unique chemical. As the names imply, the **Value** field contains the actual value and the **Note** field contains a description of the source of the information.

An overview of the **ValueCode** codes that are included for each chemical given in Table 2. The value codes are broken down into three groups: descriptors, chemical properties, and modeling assumptions. There are three descriptors: **Desc**, **Name**, and **PSTNAM**. **Name** and **PSTNAM** are most often the same and are simply the common name of the chemical as listed in Table 1. **PSTNAM** is the name that is entered into the chemical input file in the GLEAMS runs. In GLEAMS, the chemical name is limited to 16 characters. Thus, if the common name of the chemical is over 16 characters – i.e., sulfometuron methyl – the **Name** could be designated as **Sulfometuron methyl** but the **PSTNAM** would need to be truncated – e.g., **Sulfometuron met**. Other than making the data base and the selection list in Gleams-Driver easier to understand, the values that are entered for the **Name** and **PSTNAM** codes have no impact on the model runs. The output is determined by the numeric input parameters such as water solubility and soil halftime, as discussed further below.

The third descriptor, the **Desc** value code, specifies both the name of the chemical and may indicate the general applicability of the values to certain situations. There can be only one set of values for each **Desc** value code while there may be many sets of values for a given **Name** or **PSTNAM**. This is detailed further in Section 3 in terms of the variability of some chemical properties under different conditions.

The other chemical value codes illustrated in Table 2 refer to either modeling assumptions or chemical properties. The modeling assumptions include the coefficient of transformation, coefficient of uptake, and number of metabolites. Each of these are described briefly in Table 2 and discussed further in the documentation for GLEAMS (Knisel and Davis 2000).

The chemical properties needed to run GLEAMS include foliar and soil halftimes, foliar washoff fraction, the soil adsorption coefficient based on organic carbon (K_{oc}), and the solubility of the chemical in water. Additional properties that are needed by Gleams-Driver for the post-processing of GLEAMS output include the sediment-water distribution coefficient (Kd) and the halftimes in sediment and water.

3. RESULTS and DISCUSSION

The common names and the chemical and physical properties that have been added to the **Chemicals** data table in **Chemcials.mdb** is given in Table 3. It will be noted that 3 entries have been added for each of the 16 chemicals designated in Table 1. This approach is taken because virtually all of the chemical and physical properties that are given in Table 3 are not physical constants, in the sense that molecular weight, boiling point, and vapor pressure can be viewed as physical constants.

In Table 3, the entries for each chemical are designated by soil texture: clay, loam, and sand. This approach is taken because the binding characteristics of all of the chemicals specified in Table 1 are influenced by the specific characteristics of different soils. This is most easily appreciated in the consideration of K_{oc} and K_d.

The K_d is the sediment-water distribution coefficient and is defined as the concentration of the chemical in soil (C_s) divided by the concentration of the chemical in water (C_w) at equilibrium:

$$K_d = C_s/C_w \qquad \text{(Eq. 1)}$$

Many neutral organic molecules are bound almost exclusively to the organic carbon in soil (Winegardner 1996). Consequently, soil binding is often expressed as the soil adsorption coefficient based on the organic carbon content of a particular soil (K_{oc}). The K_{oc} is calculated as the K_d divided by the proportion of the soil that consists of organic carbon (*oc*):

$$K_{oc} = K_d / oc. \qquad \text{(Eq. 2)}$$

Conversely, the K_d for a particular soil can be calculated as:

$$K_d = K_{oc} \times oc. \qquad \text{(Eq. 3)}$$

These general relationships are often referred to as the *K_{oc} model* (EFED, 2002a).

While the K_{oc} model is applicable to some compounds, particularly neutral organics, other compounds (including many pesticides) display much more complicated binding patterns that are generally described as Freundlich sorption models (e.g., Otte et al. 2001). One of the simpler Freundlich sorption models is the Freundlich isotherm, in which the Freundlich adsorption coefficient (K_f) is defined as:

$$K_f = C_s/C_w^{\,n}. \qquad \text{(Eq. 4)}$$

K_f is not constant unless *n*, referred to as the *Freundlich exponent*, is equal to 1. When n does equal 1, the Freundlich adsorption coefficient reduces to the K_d in the K_{oc} model (Eq. 1). Various analyses conducted by the U.S. EPA's Environmental Fate and Effects Division provide

examples of compounds that either do fit the K_{oc} model (e.g., EFED 1998) or deviate from the K_{oc} model (e.g., EFED 2002b).

For all of compounds listed in Table 1, data are available indicating either differences in K_{oc} for different soils and/or differences in the K_d values in different types of aquatic sediments. The specific information for each compound is detailed in the various risk assessments as indicated in Table 1. It is for this reason that three values are entered for each compound for the three basic soil textures, clay, loam, and sand.

It should be noted that the K_{oc} values given in Table 3 are used within GLEAMS to model binding to soil. GLEAMS is based on the K_{oc} model and the value of the K_{oc} is used with information on the organic carbon content of the soil to characterize soil binding. In the Gleams-Driver post-processing, binding to aquatic sediment is based directly on a K_d.

Variability is also characteristic of most of the other properties listed in Table 3. Water solubility, for example, is often listed as physical property (e.g., Tomlin 2005) but the solubility of many ionizable compounds will vary with pH and the solubility of most compounds in natural water will vary with temperature as well as the concentrations of other materials in water. Similarly, halftimes in soil, sediment, water, and vegetation may vary substantially based on a number of site-specific conditions. These conditions, however, do not relate primarily to differences in soil type. Thus, these factors are generally constant within the listings for a given compound for clay, loam, and sand in Table 3. Nonetheless, all of these properties may be highly variable.

The variability and uncertainties in the estimates given in Table 3 are important in interpreting the results from Gleams-Driver. The risk assessments listed in Table 1 all involve the development of generic exposure assessments. Thus, only three groups of K_d in the K_{oc} are designated in the risk assessments for the three basic soil textures. All of these should be regarded general approximations. Much more detailed information is available in other sources such as the USDA Pesticide Properties Database (USDA/ARS 2005). If you are using Gleams-Driver to get a rough estimate of how exposures might change with different soils or other conditions, the values given in Table 3 may be reasonable starting points. Depending on the soil profile that you using (i.e., GLEAMS and Gleams-Driver allow up to four soil horizons in a given run), you might select the values for clay, loam, or sand to reflect the predominant soil texture in the soil horizons that you have defined. On the other hand, if you are attempting a more refined or site-specific assessment, it may be worth the effort to either obtain more representative values for the conditions that you are attempting to simulate and/or to explore the Monte Carlo features in Gleams-Driver.

Note on Installation

In the preparation of the expanded version of **Chemicals.mdb** no changes were made to the Gleams-Driver code. To activate the expanded **Chemicals.mdb**, simply copy the new version of **Chemicals.mdb** to the **SupportFiles** subdirectory where the Gleams-Driver program is installed. If you do not want to over-write the existing version of **Chemicals.mdb**, just

move it to a different location before copying the new version of **Chemicals.mdb** to the **SupportFiles** subdirectory.

4. REFERENCES

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Table 1: Sources of information for the chemicals included in the expanded chemical database, **Chemicals.mdb** [a]

Chemical	SERA TR Number	Report Date	Source in Document
2,4-D	06-43-29-01d	July 2, 2006	Table 3-5
Chlorsulfuron	04-43-18-01c	November 21, 2004	Table 3-2
Clopyralid	04-43-17-03c	December 5, 2004	Table 3-1
Dicamba	04-43-17-06d	November 24, 2004	Table 3-1
Diflubenzuron	04-43-05-03b	July 30, 2004	Table 3-1
Glyphosate	02-43-09-04a	March 1, 2003	Table 3-4
Imazapic	04-43-17-04b	December 23, 2004	Table 3-1
Imazapyr	04-43-17-05b	December 18, 2004	Table 3-3
Imidacloprid	05-43-24-03a	December 28, 2005	Table 3-2
Metsulfuron Methyl	04-43-17-01c	December 9, 2004	Table 3-2
Oxyfluorfen	05-43-26-03b	December 22, 2005	Table 3-3
Picloram	03-43-16-01b	June 30, 2003	Table 3-2
Sethoxydim	01-43-01-01c	October 31, 2001	Table 3-3
Sulfometuron Methyl	03-43-17-02c	December 14, 2004	Table 3-1
Tebufenozide	04-43-05-06c	August 8, 2004	Table 3-1
Triclopyr	02-43-13-03b	March 15, 2003	Table 3-7

[a] All documents were prepared under USDA Forest Service BPA: WO-01-3187-0150. Except 2,4-D are available on Forest Service web site, http://www.fs.fed.us/foresthealth/pesticide/risk.shtml. The values for 2,4-D are from the peer review draft. The values used in this report will not change and the 2,4-D final report should be on the Forest Service web site by October, 2006.

Table 2: Chemical Fields Used in GLEAMS and Gleams-Driver		
Parameter	**Value Code**	**Description**
Descriptors		
Description	Desc	This is the fully descriptive name of the chemical. It should indicate the name of the chemical and information on the run – i.e., "Hexazinone for Run of ....". This approach is taken because some of the properties such as soil halftime may differ from site to site. This field is a "Primary Key" in the database supplied with Gleams-Driver. It must be a unique name that is not already in the database.
Chemical name	Name	The common name of the chemical.
GLEAMS Name	PSTNAM	Short name (up to 16 characters) used in GLEAMS files. This will often be the common name, so long as the common name is less than 16 characters.
Chemical Properties		
Foliar halftime	HAFLIF	Foliar halftime in days. Used in GLEAMS.
Foliar washoff fraction	WSHFRC	Fraction of pesticide on the foliage available for washoff by rainfall. Used in GLEAMS.
Koc	KOC	Partitioning coefficient, ratio of the concentration of the pesticide on organic carbon in soil to concentration of the pesticide in water. Used in GLEAMS.
Sediment partition coefficient	SedKd	Partition coefficient for sediment. This is used only in GLEAMS post-processing.
Sediment halftime	SedHT	Halftime in aquatic sediment in days. This should reflect all routes of degradation (photolysis, hydrolysis, volatilization, biodegradation etc.) but should not consider dissipation. Use aerobic or anaerobic data depending on the site and conditions (e.g., depth of soil layer). This is used only in GLEAMS post-processing.
Soil halftime(s)	SOLIF(I)	A pipe (|) delimited set of halftime, one for each soil horizon that is modeled – e.g., 90 | 120 | 180 | 240. These can be entered as distributions. Used in GLEAMS.
Water halftime	WatHT	Halftime in water in days. Can consider routes of degradation – i.e., hydrolysis, photolysis, and biological. Should not consider dissipation. This is used only in GLEAMS post-processing.
Water solubility	H2OSOL	Water solubility in mg/L. Used in GLEAMS.
Modeling Assumptions (all used in GLEAMS)		
Coefficient of transformation	COFTRN	Pesticide concentrations simulated in GLEAMS are mass per volume, or weight per weight (µg/L or µg/kg) and not molar concentrations. Therefore, if significant changes in molecular weight occurs from parent to metabolite or from metabolite to metabolite, the ratio of mass change can be reflected in COFTRN, also (GLEAMS documentation, p. 110). **Default Value = 1**.
Coefficient of uptake	COFUP	Consider uptake by plant (COFUP = 1) or assume no uptake (COFUP = 0). For soluble, low KOC pesticides, uptake can be significant and will reduce amounts potentially leached below the root zone. For pesticides with large KOC, little uptake in the transpiration stream will be simulated because of the reduced concentrations in solution, even with COFUP = 1. **Default Value = 0**.
Number of metabolites	NumMetabs	Number of metabolites that are model in this run. For each metabolite, a full set of chemical records must be in the database. **Default Value = 0**.

Table 3: Information Entered into Chemical Library for Gleams-Driver

Chemical Name	Foliar Halftime (days)	Foliar washoff fraction (unitless)	K_{oc} (mL/g)	K_d for Aquatic Sediment (mL/g)	Aquatic Sediment Halftime (days)	Soil Halftime (days)	Water Halftime (days)	Water solubility (mg/L)
2,4-D, clay	8.8	0.5	61.7	1	231	6.2	45	569
2,4-D, loam	8.8	0.5	61.7	1.1	231	6.2	45	569
2,4-D, sand	8.8	0.5	61.7	0.08	231	6.2	45	569
Chlorsulfuron, clay	30	0.75	40	0.24	154	168	200	27,900
Chlorsulfuron, loam	30	0.75	40	0.18	154	37	200	27,900
Chlorsulfuron, sand	30	0.75	40	0.12	154	47	200	27,900
Clopyralid, clay	2	0.95	0.4	0.0094	1000	14	261	1,000
Clopyralid, loam	2	0.95	3.15	0.02	1000	25	261	1,000
Clopyralid, sand	2	0.95	12.9	0.0935	1000	29	261	1,000
Dicamba, clay	9	0.65	2.4	0.1	58	31	39	6500
Dicamba, loam	9	0.65	13.6	0.16	58	31	39	6500
Dicamba, sand	9	0.65	32.5	0.07	58	31	39	6500
Diflubenzuron, clay	9.3	0.5	8700	261	34	10	5.4	0.926
Diflubenzuron, loam	9.3	0.5	8700	130	34	1.1	5.4	0.926

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Chemical Name	**Foliar Halftime (days)**	**Foliar washoff fraction (unitless)**	**K_{oc} (mL/g)**	**K_d for Aquatic Sediment (mL/g)**	**Aquatic Sediment Halftime (days)**	**Soil Halftime (days)**	**Water Halftime (days)**	**Water solubility (mg/L)**
Diflubenzuron, sand	9.3	0.5	8700	26.1	34	2.1	5.4	0.926
Glyphosate, clay [a]	10	0.5	2000	60	203	30	1000	12000
Glyphosate, loam [a]	10	0.5	2000	30	203	30	1000	12000
Glyphosate, sand [a]	10	0.5	2000	6	203	30	1000	12000
Imazapic, clay	4	0.8	112	4.05	2400	113	30	36000
Imazapic, loam	4	0.8	112	0.6	2400	113	30	36000
Imazapic, sand	4	0.8	112	0.13	2400	113	30	36000
Imazapyr, clay	26	0.9	99.8	4.55	10000 [b]	25	325	13100
Imazapyr, loam	26	0.9	99.8	4.55	10000 [b]	67	325	13100
Imazapyr, sand	26	0.9	99.8	4.55	10000 [b]	180	325	13100
Imidacloprid, clay	10	0.5	779	11.3	27	40	22	610
Imidacloprid, loam	10	0.5	296	3.45	27	40	22	610
Imidacloprid, sand	10	0.5	203	1.18	27	40	22	610
Metsulfuron methyl, clay	30	0.8	35	0.25	140	120	1213	2790

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Chemical Name	**Foliar Halftime (days)**	**Foliar washoff fraction (unitless)**	**K_{oc} (mL/g)**	**K_d for Aquatic Sediment (mL/g)**	**Aquatic Sediment Halftime (days)**	**Soil Halftime (days)**	**Water Halftime (days)**	**Water solubility (mg/L)**
Metsulfuron methyl, loam	30	0.8	35	0.2	140	120	1213	2790
Metsulfuron methyl, sand	30	0.8	35	0.15	140	120	1213	2790
Oxyfluorfen, clay	8	0.4	5585	755	230	870.5	1741	0116
Oxyfluorfen, loam	8	0.4	5585	52	230	870.5	1741	0116
Oxyfluorfen, sand	8	0.4	5585	9.44	230	870.5	1741	0116
Picloram, clay [c]	8	0.6	48	1.44	2000	320	14	200000
Picloram, loam [c]	8	0.6	29	0.43	2000	320	14	200000
Picloram, sand [c]	8	0.6	7	0.021	2000	320	14	200000
Sethoxydim, clay	3	0.7 [d]	100	0.03	190	22	155.2	4700
Sethoxydim, loam	3	0.7 [d]	100	0.84	190	22	155.2	4700
Sethoxydim, sand	3	0.7 [d]	100	0.06	190	22	155.2	4700
Sulfometuron methyl, clay	10	0.65	78	0.15	60	10	300	300
Sulfometuron methyl, loam	10	0.65	78	0.6	60	30	300	300
Sulfometuron methyl, sand	10	0.65	78	1	60	100	300	300

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Chemical Name	Foliar Halftime (days)	Foliar washoff fraction (unitless)	K_{oc} (mL/g)	K_d for Aquatic Sediment (mL/g)	Aquatic Sediment Halftime (days)	Soil Halftime (days)	Water Halftime (days)	Water solubility (mg/L)
Tebufenozide, clay	13.4	0.5	572	7.8	179	100	67	0.83
Tebufenozide, loam	13.4	0.5	572	4.4	179	270	67	0.83
Tebufenozide, sand	13.4	0.5	572	1.7	179	730	67	0.83
Triclopyr, clay	15	0.95	20	0.6	365	46	196	435
Triclopyr, loam	15	0.95	20	0.3	365	46	196	435
Triclopyr, sand	15	0.95	20	0.06	365	46	196	435

[a] The K_{oc} values reported for glyphosate are highly variable. The K_{oc} values listed are very similar to the value of 2100 recommended by USDA/ARD (2005). The K_d values for clay, loam, and sand are based on the equation, $K_d = K_{oc}$ x *oc*, where *oc* is the proportion of organic carbon. The values for *oc* are taken as 0.003 for sand, 0.015 for loam, and 0.03 for clay. See Gleams-Driver documentation.

[b] Stable. The halftime is set to an arbitrarily long halftime.

[c] Substantial increase in soil halftime with soil depth. The value given in table is for 1 to 2 feet below the soil surface.

[d] Taken from Knisel and Davis (2000).

[e] The K_d value for triclopyr is not specified in the risk assessment. The values for clay, loam, and sand are based on the equation, $K_d = K_{oc}$ x *oc*, where *oc* is the proportion of organic carbon. The values for *oc* are taken as 0.003 for sand, 0.015 for loam, and 0.03 for clay. See Gleams-Driver documentation.