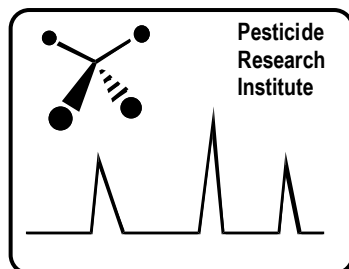


Marin Municipal Water District Herbicide Risk Assessment

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Susan Kegley, PhD
Erin Conlisk, PhD
Marion Moses, MD

Pesticide Research Institute
2768 Shasta Road
Berkeley, CA 94708
E-mail: skegley@pesticideresearch.com
Phone: (510) 759-9397
Fax: (510) 848-5271
Web: www.pesticideresearch.com

Acronyms, Abbreviations and Symbols

| | |
|-------------------|--|
| AQUIRE | US EPA's aquatic ecotoxicity database |
| a.e. | carboxylic acid equivalents |
| a.i. | active ingredient |
| ACGIH | American Conference of Governmental Industrial Hygienists |
| AChE | acetylcholinesterase |
| AHS | Agricultural Health Study |
| AMPA | aminomethylphosphonic acid, degradation product of glyphosate |
| CA ARB | California Air Resources Board |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BCF | bioconcentration factor |
| bw | body weight |
| cm | centimeter |
| DRV | dietary reference value |
| EC ₅₀ | concentration causing 50% inhibition of a process |
| EAD | estimated absorbed dose |
| EC ₁₀₀ | concentration causing complete inhibition of a process |
| Ecotox | US EPA's ecotoxicity database collection |
| EIS | environmental impact statement |
| F | female |
| F ₀ | Parental generation in a multigenerational animal study |
| F ₁ | first filial generation in a multigenerational animal study |
| FFES | Farm Family Exposure Study |
| FIFRA | Federal Insecticide, Fungicide and Rodenticide Act |
| FR | fecundity ratio |
| FS | Forest Service |
| FQPA | Food Quality Protection Act |
| g | gram |
| GLEAMS | Groundwater Loading Effects of Agricultural Management Systems |
| GM | Geometric mean |
| GRAS | generally recognized as safe |
| HQ | hazard quotient |
| IARC | International Agency for Research on Cancer |
| IPA | isopropylamine |
| IRIS | Integrated Risk Information System |
| kg | kilogram |
| K _{oc} | organic carbon partition coefficient |
| K _{ow} | octanol-water partition coefficient |
| K _p | skin permeability coefficient |
| L | liter |
| lb | pound |
| LC ₅₀ | lethal concentration, 50% mortality |
| LD ₅ | lethal dose, 5% mortality |
| LD ₅₀ | lethal dose, 50% mortality |

| | |
|------------------|--|
| LD ₉₅ | lethal dose, 95% mortality |
| LOAEL | lowest-observed-adverse-effect level |
| LOC | level of concern |
| LOD | limit of detection |
| m | meter |
| M | male |
| MCL | maximum contaminant level |
| mg | milligram |
| mg/kg-day | milligrams of agent per kilogram of body weight per day |
| mL | milliliter |
| MRID | master record identification number |
| MS | mass spectrometry |
| MMWD | Marin Municipal Water District |
| MSDS | material safety data sheet |
| MW | molecular weight |
| NCI | National Cancer Institute |
| NHL | non-Hodgkins lymphoma |
| NIH | National Institutes of Health |
| NNG | N-nitrosoglyphosate |
| NOAEL | no observed adverse effect level |
| NOEC | no observed adverse effect concentration |
| NOEL | no observed effect level |
| NPE | nonylphenol polyethoxylate |
| NRC | National Research Council |
| NTP | National Toxicology Program |
| NTD | neural tube defect |
| OFFHS | Ontario Farm Family Health Study |
| OPP | Office of Pesticide Programs |
| OR | odds ratio |
| PAD | Population Adjusted Dose, similar to a reference dose, but often contains an additional uncertainty factor for vulnerable populations. |
| PHED | Pesticide Handler's Exposure Database |
| PHG | Public Health Goal |
| PISP | Pesticide Illness Surveillance Program (CA) |
| pKa | negative logarithm of a chemical's acid dissociation constant |
| POEA | Polyoxyethyleneamine, a surfactant used in Roundup products |
| PPE | Personal protective equipment (e.g., gloves, boots, goggles) |
| ppm | parts per million |
| RBC | red blood cells |
| RED | US EPA reregistration eligibility decision |
| RfD | reference dose |
| RTU | ready to use |
| RR | Relative risk or rate ratio |
| SD | standard deviation |
| SCE | sister chromatid exchange |
| SENSOR | Sentinel Event Notification System of Occupational Risk |

| | |
|----------|---|
| SERA | Syracuse Environmental Research Associates |
| TCP | 3,5,6-trichloro-2-pyridinol, degradation product of triclopyr |
| TMP | 3,5,6-trichloro-2-methoxypyridine, degradation product of triclopyr |
| Terretox | US EPA's terrestrial ecotoxicity database |
| TESS | Toxic Exposure Surveillance System |
| TRV | Toxicity Reference Value |
| UF | uncertainty factor |
| US | United States |
| US EPA | U.S.Environmental Protection Agency |
| USDA | United States Department of Agriculture |
| USGS | United States Geological Survey |
| VMP | Vegetation Management Plan |
| > | greater than |
| ≥ | greater than or equal to |
| < | less than |
| ≤ | less than or equal to |
| = | equal to |
| ≈ | approximately equal to |

Commonly Used Terms and Definitions

| | |
|--------------------------|---|
| Acid equivalent (a.e.) | For a chemical that is an ester or salt of a carboxylic acid, concentrations or weights are often given in acid equivalents, in order to express all concentrations in the consistent unit of the parent carboxylic acid, which is generally the active moiety of a compound. |
| Active ingredient (a.i.) | The individual pesticide chemical that is responsible for the pesticidal activity. Contrast the active ingredient with the acid equivalent and with the pesticide product that may contain additional ingredients. |
| Contaminated | Containing any amount of a chemical residue in a given medium. “Contaminated” does not necessarily equate to hazardous, but indicates only that the compound is present at some level. |
| Conventional herbicide | An herbicide with synthetic active ingredients not approved for use in organic agriculture. |
| Organic herbicide | An herbicide approved for use in organic agriculture with active ingredients comprised of naturally occurring compounds. |
| Pesticide | Any insecticide, herbicide, fungicide, rodenticide, avicide (bird killing), acaricide (mite killing), microbiocide or other compound designed to kill or deter pests. |
| Pesticide product | The mixture of ingredients sold in the marketplace that contains the active ingredient and other ingredients such as surfactants, solvents, preservatives, etc. Products are often referred to as “formulated products” to clarify the distinction between active ingredients and products. |
| Surfactant | A chemical compound added to a pesticide that acts as an emulsifier, enhances absorption and effectiveness of the pesticide, and/or changes the surface tension of a solution as a control for spray drift. |

Chapter 1 — Overview and Executive Summary

1 Table of Contents — Overview and Executive Summary

- 1.1 PURPOSE OF THE REPORT..... 1-3**
- 1.2 SUMMARY OF CONCLUSIONS 1-3**
- 1.3 REPORT OVERVIEW 1-5**
- 1.4 HERBICIDES AND ADJUVANTS UNDER CONSIDERATION 1-5**
 - 1.4.1 HERBICIDES..... 1-5
 - 1.4.2 SURFACTANTS..... 1-6
 - 1.4.3 MARKER DYES AND COLORANT 1-7
- 1.5 ASSESSING THE FATE OF CHEMICALS IN THE ENVIRONMENT 1-7**
- 1.6 RISK ASSESSMENT PROCESS 1-9**
 - 1.6.1 HAZARD ASSESSMENT..... 1-9
 - 1.6.2 EXPOSURE ASSESSMENT 1-10
 - 1.6.3 RISK CHARACTERIZATION..... 1-10
- 1.7 RISK ASSESSMENT RESULTS 1-11**

1.1 Purpose of the Report

This report focuses on the main concerns of the southern Marin County community and the MMWD decision-makers – what are the potential health effects of herbicides so a decision can be made whether herbicides should be considered as part of an integrated pest management program that would be incorporated into the Vegetation Management Plan. The risks from exposing humans and other organisms to various herbicides and additives to the herbicides are assessed and compared. The assessment and comparison determines the potential health risks of using a specified and limited range of possible methods of applying herbicides along with other protective restrictions on transport and use of these herbicides.

The risk assessment provides information on the inherent hazards of the chemicals, possible routes of exposure for humans and wildlife, and an estimated magnitude of exposure from which the likelihood of adverse effects and consequent risk may be estimated. The consulting team and MMWD will assess these risk assessment data along with risk data from using techniques and tools that do not involve the use of herbicides, risks from wildfire, and risks to the biological diversity of the watersheds when developing alternative approaches to managing vegetation on the watersheds. This comparison of alternative approaches will be presented in subsequent reports prepared by the consulting team. This report focuses solely on the health impacts on humans and other organisms if herbicides were used.

1.2 Summary of Conclusions

Three conventional herbicides containing synthetic active ingredients: Aquamaster (active ingredient is glyphosate); Transline (active ingredient is clopyralid), and Garlon 4 Ultra (active ingredient is triclopyr); two organic herbicides with active ingredients derived from essential oils or naturally occurring organic acids: Matran (active ingredient is eugenol from clove oil) and Scythe (active ingredient is pelargonic acid), two surfactants (Sylgard 309 and Competitor) and one dye (Blazon) that are being considered for possible inclusion into the integrated pest management (IPM) program were evaluated.

The herbicides and additives being considered for use are all materials that are potentially toxic to humans and other life. They can all cause illness or death if people or other organisms are exposed to hazardous amounts of the materials for a sufficient period of time. There is no such thing as a "safe" herbicide; all herbicides have the potential to cause adverse health effects at some level of exposure.

There are many data gaps and uncertainties involved in assessing the risk of these chemicals and it should be recognized that the conclusions drawn in the risk assessment are only as good as the available toxicity studies. This report contains a full and detailed accounting of the uncertainties and data gaps. Specifically, there are uncertainties about the hazard of all these chemicals as regards their ability to disrupt the endocrine system. In addition, there is less known about clopyralid and triclopyr as compared to glyphosate, and little is known about the surfactants or the dye. This report uses the best available scientific data account for these uncertainties.

To summarize the findings for the five herbicides that were assessed:

- Triclopyr poses the highest risk to workers, the general public and most aquatic and terrestrial wildlife. The primary factor contributing to high human risks is dermal exposure from handling the chemical during applications or from vegetation contact.

- Glyphosate poses the least risk to workers and the general public, moderate risks to terrestrial wildlife from direct sprays, and low risks to aquatic species.
- Clopyralid poses the least risk to terrestrial and aquatic wildlife. The primary factor contributing to the lower risk for clopyralid is the lower application rates used for this herbicide—approximately 0.14 pounds per acre compared to 2.0 pounds per acre for glyphosate and triclopyr.
- Clove oil/eugenol poses high worker risks for accidental exposure scenarios and accidental spills into water. The primary factor contributing to these risks is dermal exposure. Direct sprays and consumption of contaminated food poses some risk to terrestrial animals.
- Pelargonic acid poses low risks to workers, the general public and aquatic and terrestrial wildlife.
- Co-application of herbicides with the “inerts” they contain and/or the surfactants Competitor and Sylgard 309 may change the risks associated with exposure to the herbicide active ingredients; available data indicate that these differences would small, but the data set is incomplete.
- There is some potential for winter storm water runoff from treated areas to carry herbicide residue into MMWD reservoirs if many acres are treated in a single year or if applications are made close to reservoirs. Runoff is unlikely to occur at all with the less toxic herbicides Scythe (pelargonic acid) and Matran (clove oil) because they are rapidly degraded in the environment and will not persist into the rainy season. Of the three conventional herbicides, runoff is less likely with glyphosate because it binds strongly to soils. Clopyralid runoff is also anticipated to be low because the application rates are low. Triclopyr is the herbicide of greatest concern for runoff into water bodies, both because of its high mobility and high toxicity. Use of no-spray buffer zones around water bodies and placing limits on the total acreage treated in a single year would significantly reduce the likelihood of herbicide runoff into water bodies.
- A highly improbable worst-case estimate of herbicide concentrations in water after winter stormwater runoff indicates that up to 2,600 acres in the Phoenix Lake watershed could be treated with glyphosate without exceeding 10% of the human Reference Dose (RfD, the dose below which no adverse human health effects are anticipated by EPA) from drinking water exposure. Only 80 acres in the watershed could be treated with triclopyr, and 4,870 acres could be treated with clopyralid before exceeding 10% of the human RfD.

This estimate assumes that 100% of the applied herbicide runs off into Phoenix Lake several months after the application. Field experiments show that the fraction of herbicide lost in runoff is typically closer to 1–10%, so this calculation overestimates the potential for herbicide runoff by about 10–100 times. Thus, a more realistic statement would be that up to 2,600 acres in the Phoenix Lake watershed could be treated with glyphosate without exceeding one-tenth of a percent to one percent (0.1–1%) of the RfD for drinking water exposure. Concentrations in the Bon Tempe Reservoir (this reservoir is actually used as part of the MMWD water supply, while Phoenix Lake is only used in drought years) would be lower by an additional factor of 10 because Bon Tempe is 10 times larger than Phoenix Lake and any runoff would be diluted further.

- Even with the highly improbable 100% runoff scenario, our calculations indicate that treatment of the entire acreage of invasive weeds with glyphosate or clopyralid would not exceed the EPA Reference Dose (RfD) for human exposures to glyphosate or clopyralid through drinking water. Nevertheless, it is important to recognize the uncertainties and limitations of the hazard assessment process through which the RfDs are set, particularly for herbicides or adjuvants with minimal data. Because of these uncertainties, if the MMWD Board does decide to allow the use of herbicides, we recommend that limitations on their use be institutionalized into MMWD policy. Buffer zones around water bodies in which only manual weed-removal techniques can be used should be implemented. Triclopyr use should be limited to spot treatments only, and the more readily degradable herbicides like Scythe (pelargonic acid) and Matran (clove oil) should be used in areas upslope of water bodies. Limits should be set on the maximum number of acres that can be treated with glyphosate and clopyralid in a single year, and MMWD Board approval should be required for any requests to change these limits.

1.3 Report Overview

Following this Introduction and Summary Chapter, Chapter Two provides the essential background information necessary for interpreting the different parts of the risk assessment and is divided into the following sections:

- Human health impacts of chemical exposure
- Effects of chemical exposure on animals and other organisms
- Pathways by which chemicals are transported and degrade in the environment
- Development of application guidelines to minimize risks and assessment of exposure pathways and anticipated exposures
- Risk characterization, comparing plausible levels of exposure with levels of concern
- An assessment of the USFS approach

Chapters 3 through 8 provide a summary of available information on the above-mentioned topics for each active ingredient, as well as information about the specific products selected for potential use in the MMWD watershed. Chapter 9 provides recommendations for minimizing herbicide use and mitigating potential adverse effects.

The summary of human health and ecological impacts presented in this document are not, and are not intended to be, comprehensive summaries of all of the available information, and these risk assessments do not cite all of the available literature. However, the studies most relevant to the MMWD watershed are discussed in detail, and summary data are provided in the Appendices for the remaining studies. This document focuses on the information necessary to assess the risks of use of a few specific herbicide products in the MMWD watershed.

1.4 Herbicides and Adjuvants Under Consideration

After a preliminary review of risks by PRI and the other members of the consulting team, three conventional herbicides, two organic herbicides, two surfactants, and one dye were selected for the risk assessment. These chemicals are described below.

1.4.1 Herbicides

Aquamaster (the active ingredient [a.i.] is glyphosate) is formulated as a four pound a.i./gallon isopropyl amine salt without any surfactant. Aquamaster is a broad-spectrum, non-selective, systemic, post-

emergent herbicide used to control annual and perennial plants, including grasses, sedges, broad-leaved weeds, and woody plants. It has no pre-emergent activity. If included in MMWD's IPM tool box, Aquamaster would be prescribed for a wide variety of weeds and applied as a 1–3 percent solution for low-volume, spot treatment delivery not to exceed two quarts of formulated product per acre. Broadcast applications would be made at a two quart per acre rate.

Garlon 4 Ultra (the active ingredient is triclopyr ester) is a broadleaf selective, post-emergent, terrestrial herbicide used for control of most annual and perennial broadleaf weeds and brush in crop and non-crop sites. Garlon 4 Ultra is an auxin-mimicking herbicide, specifically, Indole-3-acetic acid (IAA), a plant hormone that regulates cell division and expansion. It is transported through the phloem and xylem of the plant and accumulates in the meristematic tissue of the shoots of susceptible plants, accelerating growth and resulting in ruptured cell walls. Triclopyr is rapidly metabolized in the plant with 85% of a dose being metabolized within three days. If included in the final IPM, Garlon 4 Ultra would be prescribed for the control of brush and broadleaf weeds. A 0.5% solution of Garlon 4 Ultra would be spot applied. Prescribed use rates would not exceed 40 ounces of formulated product per acre.

Transline (the active ingredient is clopyralid) is a selective, post-emergent herbicide. Transline is also an auxin-mimicking herbicide. It stimulates rapid cell elongation which results in a ruptured cell wall and the destruction of the cell wall. Transline is rapidly absorbed with 97% of a dose being absorbed within 24 hours. Transline translocates readily within the plant, with 50% of the dose being translocated out of the leaf within 24 hours. If included in the final IPM, Transline would be used primarily for the control of yellow star thistle. It would be prescribed at a rate of four ounces per acre of formulated product.

Scythe (the active ingredient is pelargonic acid) is formulated as a 4.2 pound a.i./gallon of pelargonic acid with a fatty acid component. Scythe is a broad-spectrum, non-selective contact, post-emergent herbicide used to burn down annual and perennial plants including grasses, sedges, broad-leaved weeds, woody plants, moss, lichens, and algae. Scythe causes rapid cell death by electrolyte loss. If included in the final IPM, Scythe would be applied at a concentration of 3% to 5% for non-selective high volume foliar applications. It would be used for the control of herbaceous grass and broadleaf weeds.

Matran (the active ingredient is clove oil) is a non-selective, post-emergent, contact herbicide used for the removal of annual and perennial vegetation. Matran is 50% clove oil and 50% "other" (listed as winter green oil, butyl lactate and lecithin). Cell disruption via loss of membrane integrity appears to be the primary mechanism of action in plants. If included in the final IPM, Matran would be prescribed at 3% to 8% for the control of herbaceous vegetation. It would be applied as a high volume foliar treatment.

Acetic acid is available in many formulations. Common formulations available for weed control include a 25% concentrate and a 6.25% "Ready to Use" (RTU). Acetic acid is non-selective and used for the control of herbaceous grass and broadleaf weeds. Acetic acid, like clove oil and pelargonic acid, acts to rapidly disrupt cell membrane integrity. Only vegetation being treated is effected. If included in the final IPM, acetic acid would be used for the control of annual herbaceous weeds and broom seedlings. It would be applied at a concentration of 15% as a high volume foliar application.

1.4.2 Surfactants

Surface active agents, or surfactants, are additives used to enhance the activity of foliar applied herbicides. Many commercial herbicides already contain internal surfactants in the formulation. While the

label might not require adding a surfactant, the addition of one will improve herbicidal activity. Herbicides formulated without surfactants have little to no activity without the addition of a surfactant. There are several classes of surfactant. If herbicides are included in the final IPM, the plan would utilize two surfactants: a modified seed oil (MSO) for both foliar and basal applications and an organo-silicone surfactant for foliar applications.

Competitor is in a class of surfactants known as modified seed oils (MSOs). Competitor reduces the surface tension of water on the surface of the leaf, breaks down the waxy surface of the leaf, and aids in moisture retention on the leaf surface. These combined characteristics work to enhance the uptake of the herbicide. Competitor would be used as a surfactant in low volume foliar applications and as a diluent for basal and cut stump applications. As a surfactant, Competitor would be used at concentrations of 1% to 3%. As a diluent, Competitor would comprise 75% to 80% of a mixture with Garlon4 Ultra for basal and cut stump treatments

Sylgard 309 is a silicone-based surfactant known as an organo-silicone surfactant. These types of surfactants are sometimes referred to as a "super wetter" because of their superior ability to reduce surface tension. Sylgard 309 reduces the surface tension of water allowing the herbicide mixture to spread evenly and thoroughly across the leaf surface. Sylgard 309 would be prescribed as a surfactant for use in foliar applications. It would be prescribed at a concentration of 0.06 to 0.12% by volume or 8 to 12 ounces per 100 gallons of water.

1.4.3 Marker Dyes and Colorant

Dyes are used to show where an herbicide application has been made to avoid retreatment and ensure that all target plants are treated. They are beneficial as they help prevent skips, overlap and incidental exposure during reentry. They also help determine potential off-target injury. One marker dye is proposed for possible use in the MMWD vegetation management project.

Blazon is a marker dye that will be used with all foliar applications and with some cut stump applications. Blazon is a water-soluble dye used as a pattern indicator. The primary function is to prevent overlap or skip.

1.5 Assessing the Fate of Chemicals in the Environment

Once released into the environment, herbicides, surfactants and dyes are subject to a number of processes that transport them away from the application site or degrade them into smaller molecules. Specifically, these chemicals are transported off-site by water and air and degraded or inactivated by microbial and chemical reactions. Understanding these processes is critical for the assessment of questions of actual risk of exposure, such as 1) are reservoirs or streams likely to be contaminated by herbicide use; 2) are MMWD visitors likely to be exposed to herbicides by picnicking near an application site; and 3) will wildlife be exposed to herbicides from eating contaminated vegetation?

Herbicides can be transported away from the site where they were applied by water, air and soil movement. They can also be degraded by chemical or biological processes. Water transports herbicides off-site by leaching of dissolved herbicides through soil to groundwater, surface runoff of dissolved herbicides, and by surface runoff of soil-bound herbicides.

- **Leaching to groundwater:** Herbicides can dissolve in water and percolate through the soil, sometimes traveling as far as the water table. Herbicides most prone to this process have high water solubility, low ability to adsorb to soils, and long half-lives. Even herbicides that do not have these characteristics may still contaminate groundwater by traveling through rocky or fractured soils that provide a direct pathway to groundwater. High pesticide application rates and heavy rains will enhance transport to groundwater. Once in groundwater, herbicides are not exposed to sunlight and microbes, and typically degrade much more slowly than in soils or surface waters.
- **Surface runoff of dissolved and adsorbed herbicides:** During heavy rains or high irrigation flows, herbicides can be dissolved and transported in runoff water. If the runoff event has sufficient volume and energy to carry sediment particles, even herbicides that are not particularly water soluble can still be transported in the flow adsorbed to sediment and deposited in a new location.

Herbicides may also be transported off-site through the air, by spray drift during the application and/or volatilization drift that occurs both during and after the application.

- **Spray drift:** Spray drift occurs during and for a few hours after a pesticide spray application, as fine droplets or dust particles created by spray equipment are carried off-site by prevailing winds. Spray drift of herbicides can affect non-target plants, animals, and humans near an application site at the time of the application. Both dermal and inhalation exposure are possible.
- **Volatilization drift:** Volatilization drift occurs primarily with herbicides with moderate to high vapor pressures. Higher vapor pressure and temperature lead to greater volatilization and subsequent wind transport.
- **Wind erosion:** Transport of herbicides on dust particles can occur through wind erosion of dry and exposed soils. Deposition of herbicide-contaminated soils can damage non-target plants and contaminate waterways far from the original application site.

Most herbicides are degraded in the environment by microbial activity, photolysis, hydrolysis and other chemical reactions.

- **Microbial activity:** Soil microbes—bacteria and fungi—metabolize most chemicals, using them as a source of organic carbon. Some microbes have been observed to adapt to applications of herbicides by increasing the rate at which they metabolize that particular chemical.
- **Photolysis:** Sunlight, particularly in combination with oxygen in the air, can break chemical bonds and degrade herbicides in air, water and soil.
- **Hydrolysis and other chemical reactions:** Herbicides can also be degraded through reaction with water (hydrolysis) or other substances in the environment. Some chemical reactions do not necessarily degrade the chemical structure, but may result in the formation of a new molecule or complex that changes the reactivity of the parent pesticide. An example of this is the complexation of glyphosate to clay soils, which decreases the bioavailability and the toxicity of this herbicide.

1.6 Risk Assessment Process

Risk assessment is defined as the qualitative and quantitative evaluation of the risk posed to human health and/or the environment by the actual or potential presence and/or use of specific pollutants. **Risk** is a measure of the probability that damage to life, health, and/or the environment will occur as a result of a given hazard. The assessment of risk requires knowledge of the inherent toxicity of chemical being assessed (the **hazard**), the amount and time of **exposure**, and the **probability** of that exposure occurring.

1.6.1 Hazard Assessment

The **hazard** data described in this report provide information on the types of adverse effects that the herbicide may cause at the various doses (i.e., how much exposure per unit of body weight) evaluated in animal tests. Acute effects are short-term effects that occur close in time to the exposure—within a few minutes to 24 hours. Chronic effects such as cancer or sterility occur after longer exposure times, a few weeks to a lifetime. Local (topical) effects are those that affect only the surfaces contacted that come in contact with the pesticide, such as the eyes, skin, nose and throat. Systemic poisoning occurs when a toxic chemical enters the blood stream and is carried throughout the body, adversely affecting internal organs and body systems.

There are uncertainties in hazard assessment, including translation of results in laboratory animals to humans; failure of study designs to adequately measure all toxic effects, especially in developing organisms; misinterpretation of study results; and failure to assess the effects of exposure to multiple chemicals that may be present in a product. These uncertainties are discussed in detail in Section 2.4.9.A.

The U.S. Environmental Protection Agency (EPA) classifies herbicides into four categories based on **acute health effects** (toxicity) in animals: Toxicity Class I (called Tox I) are the most toxic, Tox II are moderately toxic, Tox III are of low acute toxicity and Tox IV are the least acutely toxic. The EPA also estimates a lowest **no observable adverse effect level (NOAEL)**; this is the level where the bulk of the scientific research has shown that exposure at that level would have no adverse health effects. The daily oral exposure to humans that is not expected to cause non-cancer adverse effects during a lifetime is known as the **reference dose (RfD)**.

Chronic health effects are long-term effects that include cancer, reproductive problems, impaired development and neurological disease, among others. The EPA assesses the risk of human chronic health effects of herbicides based on animal data submitted by the pesticide manufacturer to register a product. There are no human data available for most herbicides, so the effects are based on studies done on animals and epidemiological studies that evaluate the links between exposure and incidence of disease. Cancer cases related to pesticide exposure typically develop years after exposure and can result from legal use of herbicides that does not cause any apparent acute illness. It is uncommon for a single pesticide to be directly associated with a specific cancer, because of exposure to multiple herbicides, and changing patterns of use over time. Herbicides might act synergistically, and cumulative exposures over time are difficult to document. If the type of cancer is rare or infrequent, or the number of people in an exposed group is small, an association with pesticide exposure may not be found, even if one exists.

Chemically-induced endocrine disruption is a new area of research that current toxicology tests do not address. The endocrine system is composed of glands that secrete hormones directly into the blood system, including the ovaries and testes, the thyroid, parathyroid, adrenals, pituitary, and pancreas. Small

changes in hormone levels are known to affect reproduction, neurological development, sexual development, metabolic processes, and mood, and may have other effects. Hormones play a crucial role in guiding normal cell differentiation in early life forms, and exposure to endocrine disrupting substances in the egg or in the womb can alter the normal process of development. Mature animals can also be affected, but it is the developing organism that is especially vulnerable. Exposure at this sensitive time may cause effects that are not evident until later in life, such as adverse effects on learning ability, behavior, reproduction and increased susceptibility to cancer and other diseases. The toxicologists' mantra of "The dose makes the poison" does not necessarily hold true in the domain of endocrine effects. Endocrine-disrupting substances have effects at very low, potentially environmentally relevant, doses far below those used in typical toxicology studies. These effects often disappear at higher doses that may trigger an organism's chemical detoxification mechanisms and/or inhibition pathways. Unfortunately, to date little testing has been done specifically for endocrine disrupting effects.

There is no evidence suggesting that any of the pesticide active ingredients, identified "inert" ingredients, or surfactants being considered for use by MMWD are endocrine disruptors at low doses in humans or animals. However, some of the pesticide products contain unidentified "inert" ingredients that have the potential to be endocrine disruptors. In addition, no definitive testing has been done to confirm the endocrine-disrupting status of any of the pesticide active ingredients, surfactants, or mixtures of these ingredients.

1.6.2 Exposure Assessment

Exposure assessment involves estimation of exposures through all available routes, including drinking water, skin (dermal) contact, inhalation, and ingestion of contaminated food sources. A number of computer models have been developed to facilitate this type of analysis. The exposure analysis is divided into four broad categories: workers, the general public, terrestrial animals, and aquatic organisms. Hazard quotients above one suggest that a species or taxa is likely to encounter environmental concentrations/doses that may pose a risk to individuals of a species.

Water contamination estimates are developed for several acute spill scenarios, peak runoff, and long-term runoff that might result in exposure through drinking water. These concentration estimates are used to estimate exposures from consuming contaminated water for humans, terrestrial and aquatic animals, and aquatic plants. Aquatic exposure scenarios include both short-term accidental and long-term runoff from treated sites (in milligrams [mg] of the chemical per liter of water per pound applied per acre).

Human exposure estimates are developed for both workers and the general public. Worker exposure estimates consider both everyday and accidental exposures, where exposure rates are expressed in units of mg of absorbed dose per kilogram of body weight per pound of chemical handled. The exposure assumptions were derived using proposed application rates, the physical properties of the herbicides, and observational exposure data for workers mixing, loading, or applying herbicides.

1.6.3 Risk Characterization

Risk is a measure of the probability that adverse effects will occur given a particular exposure scenario for a particular chemical. High toxicity alone does not necessarily equal high risk. If there are few routes of exposure or if organisms are only exposed to very small quantities of the chemical, risk is generally anticipated to be low. Exceptions to this "dose-makes-the-poison" paradigm are the low-dose effects observed from exposures to endocrine-disrupting chemicals. Endocrine disruption may occur at doses

below those known to cause the toxicity that is typically evaluated in high-dose animal studies. Endocrine-disrupting chemicals may be more toxic at very low doses than at low to moderate doses. Although some information is available in the peer-reviewed literature, EPA is only now beginning a large-scale endocrine disruptor screening program with validated assays.

To evaluate risk, *exposure estimates* are compared to a standardized reference value defined as the *toxicity reference value (TRV)* to obtain a *hazard quotient* (which is the ratio of the estimated exposure to the TRV). For humans, the TRV is defined as being the equivalent to US EPA's "*reference dose*" (**RfD**) (i.e., the level of exposure below which no adverse effects are anticipated). Thus, if the exposure has the potential to cause a known adverse health effect, then the hazard quotient would be greater than 1.0. Hazard quotients above one indicate that exposure exceeds the level of concern, and humans or wildlife may be at risk of adverse effects. These scenarios are flagged as potentially problematic and recommendations are made for avoiding them. Hazard quotients between 0.1 and 1.0 suggest that there may be particularly sensitive individuals or species that may be affected. Hazard quotients below 0.1 indicate low levels of risk for the effects that have been studied and are represented by the TRVs. In this report, hazard quotients (HQs) less than one are reported as a percent of the TRV; HQs greater than one are reported as a multiplier of the TRV, e.g. "the HQ was 2.4 times the TRV," or it was 2.4 times greater than the level where adverse health effects are possible.

Risk assessments can only be conducted for chemicals for which toxicity data and physical properties are available. For the MMWD project, sufficient data were not available to conduct a risk assessment for the two surfactants—Competitor and Sylgard—and Blazon dye.

1.7 Risk Assessment Results

When considering the potential impacts of herbicide use in the MMWD watershed, five basic questions were evaluated, specifically:

What are the levels of concern for each herbicide for humans and wildlife? Based on published toxicological reports, the report identifies what levels of exposure are harmful to humans and other species as well as what exposure thresholds are below the level where no adverse effects are anticipated. Epidemiological studies (where available) are used to provide a population-based view of the links between herbicide exposures and disease in humans. This report summarizes the available studies as well as highlighting data gaps (i.e., risks and hazards that have not been sufficiently studied to conclusively summarize impacts).

Table 1-1 provides the reference doses (RfDs) and toxicity reference values (TRVs) used in the analysis for the different herbicides. For example, the reference dose for glyphosate is 2 milligrams of glyphosate per kilogram (mg/kg) of body weight per day. This means that no adverse effects would be anticipated if a person were exposed to a dose of glyphosate up to 2 mg/kg per day. Lower values for the RfDs or TRVs mean that the chemical is more toxic, and adverse effects occur at lower doses. For plants, TRVs are expressed as an application rate in pounds per acre at which vegetative growth (vegetative vigor) or seed emergence is not inhibited. For aquatic species, TRVs are expressed as concentrations in water in milligrams per liter (mg/L), below which no adverse effects are anticipated. For some chemicals, certain aquatic species are particularly sensitive and others particularly tolerant to chemical exposures, and different TRVs are used for these two groups.

Table 1-1: Comparison of RfDs and TRVs for Five Herbicide Active Ingredients

| Taxa and Exposure Type | Glyphosate Dose | Triclopyr BEE Dose | Clopyralid MEA Dose | Clove Oil/Eugenol Dose | Pelargonic Acid Dose* |
|---------------------------------|-----------------|---|---------------------|------------------------|-----------------------|
| Humans | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) |
| acute RfD | 2 | 1.0 (male) 0.05 (female) | 0.75 | 2.5 | 20 |
| chronic RfD | 2 | 0.05 (male) 0.012 (female) | 0.15 | 2.5 | 20 |
| Mammals | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) |
| acute TRV | 175 | 100 | 75 | 250 | >1,000 |
| chronic TRV | 175 | 5 | 15 | 250 | >1,000 |
| Birds | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) |
| acute TRV | 562 | 65 | 77 | NA | 333 |
| chronic TRV | 100 | 10 | 15 | NA | 333 |
| Honeybees | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) |
| honeybees, chronic TRV | 540 | 179 | 1,075 | 5,000 | >45 |
| Plants | (lb/acre) | (lb/acre) | (lb/acre) | (lb/acre) | (lb/acre) |
| vegetative vigor TRV, tolerant | 0.56 | 0.0039 | 0.5 | NA | 2.7 L/ha |
| vegetative vigor TRV, sensitive | 0.035 | --- | 0.0005 | NA | NA |
| seed emergence, TRV tolerant | 4.5 | 0.003 | 0.5 | NA | NA |
| seed emergence, TRV sensitive | --- | --- | 0.025 | NA | NA |
| Fish | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) |
| tolerant fish, acute TRV, | 25.7 | 0.013 | 82 (MEA) | 0.45 | 0.46 |
| tolerant fish, chronic TRV, | 25.7 | 0.075 | 23 (MEA) | 0.45 | 0.46 |
| sensitive fish, acute TRV, | 2.57 | --- | 5 (acid) | --- | --- |
| sensitive fish, chronic TRV, | 2.57 | --- | 5 (acid) | --- | --- |
| Amphibians | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) |
| acute TRV | 6.5 | 6.7 | NA | NA | NA |
| chronic TRV | 1.8 | 1.2 | NA | NA | NA |
| Aquatic Invertebrates | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) |
| acute TRV | 130 | 0.1 | 23 | 22 | 3.3 |
| chronic TRV | 50 | 0.1 | 23 | 22 | 0.03 |
| Aquatic Plants | (mg/L) | (mg/L) | (mg/L) | (mg/L) | (mg/L) |
| tolerant algae TRV | 3 | 0.07 | 449 | NA | 30 |
| sensitive algae TRV | --- | --- | 6.9 | NA | --- |
| macrophyte TRV | 3 | 0.07 | 0.1 | NA | --- |

RfD = Reference Dose, a dose for humans below which no adverse effects are anticipated; TRV = Toxicity Reference Value, a dose or exposure below which no adverse effects on terrestrial and aquatic wildlife are anticipated. BEE = butoxyethyl ester; MEA = monoethanolamine salt; acid = triclopyr carboxylic acid; NA = not available. **Bold** values highlight the most toxic pesticide for a particular taxa group.

* Since pelargonic acid occurs naturally in foods and is a part of the typical human diet, a Dietary Reference Value (DRV) was developed that describes the amount of pelargonic acid a person might reasonably be expected to consume in a typical daily diet, and was used in place of the RfD for humans.

The RfDs and TRVs in Table 1-1 are given for both acute and chronic exposure times, with the acute RfDs for exposures lasting a few hours to 24 hours and the chronic RfDs representing exposure over a longer time period—a few months to a lifetime. Chronic RfDs are generally lower than acute RfDs because an organism is more vulnerable to adverse effects if exposure continues over a longer period of time. Chapters 3 through 7 provide detailed analyses of the studies on which these reference values are based.

In general, triclopyr and clopyralid have lower human RfDs and mammalian TRVs (i.e., less exposure is needed to cause adverse health effects) than the other herbicides, suggesting that these chemicals are inherently more toxic to mammals. Triclopyr is particularly toxic to pregnant animals, causing severe birth defects in the fetus if the mother is exposed during pregnancy. As a result, for the acute triclopyr RfD for women of childbearing age is 20 times lower than the RfD for men or children. The least toxic herbicides to humans are pelargonic acid, clove oil and glyphosate. Triclopyr and clopyralid are an order of magnitude more toxic to birds than the other herbicides, and triclopyr is the most toxic of the five herbicides to bees. Glyphosate is the least toxic to birds, and clove oil is the least toxic to bees.

Triclopyr, clove oil and pelargonic acid are more toxic to fish than clopyralid and glyphosate. Aquatic invertebrates are most sensitive to triclopyr and clove oil and quite tolerant of glyphosate. The data set is not complete for amphibians, aquatic invertebrates or aquatic plants.

How definitive are the toxicological study results? A risk assessment does not provide a precise measure of risk, and even the most thorough risk assessments contain unverified assumptions and data gaps. Risk assessments are useful in highlighting knowledge gaps that require additional studies, trials, or monitoring programs, but do not provide information about risks associated with chemicals for which no toxicity data exist. Results and study parameters often vary from study to study, and multiple studies are necessary to determine where the weight of the evidence lies. Outlier results (i.e., results that are not consistent with the bulk of the studies) may still be important, since most studies work with small numbers of test subjects and may not have the statistical power to reveal infrequent effects. The herbicide risk assessments in this report are based on the available data in the scientific literature and in government reports on the chemicals. The risk assessment process also clearly identifies hazards and risks that are not clearly understood and/or where there are data gaps.

In evaluating toxicological studies, it is important to note that this work is conducted by several different parties, including herbicide manufacturers, consultants and academic scientists hired by herbicide manufacturers, academic scientists funded by government or foundation grants, or government researchers. Where this information is available, the source of the work is included. While US EPA has developed study guidelines for manufacturer-conducted tests used in the pesticide registration process, complete study details are typically not available—only US EPA or USFS summaries of the results are publicly available. Because these studies are only rarely published in the peer-reviewed literature, it is often difficult to confirm their scientific relevance to actual exposure scenarios. See Section 2.4.11 in Chapter 2 for a more detailed discussion of the uncertainties associated with the risk assessments.

What is the probability that herbicide applications might contaminate drinking water reservoirs in amounts exceeding levels of concern? Herbicides do not always stay where they are applied and can move off-site through runoff, leaching through soils, and spray drift. Because some watershed lands drain

to reservoirs that are used to supply water to southern Marin County, careful attention is given to assessing the potential for off-site movement of herbicides to surface and ground water.

If MMWD adheres to the application guidelines (see Section 2.4.1A for a listing of these guidelines), the probability of an accidental spill occurring can be reduced to Highly Improbable by keeping large quantities of herbicides away from the drinking water reservoirs. Peak runoff is also reduced to Highly Improbable if the June 1–September 15th application window is observed and appropriate “no-spray” buffer zones adhered to. The long-term runoff scenario is "probable," and much of the risk assessment for drinking water is focused on this route of water contamination. Two methods were used to assess this risk.

The USFS-derived water contamination rates were used to calculate anticipated concentrations of glyphosate, triclopyr and clopyralid in water after long-term runoff. Contamination by long-term runoff is not anticipated for clove oil and pelargonic acid because they both degrade rapidly enough that little of the applied herbicide would remain to contaminate runoff. To obtain more accurate estimates for the conventional herbicides, the USFS water contamination rates were adjusted for herbicide degradation during the time between the application and the occurrence of a heavy rainstorm with sufficient volume to cause overland runoff of storm water. The results indicate that none of the hazard quotients for human or terrestrial wildlife water consumption are greater than 5.2% of the respective RfD for runoff into the smallest continuously utilized reservoir (Bon Tempe). The hazard quotient for glyphosate is 0.0062% of the RfD, for triclopyr, 5.2% of the RfD, and for clopyralid, 0.038% of the RfD (see Tables 1-3 and 1-4). This means, for example, that the predicted exposure to glyphosate from runoff to a reservoir is less than one hundredth of one percent of the exposure level deemed acceptable by EPA. Unfortunately, the USFS method does not account for the number of acres treated and the size of the receiving water body, both important parameters that ultimately determine herbicide concentrations after long-term runoff.

The second method used in this report provides a means to evaluate herbicide concentrations in water based on the number of acres treated in a particular watershed and assuming some fraction of the applied herbicide runs off into a small reservoir. The calculation specifically evaluated the amount of herbicide that could be used (and corresponding number of acres that could be treated) in the Phoenix Lake watershed. Phoenix Lake is not used as part of the MMWD water supply except in drought years, but the watershed provides a worst-case scenario because of the relatively small volume of the lake and the large amount of broom in the watershed.

Scenarios for 100% ("Highly Improbable") and 5% ("Possible") runoff of applied herbicide were evaluated. The volume of Phoenix Lake was used to calculate the anticipated concentrations of herbicides in the water for these scenarios for hazard quotients of 0.1, 0.5 and 1.0. The result is an estimate of the maximum volume of pesticide products that could be applied in the Phoenix Lake watershed (or maximum acres treated) without exceeding hazard quotients of 0.1, 0.5 and 1.0. The results for a hazard quotient of 0.1 for runoff into a well-mixed water body characteristic of winter storm conditions are described in Table 1-5. Chapters 3 through 5 provide more detail on this calculation and the estimates of exposure for the three conventional herbicides glyphosate, triclopyr and clopyralid.

Table 1-5: Maximum Volume of Three Herbicides That Can Be Applied in Phoenix Lake Watershed Without Exceeding a Hazard Quotient of 0.1 for Long-Term Runoff

| Scenario | Volume of Product Applied (gal) | Maximum Area Treated (acres) |
|--|---------------------------------|------------------------------|
| HQ = 0.1, Aquamaster (glyphosate, applied at 2 lbs/acre) | | |
| 100% runoff, degradation for 60 days | 1,308 | 2,616 |
| 5% runoff, degradation for 60 days | 26,167 | 52,334 |
| HQ = 0.1, Garlon 4 Ultra (triclopyr, applied at 2 lbs/acre) | | |
| 100% runoff, degradation for 60 days | 40 | 80 |
| 5% runoff, degradation for 60 days | 791 | 1,582 |
| HQ = 0.1, Transline (clopyralid, applied at 0.14 lbs/acre) | | |
| 100% runoff, degradation for 60 days | 69 | 4,872 |
| 5% runoff, degradation for 60 days | 1,384 | 97,916 |

To summarize the findings for the worst-case scenario (i.e., 100% of the applied material in the watershed runs off to Phoenix Lake), in order to exceed the 0.1 hazard quotient (this is 10% of the exposure deemed acceptable by EPA), MMWD would have to apply 1,308 gallons of Aquamaster in the previous dry season to 2,616 acres. This substantially exceeds the amount of glyphosate MMWD would ever apply, given that the number of acres with invasive weed species is on the order of 200–300 and not all of the acreage would be treated in a single season. Only 80 acres in the watershed could be treated with triclopyr, and 4,870 acres could be treated with clopyralid before exceeding 10% of the human RfD.

Field experiments show that the fraction of herbicide lost in runoff is typically closer to 1–10%, so this calculation overestimates the potential for herbicide runoff by about 10–100 times. Thus, a more realistic statement would be that up to 2,600 acres in the Phoenix Lake watershed could be treated with glyphosate without exceeding *one-tenth of a percent to one percent (0.1–1%) of the RfD* for drinking water exposure. Extending this calculation to the Bon Tempe watershed provides a more realistic scenario, since Bon Tempe is continuously used as a drinking water supply, while Phoenix Lake is only used in drought years. Concentrations in Bon Tempe would be lower by an additional factor of 10 because Bon Tempe is 10 times larger than Phoenix Lake and any runoff would be diluted further.

Even with the highly improbable 100% runoff scenario, our calculations indicate that treatment of the entire acreage of invasive weeds with glyphosate or clopyralid would not exceed the EPA Reference Dose (RfD) for human exposures to glyphosate or clopyralid through drinking water. Nevertheless, it is important to recognize the uncertainties and limitations of the hazard assessment process through which the RfDs are set, particularly for herbicides or adjuvants with minimal data. Because of these uncertainties, if the MMWD Board does decide to allow the use of herbicides, we recommend that limitations on their use be institutionalized into MMWD policy. Buffer zones around water bodies in which only manual weed-removal techniques can be used should be implemented. Triclopyr use should be limited to spot treatments only, and the more readily degradable herbicides like Scythe (pelargonic acid) and Matran (clove oil) should be used in areas upslope of water bodies. Limits should be set on the maximum number of acres that can be treated with glyphosate and clopyralid in a single year, and MMWD Board approval should be required for any requests to change these limits.

What is the probability that humans, wildlife and non-target plants will be exposed through non-drinking water routes to herbicides in amounts exceeding levels of concern? Drinking water is not the only potential source of exposure to herbicides that might be applied on MMWD lands. Herbicide applicators are likely to have the highest exposures, since they would be working directly with the chemicals. Visitors to MMWD lands could be exposed through contact with treated plants or nearby soils, rocks and logs. Terrestrial wildlife could be exposed through direct spray contact, by eating contaminated food or drinking contaminated water, and through contact with treated surfaces; aquatic organisms could be exposed if herbicides are spilled into surface waters or if runoff of herbicide-contaminated water from treated sites occurs. All of these exposure sources are evaluated in this report.

Because the different herbicides are used at different application rates, the hazard quotients that describe the extent of exposure do not necessarily parallel the inherent toxicity of each herbicide described by Table 1-1. For example, glyphosate and triclopyr are used at application rates of 2 lb/acre and clopyralid is used at 0.14 lb/acre. Although clopyralid is more toxic than glyphosate, it is used at a lower application rate, resulting in smaller hazard quotients for some scenarios.

An additional variable that is not directly addressed by this risk assessment is the absolute amount of herbicide that is likely to be used in the watershed in a given year. The number of acres treated per year is one of the variables MMWD can adjust to reduce risks.

Tables 1-2 and 1-3 compare the hazard quotients for the most likely use scenarios for a set of five herbicides. Selected scenarios are presented for humans (Table 1-2) and wildlife (Table 1-3). The tables are not meant to encompass all scenarios evaluated, but to provide a means of visualizing the relative toxicity of the five herbicides. See Chapters 3 through 7 for a comprehensive assessment of hazard and risk. Several major conclusions can be drawn from viewing the data in this way.

- Triclopyr poses the highest risk to workers, the general public and most aquatic and terrestrial wildlife. The primary factor contributing to high human risks is dermal exposure from handling the chemical during applications or from vegetation contact.
- Glyphosate poses the least risk to workers and the general public, moderate risks to terrestrial wildlife from direct sprays, and low risks to aquatic species.
- Clopyralid poses the least risk to terrestrial and aquatic wildlife. The primary factor contributing to the lower risk for clopyralid is the lower application rates used for this herbicide—approximately 0.14 pounds per acre compared to 2.0 pounds per acre for glyphosate and triclopyr.
- Clove oil/eugenol poses high worker risks for accidental exposure scenarios and accidental spills into water. The primary factor contributing to these risks is dermal exposure. Direct sprays and consumption of contaminated food poses some risk to terrestrial animals.
- Pelargonic acid poses low risks to workers, the general public and aquatic and terrestrial wildlife.
- Small mammals and honeybees are particularly vulnerable to direct sprays, which also translates to risks for predators of these animals.

- Herbivorous mammals (deer, gophers) and birds (geese, turkeys) are at risk from consuming contaminated vegetation. The exposure potential is lowered by the fact that invasive weed species do not normally constitute a major part of the diet for herbivores.
- Co-application of herbicides with the “inerts” they contain and/or the surfactants Competitor and Sylgard 309 may change the risks associated with exposure to the herbicide active ingredients; available data indicate that these differences would be small, but the data set is incomplete

Pelargonic acid exposure for humans is handled differently from the other herbicides. Exposures to pelargonic acid are expressed as a Fraction of Daily Intake (FDI), instead of a hazard quotient. Amounts above the DRV are not necessarily harmful; instead, this approach is meant to flag exposures that are above naturally occurring dietary levels.

Tables 1-2 and 1-3 show that the reference dose (the level where adverse health effects occur) for glyphosate is defined as "2 milligrams of glyphosate per kilogram of body weight per day (mg/kg-day)." The hazard quotient* for the most likely exposure scenario for someone who wears contaminated gloves for one minute (an event that is considered to be likely to occur for workers applying herbicide) is 0.000021, which is less than one hundredth of one percent of the reference dose of 2 mg/kg-day.

If it is determined that herbicides will be a part of MMWD's integrated pest management program, what steps can be taken to minimize the possibility of concomitant adverse effects? Methods for minimizing risk are described in this document and can be found in Chapter 2, Section 2.4.1 and include strategies such as using non-chemical methods of weed control whenever feasible—especially near waterways, reservoirs, and sensitive habitats; limiting the amount of herbicide to be used each year in the watershed; using application methods that minimize herbicide application rates; utilizing herbicide mixing protocols that reduce potential hazard from spills; minimizing spray drift through use of proper droplet size and sprayer pressure and by avoiding applications on windy days; timing applications to provide the maximum amount of time between application and rainfall events to allow for degradation to occur; timing applications to fall on days when fewer park visitors are present; timing applications to avoid sensitive wildlife life stages; timing with regards to burning done in conjunction with herbicide applications to minimize volatilization; and adequate applicator protection.

* The hazard quotient is the ratio of the estimated exposure to the toxicity reference value (TRV), which for humans is the same as the reference dose (RfD).

Table 1-2: Humans—Comparison of Herbicide TRVs and Hazard Quotients for Selected Exposure Scenarios

| | Scenario Probability | Glyphosate | | Triclopyr | | Clopyralid | | Clove Oil | | Pelargonic Acid | |
|---|----------------------|------------|-------------------------|-----------|-------------------------|------------|-------------------------|-----------|-------------------------|------------------------|--------------------------|
| | | RfD mg/kg | Central HQ ^a | RfD mg/kg | Central HQ ^a | RfD mg/kg | Central HQ ^a | RfD mg/kg | Central HQ ^a | DRV ^b mg/kg | Central FDI ^b |
| Herbicide Applicators | | | | | | | | | | | |
| Accidental exposure to diluted product | | | | | | | | | | | |
| Contaminated gloves worn for 1 min | Probable | 2 | 2.1x10 ⁻⁶ | 1 | 0.016 | 0.75 | 7.7x10 ⁻⁷ | 2.5 | 0.0083 | 20 | 0.0075 |
| Contaminated gloves worn for 1 h | Improbable | 2 | 0.00013 | 1 | 0.94 | 0.75 | 4.6x10 ⁻⁵ | 2.5 | 0.50 | 20 | 0.44 |
| Spill on hands, unwashed for 1 h | Improbable | 2 | 0.00028 | 1 | 0.037 | 0.75 | 0.00013 | 2.5 | 0.0068 | 20 | 0.0017 |
| Spill on lower legs, unwashed for 1 h | Improbable | 2 | 0.00068 | 1 | 0.091 | 0.75 | 0.00034 | 2.5 | 0.017 | 20 | 0.0042 |
| Accidental exposure to concentrated product | | | | | | | | | | | |
| Contaminated gloves worn for 1 min | Probable | 2 | 7.2x10 ⁻⁵ | 1 | 0.20 | 0.75 | 0.00016 | 2.5 | 0.28 | 20 | 0.26 |
| Contaminated gloves worn for 1 h | Improbable | 2 | 0.0043 | 1 | 11.8 | 0.75 | 0.0098 | 2.5 | 17 | 20 | 16 |
| Spill on hands, unwashed for 1 h | Improbable | 2 | 0.0094 | 1 | 0.46 | 0.75 | 0.029 | 2.5 | 0.23 | 20 | 0.061 |
| Spill on lower legs, unwashed for 1 h | Improbable | 2 | 0.023 | 1 | 1.14 | 0.75 | 0.072 | 2.5 | 0.57 | 20 | 0.15 |
| General exposure for applicators | | | | | | | | | | | |
| Backpack spraying (diluted product, foliar applications) | Highly Probable | 2 | 0.013 | 0.05 | 0.53 | 0.15 | 0.012 | 2.5 | 0.042 | 20 | 0.0055 |
| Backpack spraying (concentrated product, cut-stump and basal bark applications) | Highly Probable | 2 | 0.0066 | 0.05 | 0.53 | c | c | c | c | 20 | 0.009 |
| Ground spraying (diluted product, foliar applications) | Highly Probable | 2 | 0.022 | 0.05 | 0.90 | 0.15 | 0.021 | 2.5 | 0.0014 | 20 | 0.00033 |
| General Public | | | | | | | | | | | |
| Vegetation contact after spray, shorts & T-shirt, woman | Improbable | 2 | 0.0011 | 0.05 | 2.80 | 0.75 | 0.00025 | 2.5 | 0.064 | 20 | 0.0065 |
| Contaminated fruit consumption after spray, acute | Improbable | 2 | 0.012 | 0.05 | 0.48 | 0.75 | 0.0022 | 2.5 | 0.025 | 20 | 0.0013 |
| Woman (triclopyr) or child (other herbicides) drinking water after a 20-gallon spill of concentrated product into Bon Tempe | Highly Improbable | 2 | 0.00028 | 0.05 | 0.0012 | 0.75 | 0.00055 | 2.5 | 11 | 20 | 0.000029 |
| Woman (triclopyr) or child (other herbicides) drinking water after a 20-gallon spill of diluted product into Bon Tempe | Highly Improbable | 2 | 8.2x10 ⁻⁶ | 0.05 | 9.1x10 ⁻⁵ | 0.75 | 2.6x10 ⁻⁶ | 2.5 | 3.2 | 20 | 8.1x10 ⁻⁷ |
| Woman (triclopyr) or child (other herbicides) drinking water after long-term runoff into Bon Tempe | Probable | 2 | 6.2x10 ⁻⁵ | 0.012 | 0.052 | 0.15 | 0.00038 | 2.5 | d | 20 | d |

HQ = hazard quotient, the ratio of anticipated exposure to the TRV or RfD; RfD = reference dose, the dose at which no adverse effects are anticipated by EPA.

Hazard Quotients greater than 0.1 are shaded. Hazard Quotients greater than one are also bolded.

^aThe Central hazard quotient is calculated from the most likely exposure estimate.

^bPelargonic acid exposures are compared to estimated daily dietary intake, the Dietary Reference Value (DRV), with comparisons expressed as the Fraction of Dietary Intake (FDI). See Chapter 7 for discussion of these concepts.

^cNo cut-stump or basal bark applications are anticipated for clopyralid.

^dClove oil and pelargonic acid both dissipate rapidly due to volatilization and microbial degradation. It is Highly Improbable that any substantial amount of these two chemicals would remain at the application site long enough for fall rains to result in runoff.

Table 1-3: Wildlife—Comparison of Herbicide TRVs and Hazard Quotients for Selected Exposure Scenarios

| | Scenario Probability | Glyphosate | | Triclopyr | | Clopyralid | | Clove Oil | | Pelargonic Acid | |
|---|----------------------|------------|-------------------------|--------------|-------------------------|--------------|-------------------------|--------------|-------------------------|-----------------|-------------------------|
| | | TRV mg/kg | Central HQ ^a | TRV mg/kg | Central HQ ^a | TRV mg/kg | Central HQ ^a | TRV mg/kg | Central HQ ^a | TRV mg/kg | Central HQ ^a |
| Terrestrial Wildlife | | | | | | | | | | | |
| Direct spray of small mammal, 50% of body, first-order absorption | Possible | 175 | 0.0027 | 100 | 0.30 | 75 | 0.00068 | 250 | 0.20 | 1,000 | 0.089 |
| Direct spray of small mammal, 50% of body, 100% absorption | Improbable | 175 | 0.27 | 100 | 0.48 | 75 | 0.045 | 250 | 0.78 | 1,000 | 0.19 |
| Direct spray to 50% of honeybee body, 100% absorption | Improbable | 540 | 0.59 | 179 | 1.79 | 1,075 | 0.022 | 5,000 | 0.26 | 45 | 28 |
| Consumption of contaminated fruit by small mammal | Possible | 175 | 0.014 | 100 | 0.025 | 75 | 0.0023 | 250 | 0.010 | 1,000 | 0.0026 |
| Consumption of contaminated grass by large mammal | Possible | 175 | 0.19 | 100 | 0.34 | 75 | 0.032 | 250 | 0.55 | 1,000 | 0.14 |
| Consumption of contaminated grass by large bird | Possible | 562 | 0.096 | 65 | 0.83 | 77 | 0.049 | 250 | 0.86 | 333 | 0.65 |
| Consumption of contaminated insects by small mammal | Probable | 175 | 0.26 | 100 | 0.46 | 75 | 0.043 | 250 | 0.74 | 1,000 | 0.19 |
| Consumption of contaminated insects by small bird | Probable | 562 | 0.13 | 65 | 1.2 | 77 | 0.068 | 250 | 1.2 | 333 | 0.90 |
| Consumption of contaminated prey, carnivorous small mammal | Possible | 175 | 0.024 | 100 | 0.042 | 75 | 0.0039 | 250 | 0.068 | 1,000 | 0.017 |
| Consumption of contaminated prey, carnivorous bird | Possible | 562 | 0.012 | 65 | 0.099 | 77 | 0.0058 | 250 | 0.10 | 333 | 0.078 |
| Aquatic Wildlife | | | | | | | | | | | |
| | | mg/L | | mg/L | | mg/L | | mg/L | | mg/L | |
| Sensitive fish, long-term runoff into Bon Tempe Reservoir | Probable | 2.57 | 0.00032 | 0.042 | 0.48 | 5 | 0.00015 | 0.45 | ^d | 0.46 | ^d |
| Tolerant fish, long-term runoff into Bon Tempe Reservoir | Probable | 25.7 | 8.5x10 ⁻⁶ | ^b | ^b | 23.1 | 0.000032 | ^b | ^d | ^b | ^d |
| Tadpoles, long-term runoff into Bon Tempe Reservoir | Probable | 1.8 | 0.00045 | 6.7 | 0.017 | ^c | ^c | ^d | ^d | 2.2 | ^d |
| Aquatic invertebrates, long-term runoff into Bon Tempe Reservoir | Probable | 50 | 0.000016 | 0.1 | 0.20 | 23.1 | 0.000032 | 22 | ^d | 3.3 | ^d |
| Aquatic plants, long-term runoff into Bon Tempe Reservoir | Probable | 3 | 0.00027 | 0.07 | 0.29 | 6.9 | 0.00011 | NA | ^d | 30 | ^d |

NA = not available; HQ = hazard quotient, the ratio of anticipated exposure to the TRV or RfD.

Hazard Quotients greater than 0.1 are **shaded**. Hazard Quotients greater than one are also **bolded**.

^a The Central hazard quotient is calculated from the most likely exposure estimate.

^b No distinction between sensitive and tolerant fish for triclopyr, clove oil and pelargonic acid.

^c No amphibian TRV is available.

^d Clove oil and pelargonic acid both dissipate rapidly due to volatilization and microbial degradation. It is Highly Improbable that any substantial amount of these two chemicals would remain at the application site long enough for fall rains to result in runoff.