Marin Municipal Water District Herbicide Risk Assessment

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Acronyms, Abbreviations and Symbols

AQUIRE	US EPA's aquatic ecotoxicity database
a.e.	acid equivalent, or more specifically, a carboxylic acid equivalent, characterized by the presence of a carboxyl group, -C(=O)OH.
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
EAD	estimated absorbed dose
EC_{50}	the Effective Concentration of a pesticide that produces a specific measurable effect in 50% of the test organisms within the stated study time
EAD	estimated absorbed dose
EC_{100}	the Effective Concentration of a pesticide that produces a specific measurable effect in 50% of the test organisms within the stated study time
Ecotox	US EPA's ecotoxicity database collection
EIS	environmental impact statement
F	female
F_0	pParental generation in a multigenerational animal study
F_1	first generation of offspring in a multigenerational animal study
FFES	Farm Family Exposure Study
FIFRA	Federal Insecticide, Fungicide and Rodenticide Act
FR	fecundity ratio, defined on page 2-10 under "Fecundability"
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
HR	hazard ratio
IARC	International Agency for Research on Cancer
IPA	isopropylamine
IRIS	Integrated Risk Information System
K_a	acid dissociation constant, defined on page 2-23 of Chapter 2
kg	kilogram
K_{oc}	organic carbon partition coefficient, defined on page 2-22 of Chapter 2
K_{ow}	octanol-water partition coefficient, defined on page 2-23 of Chapter 2

K_p	skin permeability coefficient
L	liter
lb	pound
LC_{50}	lethal concentration for 50% of the test organisms, defined comprehensively on p. 2-15
LD_5	lethal dose for 5% of the test organisms, defined comprehensively on p. 2-15
LD_{50}	lethal concentration for 50% of the test organisms, defined comprehensively on p. 2-15
LD_{95}	lethal concentration for 95% of the test organisms, defined comprehensively on p. 2-15
LOAEC	lowest observed adverse effect concentration, defined on p. 2-16
LOAEL	lowest observed adverse effect level, defined on p. 2-16
LOC	level of concern
LOD	limit of detection
LOEC	lowest observed effect concentration
LOEL	lowest observed effect level
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
NOAEC	no observed adverse effect concentration
NOAEL	no observed adverse effect level
NOEC	no observed 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, defined on page 2-12
OSHA	Occupational Safety and Health Administration
PAD	population adjusted dose, similar to a reference dose, but often contains an additional uncertainty factor for vulnerable populations.
PEL	permissible exposure limit

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, the dose below which no adverse effects are anticipated for humans
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
TLV	threshold limit value
TRV	toxicity reference value, the dose below which no adverse effects are anticipated in a wildlife population
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
WHO	World Health Organization
>	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 (where carboxylic acids are organic acids characterized by the presence of a carboxyl, or -C(=O)OH), group), 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

This report provides an assessment of the potential effects of six herbicides and three adjuvants on water quality, human health, and wildlife viability in the Marin Municipal Water District (MMWD) watersheds. The report contains information that will enable the southern Marin County community and the MMWD Board to make an informed decision as to whether herbicides should be considered as part of an integrated pest management program that would be incorporated into the Vegetation Management Plan. The risks of exposing humans and other organisms to various herbicides and additives are calculated in the context of a set of mandatory restrictions on the methods for applying and transporting herbicides that minimize the probability of accidents and adverse effects.

The risk assessment provides information on the inherent hazards of the chemicals, possible routes of exposure for humans and wildlife, an estimated magnitude of exposure, and the likelihood of adverse effects and consequent risk associated with exposure. The consulting team and MMWD will assess these risk assessment data along with risk data from using non-herbicidal techniques and tools, 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

The following conventional herbicides were evaluated for potential use in the integrated pest management program: Aquamaster (active ingredient is glysophate); Transline (active ingredient is clopyralid); Garlon 3A (active ingredient is triclopyr triethylamine salt) and Garlon 4 Ultra (active ingredient is triclopyr butoxyethyl ester). Two organic herbicides derived from essential oils or naturally occurring organic acids were evaluated: 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) were also evaluated.

The herbicides and additives being considered 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 in estimating the amount of herbicide that may run off from the treatment sites and the toxicity of these herbicides to humans and wildlife at very low doses, especially endocrine disrupting effects. In addition, less is known about clopyralid and triclopyr as compared to glyphosate, and there is very little information about the surfactants or the dye. This report uses a precautionary approach to account for uncertainty in exposure estimates, providing worst-case exposure estimates for consideration.

A summary of the findings for the five herbicides follows:

- 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. Much of this risk can be mitigated by removing vegetation prior to treatment and by only using triclopyr for cut-stump treatments.

- 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. Clopyralid is persistent in the environment and remains herbicidally active for several years, which may cause longer-term effects on the plant community in the treated area.

- 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. Clove oil is only effective as a “burn-down” herbicide when used on the leaves of growing plants.

- Pelargonic acid poses low risks to workers, the general public and aquatic and terrestrial wildlife. Pelargonic acid is only effective as a “burn-down” herbicide when used on the leaves of growing plants.

- 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 are likely to be small, but the data set is incomplete.

- There is some potential for winter storm water runoff to carry herbicide residue from treated areas into MMWD reservoirs if many acres are treated in a single year, or if applications are made close to reservoirs. Runoff is not likely 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 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). 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 adults drink between 1.4-2.4 liters of water per day and 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 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 more diluted by the larger volume of water.

- Even with the highly improbable 100% runoff scenario, our calculations indicate that treating 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 by 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 should be utilized in which only non-chemical weed-removal techniques are permitted. 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 where possible 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 2 provides the essential background information necessary for interpreting the risk assessment. Chapter 2 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 US Forest Service (USFS) approach to estimating risks from herbicide treatments

Chapters 3 through 8 provide a summary of available information on the above-mentioned topics for each active ingredient and adjuvant, 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 (active ingredient [a.i.] is glyphosate) is formulated as a four pounds a.i./gallon of the isopropyl amine salt. Water is the only "inert" ingredient; no surfactant is included in the Aquamaster formulation. 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 final IPM plan, 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 (active ingredient is triclopyr butoxyethyl 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, the auxin 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 plan, 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.

Garlon 3A (active ingredient is triclopyr TEA) is very similar to Garlon 4 Ultra and has the same mechanism of action and intended uses. Prescribed use rates would not exceed 55 ounces of formulated product per acre.

Transline (active ingredient is clopyralid) is a selective, post-emergent herbicide. Like Garlon, 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 by plants, 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 plan, Transline would be used primarily for the control of yellow star thistle. It would be prescribed at a rate of four ounces of formulated product per acre.

Scythe (active ingredient is pelargonic acid) is formulated as a 4.2 pound a.i./gallon of pelargonic acid, a naturally occurring fatty acid. Scythe is a broad-spectrum, non-selective, post-emergent contact 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 plan, 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 plan, 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 affected. If included in the final IPM plan, 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 herbicide formulations already contain internal surfactants. While the label might not require adding a surfactant, the addition of one will generally 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 vegetation management plan, two surfactants would be utilized: 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), comprised of a mixture of ethyl oleate, sorbitan alkylpolyethoxylate, and dialkyl polyoxyethylene glycol (PEG). 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 at concentrations of 1% to 3%. As a diluent, Competitor would comprise 75% to 80% of a mixture with Garlon 4 Ultra for basal and cut-stump treatments.

Sylgard 309 is a silicone-based surfactant known as an organo-silicone surfactant. This type of surfactant is sometimes referred to as a "super wetter" because of its superior ability to reduce surface tension of water and allow 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 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—Blazon blue dye—is proposed for possible use in the MMWD vegetation management project for use with all foliar applications and with some cut stump applications.

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. None of the herbicides reviewed in this risk assessment have high vapor pressures, indicating that volatilization drift is not a significant source of herbicide transport for these herbicides.

- **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 The 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 typically 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 2.5.9.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 dose below which no adverse health effects are anticipated. The daily dose that is not anticipated to cause non-cancer adverse effects is known as the ***reference dose (RfD)***. Reference doses are given for oral, dermal and inhalation exposures, and for acute, subchronic, and chronic time periods of exposure.

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 dosing studies available for most herbicides, so the anticipated effects on humans are determined based on animal studies and human 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 difficult for an epidemiological study to single out a particular pesticide as the cause of a specific cancer, because those who are exposed to the pesticide of interest are typically also exposed to other pesticides, and use patterns of these pesticides have changed over time. In addition, pesticides 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, and current toxicology tests do not evaluate endocrine disrupting potential. 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 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. In the fall of 2009, US EPA initiated its endocrine disruptor screening program for approximately 70 pesticide active ingredients. Results will not be available for several years.

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 for which no information is available. 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 group is likely to encounter environmental concentrations/doses that are likely to pose a risk to individuals of a species.

Water contamination estimates were developed for several acute spill scenarios, peak runoff, and long-term runoff that might result in exposure through drinking water. These concentration estimates were used to estimate exposures from consuming contaminated water for humans, terrestrial and aquatic animals, and aquatic plants. Aquatic exposure scenarios included 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 were developed for both workers and the general public. Worker exposure estimates considered 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 would be 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 with standard 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 multiple of the TRV, e.g. "the HQ was 2.4 times the TRV," or it was 2.4 times greater than the level below which no adverse effects are anticipated.

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 known to be 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 of 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 herbicides, certain aquatic species are particularly sensitive and others particularly tolerant to chemical exposures, and different TRVs are used for these two groups.

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, 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.

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

Taxa and Exposure Type	Glyphosate Dose	Triclopyr BEE 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)**	**(mg/kg)**
acute RfD	2	**1.0 (male) 0.05 (female)**	**1.0 (male) 0.05 (female)**	0.75	2.5	20
chronic RfD	2	**0.05 (male) 0.012 (female)**	**0.05 (male) 0.012 (female)**	0.15	2.5	20
Mammals	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**
acute TRV	175	100	100	**75**	250	>1,000
chronic TRV	175	**5**	**5**	15	250	>1,000
Birds	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**
acute TRV	562	**65**	**65**	77	NA	333
chronic TRV	100	**10**	**10**	15	NA	333
Honeybees	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**	**(mg/kg)**
honeybees, chronic TRV	540	179	179	1,075	5,000	**>45**
Plants	**(lb/acre)**	**(lb/acre)**	**(mg/kg)**	**(lb/acre)**	**(lb/acre)**	**(lb/acre)**
vegetative vigor TRV, tolerant	0.56	**0.0039**	**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**	**0.003**	0.5	NA	NA
seed emergence, TRV sensitive	---	---	---	0.025	NA	NA
Fish	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**
tolerant fish, acute TRV	25.7	**0.013**	104	82 (MEA)	0.45	0.46
tolerant fish, chronic TRV	25.7	**0.075**	**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)**	**(mg/L)**
acute TRV	**6.5**	6.7	6.7	NA	NA	NA
chronic TRV	1.8	**1.2**	**1.2**	NA	NA	NA
Aquatic Invertebrates	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**
acute TRV	130	**0.1**	58	23	22	3.3
chronic TRV	50	0.1	58	23	22	**0.03**
Aquatic Plants	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**	**(mg/L)**
tolerant algae TRV	3	**0.07**	4.2	449	NA	30
sensitive algae TRV	---	---	---	6.9	NA	---
macrophyte TRV	3	**0.07**	4.2	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.

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 involve 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 data set is most complete for glyphosate, clove oil, and pelargonic acid, while triclopyr and clopyralid have more data gaps. Pelargonic acid is found naturally in foods and has been studied extensively in the context of fatty acid metabolism.

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 2.5.11 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 was 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 2.5.1A for a listing of these guidelines), the probability of an accidental spill occurring can be reduced to Highly Improbable by preventing large quantities of herbicides from being transported near 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 are implemented. 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 these pesticides both degrade rapidly enough that none 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. The results indicate that the hazard quotients for human or terrestrial wildlife water consumption are less 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 to estimate water contamination 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. We specifically determined the amount of herbicide that could be used (and the corresponding number of acres that could be treated) in the Phoenix Lake watershed without exceeding 0.1, 0.5 or 1.0 times the RfD for the particular herbicide. Phoenix Lake provides a worst-case scenario because of the relatively small volume of the lake and the large amount of broom in the watershed, but is not used as part of the MMWD water supply except in drought years.

Scenarios for 100% ("Highly Improbable") and 5% ("Possible") runoff of applied herbicide were evaluated 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 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 1-2. Chapters 3 through 5 provide more detail on this calculation and the estimates of exposure for the three conventional herbicides glyphosate, triclopyr and clopyralid.

For the worst-case scenario for glyphosate (i.e., 100% of the applied material in the watershed runs off to Phoenix Lake), MMWD would have to apply 1,308 gallons of Aquamaster in the previous dry season to 2,616 acres in order to exceed the 0.1 hazard quotient (this is 10% of the exposure deemed acceptable by EPA). This substantially exceeds the amount of glyphosate MMWD would 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 before exceeding 10% of the human RfD, and 4,870 acres could be treated with clopyralid.

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. 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, where their efficacy permits. 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.

Table 1-2: 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

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 1-3 and 1-4 provide a comparison of the hazard quotients for the most likely use scenarios for a set of five herbicides. Selected scenarios are presented for humans (Table 1-3) and wildlife (Table 1-4). The tables are not meant to encompass all scenarios evaluated, but to provide a means of visualizing the relative toxicity of the six 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 1-3 and 1-4 show that the reference dose (the level where adverse health effects may begin to occur) for glyphosate is defined as "2 milligrams of glyphosate per kilogram of body weight per day (mg/kg-day)." The hazard quotient[1] 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 herbicde) is 0.000021, which is less than one hundredth of one percent of the reference dose of 2 mg/kg-day.

[1] 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).

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 can be found in Chapter 2, Section 2.5.1 and include:

- 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; 3
- timing applications to provide the maximum amount of time between application and rainfall events to allow for degradation to occur;
- timing applications to occur 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.

These precautions will reduce the risk of herbicide use.

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

	Scenario Probability	Glyphosate RfD mg/kg	Glyphosate Central HQ[a]	Triclopyr BEE RfD mg/kg	Triclopyr BEE Central HQ[a]	Clopyralid RfD mg/kg	Clopyralid Central HQ[a]	Clove Oil RfD mg/kg	Clove Oil Central HQ[a]	Pelargonic Acid DRV[b] mg/kg	Pelargonic Acid 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[c]											
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	[d]	[d]	[d]	[d]	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	[e]	20	[e]

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. BEE = butoxyethyl ester.
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] Pelargonic 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.

[c] The central exposure estimate for "concentrated" triclopyr is for Garlon 4 Ultra or Garlon 3A diluted to 25% product by volume because this is likely to be the highest concentration of triclopyr used in the field. The Upper worker exposure estimates in Chapter 4 are for undiluted Garlon 4 Ultra or Garlon 3A. The undiluted scenario is designed to estimate worker exposure while mixing the pesticide for use.

[d] No cut-stump or basal bark applications are anticipated for clopyralid.

[e] 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.

Table 1-4: Wildlife—Comparison of Herbicide TRVs and Hazard Quotients for Selected Exposure Scenarios

	Scenario Probability	Glyphosate TRV	Glyphosate Central HQ[a]	Triclopyr BEE TRV	Triclopyr BEE Central HQ[a]	Clopyralid TRV	Clopyralid Central HQ[a]	Clove Oil TRV	Clove Oil Central HQ[a]	Pelargonic Acid TRV	Pelargonic Acid Central HQ[a]
Terrestrial Wildlife		**mg/kg**		**mg/kg**		**mg/kg**		**mg/kg**		**mg/kg**	
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	8.5×10^{-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.