Candidate Contaminant List Regulatory Determination Support Document for Metribuzin

Contaminant Candidate List
Regulatory Determination Support Document
for Metribuzin

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CANDIDATE CONTAMINANT LIST REGULATORY DETERMINATION SUPPORT DOCUMENT FOR METRIBUZIN

EXECUTIVE SUMMARY

Metribuzin was a 1998 Contaminant Candidate List (CCL) regulatory determination priority contaminant. Metribuzin was one of the contaminants being considered by the U.S. Environmental Protection Agency (EPA) for a regulatory determination. The available data on occurrence, exposure, and other risk considerations suggest that regulating metribuzin may not present a meaningful opportunity to reduce health risk. EPA presented preliminary CCL regulatory determinations and further analysis in the June 3, 2002 *Federal Register* (FR) Notice (USEPA, 2002; 67 FR 38222), and confirmed the final CCL regulatory determinations in the July 18, 2003 *Federal Register* Notice (USEPA, 2003a; 68 FR 42898).

To make the regulatory determination for metribuzin, EPA used approaches guided by the National Drinking Water Advisory Council's (NDWAC) Work group on CCL and Six-Year Review. The Safe Drinking Water Act (SDWA) requirements for National Primary Drinking Water Regulation (NPDWR) promulgation guided protocol development. The SDWA Section 1412(b)(1)(A) specifies that the determination to regulate a contaminant must be based on a finding that each of the following criteria are met: (i) "the contaminant may have adverse effects on the health of persons"; (ii) "the contaminant is known to occur or there is substantial likelihood that the contaminant will occur in public water systems with a frequency and at levels of public health concern"; and (iii) "in the sole judgement of the Administrator, regulation of such contaminant presents a meaningful opportunity for health risk reduction for persons served by public water systems." Available data were evaluated to address each of the three statutory criterion.

Metribuzin, a synthetic organic compound (SOC), is a selective triazinone herbicide used mostly to discourage growth of broadleaf weeds and annual grasses among vegetable crops and turf grass. Metribuzin accomplishes this by inhibiting photosynthesis. It is commonly applied to soybeans, potatoes, alfalfa, sugarcane, barley, and tomatoes. Use patterns for metribuzin show that use is concentrated in the soybean producing regions in the Midwest States (equivalent to the corn belt) and along the Mississippi River Valley production region.

Metribuzin was monitored from 1993 to 1999 under the SDWA Unregulated Contaminant Monitoring (UCM) program. In addition, EPA has recommended guidelines for exposure to metribuzin in drinking water through a health advisory of 200 µg/L. The sale, use, and distribution of metribuzin is controlled under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) and metribuzin is also a Toxic Release Inventory (TRI) chemical requiring public reporting of environmental releases from certain industrial sectors. Releases of metribuzin to the environment were reported in the TRI from three States and one territory.

Metribuzin has been detected in ambient surface and ground waters as noted by the United States Geological Survey's (USGS) National Water Quality Assessment (NAWQA) program. Detection frequencies and concentrations are low, especially in ground water. Even so, metribuzin was one of the 21 most commonly detected pesticides in ground water from the first round of NAWQA intensive data collection. The annual mean frequency of metribuzin detection in surface water is less than 15% of all samples for all land-use settings. For ground water, the annual mean detection frequency is less than 4% of all samples across land-uses. Maximum concentrations are below 1 µg/L for all surface and ground water sites, well below the Health Reference Level (HRL) of 91 µg/L, a preliminary reference level used for this analysis. Midwestern ambient surface and ground water concentrations and detection frequencies are also low.

Metribuzin has also been detected in public water system (PWS) samples collected under SDWA. Occurrence estimates from a cross-section of States with UCM data are very low with only 0.003% of samples showing detections. For the cross-section samples with detections, both the median and the 99^{th} percentile concentrations are 0.10 µg/L. Systems with detections constitute approximately 0.007% of cross-section systems. Estimates of the national population served by PWSs with detections using the cross-section data are also low: approximately 1,000 people (about 0.0003% of the national PWS population) may be served by PWSs with metribuzin detections. No PWSs reported detections greater than half the HRL. Using more conservative estimates of occurrence from all States reporting SDWA monitoring data, including States with biased data, 0.28% of the nation's PWSs (approximately 182 systems and 3.4 million people served) are affected by metribuzin concentrations greater than the minimum reporting level (MRL), while no PWSs are affected by concentrations above one half the HRL or above the HRL.

Because the heaviest use of metribuzin is across the nation's corn-soybean production area, additional data from the Midwest corn belt were also evaluated to supplement the cross-section data. Drinking water data from the corn belt States of Iowa, Indiana, Illinois, and Ohio also show very low occurrence of metribuzin. Special, targeted surface water studies from Ohio have the highest detection frequency of metribuzin (79.9% of systems). The pesticide was not detected above the HRL in any sample, with the highest concentration at 20 µg/L.

Exposure to metribuzin occurs primarily in occupational settings, particularly in the agriculture industry where it is used as an herbicide. Although there are no studies reporting the adverse effects of metribuzin on human health, animal studies indicate that metribuzin has the potential to cause adverse health effects at high doses. Chronic studies of metribuzin, for instance, have reported effects on body weight increases, liver enzyme activities, histopathological changes, and mortality.

Although there is evidence from animal studies that metribuzin may cause adverse health effects at high doses, its occurrence in public water systems and the numbers of people potentially exposed through drinking water are low. Thus metribuzin does not appear to occur with a frequency, or at levels, of public health concern.

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1.0 INTRODUCTION

1.1 Purpose and Scope

This document presents scientific data and summaries of technical information prepared for, and used in, the United States Environmental Protection Agency's (EPA) regulatory determination for metribuzin. Information regarding metribuzin's physical and chemical properties, environmental fate, occurrence and exposure, and health effects is included. Analytical methods and treatment technologies are also discussed. Furthermore, the regulatory determination process is described to provide the rationale for the decision.

1.2 Statutory Framework/Background

The Safe Drinking Water Act (SDWA), as amended in 1996, requires EPA to publish a list of contaminants (referred to as the Contaminant Candidate List, or CCL) to assist in priority-setting efforts. The contaminants included on the CCL were not subject to any current or proposed National Primary Drinking Water Regulations (NPDWR), were known or anticipated to occur in public water systems, and were known or suspected to adversely affect public health. These contaminants therefore may require regulation under SDWA. The first Drinking Water CCL was published on March 2, 1998 (USEPA, 1998d; 63 FR 10273), and a new CCL must be published every five years thereafter.

The 1998 CCL contains 60 contaminants, including 50 chemicals or chemical groups, and 10 microbiological contaminants or microbial groups. The SDWA also requires the Agency to select 5 or more contaminants from the current CCL and determine whether or not to regulate these contaminants with an NPDWR. Regulatory determinations for at least 5 contaminants must be completed 3½ years after each new CCL.

Language in SDWA Section 1412(b)(1)(A) specifies that the determination to regulate a contaminant must be based on a finding that each of the following criteria are met:

Statutory Finding i: the contaminant may have adverse effects on the health of persons;

Statutory Finding ii: the contaminant is known to occur or there is substantial likelihood that the contaminant will occur in public water systems with a frequency and at levels of public health concern; and

Statutory Finding iii: in the sole judgement of the Administrator, regulation of such contaminant presents a meaningful opportunity for health risk reduction for persons served by public water systems.

The geographic distribution of the contaminant is another factor evaluated to determine whether it occurs at the national, regional or local level. This consideration is important because the Agency is charged with developing national regulations and it may not be appropriate to develop NPDWRs for regional or local contamination problems.

EPA must determine if regulating this CCL contaminant will present a meaningful opportunity to reduce health risk based on contaminant occurrence, exposure, and other risk considerations. The Office of Ground Water and Drinking Water (OGWDW) is charged with gathering and analyzing the occurrence, exposure, and risk information necessary to support this regulatory decision. The OGWDW must evaluate when and where this contaminant occurs, and what would be the exposure and risk to public health. EPA must evaluate the impact of potential regulations as well as determine the appropriate measure(s) for protecting public health.

For each of the regulatory determinations, EPA first publishes in the *Federal Register* the draft determinations for public comment. EPA responds to the public comments received, and then finalizes regulatory determinations. If the Agency finds that regulations are warranted, the regulations must then be formally proposed within 24 months, and promulgated 18 months later. EPA has determined that there is sufficient information to support a regulatory determination for metribuzin.

1.3 Statutory History of Metribuzin

Metribuzin has been monitored under the SDWA Unregulated Contaminant Monitoring (UCM) program since 1993 (USEPA, 1992; 57 FR 31776). Monitoring ceased for small public water systems (PWSs) under a direct final rule published January 8, 1999 (USEPA, 1999a; 64 FR 1494), and ended for large PWSs with promulgation of the new Unregulated Contaminant Monitoring Regulation (UCMR) issued September 17, 1999 (USEPA, 1999b; 64 FR 50556) and effective January 1, 2001. At the time the UCMR lists were developed, the Agency concluded there were adequate monitoring data for a regulatory determination. This obviated the need for continuing monitoring under the new UCMR list.

EPA previously recommended guidelines for exposure to metribuzin in drinking water through a health advisory (USEPA, 1988). As part of the CCL process, health effects data have been reviewed. These are summarized in section 4.0 of this document.

Metribuzin is regulated or monitored by other federal programs as well. As a pesticide, its sale, use, and distribution is controlled under the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA). FIFRA was amended in 1996 under the Food Quality Protection Act (FQPA). FIFRA requires registration of all pesticides with EPA, and certain labeling, application, and use restrictions. Moreover, pesticide manufacturing plants must be registered, and the manufacturer must provide EPA with scientific data regarding the product's efficacy and demonstrating that it does not pose an unreasonable risk to people or the environment (USEPA, 1998c). Metribuzin was first registered in the U.S. in 1973, and a Registration Standard was issued for it by EPA in 1985 (USEPA, 1998b). The registration standard classified metribuzin as "restricted use" because of questions regarding its potential to leach to ground water and chronic toxicity. Data submitted by the manufacturer later resolved those questions and the restricted use classification was discontinued (Extension Toxicology Network, Pesticide Management Education Program (EXTOXNET), 1998). Data Call-Ins (DCIs) were issued in 1991 and 1995, requiring additional scientific data on ecological effects, product chemistry,

environmental fate, and ground water impacts (USEPA, 1998b). Metribuzin was reregistered in 1998 and is classified as a general use pesticide (USEPA, 1998a).

Metribuzin is also a Toxic Release Inventory (TRI) chemical. The TRI was established by the Emergency Planning and Community Right-to-Know Act (EPCRA). EPCRA requires certain industrial sectors to publicly report the environmental release or transfer of chemicals included in this inventory.

1.4 Regulatory Determination Process

In developing a process for the regulatory determinations, EPA sought input from experts and stakeholders. EPA asked the National Research Council (NRC) for assistance in developing a scientifically sound approach for deciding whether or not to regulate contaminants on the current and future CCLs. The NRC's Committee on Drinking Water Contaminants recommended that EPA: (1) gather and analyze health effects, exposure, treatment, and analytical methods data for each contaminant; (2) conduct a preliminary risk assessment for each contaminant based on the available data; and (3) issue a decision document for each contaminant describing the outcome of the preliminary risk assessment. The NRC noted that in using this decision framework, EPA should keep in mind the importance of involving all interested parties.

One of the formal means by which EPA works with its stakeholders is through the National Drinking Water Advisory Council (NDWAC). The NDWAC comprises members of the general public, State and local agencies, and private groups concerned with safe drinking water, and advises the EPA Administrator on key aspects of the Agency's drinking water program. The NDWAC provided specific recommendations to EPA on a protocol to assist the Agency in making regulatory determinations for current and future CCL contaminants. Separate but similar protocols were developed for chemical and microbial contaminants. These protocols are intended to provide a consistent approach to evaluating contaminants for regulatory determination, and to be a tool that will organize information in a manner that will communicate the rationale for each determination to stakeholders. The possible outcomes of the regulatory determination process are: a decision to regulate, a decision not to regulate, or a decision that some other action is needed (e.g., issuance of guidance).

The NDWAC protocol uses the three statutory requirements of SDWA Section 1412(b)(1)(A)(i)-(iii) (specified in section 1.2) as the foundation for guiding EPA in making regulatory determination decisions. For each statutory requirement, evaluation criteria were developed and are summarized below.

To address whether a contaminant may have adverse effects on the health of persons (statutory requirement (i)), the NDWAC recommended that EPA characterize the health risk and estimate a health reference level for evaluating the occurrence data for each contaminant.

Regarding whether a contaminant is known to occur, or whether there is substantial likelihood that the contaminant will occur, in public water systems with a frequency, and at levels, of public health

concern (statutory requirement (ii)), the NDWAC recommended that EPA consider: (1) the actual and estimated national percent of PWSs reporting detections above half the health reference level; (2) the actual and estimated national percent of PWSs with detections above the health reference level; and (3) the geographic distribution of the contaminant.

To address whether regulation of a contaminant presents a meaningful opportunity for health risk reduction for persons served by public water systems (statutory requirement (iii)) the NDWAC recommended that EPA consider estimating the national population exposed above half the health reference level and the national population exposed above the health reference level.

The approach EPA used to make regulatory determinations followed the general format recommended by the NRC and the NDWAC to satisfy the three SDWA requirements under section 1412(b)(1)(A)(i)-(iii). The process was independent of many of the more detailed and comprehensive risk management factors that will influence the ultimate regulatory decision making process. Thus, a decision to regulate is the beginning of the Agency regulatory development process, not the end.

Specifically, EPA characterized the human health effects that may result from exposure to a contaminant found in drinking water. Based on this characterization, the Agency estimated a health reference level (HRL) for each contaminant.

For each contaminant EPA estimated the number of PWSs with detections >½HRL and >HRL, the population served at these benchmark values, and the geographic distribution, using a large number of occurrence data (approximately seven million analytical points) that broadly reflect national coverage. Round 1 and Round 2 UCM data, evaluated for quality, completeness, bias, and representativeness, were the primary data used to develop national occurrence estimates. Use and environmental release information, additional drinking water data sets (e.g., State drinking water data sets, EPA National Pesticide Survey, and Environmental Working Group data reviews), and ambient water quality data (e.g., National Water Quality Assessment (NAWQA) program, State and regional studies, and the EPA Pesticides in Ground Water Database) were also consulted.

The findings from these evaluations were used to determine if there was adequate information to evaluate the three SDWA statutory requirements and to make a determination of whether to regulate a contaminant.

1.5 Determination Outcome

After reviewing the best available public health and occurrence information, EPA has made a determination not to regulate metribuzin with an NPDWR. This determination is based on the finding that metribuzin is not known to occur, nor is it likely to occur, in public water systems with a frequency, or at levels, of public health concern. All CCL regulations determinations and further analysis are formally presented in the CCL *Federal Register* Notices (USEPA, 2002; 67 FR 38222, and USEPA, 2003a; 68 FR 42898). The following sections summarize the data used by the Agency to reach this decision.

2.0 CONTAMINANT DEFINITION

Metribuzin, a synthetic organic compound (SOC), is a white crystalline solid with a moderately sharp sulfurous odor (EXTOXNET, 1998; USEPA, 1998a). It is a selective triazinone herbicide used primarily to discourage growth of broadleaf weeds and annual grasses among vegetable crops and turf grass. Metribuzin accomplishes this by inhibiting photosynthesis (EXTOXNET, 1998; USEPA, 1998a). Common uses include application to soybeans, potatoes, alfalfa, sugarcane, barley, and tomatoes (Larson et al., 1999; USEPA, 1998a).

2.1 Physical and Chemical Properties

Table 2-1 lists summary information regarding metribuzin's physical and chemical properties. Also included are its Chemical Abstract Number (CAS) Registry Number and molecular formula.

Table 2-1: Physical and chemical properties

Identification	
CAS number	21087-64-9
Molecular Formula	$C_8H_{14}N_4OS$
Physical and Chemical Properties	
Boiling Point	----------
Melting Point	approx.126 °C
Molecular Weight	214.28 grams per mole (g/mol)
Log K_{oc}	1.61
Log K_{ow}	1.70*
Water Solubility	1,200 ppm at 20 °C
Vapor Pressure	$\geq 10^{-5}$ mm Hg at 25 °C
Henry's Law Constant †	1.43×10^{-9}

*after USEPA, 1998a; * USDA, 1999*

†*note: this quantity is expressed in a dimensionless form.*

2.2 Environmental Fate/Behavior

When metribuzin is released to the environment, it does not volatilize from either water or land surfaces. This property, along with its high solubility in water and low soil adsorption potential, make it

available to runoff to surface waters and likely to leach to ground water (USEPA, 1998b). EPA considers it among a group of pesticides most likely to contaminate ground water (EXTOXNET, 1998). Once in the saturated zone, it is expected to persist because its primary degradation routes are through soil microbial degradation and photolytic degradation on soil surfaces. Moreover, it is not subject to hydrolysis with a hydrolysis half-life of 9-28 weeks (USEPA, 1998b; EXTOXNET,1998).

Metribuzin has a low soil adsorption potential, and is consequently easily leached, except where soils have a high clay and/or organic matter content. Under these conditions, the half life of metribuzin can be extended to several months. Other soil properties that promote adsorption of metribuzin, and therefore increase the persistence of the compound in soil, are low soil moisture, low temperatures, and acidic conditions (EXTOXNET,1998). While photodegradation from soil surfaces is a primary degradation route (half life: 2.5 days), its importance is diminished because probably only the top 1 millimeter of soil is exposed to direct sunlight. This is reflected in terrestrial field dissipation half lives of 15-149 days. Its aerobic soil metabolism half-life is estimated to be between 40-106 days (USEPA, 1998a).

In shallow surface waters with good light penetration, degradation by aqueous photolysis may be rapid (half life: 4.3 hours). However, if the surface water is turbid, metribuzin will be more likely to persist since light penetration will be minimal and metribuzin is stable to hydrolysis (USEPA, 1998a; EXTOXNET,1998).

3.0 OCCURRENCE AND EXPOSURE

This section examines the occurrence of metribuzin in drinking water. While no complete national database exists of unregulated or regulated contaminants in drinking water from PWSs collected under the SDWA, this report aggregates and analyzes existing State data that have been screened for quality, completeness, and representativeness. Populations served by PWSs exposed to metribuzin are estimated, and the occurrence data are examined for regional or other special trends. To augment the incomplete national drinking water data and aid in the evaluation of occurrence, information on the use and environmental release, as well as ambient occurrence of metribuzin, is also reviewed.

3.1 Use and Environmental Release

3.1.1 Production and Use

Recent national estimates of agricultural use for metribuzin are available. Using its own proprietary data, data from the United States Department of Agriculture (USDA) and the National Center for Food and Agricultural Policy (NCFAP), the USEPA (1998a) estimates U.S. average annual use for the years 1990-94 at approximately 2.8 million pounds of active ingredient (a.i.) with approximately 8.5 million acres treated. The USGS estimates approximately 2.7 million pounds of active ingredient used for the year 1992, with roughly 8.4 million acres treated (USGS, 1999a). These estimates were derived using State-level data sets on pesticide use rates available from NCFAP combined with county-level data on harvested crop acreage from the Census of Agriculture (CA) (Thelin and Gianessi, 2000).

Figure 3-1 shows the geographic distribution of estimated average annual metribuzin use in the U.S. for 1992. A breakdown of use by crop is also included. Again, the map was compiled using State-level data sets on pesticide use rates available from the NCFAP and county-level data on harvested crop acreage from the CA. As such, non-agricultural uses are not reflected here and any sharp spatial differences in use within a county are not well represented (USGS, 1998a). Existing data suggest that non-agricultural use of metribuzin is minimal (USEPA, 1998a).

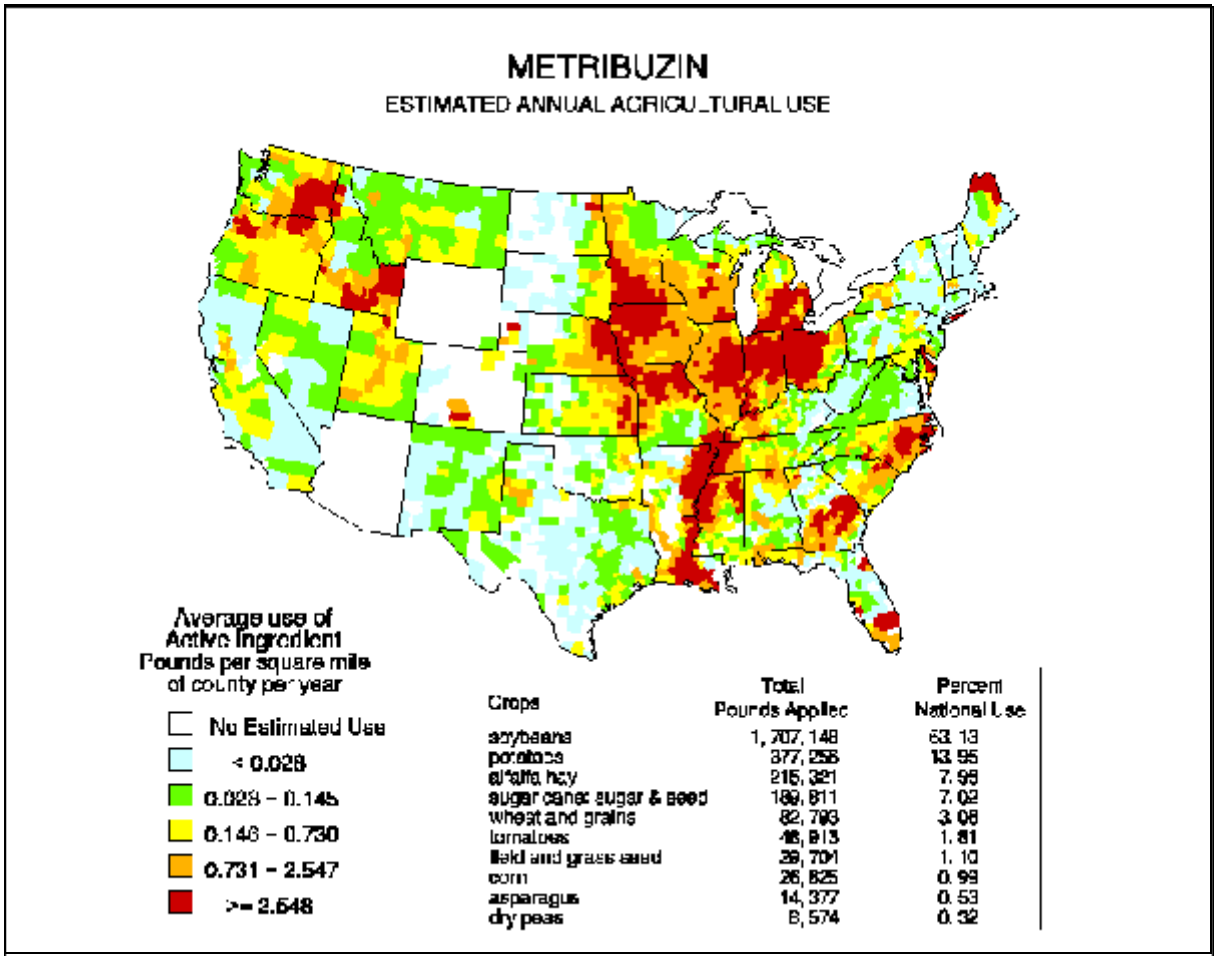
Metribuzin use patterns have been documented by the USDA as well. USDA Cropping Practices Survey (CPS) for field crops (1964-1995) merged with the Farm Costs and Returns Survey (FCRS) in 1996 to form the Agricultural Resources Management Study (ARMS). As was the case with the CPSs, the ARMS is conducted in major producing States and provides information on metribuzin use on particular field crops (corn, soybeans, cotton, winter wheat, spring and durum wheat, and fall potatoes). Farm operators are surveyed for crop practice information on a field-by-field basis (USDA, 1997; USDA, 2000). Table 3-1 shows the amount of metribuzin used annually and the number of acres treated. Metribuzin use appears to be modestly declining over the ten-year period.

Table 3-1: Metribuzin use, 1990-1999

year	pounds of active ingredient (x 1000)	acres treated (x 1000)
1999	1,214	4,542*
1998	1,261	6,432
1997	2,207	8,646
1996	1,785	6,547
1995	1,498	5,892
1994	1,773	5,811
1993	2,003	6,437
1992	1,975	6,705
1991	2,537	7,706
1990	2,959	8,924

Data for the years 1990-1995, after USDA, 1997
Data for the years 1996-1999, after USDA, 2000
**average figure based on available data*

Figure 3-1: Estimated annual agricultural use for metribuzin (1992)
after USGS, 1998b



Metribuzin is also listed as a TRI chemical. In 1986, the EPCRA established the TRI of hazardous chemicals. Created under the Superfund Amendments and Reauthorization Act (SARA) of 1986, EPCRA is also sometimes known as SARA Title III. The EPCRA mandates that larger facilities publicly report when TRI chemicals are released into the environment. This public reporting is required for facilities with more than 10 full-time employees that annually manufacture or produce more than 25,000 pounds, or use more than 10,000 pounds, of a TRI chemical (USEPA, 1996; USEPA, 2000d).

3.1.2 Environmental Release

Under these conditions, facilities are required to report the pounds per year of metribuzin released into the environment both on- and off-site. The on-site quantity is subdivided into air emissions, surface water discharges, underground injections, and releases to land (see Table 3-2). For metribuzin, air emissions constitute most of the on-site releases, and decrease throughout the period of record. A sharp decrease is evident between the 1996 and 1997 reporting years, resulting in a decreasing trend for total on- and off-site releases. Interestingly, over the period for which data is available (1995-1998), surface water discharges generally increase. Again, the trend is exaggerated between the reporting years 1996 and 1997. Whether these abrupt shifts reflect actual jumps or drops in surface water discharges and air emissions, respectively, is unclear. Interpretation is confounded by the relatively short period of record. These TRI data for metribuzin were reported from three States and one territory (IA, MO, NB, Puerto Rico; USEPA, 2000b).

Although the TRI data can be useful in giving a general idea of release trends, it is far from exhaustive and has significant limitations. For example, only industries that meet TRI criteria (at least 10 full-time employees and manufacture and processing of quantities exceeding 25,000 lbs/yr, or use of more than 10,000 lbs/yr) are required to report releases. These reporting criteria do not account for releases from smaller industries. In addition, the TRI data is meant to reflect releases and should not be used to estimate general exposure to a chemical (USEPA, 2000c; USEPA, 2000a).

Table 3-2: Environmental releases (in pounds) for metribuzin in the United States, 1995-1998

Year	On-Site Releases				Off-Site Releases	Total On- & Off-site Releases
	Air Emissions	Surface Water Discharges	Underground Injection	Releases to Land		
1998	339	26	0	0	255	620
1997	359	24	0	0	0	383
1996	1,012	5	0	0	0	1,017
1995	1,936	9	0	0	0	1,945

after USEPA, 2000b

In summary, metribuzin is used as an herbicide on crops and has limited non-agricultural use. Applications are primarily targeted to soybeans, potatoes, alfalfa, and sugar cane, and the geographic distribution of use largely reflects the distribution of these crops across the U.S. (Figure 3-1).

Estimated annual use appears to be modestly declining in the last decade (Table 2-1). Metribuzin is also a TRI chemical. Industrial releases have been reported since 1995 in three States and one U.S. territory. On- site releases to air constitute the majority of these reported releases, and decline throughout the period of record.

3.2 Ambient Occurrence

To understand the presence of a chemical in the environment, an examination of ambient occurrence is useful. In a drinking water context, ambient water is source water existing in surface waters and aquifers before treatment. The most comprehensive and nationally consistent data describing ambient water quality in the U.S. are being produced through the USGS's NAWQA program. (NAWQA, however, is a relatively young program, and complete national data are not yet available from their entire array of sites across the nation.)

3.2.1 Data Sources and Methods

The USGS instituted the NAWQA program in 1991 to examine water quality status and trends in the United States. NAWQA is designed and implemented in such a manner as to allow consistency and comparison between representative study basins located around the country, facilitating interpretation of natural and anthropogenic factors affecting water quality (Leahy and Thompson, 1994).

The NAWQA program consists of 59 significant watersheds and aquifers referred to as "study units." The study units represent approximately two thirds of the overall water usage in the U.S. and a similar proportion of the population served by public water systems. Approximately one half of the nation's land area is represented (Leahy and Thompson, 1994).

To facilitate management and make the program cost-effective, approximately one third of the study units at a time engage in intensive assessment for a period of 3 to 5 years. This is followed by a period of less intensive research and monitoring that lasts between 5 and 7 years. This way all 59 study units rotate through intensive assessment over a ten-year period (Leahy and Thompson, 1994). The first round of intensive monitoring (1991-96) targeted 20 study units. This first group was more heavily slanted toward agricultural basins. A national synthesis of results from these study units, focusing on pesticides and nutrients, has been compiled and analyzed (Kolpin et al., 2000; Larson et al., 1999; USGS, 1999b).

Metribuzin is an analyte for both surface and ground water NAWQA studies. Two of the first round study units, the Central Nebraska Basins and the White River Basin in Indiana, are located in the corn belt where metribuzin is heavily used (see Figure 3-1). The Minimum Reporting Level (MRL) for metribuzin is 0.004 µg/L (Kolpin et al., 1998), substantially lower than most drinking water monitoring reporting levels.

Data are also available for metribuzin occurrence in ground water and surface water for key corn belt States. The majority of these data are the result of USGS regional water quality investigations with

a focus on near-surface aquifers and surface waters. Additionally, USEPA's Pesticides in Ground Water Database (PGWD) provides a large data set on pesticide occurrence in ground water that spans a period of 20 years and contains data from 68,824 sites. It is a compilation of numerous national, regional, State, and local studies and therefore the data are a mix of the results of a variety of study designs, sampling techniques, and reporting limits. However, the size and temporal scope of the data set make it a valuable resource. Details regarding sampling and analytical methods for the USGS studies and the PGWD report are described in the respective reports.

3.2.2 Results

3.2.2.1 NAWQA National Synthesis

Detection frequencies and concentrations of metribuzin in ambient surface and ground water are low, especially in ground water (Table 3-3). Most herbicides monitored in the first round of the NAWQA program were detected in the greatest concentrations and frequencies in surface water as compared to ground water. Surface waters show the highest maximum concentration of metribuzin at 0.5 µg/L, well below the HRL of 91 µg/L.

Frequencies and concentrations of metribuzin in streams in agricultural settings are greater than those in urban settings, with integrator sites (a combination of agricultural and urban) having the highest occurrence (Table 3-3). Larson and others (1999) found that for 50 stream sites monitored over a 1 year period, one site had a detection frequency of greater than 50% of all samples (detections were reported for metribuzin concentrations $\geq$0.01 µg/L). Ninety percent of sites, however, had detection frequencies of less than 20% of all samples. The annual mean frequency of metribuzin detection was less than 15% in all land-use settings at all concentrations (calculated as the average of the 12 monthly detection frequencies from each site; Larson et al., 1999).

While occurrence in ground water is considerably lower than surface water, detection in more than 1% of ground water samples at concentrations greater than or equal to 0.05 µg/L make metribuzin one of the 21 most commonly detected pesticides in the first round of intensive NAWQA monitoring (the 21 are detected at concentrations $\geq$ 0.05 µg/L in more than 10% of stream samples or more than 1% of ground water samples). Metribuzin exceeded the ground water criteria partly because its high water solubility and low soil adsorption potential allow it to leach to ground water (USGS, 1998c; USEPA, 1998b; EXTOXNET, 1998). Also, the herbicide ranks among the top 200 agricultural pesticides in use (USGS, 1999b).

Herbicides often demonstrate detection frequencies in streams that correlate with patterns of use (USGS, 1998c). Patterns of pesticide use often do not correlate with detection frequency in ground water, probably because of the variable effect of local hydrogeologic conditions (depth and type of aquifer, soil conditions) on pesticides in ground water (USGS, 1998c). Metribuzin, however, is one of six pesticides that, for shallow ground water, demonstrate a statistically significant correlation between detection frequency and intensity of use (Kolpin et al., 1998). Metribuzin detection frequencies are higher in shallow ground water in agricultural areas when compared with shallow

Table 3-3: Metribuzin detections and concentrations in streams and ground water

	Detection frequency (% samples ≥ MRL*)		Concentrations (all samples; µg/L)		
	% ≥ 0.004 µg/L	% ≥ 0.01 µg/L	median	95th percentile	maximum
streams					
urban	6.73%	5.50%	nd**	0.011	0.100
integrator	14.29%	9.39%	nd	0.020	0.130
agricultural	13.70%	8.20%	nd	0.016	0.330
all sites	13.82%	9.94%	nd	0.026	0.530
ground water					
shallow urban	1.66%	0.33%	nd	nd	0.043
shallow agricultural	3.46%	2.81%	nd	nd	0.300
major aquifers	0.75%	0.32%	nd	nd	0.045
all sites	1.95%	1.36%	nd	nd	0.300

after USGS, 1998c

** MRL (Minimum Reporting Level) for metribuzin in water studies:0.004 µg/L*

***not detected in concentration greater than MRL*

ground water in urban areas (Table 3-3). This is most likely a result of metribuzin's primary use as an agricultural pesticide (USEPA, 1998a). Metribuzin is detected most frequently in shallow ground water from land-use categories containing wheat, wheat and alfalfa, corn and soybeans, and corn and alfalfa as major crops or crop-groups (Table 3-4).

3.2.2.2 Water Quality Investigations from the Corn Belt

USGS regional water quality investigations and other State and national studies are summarized below to provide ambient data in States where metribuzin use is high (see Figure 3-1). Midwest ground water concentrations and detection frequencies were low during the years 1991-1994 (Table 3-5). The highest detected ground water concentration, 25.1 µg/L, is found in the national Pesticides in Ground Water Database that draws only a portion of its data from Midwestern States. This concentration is still well below the HRL of 91 µg/L.

Maximum concentrations of metribuzin in surface waters of the Mississippi River and major tributaries, peaking at less than 0.1µg/L, were considerably lower than the HRL for all years. Although

Table 3-4: Metribuzin detections in shallow ground water from various land-use settings

Land-use settings*	Detection frequency ≥0.004 µg/L	Detection frequency ≥0.010 µg/L
All	3.1%	nr**
Corn and soybeans > 20%	6.6%	≤ 10%
Corn and alfalfa > 20%	2.1%	0 - 2%
Corn > 50%	0.0%	0 - 2%
Peanuts > 50%	1.6%	< 5%
Wheat and small grains> 50%	9.3%	< 10%
Wheat and small grains and alfalfa > 20%	6.2%	≤ 5%
Alfalfa > 50%	0.0%	0 - 2%
Pasture > 90%	0.0%	0 - 2%
Orchards or vineyards > 50%	0.0%	0 - 2%
Urban	1.8%	0 - 2%

after Kolpin et al., 1998

**evaluated as crop-groups occupying a percent of the total land*

***not reported*

all 9 sampling sites in the Mississippi River and major tributaries had a least one detection of metribuzin (100% of sites) from April, 1991 to March, 1992, the percent of samples with detections was considerably less (40%).

3.3 Drinking Water Occurrence

The SDWA, as amended in 1986, required PWSs to monitor for specified "unregulated" contaminants, on a five year cycle, and to report the monitoring results to the States. Unregulated contaminants do not have an established or proposed NPDWR, but they are contaminants that were formally listed and required for monitoring under federal regulations. The intent was to gather scientific information on the occurrence of these contaminants to enable a decision as to whether or not regulations were needed. All non-purchased community water systems (CWSs) and non-purchased non-transient non-community water systems (NTNCWSs), with greater than 150 service connections, were required to conduct this unregulated contaminant monitoring. Smaller systems were not required to conduct this monitoring under federal regulations, but were required to be available to monitor if the State decided such monitoring was necessary. Many States collected data from smaller systems. Additional contaminants were added to the UCM program in 1991 (USEPA, 1991; 56 FR 3526) for required monitoring that began in 1993 (USEPA, 1992; 57 FR 31776).

Metribuzin has been monitored under the SDWA UCM program since 1993 (USEPA, 1992; 57 FR 31776). Monitoring ceased for small PWSs under a direct final rule published January 8, 1999

Table 3-5: Metribuzin occurrence in Midwest surface and ground water

	ground water ≥ MRL		surface water ≥ MRL		max. conc. µg/L
	% sites	% samples	% sites	% samples	
USGS					
Midwest Near-Surface Aquifers (1991)[1]	1.3%	1.0%	-	-	0.57
Midwest Near-Surface Aquifers (1992-94)[2]	nr	1.4%	-	-	0.22
Miss. River and Major Tributaries (1991)[3]	-	-	54%	nr	0.08
Miss. River and Major Tributaries (1991-92)[4]	-	-	100%	40%	0.03
Midwest Reservoirs (1992)[5]	-	-	12%	6.5%	nr
Pesticides in Ground Water Database (1971-91)[6]	4.3%	nr	-	-	25.1

[1] *Kolpin et al., 1994*
[2] *Kolpin et al., 1996*
[3] *Periera and Hostettler, 1993*
[4] *Goolsby and Battaglin, 1993*
[5] *Goolsby et al., 1993*
[6] *Barbash and Resek, 1996; data are national results including some Midwestern States*
- The Health Reference Level (HRL) used for metribuzin is 91 µg/L. This is a draft value for working review only.
- Minimum Reporting Levels (MRL) vary by study.
- nr = "not reported"

(USEPA, 1999a; 64 FR 1494), and ended for large PWSs with promulgation of the new UCMR issued September 17, 1999 (USEPA, 1999b; 64 FR 50556) and effective January 1, 2001. At the time the UCMR lists were developed, the Agency concluded there were adequate monitoring data for a regulatory determination. This obviated the need for continued monitoring under the new UCMR list.

3.3.1 Data Sources, Data Quality, and Analytical Approach

Currently, there is no complete national record of unregulated or regulated contaminants in drinking water from PWSs collected under SDWA. Many States have submitted unregulated contaminant PWS monitoring data to EPA databases, but there are issues of data quality, completeness, and representativeness. Nonetheless, a significant amount of State data are available for UCM contaminants that can provide estimates of national occurrence. The contaminant occurrence analyses findings presented in this report are based on a national cross-section of aggregated state data (i.e., a representative subset of available State data) derived from the Safe Drinking Water Information System/Federal version (SDWIS/FED) database.

The National Contaminant Occurrence Database (NCOD) is an interface to the actual occurrence data stored in the SDWIS/FED and can be queried to provide a summary of the data in SDWIS/FED for a particular contaminant. The drinking water occurrence data for metribuzin presented here were derived from monitoring data available in the SDWIS/FED database. Note, however, that the

SDWIS/FED data in this report have been reviewed, edited, and filtered to meet various data quality objectives for the purposes of this analysis. Hence, not all data from a particular source were used, only data meeting the quality objectives described below were included. The sources of these data, their quality and national aggregation, and the analytical methods used to estimate a given contaminant's national occurrence (from these data) are discussed in this section (for further details see USEPA, 2001a, 2001b).

3.3.1.1 UCM Rounds 1 and 2

The 1987 UCM contaminants include 34 volatile organic compounds (VOCs) (USEPA, 1987; 52 FR 25690). Metribuzin, a SOC, was *not* among these contaminants. The UCM (1987) contaminants were first monitored coincident with the Phase I regulated contaminants, during the 1988-1992 period. This period is often referred to as "Round 1" monitoring. The monitoring data collected by the PWSs were reported to the States (as primacy agents), but there was no protocol in place to report these data to EPA. These data from Round 1 were collected by EPA from many States over time and put into a database called the Unregulated Contaminant Information System (URCIS).

The 1993 UCM contaminants include 13 SOCs and 1 inorganic contaminant (IOC) (USEPA, 1992; 57 FR 31776). Monitoring for the UCM (1993) contaminants began coincident with the Phase II/V regulated contaminants in 1993 through 1998. This is often referred to as "Round 2" monitoring. The UCM (1987) contaminants were also included in the Round 2 monitoring. As with other monitoring data, PWSs reported these results to the States. EPA, during the past several years, requested that the States submit these historic data to EPA and they are now stored in the SDWIS/FED database.

Monitoring and data collection for metribuzin, a UCM (1993) contaminant, began in Round 2. Therefore, the following discussion regarding data quality screening, data management, and analytical methods focuses on SDWIS/FED. Discussion of the URCIS database is included where relevant, but it is worth noting that the various quality screening, data management, and analytical processes were nearly identical for the two databases. For further details on the two monitoring periods, as well as the databases, see USEPA (2001a) and USEPA (2001b).

3.3.1.2 Developing a Nationally Representative Perspective

The Round 2 data contain contaminant occurrence data from a total of 35 primacy entities (including 34 States and data for some tribal systems). However, data from some States are incomplete and biased. Furthermore, the national representativeness of the data is problematic because the data were not collected in a systematic or random statistical framework. These State data could be heavily skewed to low-occurrence or high-occurrence settings. Hence, the State data were evaluated based on pollution-potential indicators and the spatial/hydrologic diversity of the nation. This evaluation enabled the construction of a cross-section from the available State data sets that provides a reasonable representation of national occurrence.

A national cross-section comprised of the Round 2 state contaminant occurrence databases was established using the approach developed for the EPA report *A Review of Contaminant Occurrence in Public Water Systems* (USEPA, 1999d). This approach was developed to support occurrence analyses for EPA's Chemical Monitoring Reform (CMR) evaluation, and was supported by peer reviewers and stakeholders. The approach cannot provide a "statistically representative" sample because the original monitoring data were not collected or reported in an appropriate fashion. However, the resultant "national cross-section" of states should provide a clear indication of the central tendency of the national data. The remainder of this section provides a summary description of how the national cross-section from the SDWIS/FED (Round 2) database was developed. The details of the approach are presented in other documents (USEPA, 2001a, 2003); readers are referred to these for more specific information.

3.3.1.2.1 Cross-Section Development

As a first step in developing the cross-section, the State data contained in the SDWIS/FED database (that contains the Round 2 monitoring results) were evaluated for completeness and quality. Some State data in SDWIS/FED were unusable for a variety of reasons. Some States reported only detections, or the data was recorded with incorrect units. Data sets only including detections are obviously biased, over-representing high-occurrence settings. Other problems included substantially incomplete data sets without all PWSs reporting (USEPA, 2001a Sections II and III).

The balance of the States remaining after the data quality screening were then examined to establish a national cross-section. This step was based on evaluating the States' pollution potential and geographic coverage in relation to all States. Pollution potential is considered to ensure a selection of States that represent the range of likely contaminant occurrence and a balance with regard to likely high and low occurrence. Geographic consideration is included so that the wide range of climatic and hydrogeologic conditions across the United States are represented, again balancing the varied conditions that affect transport and fate of contaminants, as well as conditions that affect naturally occurring contaminants (USEPA, 2001b Sections III.A. and III.B.).

The cross-section States were selected to represent a variety of pollution potential conditions. Two primary pollution potential indicators were used. The first factor selected indicates pollution potential from manufacturing/population density and serves as an indicator of the potential for VOC contamination within a State. Agriculture was selected as the second pollution potential indicator because the majority of SOCs of concern are pesticides (USEPA, 2001b Section III.A.). The 50 individual States were ranked from highest to lowest based on the pollution potential indicator data. For example, the State with the highest ranking for pollution potential from manufacturing received a ranking of 1 for this factor and the State with the lowest value was ranked as number 50. States were ranked for their agricultural chemical use status in a similar fashion.

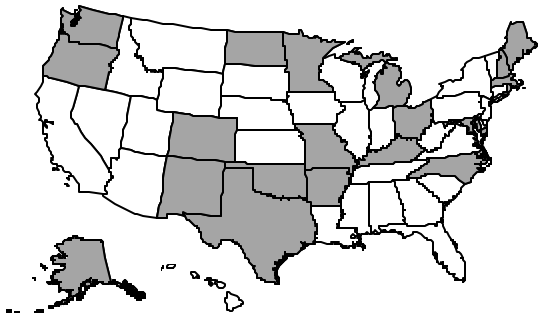
The States' pollution potential rankings for each factor were subdivided into four quartiles (from highest to lowest pollution potential). The cross-section States were chosen equally from all quartiles for both pollution potential factors to ensure representation, for example, from: States with high agrochemical pollution potential rankings and high manufacturing pollution potential rankings; States

with high agrochemical pollution potential rankings and low manufacturing pollution potential rankings; States with low agrochemical pollution potential rankings and high manufacturing pollution potential rankings; and States with low agrochemical pollution potential rankings and low manufacturing pollution potential rankings (USEPA, 2001b Section III.B.). In addition, some secondary pollution potential indicators were considered to further ensure that the cross-section States included the spectrum of pollution potential conditions (high to low). At the same time, States within the specific quartiles were considered collectively across all quartiles in an attempt to provide geographic coverage across all regions of the U.S.

The data quality screening, pollution potential rankings, and geographic coverage analysis established a national cross-section of 20 Round 2 (SDWIS/FED) States. The cross-section States provide good representation of the nation's varied climatic and hydrogeologic regimes and the breadth of pollution potential for the contaminant groups (Figure 3-2).

Figure 3-2: Geographic distribution of cross-section States for Round 2 (SDWIS/FED)

Round 2 (SDWIS/FED) Cross-Section States	
Alaska	New Hampshire
Arkansas	New Mexico
Colorado	North Carolina
Kentucky	North Dakota
Maine	Ohio
Maryland	Oklahoma
Massachusetts	Oregon
Michigan	Rhode Island
Minnesota	Texas
Missouri	Washington



3.3.1.2.2 Cross-Section Evaluation

To evaluate and validate the method for creating the national cross-sections, the method was used to create smaller State subsets from the 24-State, Round 1 (URCIS) cross-section. Again, States were chosen to achieve a balance from the quartiles describing pollution potential, and a balanced geographic distribution, to incrementally build subset cross-sections of various sizes. For example, the Round 1 cross-section was tested with subsets of 4, 8 (the first 4 State subset plus 4 more States), and 13 (8 State subset plus 5) States. Two additional cross-sections were included in the analysis for comparison; a cross-section composed of 16 States with biased data sets eliminated from the 24 State cross-section for data quality reasons, and a cross-section composed of all 40 Round 1 States (USEPA, 2001b Section III.B.1).

These Round 1 incremental cross-sections were then used to evaluate occurrence for an array of both high and low occurrence contaminants. The comparative results illustrate several points. The results are quite stable and consistent for the 8-, 13- and 24-State cross-sections. They are much less so for the 4-State, 16-State (biased), and 40-State (all Round 1 States) cross-sections. The 4-State cross-section is apparently too small to provide balance both geographically and with pollution potential, a finding that concurs with past work (USEPA, 1999c). The CMR analysis suggested that a minimum of 6-7 States was needed to provide balance both geographically and with pollution potential, and the CMR report used 8 States out of the available data for its nationally representative cross-section (USEPA, 1999c). The 16-State and 40-State cross-sections, both including biased States, provided occurrence results that were unstable and inconsistent for a variety of reasons associated with their data quality problems (USEPA, 2001b Section III.B.1).

The 8-, 13-, and 24-State cross-sections provide very comparable results, are consistent, and are usable as national cross-sections to provide estimates of contaminant occurrence. Including greater data from more States improves the national representation and the confidence in the results, as long as the States are balanced related to pollution potential and spatial coverage. The 20-State cross-section provides the best, nationally representative cross-section for the Round 2 data.

3.3.1.3 Data Management and Analysis

The cross-section analyses focused on occurrence at the water system level; i.e., the summary data presented discuss the percentage of public water *systems* with detections, not the percentage of *samples* with detections. By normalizing the analytical data to the system level, skewness inherent in the sample data is avoided. System level analysis was used since a PWS with a known contaminant problem usually has to sample more frequently than a PWS that has never detected the contaminant. Obviously, the results of a simple computation of the percentage of samples with detections (or other statistics) can be skewed by the more frequent sampling results reported by the contaminated site. The system level of analysis is conservative. For example, a system need only have a single sample with an analytical result greater than the MRL, i.e., a detection, to be counted as a system with a result "greater than the MRL."

Also, the data used in the analyses were limited to only those data with confirmed water source and sampling type information. Only standard SDWA compliance samples were used of 20 SDWIS/FED Round 2 cross-section States with usable data for IOCs and VOCs. "Special" samples, or "investigation" samples (investigating a contaminant problem that would bias results) and samples of unknown type, were not used in the analyses. Various quality control and review checks were made of the results, including follow-up questions to the States providing the data. Many of the most intractable data quality problems encountered occurred with older data. These problematic data were, in some cases, simply eliminated from the analysis. For example, when the number of problematic data were insignificant relative to the total number of observations, they were dropped from the analysis (for further details see Cadmus, 2000).

As indicated above, Massachusetts is included in the 20-State, Round 2 national cross-section. Massachusetts' SOC data were problematic. Massachusetts reported Round 2 sample results for

SOCs from only 56 PWSs, while reporting VOC results from over 400 different PWSs. Massachusetts SOC data also contained an atypically high percentage of systems with analytical detections when compared to all other States. Through communications with Massachusetts data management staff it was learned that the State's SOC data were incomplete and that the SDWIS/FED record for Massachusetts SOC data was also incomplete. For instance, the SDWIS/FED Round 2 data for Massachusetts indicates 14.3% of systems reported detections of metribuzin. The cross-section State with the next highest detection frequency reported only 0.2% of systems with detections. In contrast, Massachusetts data characteristics and quantities for IOCs and VOCs were reasonable and comparable with other States' results. Therefore, Massachusetts was included in the group of 20 SDWIS/FED Round 2 cross-section States with usable data for IOCs and VOCs, but its metribuzin (SOC) data were omitted from Round 2 cross-section occurrence analyses and summaries presented in this report.

3.3.1.4 Occurrence Analysis

To evaluate national contaminant occurrence, a two-stage analytical approach has been developed. The first stage of analysis provides a straightforward, conservative, non-parametric evaluation of occurrence of the CCL regulatory determination priority contaminants as described above. These Stage 1 descriptive statistics are summarized here. Based in part on the findings of the Stage 1 Analysis, EPA will determine whether more rigorous parametric statistical evaluations, the Stage 2 Analysis, may be warranted to generate national probability estimates of contaminant occurrence and exposure for priority contaminants (for details on this two stage analytical approach see Cadmus, 2000, 2001).

The summary descriptive statistics presented in Table 3-6 for metribuzin are a result of the Stage 1 analysis and include data from Round 2 (SDWIS/FED, 1993-1997) cross-section States (minus Massachusetts). Included are the total number of samples, the percent of samples with detections, the 99th percentile concentration of all samples, the 99th percentile concentration of samples with detections, and the median concentration of samples with detections. The percentages of PWSs and population served indicate the proportion of PWSs whose analytical results showed a detection(s) of the contaminant (simple detection, > MRL) at any time during the monitoring period; or a detection(s) greater than half the HRL; or a detection(s) greater than the HRL.

Metribuzin is not considered to be a linear carcinogen by the oral route of exposure. Accordingly, the Maximum Contaminant Level Goal (MCLG) is derived using a Reference Dose (RfD) approach. The value used as the HRL for this occurrence evaluation is derived from the RfD using the following equation:

$$HRL = \frac{RfD \times Body\ Weight}{Drinking\ Water\ Intake} \times Relative\ Source\ Contribution$$

The body weight used in the calculation is an average adult body weight (70 Kg) and the value for daily water intake is 2 L. In the calculation of the HRL, the relative source contribution is 20%. A different

relative source factor might be used to calculate the MCLG if a determination is made to regulate metribuzin.

The 99th percentile concentration is used here as a summary statistic to indicate the upper bound of occurrence values because maximum values can be extreme values (outliers) that sometimes result from sampling or reporting error. The 99th percentile concentration is presented for both the samples with only detections and all of the samples because the value for the 99th percentile concentration of all samples is below the MRL (denoted by "<" in Table 3-6). For the same reason, summary statistics such as the 95th percentile concentration of all samples or the median (or mean) concentration of all samples are omitted because these also are all "<" values. This is the case because only 0.003% of all samples recorded detections of metribuzin in Round 2.

As a simplifying assumption, a value of half the MRL is often used as an estimate of the concentration of a contaminant in samples/systems whose results are less than the MRL. For a contaminant with relatively low occurrence, such as metribuzin in drinking water occurrence databases, the median or mean value of occurrence using this assumption would be half the MRL (0.5 * MRL). However, for these occurrence data this is not straightforward. For Round 2, States have reported a wide range of values for the MRLs. This is in part related to State data management differences as well as real differences in analytical methods, laboratories, and other factors.

The situation can cause confusion when examining descriptive statistics for occurrence. For example, most Round 2 States reported non-detections as zeros resulting in a modal MRL value of zero. By definition the MRL cannot be zero. This is an artifact of State data management systems. Because a simple meaningful summary statistic is not available to describe the various reported MRLs, and to avoid confusion, MRLs are not reported in the summary table (Table 3-6).

In Table 3-6, national occurrence is estimated by extrapolating the summary statistics for the 20 State cross-section (minus Massachusetts) to national numbers for systems, and population served by systems, from the *Water Industry Baseline Handbook, Second Edition* (USEPA, 2000e). From the handbook, the total number of CWSs, plus NTNCWSs, is 65,030, and the total population served by CWSs plus NTNCWSs is 213,008,182 persons (see Table 3-6). To generate the estimate of national occurrence based on the cross-section occurrence findings, the national number of PWSs (or population served by PWSs) is simply multiplied by the percentage value for the particular cross-section occurrence statistic (e.g., the national estimate for the total number of PWSs with detections (5) is the product of the total national number of PWSs (65,030) and the percentage of PWSs with detections (0.007%)).

Included in Table 3-6 in addition to the results from the cross-section data are results and national extrapolations from all Round 2 reporting States. The data from the biased States are included because of metribuzin's very low occurrence in drinking water samples in all States. For contaminants with very low occurrence, such as metribuzin where very few States have detections, any occurrence becomes more important, relatively. For such contaminants, the cross-section process can easily miss a State with occurrence that becomes more important. This is the case with metribuzin.

Extrapolating only from the cross-section States, metribuzin's very low occurrence clearly underestimates national occurrence. For example, while data from biased States like Massachusetts exaggerate occurrence because of incomplete reporting, the detections are real and need to be accounted for because extrapolations from the cross-section States do not predict enough detections in the biased States. Therefore, results from all reporting Round 2 States, including the biased States, are also used here to extrapolate to a national estimate. Using the biased States' data should provide conservative estimates, likely overestimates, of national occurrence for metribuzin.

As exemplified by the cross-section extrapolations for metribuzin, national extrapolations of these Stage 1 analytical results can be problematic, especially for contaminants with very low occurrence, because the State data used for the cross-section are not a strict statistical sample. For this reason, the nationally extrapolated estimates of occurrence based on Stage 1 results are not presented in the Federal Register Notice. The presentation in the Federal Register Notice of only the actual results of the cross-section analysis maintains a straight-forward description, and the integrity of the data, for stakeholder review. The nationally extrapolated Stage 1 occurrence values are presented here, however, to provide additional perspective. A more rigorous statistical modeling effort, the Stage 2 analysis, could be conducted on the cross-section data (Cadmus, 2001). The Stage 2 results would be more statistically robust and more suitable to national extrapolation. This approach would provide a probability estimate and would also allow for better quantification of estimation error.

3.3.1.5 Additional Drinking Water Data from the Corn Belt

To augment the SDWA drinking water data analysis described above, and to provide additional coverage of the corn belt states where metribuzin use is highest (Figure 3-1), independent analyses of finished drinking water data from the states of Iowa, Illinois, Indiana, and Ohio are reviewed below. The Iowa analysis examined SDWA compliance monitoring data from surface and ground water PWSs for the years 1988-1995 (Hallberg et al., 1996). Illinois and Indiana compliance monitoring data for surface and ground water PWSs were evaluated. The data were mostly for the years from 1993 to 1997, though some earlier data were also analyzed (after USEPA, 1999c). These state data sets were available from an independent review of contaminant monitoring in drinking water (USEPA, 1999c). Finally, the Ohio Round 2 data analyzed with the 20-state cross-section are examined independently for comparison with the other supplemental data sets from corn belt states.

Additional reviews of national and state drinking water monitoring results are included for further perspective on corn belt occurrence of metribuzin. The Iowa State-Wide Rural Well-Water Survey was conducted in 1988-1989 to assess pesticide occurrence in rural private wells (Kross et al., 1990). The National Pesticide Survey (NPS) provides extensive national monitoring data for drinking water, including data from Midwestern states, for the years 1988-1990 (USEPA, 1990). Hallberg (1989) reviewed special contaminant occurrence studies of raw surface water supplies in Illinois (1985-1987), and both raw and finished drinking water from surface water in Iowa (1986). Data sources, data quality, and analytical methods for these analyses are described in the respective reports.

3.3.2 Results

3.3.2.1 Occurrence Estimates

As noted, the extrapolation from cross-section states underestimates national metribuzin occurrence, and the resulting percentages of PWSs with detections are very low (Table 3-6). The cross-section shows approximately 0.007% of PWSs (about 5 PWSs nationally) experienced detections of metribuzin above the MRL, affecting less than 0.0003% of the population served (approximately 1,000 people nationally). No PWSs reported detections at levels above ½ HRL or above the HRL. Detection frequencies are higher for ground water systems when compared to surface water systems, as surface water systems reported zero detections. Concentrations are also low: for samples with detections the median and 99th percentile concentrations are 0.10 µg/L. These figures are identical because for metribuzin, Washington was the only state that reported a detection (0.10 µg/L) and thus this statistic is both the median and 99th percentile concentration.

Because metribuzin's low occurrence yields an underestimate from cross-section states, all data are used, even the biased data, to present a conservative upper bound estimate. Conservative estimates of metribuzin occurrence using all of the Round 2 reporting states still show relatively low detection frequencies (Table 3-6). Approximately 0.28% of PWSs (estimated at 182 PWSs nationally) experienced detections above the MRL, while no PWSs experienced detections greater than ½ HRL or HRL. These figures indicate that about 1.61% of the population is affected by concentrations above the MRL (approximately 3.4 million people nationally), and 0% of the population is affected by concentrations above ½ HRL or HRL. The proportion of surface water PWSs with detections was greater than ground water systems. The median and 99th percentile concentrations of detections are 1 µg/L and 3 µg/L, respectively.

The Round 2 reporting states and the Round 2 national cross-section show a proportionate balance in PWS source waters compared to the national inventory. Nationally, 91% of PWSs use ground water (and 9% surface waters); Round 2 national cross-section states show 88% use ground water (and 12% surface waters); Round 2 reporting states show 87% use ground water (and 13% surface waters). The relative populations served are not as comparable. Nationally, about 40% of the population is served by PWSs using ground water (and 60% by surface water). For the Round 2 cross-section, 29% of the cross-section population is served by ground water PWSs (and 71% by surface water). For all Round 2 reporting States, 26% of the population is served by ground water PWSs (and 74% by surface water). The resultant national extrapolations are not additive as a consequence of these disproportions (Table 3-6).

3.3.2.2 Occurrence in the Corn Belt

SDWA compliance monitoring data from the corn belt States of Illinois, Indiana, and Ohio also show very low occurrence of metribuzin. The pesticide was not detected above the Health Reference Level in any case, and the highest 99th percentile concentration of detections among the three States was for Illinois at 0.7 µg/L (Table 3-7). Illinois also had the highest maximum concentration at 20 µg/L, still well below the HRL (after USEPA, 1999c). SDWA compliance monitoring from Iowa for the years 1988-1995 show similar results, although the data are not presented in Table 3-7 because they were not compiled at the system level in the same manner. Approximately 0.8% of samples analyzed

Table 3-6: Summary occurrence statistics for metribuzin

Frequency Factors	20 State Cross-Section[1] (Round 2)	All Reporting States[2] (Round 2)	National System & Population Numbers[3]	
Total Number of Samples	34,507	42,856	--	
Percent of Samples with Detections	0.003%	0.23%	--	
99th Percentile Concentration (all samples)	< (Non-detect)	< (Non-detect)	--	
Health Reference Level	91 µg/L	91 µg/L	--	
Minimum Reporting Level (MRL)	Variable[4]	Variable[4]	--	
99th Percentile Concentration of Detections	0.10 ug/L	3.0 ug/L	--	
Median Concentration of Detections	0.10 µg/L	1.0 µg/L	--	
Total Number of PWSs	13,512	15,333	65,030	
Number of GW PWSs	11,833	13,311	59,440	
Number of SW PWSs	1,679	2,022	5,590	
Total Population	50,633,068	62,397,416	213,008,182	
Population of GW PWSs	14,886,153	16,255,818	85,681,696	
Population of SW PWSs	35,746,915	46,141,598	127,326,486	
Occurrence by System			**National Extrapolation[5]**	
% PWSs with detections (> MRL)	0.007%	0.28%	5	182
Range	0 - 0.17%	0-14.29%	N/A	N/A
GW PWSs with detections	0.008%	0.14%	5	83
SW PWSs with detections	0.00%	1.24%	0	69
% PWSs > 1/2 Health Reference Level (HRL)	0.00%	0.00%	0	0
Range	0 - 0.00%	0-0.00%	N/A	N/A
GW PWSs > 1/2 Health Reference Level	0.00%	0.00%	0	0
SW PWSs > 1/2 Health Reference Level	0.00%	0.00%	0	0
% PWSs > Health Reference Level	0.00%	0.00%	0	0
Range	0 - 0.00%	0-0.00%	N/A	N/A
GW PWSs > Health Reference Level	0.00%	0.00%	0	0
SW PWSs > Health Reference Level	0.00%	0.00%	0	0
Occurrence by Population Served				
% PWS Population Served with detections	0.0003%	1.61%	1,000	3,420,000
Range	0 - 0.01%	0-14.92%	N/A	N/A
GW PWS Population with detections	0.00%	0.24%	1,000	208,000
SW PWS Population with detections	0.00%	2.09%	0	2,656,000
% PWS Population Served > 1/2 Health Reference Level	0.00%	0.00%	0	0
Range	0 - 0.00%	0-0.00%	N/A	N/A
GW PWS Population > 1/2 Health Reference Level	0.00%	0.00%	0	0
SW PWS Population > 1/2 Health Reference Level	0.00%	0.00%	0	0
% PWS Population Served > Health Reference Level	0.00%	0.00%	0	0
Range	0 - 0.00%	0-0.00%	N/A	N/A
GW PWS Population > Health Reference Level	0.00%	0.00%	0	0
SW PWS Population > Health Reference Level	0.00%	0.00%	0	0

[1] Summary Results based on data from 20-State Cross-Section (minus Massachusetts), from SDWIS/FED, UCM (1993) Round 2.
[2] Summary Results based on data from all reporting states from SDWIS/FED, UCM (1993) Round 2.
[3] Total PWS and population numbers are from EPA March 2000 Water Industry Baseline Handbook (USEPA, 2000e).
[4] See Section 3.3.1.4 for discussion.
[5] National extrapolations are from the 20-State cross-section data (left) and all Round 2 states reporting data (right) using the Baseline Handbook system and population numbers.
- PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; MRL = Minimum Reporting Level (for laboratory analyses); HRL = Health Reference Level, an estimated health effect level used for preliminary assessment for this review; N/A = Not Applicable"
- 99th Percentile Concentration = the concentration value of the 99th percentile of either all analytical results or just the detections (in µg/L)
- Median Concentration of Detections = the median analytical value of all the detections (analytical results greater than the MRL) (in µg/L)
- Total Number of PWSs = the total number of public water systems with records for metribuzin
- Total Population Served = the total population served by public water systems with records for metribuzin
- % PWS with detections, % PWS > ½ Health Reference Level, % PWS > Health Reference Level = percent of the total number of public water systems with at least one analytical result that exceeded the MRL, ½ Health Reference Level, Health Reference Level, respectively

for metribuzin in Iowa drinking water had detections of the compound with a maximum concentration of 1.6 µg/L. The 99th percentile concentration of all samples was a non-detect (Hallberg et al., 1996).

Metribuzin detection frequencies are generally much greater in surface water when compared to ground water (Tables 3-8 and 3-9). Two exceptions are the Iowa SDWA compliance data, in which surface and ground water detection frequencies are essentially the same (0.77% and 0.76%, respectively), and the Indiana SDWA compliance data with no metribuzin detections in surface water (Table 3-7).

Table 3-8 presents data from a number of national and State drinking water monitoring studies with results in corn belt States. The National Pesticide Survey reports no detections for metribuzin. Compliance monitoring from Ohio surface water PWSs shows the highest detection frequency of metribuzin by system (79.9%), but the data are from a targeted study of sensitive surface waters so results may not be representative. The highest reported concentration of the studies summarized in Table 3-8, 3.7 µg/L, is well below the HRL. Environmental Working Group reports were reviewed; however, only preliminary results were available from a special study of finished tap water in 29 cities. Metribuzin was found in unspecified concentrations in 7% (2) of the 29 cities (Cohen et al., 1995).

The Iowa State-Wide Rural Well-Water Survey established a statistically significant correlation between increasing well depth and decreasing pesticide contamination, as evidenced by the lower detection frequency of metribuzin in drinking water wells $\geq$50 ft deep (Table 3-8). Comparisons between raw and finished water in Iowa show detection frequencies of metribuzin in surface water increased from the raw to finished State (Table 3-8; Hallberg, 1989). This is probably a result of either analytical variance, imprecise matching between raw and finished water samples, or pesticide adsorption to–and subsequent release from–filtration/treatment materials (Hallberg, 1989).

3.3.2.3 Regional Patterns

Occurrence results are displayed graphically by State in Figures 3-3 and 3-4 to assess whether any distinct regional patterns of occurrence are present. Thirty-four States reported Round 2 data but 10 of those States have no data for metribuzin (Figure 3-3). Another 21 States did not detect metribuzin. The remaining 3 States detected metribuzin in drinking water and are located on the east and west coasts of the United States (Figure 3-3). In contrast to the summary statistical data presented in the previous section, this simple spatial analysis includes the biased Massachusetts data.

The simple spatial analysis presented in Figures 3-3 and 3-4 does not suggest any special regional patterns. Further, use and environmental release information, (section 3.1) and ambient water quality data (section 3.2), indicate that metribuzin has low detection even in non-drinking water sources. According to TRI data, industrial releases have occurred since 1995 in only three States and one U.S. territory (IA, MO, NB, Puerto Rico; USEPA, 2000b). However, the use patterns for metribuzin (Figure 3-1) do show that use is concentrated in soybean producing regions (similar to the corn belt) in the Midwest States and along the Mississippi River Valley production region. These States are missing from the Round 2 data, hence, a special review was conducted to evaluate data from Iowa, Illinois,

Table 3-7: SDWA compliance monitoring data from the States of Illinois, Indiana, and Ohio

Frequency Factors	**Illinois[1]**	**Indiana[2]**	**Ohio[3]**
Total Number of Samples	14,818	1,033	4,039
Percent of Samples with Detections	0.2%	0.1%	0.0%
99th Percentile Concentration (all samples)	< (ND)	< (ND)	< (ND)
Health Reference Level	91 µg/L	91 µg/L	91 µg/L
Minimum Reporting Level (MRL)	Variable[4]	Variable[4]	Variable[4]
99th Percentile Concentration of Detections	0.7 µg/L	0.2 µg/L	0 µg/L
Median Concentration of Detections	0.2 µg/L	0.2 µg/L	0 µg/L
Minimum Concentration of Detections	0.1 µg/L	0.2 µg/L	0 µg/L
Total Number of PWSs	1,139	392	2178
Number of GW PWSs	1,030	345	2,017
Number of SW PWSs	109	47	161
Occurrence by System			
% PWSs with detections (> MRL)	0.97%	0.26%	0.00%
GW PWSs with detections	0.10%	0.29%	0.00%
SW PWSs with detections	9.17%	0.00%	0.00%
% PWSs > 1/2 Health Reference Level (HRL)	0.00%	0.00%	0.00%
GW PWSs > 1/2 Health Reference Level	0.00%	0.00%	0.00%
SW PWSs > 1/2 Health Reference Level	0.00%	0.00%	0.00%
% PWSs > Health Reference Level	0.00%	0.00%	0.00%
GW PWSs > Health Reference Level	0.00%	0.00%	0.00%
SW PWSs > Health Reference Level	0.00%	0.00%	0.00%

[1] After an independent analysis of Illinois SDWA compliance monitoring data from 1993-1997 (USEPA, 1999c).

[2] After an independent analysis of Indiana SDWA compliance monitoring data from 1993-1997 (USEPA, 1999c).

[3] Summary results based on analysis of Ohio data from the SDWIS/FED UCM (1993), Round 2.

[4] See Section 3.3.1.4 for discussion.

- PWS = Public Water Systems; GW = Ground Water; SW = Surface Water; MRL = Minimum Reporting Level (for laboratory analyses);

HRL = Health Reference Level, an estimated health effect level used for preliminary assessment for this review

- The Health Reference Level (HRL) used for metribuzin is 91 µg/L. This is a draft value for working review only.

- Total Number of Samples = the total number of analytical records for metribuzin

- 99th Percentile Concentration = the concentration value of the 99th percentile of either all analytical results or just the detections (in µg/L)

- Median Concentration of Detections = the median analytical value of all the detections (analytical results greater than the MRL) (in µg/L)

- Total Number of PWSs = the total number of public water systems with records for metribuzin

- % PWS with detections, % PWS > ½ Health Reference Level, % PWS > Health Reference Level = percent of the total number of public water systems with at least one analytical result that exceeded the MRL, ½ Health Reference Level, or Health Reference Level, respectively

Table 3-8: Metribuzin occurrence in Midwest drinking water

	% sites ≥ MRL	% samples ≥ MRL	maximum concentration (µg/L)
Ground Water Surveys			
National Pesticide Survey (1988-90)[1]	nd	nd	nd
Iowa State-Wide Rural Well-Water Survey [2]			
wells < 50 ft deep	3.0%	nr	0.43
wells ≥ 50 ft deep	1.4%	nr	0.72
Special Surface Water Studies			
raw water			
Iowa (1986)[3]	nr	7.0%	0.89
Illinois (1985-87)[3]	nr	15.0%	3.70
finished water			
Ohio (1993-)[4]	79.9%	22.3%	1.8
Iowa (1986)[3]	nr	12.0%	0.45

[1] USEPA, 1990 ; data are national results including some Midwestern states
[2] Kross et al., 1990
[3] cited in Hallberg, 1989
[4] USEPA, 1999c
- MRLs vary by study.
- nd = results below the respective reporting level
- nr = "not reported"

Indiana, and Ohio. Occurrence rates in these States are much greater than other areas, but even in these States no PWSs had results greater than the HRL.

3.4 Conclusion

Detection frequencies and concentrations of metribuzin in ambient surface and ground water are low, especially in ground water. Even so, it is one of the 21 most commonly detected pesticides in ground water from the first round of NAWQA intensive data collection. The annual mean frequency of metribuzin detection in surface water was less than 15% for all land-use settings and concentrations. Midwestern ambient surface and ground water concentrations and detection frequencies are also low. Releases of metribuzin to the environment were reported in the TRI from only three States and one territory.

Figure 3-3: States with PWSs with detections of metribuzin for all States with data in SDWIS/FED (Round 2)

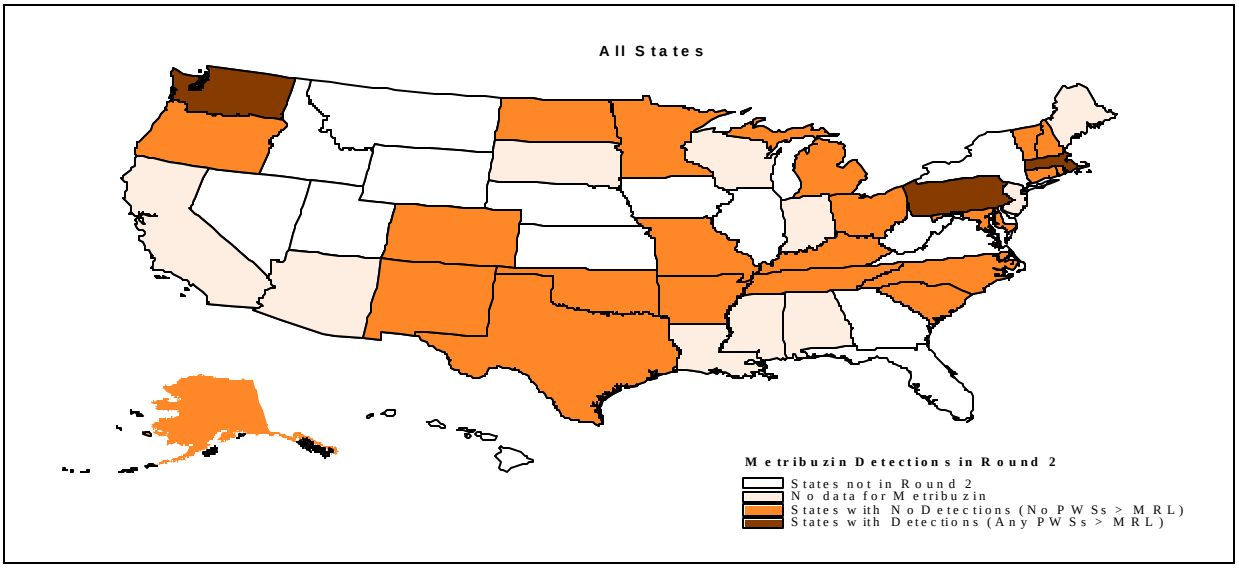
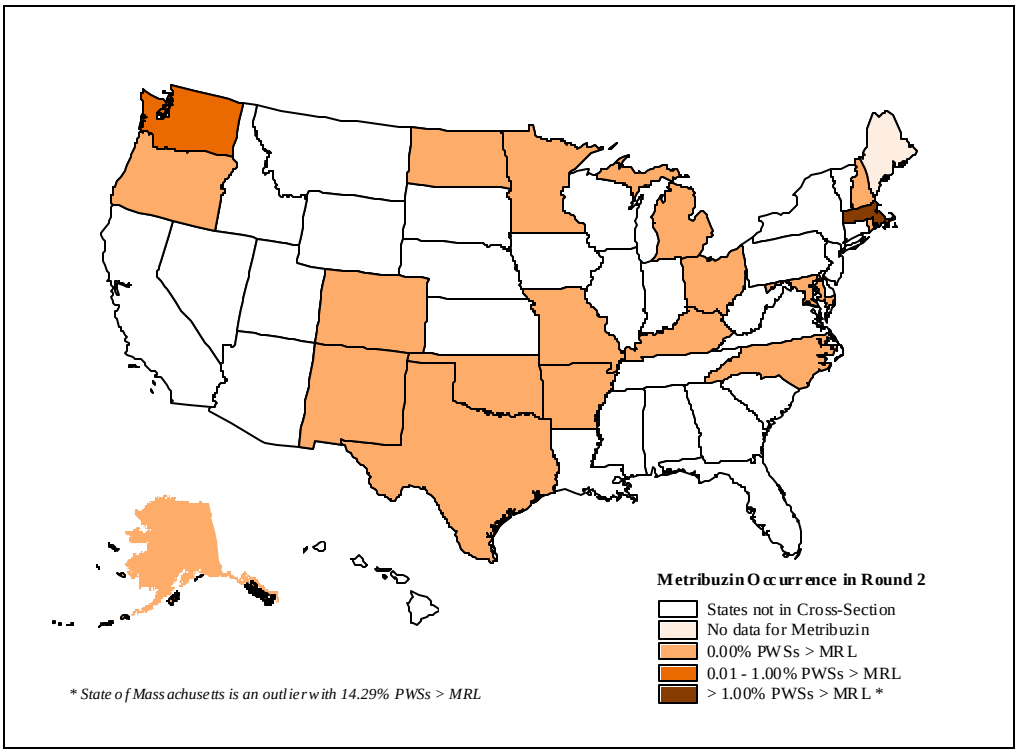
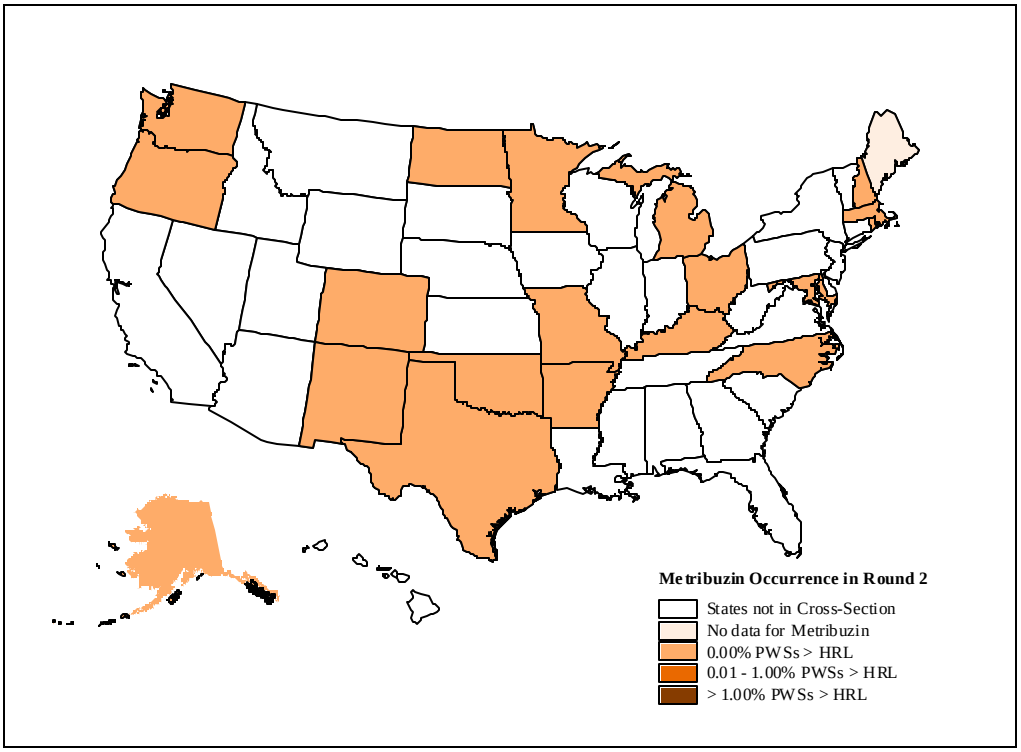


Figure 3-4: Round 2 cross-section States with PWSs with detections of metribuzin (any PWSs with results greater than the Minimum Reporting Level [MRL]; above) and concentrations greater than the Health Reference Level (HRL; below)





Metribuzin has been detected in PWS samples collected under the SDWA. Cross-section occurrence estimates are very low with only 0.003% of all samples showing detections. Significantly, the values for the 99th percentile and median concentrations of all samples are less than the MRL. For the Round 2 cross-section samples with detections, both the median and the 99th percentile concentrations are 0.10 µg/L. Systems with detections constitute approximately 0.007% of Round 2 cross-section systems. National estimates for the population served by PWSs with detections using the cross-section data are also low: approximately 1,000 people (about 0.0003% of the national PWS population) are served by PWSs with metribuzin detections greater than the MRL, and no PWSs reported detections greater than ½ HRL or HRL. Using more conservative estimates of occurrence from all States reporting SDWA Round 2 monitoring data, including States with biased data, 0.28% of the nation's PWSs (approximately 182 systems and 3.4 million people served) are affected by metribuzin concentrations greater than the MRL, while no PWSs are affected by concentrations greater than ½ HRL or HRL.

The heaviest use of metribuzin is across the nation's corn-soybean production area. These States are not well represented in the Round 2 database. Therefore, additional data from the Midwest corn belt were also evaluated. Drinking water data from the corn belt States of Iowa, Indiana, Illinois, and Ohio also show very low occurrence of metribuzin. Special, targeted surface water studies from Ohio have the highest detection frequency of metribuzin (79.9% of systems). The pesticide was not detected above the Health Reference Level in any sample, with the highest concentration at 20 µg/L.

4.0 HEALTH EFFECTS

A description of health effects and dose-response information associated with exposure to metribuzin is summarized below. For more detail, please refer to the *Health Effects Support Document for Metribuzin* (USEPA, 2003).

4.1 Hazard Characterization and Mode of Action Implications

There are no epidemiological studies that have assessed adverse human health effects caused by exposure to metribuzin. Exposure to metribuzin may occur primarily in an occupational setting, particularly in the agriculture industry where it is used as an herbicide. However, high 50% lethal dose values resulting from acute toxicity animal studies have indicated that metribuzin may potentially have low toxicity levels (Kimmerle et al., 1969; Morgan, 1982).

Subchronic studies in animals suggest that metribuzin may cause adverse effects on body and organ weight, and hematological parameters. Wistar rats, exposed to metribuzin through their diet at 1500 ppm for 3-months, exhibited a significant reduction in body weight gain, and increased liver and thyroid weights (Loser et al., 1969). However, a 3-month dietary exposure in Beagle dogs did not affect body weight gain or food consumption; only clinical parameters such as liver enzyme (SGOT and SGPT) levels were affected (Chaisson and Cueto, 1970). Metribuzin causes slight dermal irritation in rabbits, but has not been found to cause eye irritation (Kimmerle et al., 1969).

Chronic studies of metribuzin on rats also report effects on body weight gain, mortality, and liver enzyme and histopathological changes. While 2-year feeding studies conducted on rats (0, 25, 35, 100 or 300 parts/million [ppm]) and mice (0, 200, 800 or 3200 ppm) indicated no significant differences in body weight gain, food consumption, or mortality (Loser and Mohr, 1974; Hayes, 1981), another 2-year feeding study in rats using a higher dose (900 ppm) of metribuzin did report a decrease in body weight gain (Christenson and Wahle, 1993). The latter study also reported histopathological changes such as significant increases in corneal neovascularization, discolored zones in the liver, an enlarged abdomen, enlarged adrenal and thyroid glands, ocular opacity, an enlarged epididymal mass in males, and the presence of ovarian cysts in female rats. In Beagle dogs, chronic exposure to 1,500 ppm caused a significant increase in the mortality rate and liver dysfunction as evidenced by increased activity of the liver enzymes SGOT, SGPT and OCT (Loser and Mirea, 1974). Thyroid weight also increased. Histopathologic findings included liver and kidney damage at the highest dose. Liver and kidney effects, decreased body weight gain, and mortality at the highest dose are considered the critical effects of metribuzin exposure.

There are few studies that have assessed the developmental and reproductive effects of metribuzin exposure. In general, maternal toxicity effects observed in rats and rabbits include reduced body weight gain and food consumption, and are accompanied by slight toxicity to the fetus (Kowaski et al., 1986; Machemer, 1972; Unger and Shellenberger, 1981). A two-generation study in rats reported that both first and second generations consumed less food and gained less body weight (Porter et al., 1988). Autopsy findings in both generations were not affected by exposure to metribuzin. Another 3-generation reproduction study in rats found no treatment-related effects (Loser and Siegmund, 1974).

No animal studies have addressed the neurologic or immunotoxic effects of metribuzin. There is evidence of endocrine effects induced by metribuzin, including elevated plasma thyroxine levels in rats and decreased triiodothyronine levels in rats and rabbits (Porter et al. 1993; Christenson and Wahle, 1993; Flucke and Hartmann, 1989).

The EPA has classified metribuzin as class D, not classifiable as to human carcinogenicity because of inadequate data in humans or animals. A lifetime dietary study in CD-1 mice and 2-year feeding studies in Wistar rats were negative for the induction of tumors compared to control incidences (Hayes, 1981; Loser and Mohr, 1974; Christenson and Wahle, 1993).

4.2 Dose-Response Characterization and Implications in Risk Assessment

The EPA's RfD is an estimate of a daily exposure to the human population (including sensitive subgroups) that is likely to be without appreciable risk of deleterious effects over a lifetime. The principal study utilized for RfD derivation was the 2-year chronic study in rats conducted by Christenson and Wahle (1993), where 344 Fisher rats received 0, 30, 300 or 900 ppm (0, 1.3, 13.8, 42.2 mg/kg-day in males; 0, 1.6, 17.7, 53.6 mg/kg-day females) of metribuzin for 104 weeks. At 30 ppm, both sexes exhibited increased absolute and relative thyroid weights, and statistically significant increases in blood levels of thyroxine (T4) and decreases in blood levels of triiodothyronine (T3). In addition, females exhibited decreased lung weight. Since the health effects exhibited by both sexes were considered to be biologically insignificant, 30ppm was considered the no observed adverse effect

level (NOAEL). The RfD of 0.013 mg/kg-day was derived by dividing the NOAEL by an uncertainty factor of 100, which was used to account for inter- and intra-species variability. The HRL was derived from the RfD as discussed in section 3.3.1.4.

4.3 Relative Source Contribution

Relative source contribution analysis compares the magnitude of exposure to metribuzin expected via drinking water and the magnitude of exposure from other media, such as food, air and soil. The intake of metribuzin from drinking water can be calculated from the median concentrations described above for both the cross-section study and the study of all the Round 2 States. Using the median metribuzin level from the 20 State cross-section study of 0.10 μg/L, an average daily intake of 2 L/day for an adult, and an average weight of 70 kg for an adult, the corresponding dose would be 2.8×10^{-3} mg/kg-day for adults. For children, assuming an intake of 1 L/day and an average weight of 10 kg, the dose would be 0.010 mg/kg-day.

As part of the Food and Drug Administration's (FDA's) Regulatory Monitoring Program, 9,438 domestic and imported food samples were analyzed for pesticides, including metribuzin. Metribuzin was not detected in any samples of grains, milk products, fruits or vegetables. In addition, no detections were found in 218 domestic and 298 imported fish and shellfish samples. Thus, the daily intake of metribuzin from food is anticipated to be close to zero.

No data are available for the ambient levels of metribuzin in air. Metribuzin is a solid at ambient temperatures and has a low vapor pressure. Thus, partitioning of metribuzin into air is highly unlikely. While the average daily intake for the general population is anticipated to be close to zero, inhalation of metribuzin may be a potentially significant occupational exposure. The occupational subgroup may include workers involved in the mixing, loading, handling and application of metribuzin. The EPA has estimated that inhalation exposures of this subgroup range from 0.006 to 91.14 mg/day. Calculations of doses based on this range of exposure and 70 kg body weight are 8.6×10^{-5} to 1.3 mg/kg-day.

Metribuzin is not labeled for residential use and so it is not anticipated to be found in residential soils. General population exposures are anticipated to be close to zero. In agricultural regions where metribuzin is applied, metribuzin may be found in soils in concentrations as high as 0.78 mg/kg. Based on an average body weight of 70 kg and a daily soil intake of 480 mg/day, the maximum daily intake for a contact intensive worker would be 5.3×10^{-3} mg/kg-day, which is below the RfD.

For most individuals, the majority of metribuzin exposure will be from water. For the purpose of estimating the HRL from the RfD, a conservative default value of 20% was used for the relative source contribution.

4.4 Sensitive Populations

No populations sensitive to metribuzin have been identified.

4.5 Exposure and Risk Information

A cross-section survey of 20 States reported that 0.007% of Public Water Systems had detections of metribuzin above the MRL, affecting about 0.0003% of the population. A national extrapolation of this data indicates that approximately 1,000 people would be exposed to metribuzin through the drinking water. Of the 20 States in this cross-section survey, only the State of Washington reported a detection of metribuzin. Since Washington is the only State to report a metribuzin detection at 0.10 µg/L, this value is both the median and 99th percentile concentration. However, when all of the participating States in Round 2 of the UCM program were considered, 0.28% of PWSs reported detections above the MRL. National extrapolation of this data indicates that approximately 1.6% of the population, or 3.4 million people, are exposed to concentrations above the MRL.

4.6 Conclusion

In conclusion, while there is evidence from animal studies that metribuzin may cause adverse health effects at high doses, low doses do not appear to be very toxic. There are no available studies, either epidemiological studies or case-studies of accidentally exposed agricultural workers, that assess adverse health effects in humans from metribuzin exposure. Its occurrence in public water systems and the number of people potentially exposed through drinking water is generally low. Thus it is unlikely that metribuzin will occur in drinking water at frequencies that are of public health concern or that regulation represents a meaningful opportunity for health risk reduction in persons served by public water systems. All CCL regulatory determinations and further analysis are formally presented in the *Federal Register* Notices (USEPA, 2002; 67 FR 38222, and USEPA, 2003a; 68 FR 42898).

5.0 TECHNOLOGY ASSESSMENT

If a determination is made to regulate a contaminant, SDWA requires development of proposed regulations within 2 years of making the decision. It is critical to have suitable monitoring methods and treatment technologies to support regulation development according to the schedules defined in the SDWA.

5.1 Analytical Methods

The availability of analytical methods does not influence EPA's determination of whether or not a CCL contaminant *should* be regulated. However, before EPA actually regulates a contaminant and establishes a Maximum Contaminant Level (MCL), there must be an analytical method suitable for routine monitoring. Therefore, EPA needs to have approved methods available for any CCL regulatory determination contaminant before it is regulated with an NPDWR. These methods must be suitable for compliance monitoring and should be cost effective, rapid, and easy to use.

Metribuzin is an unregulated contaminant for which monitoring was required under the Unregulated Contaminant Monitoring Program (USEPA, 1987; 52 FR 25690). Monitoring for metribuzin was initiated through rulemaking in 1991 (USEPA, 1991; 56 FR 3526), and began in 1993. It already has

well-documented analytical methods developed specifically for low-level drinking water analyses (see Table 5-1).

5.2 Treatment Technology

Treatment technologies also do not influence the determination of whether or not a contaminant should be regulated. But before a contaminant can be regulated with an NPDWR, treatment technologies must be readily available. EPA's Office of Research and Development (ORD) has researched treatment technologies for all of the organic compounds listed as regulatory determination priorities on the CCL, including metribuzin. The two appropriate technologies reviewed were granular activated carbon (GAC) and air stripping.

Table 5-1: Analytical methods for metribuzin

Method	Type	Method Detection Limit (µg/L)
EPA 507	gas chromatography (GC)/ Nitrogen/Phosphorous detector	0.029
EPA 508.1	GC/ electron capture detectors (ECD)	0.009
EPA 525.2	GC/ quadrupole mass spectrometry	0.062
	GC/ ion trap mass spectrometry	0.09
EPA 551.1	GC/ECD	0.005

Granular activated carbon treatment removes contaminants via the physical and chemical process of sorption, by which the contaminants attach to the carbon surface as water passes through the carbon bed. Activated carbon has a large sorption capacity for many water impurities including synthetic organic contaminants, taste and odor causing compounds, and some species of mercury. Adsorption capacity is typically represented by the Freundlich isotherm constants, with higher Freundlich (K) values indicating greater sorption potential.

Air stripping involves the continuous contact of air with the water being treated, allowing volatile dissolved contaminants to transfer from the source water to the air. After contact, the "contaminated air" is swept from the system, taking the contaminant out of contact with the treated water. The driving force for the water-to-air transfer of the volatile contaminants is the contaminant's concentration gradient between the water and air. The Henry's Law constant is a commonly used indicator of the tendency of a contaminant to partition from water to air. A larger Henry's constant indicates a greater equilibrium of the contaminant in the air. Thus, contaminants having larger Henry's constant are more easily removed by air stripping.

Predictive computer modeling and specific chemical characteristics were used to determine the isotherm constants needed to evaluate the two treatment technologies. The rule of thumb used for SDWA compounds, learned through the development of cost-and-technology documents to support other drinking water regulations, is that GAC is considered to be cost-effective if the contaminant has a Freundlich (K) value above 200 (Speth and Adams, 1993). For air stripping, a compound with a Henry's constant above dibromochloropropane (DBCP) (0.005) or ethylene dibromide (0.037) is considered strippable at a reasonable cost.

Metribuzin has a predicted Freundlich (K) value of 25,200 and a predicted Henry's Law constant of 7.2×10^{-8}. Therefore, only GAC is an applicable treatment technology for metribuzin. Its low volatilization potential makes air stripping impractical.

6.0 SUMMARY AND CONCLUSIONS - DETERMINATION OUTCOME

Three statutory criteria are used to guide the determination of whether regulation of a CCL contaminant is warranted: 1) the contaminant may adversely affect the health of persons; 2) the contaminant is known or is likely to occur in public water systems with a frequency, and at levels, of public health concern; and 3) regulation of the contaminant presents a meaningful opportunity for health risk reduction for persons served by public water systems. As required by SDWA, a decision to regulate a contaminant commits the EPA to propose a MCLG and promulgate a NPDWR for the contaminant. A decision not to regulate a contaminant is considered a final Agency action and is subject to judicial review. The Agency can choose to publish a Health Advisory (a non-regulatory action) or other guidance for any contaminant on the CCL that does not meet the criteria for regulation.

Exposure to metribuzin occurs primarily in occupational settings, particularly in the agriculture industry where it is used as an herbicide. Although there are no studies assessing adverse effects of metribuzin on human health, animal studies indicate that metribuzin has the potential to cause adverse health effects at high doses. Chronic studies of metribuzin, for instance, have reported effects on body weight increases, mortality, liver enzyme activities, and histopathological changes. The RfD of 0.013 mg/kg-day was derived from a study reporting the adverse health effects of metribuzin in rats. Currently, metribuzin is classified as a class D carcinogen, due to inadequate carcinogenicity data in humans and animals.

While metribuzin has been detected in ambient surface and ground water, detection frequencies and concentrations from PWS samples collected under the SDWA are low. Contaminant releases to the environment have been reported in the TRI from only three States and one territory. Round 2 cross-section occurrence estimates are very low, with only 0.003% of all samples showing detections. Significantly, the values for the 99^{th} percentile (0.10 µg/L) and median concentrations (0.10 µg/L) of all samples are less than the HRL. When all the Round 2 data are considered, a national extrapolation of the data indicates that 1.6%, or approximately 3.4 million people nationally, are exposed to any concentration of metribuzin.

The heaviest use of metribuzin is across the nation's corn-soybean production area. These States are not well represented in the Round 2 database. Therefore, additional data from the Midwest corn belt were also evaluated. Drinking water data from the corn belt States of Iowa, Indiana, Illinois, and Ohio show very low occurrence of metribuzin. Special, targeted surface water studies from Ohio have the highest detection frequency of metribuzin.

Metribuzin is not labeled for residential use and so it is not anticipated to be found in residential soils. General population exposures are anticipated to be close to zero. In agricultural regions where metribuzin is applied, metribuzin may be found in soils in concentrations as high as 0.78 mg/kg. Based on an average body weight of 70 kg and a daily soil intake of 480 mg/day, the maximum daily intake for a contact intensive worker would be 5.3×10^{-3} mg/kg-day, which is below the RfD 0.013 mg/kg-day. There is no evidence to suggest that children, or any other population subgroup, would be more sensitive than others when exposed to metribuzin. In addition, EPA has applied an uncertainty factor in deriving the HRL that adequately protects sensitive subgroups of the population.

Although there is evidence from animal studies that metribuzin may cause adverse health effects at high doses, its occurrence in public water systems and the numbers of people potentially exposed through drinking water are low. Thus metribuzin may not occur in drinking water with a frequency, or at levels, of public health concern. All CCL regulatory determinations and further analysis are formally presented in the *Federal Register* Notices (USEPA, 2002; 67 FR 38222, and USEPA, 2003a; 68 FR 42898).

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APPENDIX A: Abbreviations and Acronyms

ARMS - Agricultural Resources Management Study
CA - Census of Agriculture
CAS - Chemical Abstract Service
CCL - Contaminant Candidate List
CMR - Chemical Monitoring Reform
CPS - Cropping Practices Survey
CWS - community water system
DBCP - dibromochloropropane
DCI - data call-in
ECD - electron capture detectors
EPA - Environmental Protection Agency
EPCRA - Emergency Planning and Community Right-to-Know Act
EXTOXNET - Extension Toxicology Network, Pesticide Management Education Program
FDA - Food and Drug Administration
FIFRA - Federal Insecticide, Fungicide, and Rodenticide Act
FQPA - Food Quality Protection Act
FR - federal register
GAC - granular activated carbon (treatment technology for organic compounds)
GC - gas chromatography (a laboratory method)
g/mol - grams per mole
GW - ground water
HRL - Health Reference Level
IOC - inorganic compound
K_{oc} - organic carbon partition coefficient
K_{ow} - octanol-water partitioning coefficient
L - liter
MCL - maximum contaminant level
MCLG - maximum contaminant level goal
mg - milligram
mg/kg-day - milligram per kilogram per day
mm Hg - millimeter mercury
MRL - minimum reporting level
NAWQA - National Water Quality Assessment Program
NCFAP - National Center for Food and Agricultural Policy
NCOD - National Drinking Water Contaminant Occurrence Database
NDWAC - National Drinking Water Advisory Council
nm - nanometer
NOAEL - no observed adverse effect level
NPDWR - National Primary Drinking Water Regulation
NPS - National Pesticide Survey
NTNCWS - non-transient non-community water system
OGWDW - Office of Ground Water and Drinking Water

ORD	- Office of Research and Development
PGWD	- Pesticides in Ground Water Database
ppm	- part per million
PWS	- public water system
RfD	- reference dose
SARA	- Superfund Amendments and Reauthorization Act
SDWA	- Safe Drinking Water Act
SDWIS/FED	- Federal Safe Drinking Water Information System
SOC	- synthetic organic compound
SW	- surface water
TRI	- Toxic Release Inventory
UCM	- Unregulated Contaminant Monitoring
UCMR	- Unregulated Contaminant Monitoring Regulation/Rule
ARCCOS	- Unregulated Contaminant Monitoring Information System
USDA	- United States Department of Agriculture
USEPA	- United States Environmental Protection Agency
USGS	- United States Geological Survey
VOC	- volatile organic compound
µg	- micrograms
>MCL	- percentage of systems with exceedances
>MRL	- percentage of systems with detections