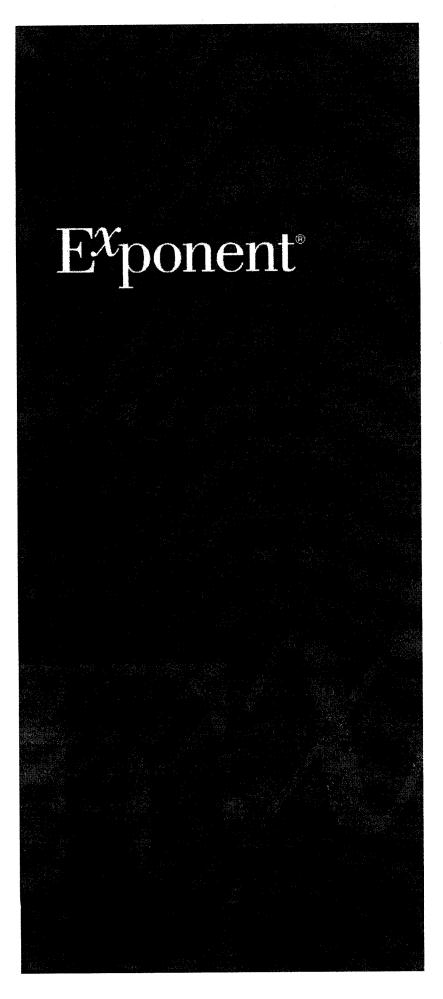


## **ATTACHMENT 9**



Center for Chemical Regulation & Food Safety

Comments on EPA-Proposed Alternatives to the Organic Arsenical Herbicides

## E<sup>x</sup>ponent<sup>\*</sup>

## Comments on EPA-Proposed Alternatives to the Organic Arsenical Herbicides

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## **Executive Summary**

In a Federal Register Notice issued on August 9, 2006, the Office of Pesticide Programs (OPP) announced the availability of the Reregistration Eligibility Decision (RED) for MSMA, DMSA, CAMA, and Cacodylic Acid, which are collectively known as the organic arsenical herbicides. In several documents published over 2006, OPP proposed alternatives for these herbicides. This document presents comparative information on the proposed alternatives, including information on efficacy, costs, potential risks and water contamination. Overall, the information presented in this document demonstrates that there is no acceptable alternative for the organic arsenical herbicides.

The OPP-proposed alternatives to the organic arsenical herbicides are less effective and more costly to users. OPP has suggested numerous potential alternatives, but there are no viable replacements for the organic arsenical herbicides thanks to their superior efficacy compared to that of the proposed alternatives, the broad spectrum of weeds controlled by the organic arsenical herbicides, and the season-long application time period (*i.e.*, the organic arsenical herbicides can be applied pre-plant, early post-emergent, and late post-emergent), as well as resistance management issues associated with the proposed alternatives. Additionally, there are toxicological and/or environmental risk concerns with a number of the proposed alternatives, and the fact that several of these proposed alternatives have been detected in surface and/or ground water monitoring programs, with some having very high rates of detection in those water monitoring programs.

In summary, replacing the organic arsenical herbicides with the alternatives proposed by OPP will not solve the weed issues that are currently solved by the organic arsenical herbicides, will create new environmental and human health risk concerns, and will cause economic hardships for users.

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#### Introduction

In a Federal Register Notice issued on August 9, 2006, OPP proposed to cancel the use of the organic arsenical herbicides. In several documents published over 2006, OPP proposed alternatives for these herbicides. This document responds to the relevant parts in the following US EPA documents:

- Memorandum Subject: Alternatives Assessment of the Organic Arsenical Herbicides
  Used in Residential and Golf Course Turfgrass, and Cotton (DP Barcode: 309117),
  Office of Prevention, Pesticides and Toxic substances; Biological and Economic Analysis
  Division, April 12, 2006. (EPA-HQ-OPP-2006-0027)
- Memorandum Subject: BEAD Response to Organic Arsenical Public Comments (DP #309116). Office of Prevention, Pesticides and Toxic Substances. Biological and Economic Analysis Division [June 28, 2006]. (EPA-HQ-OPP-2006-0073)
- Reregistration Eligibility Decision for MSMA, DSMA, CAMA, and cacodylic acid.
   Office of Prevention, Pesticides and Toxic Substances. EPA 738-R-06-021, July 2006.
   (EPA-HQ-OPP-2006-0201-0079)

In the three documents OPP proposed various different alternative herbicides. A consolidated list of the alternatives is given in Appendix I to this document. This document presents comparative information on efficacy, costs, potential risks, and water contamination by the proposed alternatives, demonstrating that there are no acceptable alternatives for the organic arsenical herbicides, and that these proposed alternatives also raise risk concerns.

The first section of this document provides a brief overview of efficacy issues and resistance management issues associated with EPA-proposed alternatives to the organic arsenical herbicides.

The second section discusses economic issues and presents a comparison of the cost involved with the use of different alternative herbicides.

The third section presents key mammalian toxicology information (e.g., carcinogenic potential), ecotoxicological information such as exceedances of risk levels of concern (LOCs), and environmental fate information (e.g., environmental persistence, leaching potential, potential for movement to surface water), on the EPA-proposed alternative compounds.

The fourth section provides a brief overview of surface water and ground water monitoring results for those compounds that have been included as analytes in surface or ground water monitoring programs.

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## **Efficacy and Resistance Management Issues**

#### **Efficacy**

The organic arsenical herbicides, and especially, MSMA and DSMA, the sodium salts of methanearsonic acid (MAA), have performed reliably for over forty years for weed control in cotton, in lawn and turf, under trees, vines and shrubs, for vegetation control along railroad rights-of-way and highways, on drainage ditchbanks, and at industrial sites such as storage yards. They are among the few herbicides available today that possess the unique combination of selectivity and low potential for development of weed resistance.

#### Turf

In lawn and turf applications, the selectivity of the organic arsenical herbicides makes them an essential weed control instrument. These herbicides distinguish between most turfgrasses and weeds, and they cannot be equaled for their selective post-emergent annual grass control and their efficacy in controlling weeds in advanced stages of growth. The few products showing comparable early stage efficacy are less effective on advanced growth stage weeds, and are substantially more expensive than the organic arsenical herbicides (e.g. dithiopyr, pendimethalin, oxadiazon, prodiamine) (Appendix II, Table II-3). This is of critical importance to consumers wanting control of weeds in lawns.

The organic arsenical herbicides provide post-emergent selective annual grass and yellow nutsedge control in cool season, as well as in warm season grasses. This is extremely important because these weeds emerge during summer when cool season turf is under stress and more vulnerable to competitive weed pressure.

In addition, the organic arsenicals are very broad-spectrum herbicides. They are very effective against a large number of weed species found in turf grasses, but at the same time the desired turf species are tolerant (as opposed to glyphosate, for example, that will kill both weeds and the desired turf species). Moreover, the organic arsenical herbicides can be applied throughout the growing season, whereas other products are more specific or limited to pre-plant or early post-emergent use. The selective weed control in turf, especially for post-emergent use, is a key property of the organic arsenical herbicides that the other products can't offer.

The organic arsenical herbicides control more weeds than any other herbicide registered for use on turf grass. Replacing the organic arsenical herbicides will take a mixture of several other herbicides, which sometimes, cannot be mixed. That means more total pounds of active

ingredients to be applied to replace the organic arsenical herbicides (greater environmental loading of pesticides). In fact, for certain key weeds, there is practically no effective replacement to the organic arsenical herbicides (Wahlin, 2006; Wildmon, 2006; Askew et. al., 2006; McCarty, 2006). Table 1 presents the efficacy of several herbicides in controlling certain weeds. It is clear from the table, that no effective chemical alternative is currently available for the control of dallisgrass, vaseygrass, morning glory, knotgrass, field paspalum, tropical signal grass, and fall panicum. Table 1 illustrates that there is no true replacement for MSMA for postemergent weed control.

Table 1: A comparisons of post-emergent weed control of several herbicides

	MSMA	foramsulfuron (Revolver)	sulosulfuron (Certainty)	dithiopyr (Dimension)	2-4,D (Trimec)	atrazine (Aatrex)	halosulfuron (Sedgehammer)	fluazifop (Fusilade)	diclofop-methyl (Iloxan)	metribuzin (Sencor)	quinclorac (Drive)
Crabgrass	×			×							×
Goosegrass	×	×	×						×	×	
Dallisgrass	×										
Vaseygrass	×										
Morningglory	×										
Yellow nutsedge	×		×				×				
Purple nutsedge	×		×				×				
Common broad leaf weeds (BLW)	×		×		×	×					Few (Clover)
Johnsongrass	×		×								
Knotgrass	×										
Field paspalum	×										
Tropical Signalgrass	×										
Fall panicum	×										
Poa annua	×	×	×			×				×	
Annual grassy weeds	×					×		×			

BEAD's report (USEPA-OPP, 2006a) acknowledges that MSMA, as well as the other organic arsenical herbicides would be difficult to replace. However, later in the document BEAD later reverses itself and erroneously presents a few products as effective competitive products although they are not. For example, according to the report introduction (page 2) and later in Table 1 (page 6 of USEPA-OPP, 2006a), fluazifop (brand name Fusilade) is a wonderful grass herbicide controlling most grasses. However, the use of this product is primarily for controlling

bermudagrass in other grasses, zoysia and tall fescue, that are a bit more tolerant to fluazifop than bermudagrass. In contrast, MSMA is very selective in removing grass weeds from the preferred turf grasses, bermudagrass, zoysia, and bluegrass. This "selective" use for fluazifop is risky because fluazifop is a pure grass killer. It is mostly used in controlling all grasses and only grasses in broadleaf ornamentals such as flowers and shrubs.

Of all the proposed alternatives, dithiopyr comes closest to the weed control efficacy of the organic arsenical herbicides. However, it is really more effective when applied as a preemergence herbicide. Its label shows an early post-emergence use for control of crabgrass, but its timing must be perfect in order to achieve control of this weed. Most of the dithiopyr that is applied post-emergent is applied in a mixture with MSMA. BEAD fails to recognize that all the proposed alternatives are already used in a mixture with MSMA. Neither fluazifop nor dithiopyr will control or suppress sedges as do the organic arsenical herbicides.

It is clear from Table 1 (page 6) of the BEAD document that there are no alternatives to the organic arsenical herbicides. Since fluazifop cannot be considered to control grassy weeds in most turf grasses, especially bermudagrass, there are only a few pre-emergent herbicides and hormone herbicides for broadleaf weed control in turf. All the proposed alternatives are either preemergent or have to be applied very early after emergence of the weed. There is not any alternative proposed by EPA that can replace the organic arsenical herbicides in both early and late post-emergence applications.

Having only pre-emergent and hormone type herbicides available for turf grass presents numerous additional problems for users. Pre-emergent herbicides control or suppress desired seedling germination, which is why their use is restricted to <u>established</u> turf. The organic arsenical herbicides have no residual herbicidal activity to interfere with grass seeding or turf thickening following application. Pre-emergent herbicides will not control weeds after the weeds have emerged, leaving the turf owner with no remedy for in season weed control for weeds not controlled by the preemergence product.

Hormone herbicides, such as 2,4-D, control only broadleaf weeds and pose a risk of injury to surrounding, desired vegetation, such as flowers, shrubs, trees, etc. Triclopyr and dicamba are excellent brush control tools, thus cannot be used under this kind of vegetation, whereas the organic arsenical herbicides can be safely applied under trees and shrubs. Thus, these hormone products are not realistic alternatives to the organic arsenical herbicides, as suggested by OPP.

Professor Bert McCarty of Clemson University estimates that if MSMA turf uses are canceled, then over 75% of the golf courses in the southern regions of the US will have moderate to severe infestations by specific weed species that are effectively controlled only by MSMA and DSMA products. These weed species include dallisgrass, tropical signal grass, and certain other

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Paspalum spp. (McCarty, 2006). Only MSMA controls these weed species. Additionally MSMA provides control of a broad spectrum of non-target weeds. Newer herbicide products typically do not provide the broad-spectrum weed control of the organic arsenical herbicides, and some are known to result in development of weeds that are resistant to these herbicides when used continuously. The loss of MSMA will cause a major shift in weed infestations, based on Dr. McCarty's experience with previous EPA cancellations of other herbicide products (McCarty, 2006).

#### Cotton

The importance of cotton and its benefits to society cannot be overestimated. The National Cotton Council of America (NCC) has published a number of documents, which emphasize the importance of cotton production to the U.S. economy (NCC, 2006). This section discusses the end-user impacts that a ban on the use of organic arsenical herbicides will have on cotton production.

The cotton industry and its suppliers, together with the cotton product manufacturers, account for more than 440,000 jobs in the U.S. (USDA, 2002). Annual cotton production (about 20 million 480 lb bales equaling 4.8 million tons) is valued at more than \$4 billion at the farm gate, the point at which the producer sells the product (NCC, 2006). In addition to the cotton fiber, cottonseed products are used for livestock feed, and cottonseed oil is used for food products ranging from margarine to salad dressing. While cotton's farm-gate value is significant, a more meaningful measure of cotton's value to the U.S. economy is its retail value. Collectively, the annual business revenue generated by cotton and its products in the U.S. economy is estimated to be in excess of \$120 billion (NCC, 2006).

The National Cotton Council (NCC) of America represents producers in America who cultivate over 13 million acres of farmland producing approximately 20 million bales of cotton. It is important to note that many public submissions to the EPA's public federal docket highlight that overall chemical dependence has decreased and crop yields have increased (NCC, 2006). However, this can only be attributed to collectively more intelligent Integrated Pest Management (IPM) strategies, which depend on the use of MSMA in combination with other herbicides to achieve the most effective pest management. MSMA is needed as an irreplaceable, economically productive weed management tool (NCC, 2006).

MSMA represents a key tool for use against several significant weeds that can adversely impact cotton yields. The organic arsenical herbicides are a critical weed management tool for the cotton industry farmers. Over the past five years the University of Georgia has conducted more than 50 on-farm management trials in search of replacement products. "[The resulting

conclusion] has developed the most effective herbicide system for the control of tropical spiderwort, which includes the use of MSMA. Tropical spiderwort cost Georgia growers over \$1.1 million in 2006, even with effective mixtures of MSMA applied at lay-by. Loss of MSMA will prevent adequate control of this cotton pest and most certainly result in significant economic loss. Tillage, along with our most effective herbicide programs emphasizing MSMA, are our only management options in cotton. The loss of MSMA would prevent adequate control of this pest in cotton with significant economic loss" (Perry, 2006). Additionally, "The cost to control [herbicide-]resistant Palmer amaranth and the corresponding [yield] losses in cotton production could be devastating and the loss of MSMA will further exacerbate these losses" (Tolar, 2006). "For control of weeds such as tropical spiderwort, MSMA is my ONLY alternative. Elimination of that tool will create more management problems with resistant weeds in the future, along with substantially higher production costs, yield loss and reduced crop value" (Virginia Cotton Farming, 2006).

It is important to emphasize that the cotton industry continues to observe an increasing number of cases of herbicide resistance. These cases are appearing in cotton fields from North Carolina across the entire cotton belt (southern-tier and mid-south states) and Texas. "One of the major components of a resistance management strategy is to include multiple modes of action in the herbicide program. We are of the opinion that continued registration of MSMA is critical in our battle against herbicide-resistant weeds" (NCSU, 2006).

A review of the public docket (Docket ID: EPA-HQ-OPP-2006-0201) illustrated many common themes concerning the benefits of the organic arsenical herbicides and EPA's proposed cancellation of these products. These themes include:

- No alternative products are comparable/available;
- MSMA is an effective, economical product;
- MSMA is currently being used in combination with alternatives listed by EPA;
- Small businesses will be impacted if MSMA is canceled;
- Management budgets are already tight (potential alternative products are very expensive).

These themes continue to stress the importance of MSMA within the cotton industry, and the impact that the cancellation of organic arsenical herbicide products will have on the cotton industry. BEAD's analysis has not adequately evaluated the economic impact of the loss of the organic arsenical herbicides, and the key role the organic arsenical herbicides, particularly MSMA, play in IPM programs and as a significant, necessary tool for resistance management. For controlling certain key weed species, MSMA is the only viable product available.

#### Resistance Issues

One of OPP's arguments for proposing the cancellation of the organic arsenical herbicides uses, is that their use has been declining in the last few years. From the reduced use, OPP has erroneously deduced that these products can be completely eliminated. This rationale is wrong for two reasons: First, the use of the organic arsenical herbicides has been reduced due to product stewardship. In the last few years, users have been educated to use the products more economically: The product is a contact herbicide and should not be used by broadcast application. Thus, users are currently using the organic arsenical herbicides in spot treatment applications. Second, the increased use of glyphosate for weed control in genetically modified glyphosate-resistant cotton has reduced the use of organic arsenical herbicide products. However, weed resistance to glyphosate has recently emerged and is quickly expanding (Robertson, 2006). For example, glyphosate does not control tropical spiderwort due to the weed species' natural tolerance to the herbicide (NCC, 2007). Weed resistance to currently available herbicides is one of the biggest threats to cost effective weed control in agriculture and vegetation control in non-agricultural applications. This problem has increased in recent years and shows no sign of abating. There are fewer new products with which to economically combat the resistance problem (Bennett, 2006). The resistance issue alone is reason enough for users to keep MSMA and other organic arsenical herbicides in their available toolbox, rather than removing a powerful tool that can address resistance issues, as EPA is proposing.

In addition, a problem that has recently been associated with the use of genetically modified crops is the unintended spread of the herbicide resistant bio-types that may reach wild populations as a result of repeated use of the modified crops. This sometimes occurs when seeds of herbicide resistant crops, such as cotton or soybeans, germinate in non-crop areas or cross-pollinate with weeds, resulting in weeds that are resistant to the herbicides (Duke, 1999). These situations require effective resistant management strategies that include the use of selective herbicides against which the modified crops have no resistance. The organic arsenical herbicides can be used to combat the herbicide resistance issues. In over 40 years of use no herbicide resistant bio-types, with the exception of isolated cases of common cocklebur (*Xanthium strumarium*), have been observed in those species controlled by the organic arsenical herbicide products. This important property of the organic arsenical herbicides has not been adequately considered by EPA in their proposed decision to cancel the organic arsenical herbicides.

Many of the alternatives listed by OPP include members of the aryloxyphenoxy propionate, imidazolinone, and sulfonylurea herbicide families. Resistance to members of these herbicide families has been reported for crabgrass (*Digitaria* spp.), goosegrass (*Eleusine indica*), and annual bluegrass (*Poa annua*), which results in restricting or eliminating the actual, realistic potential of these compounds as suitable substitutes for MSMA. Additionally, these herbicides do not provide effective control of dallisgrass (Askew et. al., 2006). According to Professor

Robert H. Walker of Auburn University, the alternative chemicals for MSMA generally will provide only 75% control of post-emergent weeds versus 98% control achieved with MSMA (Walker, 2006). Efficacy comparisons were made by Environmental & Turf Services, Inc. for the control of dallisgrass (*Paspalum dilatatum*), tropical signal grass, and other weed scenarios that would likely occur in the southern region throughout the playable golf season (Appendix II, Table II-3). No alternative listed by EPA effectively controlled the broad spectrum of weed species likely to occur on golf courses and other turf stands. MSMA does provide the necessary broad-spectrum control of nuisance weed species at an affordable price for turfgrass managers.

If the uses of the organic arsenical herbicides are cancelled, some cotton-growing farmers will be out of business, due to the overuse of glyphosate on Roundup-Ready cotton and the lack of replacement for MSMA to control the uncontrollable of glyphosate-resistant weeds (Robertson, 2006a, 2006b, 2006c).

It is important to note that weed resistance may have secondary environmental implications. For example, ineffective weed management may result in overgrowth, population shifts to naturally resistant weed species, the creation of "super weeds" (e.g., weeds resistant to multiple herbicide chemistries), and integration of herbicide-tolerant genes into surrounding ecosystems potentially disrupting natural ecologic balances in the surrounding systems (Altieri, 2000; Duke, 1999; Marshall, 1999).

#### **Economic Issues**

As explained in the previous section, for some of the weeds, there is currently no viable alternative to organic arsenical herbicides, or no alternative chemical control. For those weeds, for which alternative herbicides have been identified, the available alternative chemical controls are much more expensive than the organic arsenical herbicides. In Appendix II, examples are given of cost of weed control using proposed alternatives with the cost of weed control using MSMA. Table II-1 presents examples for the cost of post-emergent weed treatment with MSMA, compared to the cost of available alternative-post emergent herbicides. Table II-2, presents examples of the cost of treatment with proposed pre-emergent herbicides. Table II-3, presents examples of common weed scenarios occurring in the southern regions of the U.S. (e.g., Florida) and the cost of controlling them with alternatives to MSMA compared to the cost of current treatment with MSMA. Table II-3 demonstrates that the control of weeds with alternatives, when available, will be significantly higher than treatment with MSMA. The cost of the current treatment with MSMA is \$5.50/ac, and not \$9.00 as reported by BEAD (USEPA, 2006a). It should be noted that while BEAD cited higher costs for MSMA, the costs cited for the proposed alternatives were lower than the actual costs of these products to users. Some examples of the cost increase or weed treatment are given in Table 2.

Table 2: Cost increase of weed control with alternatives compared to MSMA (\$5.50/acre)

Weed Scenario	Cost of	Cost Increase				
Weeu Scenario	Alternative (\$)	Difference (\$)	Times (x)			
goosegrass and crabgrass	60	54.5	11			
goosegrass, crabgrass, and annual sedges	124.40	118.90	23			
goosegrass and Poa annua	131	126.4	24			
sedges	78.40	72.90	14			

Table 2 clearly illustrates that if the uses of the organic arsenical herbicides are cancelled, there will be a significant economic impact for herbicide use for turf users as well as for cotton users. It is also important to remember that the alternatives do not provide the same effective weed control as compared to MSMA and that many of them have been observed to cause weed resistance (e.g., sulfonylurea family products like Revolver, Certainty; also Iloxan and Atrazine as discussed earlier in this document).

If the uses of the organic arsenical herbicides are cancelled, the costs to maintain adequately playable golf courses will increase significantly, to an extent that low to mid-level courses (e.g., daily-fee, municipal, or "blue collar" courses) will not be able to bear. These mid-level courses

contribute roughly 42,200 rounds of golf played annually in the southern "sunbelt" region of the U.S. (NGF, 2006). Scott Wahlin, former President of the Florida Turfgrass Council, believes that if MSMA will not be available, the number of golf courses in Florida will decrease due to increased maintenance cost (Wahlin, 2006). The same situation will likely occur throughout the entire Sunbelt region.

If the uses of the organic arsenical herbicides are cancelled, users will likely use combinations of available herbicides attempting to achieve the same benefit that MSMA provides. This will result in additional active ingredients being applied at higher rates over greater areas compared to MSMA (Hunter, 2006; Wildmon, 2006). This increase in active ingredients may have unintended environmental implications, such as ground and/or surface water contamination or impacts on aquatic organism populations (Wildmon, 2006).

# **Toxicological and Environmental Information for OPP Proposed Alternatives**

In the previous Sections it was demonstrated that the alternatives proposed by OPP are much less cost-effective than the organic arsenical herbicides, and will result in lower efficacy and higher costs. Additionally, there are resistance issues with the alternatives that have not occurred with the organic arsenical herbicides for almost half a century that these products have been used.

In addition to these efficacy, cost and resistance issues, we have examined OPP's proposed alternatives to the organic arsenical herbicides from point of view of toxicology, ecotoxicology, and environmental fate. Summaries of pesticide-specific issues with EPA-proposed alternatives are presented in Appendix III. The information was obtained from EPA Fact Sheets, EPA documents of Reregistration Eligibility Decision (RED), Interim REDs (IRED), or Reports on FQPA Tolerance Reassessment Progress and Interim Risk Management Decision, known as TREDs for proposed alternative compounds for which such documents are available. It is important to note that TREDs do not provide key environmental fate or ecotoxicology data.

The information detailed in Appendix III reveals that the OPP-proposed alternatives are far from free of significant toxicological and ecotoxicological issues, and may cause environmental contamination. Some of the proposed alternatives have not been studied sufficiently yet, thus there is no adequate information on them, compared to the organic arsenical herbicides, which have been studied for decades.

## **Water Monitoring Data for Alternatives**

For some of the OPP-proposed alternatives to the organic arsenical herbicides, monitoring data for surface water and ground water are available at the website of the National Water Quality Assessment Program (NAWQA) of the United States Geological Survey (USGS). Data on these alternatives may be available under the NAWQA Cycle I program (1991-2001) and/or the NAWQA Cycle II program (2002-present). The NAWQA database contains monitoring data for both surface water and ground water. The USGS NAWQA Cycle I database includes monitoring data for 14 of the OPP-proposed alternative herbicides to the organic arsenical herbicides, while the NAWQA Cycle II database includes data on 16 of OPP's proposed alternatives. The available water monitoring data for EPA-proposed alternatives indicate that many of these compounds are found in both surface water and ground water. For surface water, results for all 14 (Cycle I) or all 16 (Cycle II) proposed alternatives indicate detections that have exceeded the NAWQA minimum reporting limit (MRL) for each monitored compound. The listed MRL for each compound represents the maximum of the minimum reporting limits determined by USGS for the NAWQA program for Cycle I and Cycle II. For ground water, the NAWQA results indicate that 12 (Cycle I) or 13 (Cycle II) of these proposed alternatives were detected above the applicable MRL. Some of the proposed alternatives for the organic arsenical herbicides have been detected at relatively high concentrations in surface water and in ground water. It is important to note that a number of these proposed alternatives that were detected in surface and ground water also have a relatively high percentage of detections (>10%).

The maximum detected concentrations, and the detection frequency, of the alternative herbicides proposed by OPP, in surface water and ground water, are provided in Appendix IV.

#### **Surface Water**

Detailed summaries of the NAWQA Cycle I (1991-2001) surface water monitoring data for each of the four major land use categories (agricultural, mixed, undeveloped, and urban) are provided in Tables IV-3 – IV-6, respectively. Table IV-7 provides an overall summary of the NAWQA Cycle II data for all the land use categories combined.

The agricultural, mixed, and urban land use categories indicate very high frequencies of detection for atrazine and metolachlor (approximately 60% to 90% of samples analyzed). Even the undeveloped land use category displays high rates of detections for these two alternatives.

Among agricultural sites, four additional proposed alternatives (2,4-D, diuron, EPTC, and trifluralin) display significant rates of detection (>10%), and two additional proposed

Attachment 9

alternatives, fluometuron and pendimethalin, have detection frequencies >5%. Maximum detected concentrations for these proposed alternatives ranged from <1  $\mu$ g/L (MCPA and trifluralin) to 201  $\mu$ g/L for atrazine. The maximum detected concentration for atrazine exceeded the maximum contaminant level (MCL) by nearly an order of magnitude, although the MCL is based on chronic exposure, and the highest atrazine concentrations result from intermittent events. The maximum detected concentration of atrazine also exceeded the criteria for aquatic communities. The maximum detected concentration for diuron exceeded the health advisory level (HAL) and the water quality criterion for acute effects on nonvascular plants, and the maximum detected concentration for metolachlor approaches the HAL.

Among the mixed land use sites, two additional alternatives (EPTC and trifluralin) have >10% detection frequencies, and three additional alternatives (2,4-D, diuron, and pendimethalin) have >5% detection frequencies. Maximum detected concentrations for these proposed alternatives ranged from <1  $\mu$ g/L for several alternatives to 29.6  $\mu$ g/L for EPTC. The maximum detected concentration of atrazine exceeds the MCL, and maximum detected concentration of diuron exceeds the criterion for acute effects on nonvascular plants.

In addition to high rates of detection for atrazine and metolachlor, diuron, fluometuron, MCPA, and norflurazon were detected in >5% of the samples among undeveloped land use sites, and 2,4-D, diuron, pendimethalin, and trifluralin were detected in  $\geq 10\%$  of the samples among urban land use sites. Maximum detected concentrations of these proposed alternatives ranged from <1  $\mu$ g/L for several alternatives to 19  $\mu$ g/L for MCPA at the urban sites, and were < 1  $\mu$ g/L for the undeveloped sites. For urban sites, the maximum detected concentration of atrazine again exceeds the MCL, and the maximum detected concentration of diuron again exceeds the HAL and the criterion for acute effects on nonvascular plants.

A summary of the surface water monitoring for Cycle II (2002-present) for all land use types, is presented in Table IV-7. Significant detection percentages (>10% of total samples) were found in 10 of the 16 alternative compounds. As with Cycle I, very high detection percentages were demonstrated in atrazine and metolachlor (60-80% of samples were positive), and very high rates of detection (>50% of samples) also occurred for 2,4-D, and diuron. High detection frequencies occurred for glyphosate and triclopyr (>20% of samples). Additional proposed alternatives with detection rates exceeding 10% of samples included dicamba, norflurazon, pendimethalin, and trifluralin. The maximum detected concentration of atrazine exceeds the MCL and the criterion for effects on aquatic communities, and the maximum detected concentration of diuron exceeds the criterion for acute effects on nonvascular plants and approaches the HAL.

Additionally, in a monitoring study involving 51 streams in nine Midwestern states in 2002 (Battaglin et al.,  $2005^1$ ), glyphosate was detected at a maximum concentration of 8.7  $\mu$ g/L, with a percentage of detection (concentrations of 0.1  $\mu$ g/L or above) of 35% for the pre-emergence use period, 40% for the post-emergence use period, and 31% for the harvest use period.

These data demonstrate that many of the proposed alternatives to organic arsenical herbicides continue to have a high percentage of detections in water (>10%) and in many cases, high concentrations when detected.

#### **Ground Water**

Ground water monitoring data from the NAWQA database indicate detections that exceed MRLs for 12 of the 14 OPP-proposed alternatives for which there is information in the database for Cycle I, as shown in Table IV-1.

Ground water monitoring for NAWQA Cycle I agricultural sites for OPP-proposed alternatives to the organic arsenical herbicides are presented in Table IV-8, including the frequency of detection and maximum concentration levels. In addition to the monitoring data available at the USGS NAWQA website, data for glyphosate and for fluazifop are available from EPA's Pesticide in Ground Water Database (PGWDB). Table IV-8 presents a summary of the results from both databases. As with the surface water samples, high frequencies of detection were found for atrazine and metolachlor. Metolachlor and norflurazon had the highest reported concentrations (approximately 30  $\mu$ g/L), while concentrations between 1 and 10  $\mu$ g/L were reported for 2,4-D, atrazine, and diuron. A high detection rate was also found for fluazifop in the PGWDB monitoring program, at concentrations as high as 20  $\mu$ g/L.

Tables IV-9 through IV-11 present ground water monitoring data for mixed, undeveloped, and urban land use sites for Cycle I. Atrazine also demonstrated a high frequency of detection in NAWQA Cycle I ground water samples for other land use sites (mixed, undeveloped, and urban) ranging from 13.4% to 32% of the samples (Tables IV-9-IV-11). Detection frequencies were also significant (>5%) for metolachlor for the mixed land use and urban land use sites. Diuron was detected in >3% of the samples collected from urban land use sites.

Table IV-12 presents a summary of the available ground water monitoring data for the alternative compounds for Cycle II. The ground water monitoring data for Cycle II demonstrate that atrazine and metolachlor continue to have very high frequencies of detection, 31% and 12%,

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Battaglin, W.A., Kolpin, D.W., Scribner, E.A., Kuivila, K.M., and Sandstorm M.W. 2005. Glyphosate, other herbicides, and transformation products in Midwestern streams, 2001(1). J. Amer. Water Resour. Asso. April, 2005. <a href="http://www.findarticles.com/p/articles/miga4038/is-200504/ai-n13637417">http://www.findarticles.com/p/articles/miga4038/is-200504/ai-n13637417</a>

respectively. Diuron has been detected in approximately 4% of the Cycle II samples, with fluometuron and norflurazon being found in approximately 2% of the Cycle II samples. The frequency of detection for the alternatives has remained consistent between Cycle I and Cycle II for the majority of the alternative compounds.

## **Summary and Conclusions**

In several documents published in 2006, OPP proposed 34 different alternatives to the organic arsenical herbicides. The information in this document demonstrates that none of the products proposed as alternatives has efficacy that is comparable to that of the organic arsenical herbicides. Whereas the organic arsenicals have broad-spectrum efficacy, the proposed alternatives each has a specific efficacy, and none can be used as a full replacement for the organic arsenical herbicides. That means, that for each weed a different herbicide will be required. In fact, for certain weeds, no replacement for the organic arsenical herbicides is available.

Moreover, for almost half a century that the organic arsenical herbicides have been in use, there have been no resistance issues (except for isolated cases of common cocklebur (*Xanthium strumarium*), whereas resistance issues have been developed with many of the alternatives proposed by OPP. These issues result in restricting or eliminating the actual, realistic potential of these compounds as suitable substitutes.

There are many human toxicological, ecotoxicological, and endangered species risk concerns cited in OPP's various science summaries for the alternatives. Review of the USGS-NAWQA database shows that all of the proposed alternatives (for which information is included in the database) have been detected in surface water or in ground water by the USGS. More than half of these products have been detected at least once at concentrations that exceed OPP's levels of concern.

The cost of the alternatives is several times higher than that of the organic arsenical herbicides. Replacing the organic arsenical herbicides not only will not give the users the weed control solution they need, it will also cause economic hardships.

In summary, replacing the organic arsenical herbicides will lead to performance issues, economic hardships and health & environmental issues that are greater than those for the organic arsenical herbicides.

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## Appendix I

The following is a consolidated list of the alternatives proposed by OPP in the three documents:

- US EPA. 2006. "Internal memorandum to Organic Arsenical Herbicides Docket (EPA-HQ-OPP-2006-0027) re: Alternatives Assessment of the Organic Arsenical Herbicides Used in Residential and Golf Course Turfgrass, and Cotton (DP Barcode: 309117)" Office of Prevention, Pesticides and Toxic Substances. April 12.
- US EPA. 2006. "Internal memorandum to Organic Arsenical Herbicides Docket (EPA-HQ-OPP-2006-0073) BEAD Response to Organic Arsenical Public Comments (DP #309116)."
   Office of Prevention, Pesticides and Toxic Substances. June 28.
- US EPA. 2006. "Internal memorandum to Organic Arsenical Herbicides Docket (EPA-HQ-OPP-2006-0201) re: Revised 'Reregistration Eligibility Decision for MSMA, DSMA, CAMA, and cacodylic acid' Document." Office of Prevention, Pesticides and Toxic Substances. August 10.

Note: Unless otherwise indicated, all of the MSMA and CA alternatives listed below were presented in the Alternative Assessment<sup>1</sup> document dated April 12, 2006. Some of these alternatives were also listed in BEAD response<sup>2</sup> (June 28), and in the August 10 Reregistration Eligibility Decision (RED)<sup>3</sup>. Those alternatives listed in the RED are **bolded** and those in the BEAD response are <u>underlined</u>.

#### Homeowner use:

MSMA/ CA: Alternatives: dithiopyr<sup>1,3</sup> pendimethalin<sup>1,3</sup> dithiopyr<sup>1,3</sup> 2.4-D<sup>1,2</sup> dicamba <sup>1</sup> triclopyr<sup>1</sup>

#### Cacodylic Acid Alternatives:

diquat<sup>1</sup> glufosinate<sup>1</sup> glyphosate<sup>1</sup>

MSMA Alternatives:

atrazine<sup>1,2</sup> pendimethalin<sup>1,3</sup> dithiopyr<sup>1,3</sup> fluazifop<sup>1,3</sup>
atrazine<sup>1,2</sup>
2,4-D<sup>1,2</sup>
dicamba<sup>1</sup>
MCPA <sup>1</sup>
MCPP<sup>1</sup>
propanoic acid<sup>1</sup>
triclopyr<sup>1</sup>

## **Golf Course Use:**

prodiamine<sup>1,2</sup>
oxadiazon
2,4-D<sup>1,2</sup>
halosulfuron (methyl)
napropamide oryzalin<sup>1,2</sup>
atrazine<sup>1,2</sup>

### **Cotton Weed control:**

MSMA/DSMA
EPTC¹
metolachlor¹
norflurazon¹,³
pendimethalin¹,³
prometryn¹
pyrithiobac-sodium¹
trifuralin¹,³
diuron¹
fluometuron¹
glyphosate¹,³
halosulfuron-methyl¹,²,³
clethodim¹
fenoxaprop¹
fluazifop¹,³

Harvest Aid: cacodylic acid

Organic Arsenical Desiccant		Alternative Chemistries	
	Desiccant	Defoliant	Boll Ripening
	diquat <sup>1</sup>	dimethipin <sup>1,3</sup>	dimethipin <sup>1</sup>
cacodylic acid	endothall <sup>1</sup>	ethephon <sup>1</sup>	ethephon <sup>1,2</sup>
	paraquat <sup>1</sup>	paraquat <sup>1</sup>	
	sodium chlorate <sup>1,3</sup>	thidiazuron <sup>1,3</sup>	
		sodium chlorate <sup>1</sup>	

Diclofop D, formasulfuon, metribuzin, mentioned in the BEAD response for alternatives for MSMA on golf courses, but not other documents<sup>2</sup>.

The alternatives are listed in alphabetical order in Table I-1.

Table I-1: A consolidated list of OPP-proposed alternatives

Alternative	Но	omeowner	use	Golf Courses	Cotton		
	MSMA/CA	CA	MSMA	Courses	Weed control	Harvest aid	Reference
2,4-D	+		+	+			1,2
Atrazine			+	+	+		1,2
Clethodim				<del>                                     </del>	+		1,2
Dicamba	+		+				
Dimethipin				<del></del>		+	1
Diquat		+		<del>                                     </del>		+	1,3
Dithiopyr	+		+	<del> </del>			1
Diuron				<del> </del>	+		1,3
Endothall				<del> </del>		<del></del>	1
EPTC	1	~		<del>                                     </del>	+	+	1
Ethephon				<del>  -</del>	+ +		1
Fenoxaprop				<del> </del>			1
Fluazifop			+	· · · · · · · · · · · · · · · · · · ·	+		1
Fluometuron	<del></del>			<del> </del>	+		1,3
Glufosinate	<del></del>	+					1
Glyphosate	<del>                                     </del>	+		<b>_</b>	+		1
Halosulfuron (methyl)	<del></del>	,			+		1,3
MCPA	<del>  -  </del>		+	+	+		1,2.3
MCPP	<del> </del>		+				1
Metolachlor			<del>+</del>	ļ			1
Napropamide	<del>                                     </del>				+		1
Norflurazon	<del></del>			+			1
Oryzalin	<del></del>			ļ	+		1,3
Oxadiazon	<del> </del>			+			1,2
Paraquat	+			+			1,2
Pendimethalin	+					+	1
Prodiamine	+		+		+		1,3
Prometryn	<del> </del>			+			1,2
	+				+		1
Propanoic acid			+				1
Pyrithiobac-sodium	<del>                                     </del>				+		1
Sodium chlorate	<del> </del>					+	1,3
Thidiazuron	<u> </u>					+	1,3
Triclopyr	+ +		+				1
Frifuralin					+		1.3

Table II-1. Cost Estimates for Postemergent Chemical Controls in Warm Season Turfgrass, Compared to MSMA

	_						_			_									
	Additional Comments	\$22 per gallon; applied 1 qt per acre, good control of listed weed species with little or no injury to well established turfgrasses.		great treatment for postemergent goosegrass, not as effective on crabgrass. Widely used postemergent treatment for goosegrass on bermudagrass putting	greens	"Early" postemergent activity, limited to small plants	(no larger than 3 leaf stage)	No grassy weed control	No longer commonly used. Frequent resistance	problems; soil persistence and environmental issues.	Very selective only controls sedges (purple and yellow nutsedge); controls nutsedge in one	application	No BLW control. Not widely used in turf management; more used in ornamentals and	soybeans	Unly controls goosegrass in bermudagrass stands;	Not efficacious when used alone. Usually mixed	with MSMA	Good activity on crabgrass and clover. Must be	sprayed with Methylated Seed Oil (MSO)
	Cost/ac	\$5.50		\$46.00	\$45.00	55.00		\$5	\$5	900	084		\$29.00	640 50	948.50	\$8.00		\$85	
	Price/unit	\$22/gal	4.4	\$85/qt	\$355/50z	\$110/gal		15/gal	\$12.50/gal	\$05/120	bottle	6	1b/8c¢	\$145/mil	\$143/gal	\$40/lb		\$85/lb	
A	Application Kate	3 @ 1.5 lbs ai/ac	1 5 lbs ci/cc	3 @ 0.8 lb ai/ac	3 @ 0.5 lb ai/ac	2qt /ac (2.72 lb	al/ac)	1 oz/1000 sq ft (2.72 lb ai/ac)	1-2 qt/ac (2.0-	1 07/90 (0 0K lk	ai/ac)	3/4 52 / 1000 0	(2.04 lbs ai/ac)	1 oz/1000 sa A	(2.72 lbs ai/ac)	3.2 oz/ac (0.2lb	al/ac)	1.0 lb ai/ac	
Weeds Treated	Treated Treated	Bahiagrass; barnyardgrass; brachiaria spp.; cullnettle; chickweed; cocklebur; crabgrass; dallisgrass; foxtail; goosegrass; johnsongrass; morningglory; nutsedge; pidweed; puncturevine; raoweed; sandhur; wood sorrel	12 (months) (months) (months)	Goosegrass, Poa annua; Poa trivialis, henbit; doveweed	goosegrass; Poa annua; Poa trivialis, Johnson grass; yellow/purplc/annual nutsedges; green kyllinga; Most common annual broad loaf woods (BU 10)#	crabgrass	Most BI W#	Work DLW	Poa annua; cool season grasses; most common annual grassy weeds and annual BLW#	Nutsedge (yellow, purple)		Most annual grassy weeds**		goosegrass		Poa annua; goosegrass	Ramvarderse: orsherse: fortaile and a f Dr 111#	(especially clover)	
Chemical		MSMA	MSMA	foramsulfuron	sulfosulfuron	dithiopyr	2.4-D		atrazme	halosulfuron		fluazifop		diclofop-		metribuzin	quinclorac	1	
Product/	Trade Name	MSMA 6.6	MSMA	Revolver	Certainty	Dimension	Trimec		Aaurex	Sedgehammer		Fusilade		Iloxan		Sencor	Drive		NR = Not reported

NR = Not reported

\*USEPA-OPP Estimates (04/12/06 memo by Dr. W. Phillips II, BEAD/OPP/USEPA) noted where prices differed from ETS calculations

\*\*Amual grass weeds: Poa annua; Poa trivialis; Barnyardgrass; Crabgrass; Foxtails; Goosegrass; Panicums; Witchgrass; Junglerice

\*BLW (Broadleaf weeds): Bindweed; Bitercress; Black medic; Carpetweed; Chickweed; Clover; Deadnettle; Henbit; Knotweed; Marestail; Mustard; Oxalis; Pigweed; Purslane; Sheperds-purse; speedwell; Spurge

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Table II-2. Cost Estimates for Preemergent Chemical Controls in Warm Season Turfgrass

Drodnot /	(F					
Trade Name	Chemical	Weeds Treated	Application Rate	Price	Cost/ac	Additional Comments
Barricade	prodiamine	Most common annual grassy weeds**.	1.0 lb ai/ac	\$215/201	9.46	
		many BLW#	1:0 to all ac	3213/gal	<b>645</b>	Very persistent. Use limited to southern
Pre-M	pendimethalin	Most common applied grassiv moode**.	7.011			US states.
		many BLW#	3.0 lbs al/ac	\$10/lb	\$30	No longer widely used. "Breakthrough"
Devrinol	napropamide	Annual binegrass: craborass: gooseanss: 25 lb. cites	7 5 115 01/22	11,00		problems later in season.
	1	Most common annual grassy weeds**:	2.3 IOS al/ac	\$8/Ib	\$20	Not widely used. Used primarily for
		many BLW#				ornamentals.
Surflan	oryzalin	Most common annual oracev weeds**.	201/00	. , , , ,		
	•	many BLW#	4 yrac	363/gai	<b>34</b> 1	Not widely used for turf management,
				•		best in ornamentals applied under
Ronstar	oxadiazon	Most common annual grassy weeds**.	2.2 112.01/20			nuicn
		many BLW#	2-2 10s al/ac	\$/0/Ib	\$210	Best preemergent product for
						goosegrass control. Only preemergent
						product labeled for use during
Ronetar	ovediozon					"sprigging."
TANITO ME	Ovaulazuii		2-3lbs ai/ac	NR	£104*	
Dimension	dithiopyr	Annual gracey weeds**	2-11-0		1010	
	. (1)	Annual Brassy Woods	zqvac	\$110	\$55	Applied as a preemergent but has

NR = Not reported

\*USEPA-OPP Estimates (04/12/06 memo by Dr. W. Phillips II, BEAD/OPP/USEPA) noted where prices differed from ETS calculations

\*\*Annual grass weeds: Poa annua; Poa trivialis; Barnyardgrass; Catbgrass; Foxtails; Goosegrass; Panicums; Witchgrass, Junglerice

\*BLW (Broadleaf weeds): Bindweed; Bittercress; Black medic; Carpetweed; Chickweed; Clover; Deadnettle; Herbit; Knotweed; Marestail; Mustard; Oxalis; Pigweed; Purslane; Sheperds-purse; speedwell; Spurge

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Table II-3. Weed Scenarios and Probable Costs

Scenario	Chemical(s)	Application Rate(s)	Tot. Cost/ac	
Dallisgrass	MCMA (no oftomotion)		101: 003040	Additional Comments
00000	MISIMA (no atternative)	2-3 @ 1.5 lb ai/ac	\$5.50	Only selective control oution ourseasts. com:1-11-
Faspaium spp (e.g., vaseygrass, Knotorass Rull Pasmaium etc.)	Revolver	3 @ 0.8 lb ai/ac	\$46	Sulfonylurea products have high propertity to develor wood
recogness, part 1 aspainii, cit.)	Cetainty	3 @ 0.5 lb ai/ac	\$45	used continuously, application rates are outside of labeled rates to provide
	MSMA	Multiple spot treat - 1.5lb ai/ac	\$5.50	comparable control (Walker, 2006)
		Cost Difference	+\$40	
Tropical signalgrass	MSMA (no alternative)	multiple applications 1.51b ai/ac	05 58	Touch weed in flowide marion MCMA
				Foogly would in John at region, MaxMA is only known chemical to be effective (multiple applications) - Spread of tropical signalgrass in Central and S. Florida theorized that reduction in applications of MSMA have allowed TSG to
Postemergent crabgrass and goosegrass (Early spring, some winter broadleaves)	Dimension and Trimec(2,4-D)	Dimension - 2qt/ac	\$60.00	Pronterate (Foy, 2006) Very typical scenario - "most common scenario on golf conreses" - not limited to
(Tlowe, 2006)	MSMA	1.5 lb ai/ac	0.0	southern region; Dimension gives good preemergent control of crabgrass and
	9	Cost Difference	05.50	goosegrass, while Trimec controls only broadleafs.
Postemergent crabgrass and goosegrass	Sencor	3.2 oz/ac (0.2lb ai/ac)	\$8,00	Not effective when used alone Almans and the second
(rate spring early summer)	Sencor and MSMA	Tank Mix (label instructions)	613 50	phytotoxic product.
	Revolver and MSMA	Tank Mix (Rev - 0.81b ai/ac; MSMA	\$51.50	•
Postemergent crabgrass, goosegrass,	Revolver, and Sedochammer	0.9 14 0:/00		
sedges (nutsedges, annual sedge and	9000	0.061b ai/ac	\$124.40	This is usually a second treatment using Revolver or Certainty (\$1.00 difference in price). Too late it cannot be a second treatment using Revolver or Certainty (\$1.00 difference in price).
Kyninga) (summer early Iall)	MSMA	1.5 lb ai/ac	\$5.50	Florida region (Thowe 2006)
		Cost Difference	+\$118.90	(2004; 7000)
Goosegrass, sedges (see above), Poa	lloxan, Aatrex, and	Illoxan - 2.72 lb ai/ac	\$131.90	Observed resistence problems with Howar (Distage 1)
arriag - purning greens	Sedgehammer	Aatrex - 2.0-2.72 lbs ai/ac Sedgehammer - 0.06 lb ai/ac		Florida region (Tlowe, 2006)
	MSMA	Snot trant 1 4 1h ailea		
		Cost Difference	\$5.50	
Sedges (Nutsedge, yellow &/or pumle)	Sedochammer	Of the cites	+\$126.40	
	MSMA	1 \$ 1b ai/oc	\$78.40	Very effective treatment in cool and warm season turf; MSMA also accounts for
		Cost Difference	\$5.50	other infestations (e.g., broadleaf weeds, grassy weeds, etc.)
Goosegrass (bermudagrass greens)	Revolver	0.8 lb si/sc	+\$72.90	
	Iloxan	2.72 lb ai/ac	346.00	Very common scenario. Revolver is replacing Iloxan because of Iloxan
	MSMA	1.5 lb ai/ac	346.30	resistance. Revolver is a sulfonylurea product may develop weed resistances.
	Cos	Cost Difference	93.30	
Winter annual broadleafs. Poa annua	Revolver	0.8 lb ai/ac	\$46.30-343	Stilfonylines producte wood society
	Certainty	0.5 lb ai/ac	545	Good mogram for courses that do not every Trackers 1.21
	MSMA	1.5 lb ai/ac	05.53	in dormant bermudagrass stands.
	Cos	Cost Difference	00 075+	
		AVERAGE PRICE INCREASE	671 00	
****			DA'T/6	

\*Note: These scenarios are for postemergent weed control, additional costs for preemergent controls were not included in this table.

\*\*Note: mid-season applications of other postemergent pesticides, MSMA is added in very small amounts to tank to provide control of a very broad spectrum of weed species.

Walker, Robert H., 2006. Personal Communication, September 18, 2006.

Lowe, Todd. 2006. Personal Communication, September 27, 2006.

Foy, John. 2006. Personal Communication, September 27, 2006.

## Appendix III

Below are summaries of pesticide-specific toxicology, ecotoxicology and environmental fate issues with OPP-proposed alternatives to the organic arsenical herbicides. The summaries are presented in alphabetical order of the products.

#### 2,4-D

- Neurotoxicity was demonstrated following exposure to 2,4-D at relatively high dose levels
- Developmental toxicity was observed in the rat following exposure to 2,4-D and its amine salts and esters. There is concern regarding its endocrine disruption potential.
- Most ecological risk quotient (RQ) values exceed EPA's levels of concern (LOCs).
- The Agency's screening level risk assessment for 2,4-D concluded that there is a
  potential for risk to endangered species.
- Relatively persistent in anaerobic aquatic environments (half life ranges from 41 to 333 days).
- 2,4-D has a low binding affinity in mineral soils and sediment; therefore has
  potential to leach to groundwater, or run off to surface water in high mineral soils
  and sediments.

#### (Red Fact Sheet, 06/05)

#### Atrazine

- Chronic risk LOCs are exceeded for mammals and birds.
- Some high acute risk and endangered risk LOCs are exceeded for terrestrial plants.
- High acute risk LOCs are exceeded for aquatic plants.
- Restricted use LOCs are exceeded for aquatic invertebrates.
- Endangered species risk LOCs are exceeded for aquatic invertebrates and aquatic vascular plants.
- Chronic LOCs are exceeded for aquatic plants, fish and aquatic invertebrates.
- Amphibian endocrinology and developmental issues.
- Mobile and persistent in the environment
- Expected to be in ground water and surface water confirmed by widespread detections in both surface and ground water.
- Very high rates of detections in both surface water (>90% of samples positive) and ground water (>40% of sampled wells positive).
- Detected concentrations in both surface water and well water exceed the maximum contaminant level (MCL).
- 10XFQPA safety factor because of concern for neuroendocrine mode of action and drinking water exposure assessment
- Some restricted use and endangered species ecological risk levels of concern (LOCs) are exceeded for mammals.

#### (RED, 04/06)

Clethodim	Alterations in hematology clinical abordistry recovery.
Ciethodini	Theoretical in hematology, chilical chemistry parameters, and increased absolute
ļ	& relative liver weights observed at the LOAEL of 75 mg/kg-day.  NOAEL of 1.0 mg/kg-day and uncertainty factor of 100 mg/kg-day.
	<ul> <li>NOAEL of 1.0 mg/kg-day and uncertainty factor of 100 used to calculate reference dose of 0.01 mg/kg-day.</li> </ul>
Ĭ	Surface and groundwater contemination was a second at the second and second areas are second areas and second areas are secon
	Surface and groundwater contamination may occur from the sulfoxide and sulfone degradates as well as the percent compound. The desired the sulfoxide and sulfone degradates.
	degradates, as well as the parent compound. The degradates are more persistent that the parent compound.
1	DWLOCs calculated and used as a point of comparison against modeled
	estimates. No sufficient monitoring data available.
(RED, 04/06)	
Dicamba	LOCs are exceeded for aquatic non-vascular plants
	High acute risk LOC is exceeded for small birds (including endangered birds)
ļ	Mammalian endangered species LOC is exceeded for small (15g) mammals
]	Chronic risk LOC is exceeded for mammals in some instances
]	Terrestrial plant risk LOCs are exceeded in some instances
	<ul> <li>Dicamba and metabolite DCSA are somewhat persistent in soil and would be</li> </ul>
	expected to be persistent in ground water.
	• Dicamba acid is very mobile in laboratory soil studies (high leaching potential)
	high potential to run off to surface water).
(RED, 06/06)	
Dimethipin	Data from long-term studies indicate that organ effects and decreased weight gain
	are the primary effects of exposure to dimethipin. Observed organ effects include
	toxicity in the kidney, lungs, duodenum and testes of male rats and toxicity in the
	liver kidney, glandular stomach, heart and aortic artery of female rats.
	USEPA has classified dimethipin as a possible human carcinogen, based on
	evidence of lung adenomas and carcinomas in mice. No O1* was calculated
	Dimethipin is classified as moderately toxic to small mammals on an acute oral
	basis with an LD <sub>50</sub> value of 458 mg/kg.
	Dimethipin has very high mobility in all soils.
	Dimethipin has the potential to enter surface water by runoff and enter
(DED 9/2005)	groundwater by leaching.
(RED, 8/2005)	
Diquat	Moderately toxic compound; listed by USEPA as Toxicity Class II.
	<ul> <li>Moderately toxic via ingestion; LD<sub>50</sub>s in animals range 30-188 mg/kg in various</li> </ul>
	test animals.
	MCL of 20 ppb.
	USEPA chronic Reference Dose of 0.0022 mg/kg-day based on NOEL of 0.22
	mg/kg-day and uncertainty factor of 100, based on cataracts in rats.
	Highly persistent and water soluble.
(EXTOXNET, IF	RIS, USEPA RED 5/95, TRED 4/2002)

#### Dithiopyr Oral chronic NOEL <0.5 mg/kg-day, based on a one-year study in dogs. In chronic rodent studies, rats fed dithiopyr exhibited liver toxicity (no dose given). In chronic studies with dogs, changes observed included decreased body weight, kidney, thyroid, ovarian and adrenal effects, as well as vomiting (no doses given). Subchronic and chronic exposure studies produces primarily liver and kidney toxicity Toxic to fish. (Merck Veterinary Manual, Dow Agrosciences MSDS, Monsanto Agricultural Group) Diuron Known/likely human carcinogen; Q<sub>1</sub>\* is 1.91 x 10<sup>-2</sup> mg/kg/day. Acute LOC for small mammals is exceeded for 15g mammals ingesting short grass. Acute high risk and endangered species LOCs are exceeded for small and medium sized mammals in some instances. Chronic LOC is exceeded for certain small mammals. Certain acute and chronic LOCs are exceeded for fish and invertebrates. Certain LOCs are exceeded for aquatic and terrestrial plants. Persistent and stable to hydrolysis. Mobile and has potential to leach to ground water and to contaminate surface water. (RED, 09/03) Endothall In the human health risk assessment, drinking water risk for infants less than one year old is at the level of concern. To ensure that endothall exposures from drinking water do not result in risks of concern, the Agency is requiring that direct applications to water not be applied less than 600 feet from an active drinking water intake. Food items may be exposed to residues of endothall in two ways: via direct application or via irrigation water previously treated with endothall. USEPA feels that potential risks to terrestrial organisms from the N, Ndimethylalkylamine salt may have been underestimated because terrestrial RQs were based on toxicity data using endothall acid and endothall dipotassium salt. On an acute basis, the N,N-dimethylalkylamine salt is considered to be highly toxic to very highly toxic to freshwater fish, moderately toxic to highly toxic to estuarine/marine fish, and moderately toxic to very highly toxic to estuarine/marine invertebrates. (RED, 9/2005)

## EPTC (s-ethyl-dipropylcarbamo thioate)

- Neurotoxic, causes increased cardiomyopathy, neuronal degeneration; developmental neurotoxicity study required.
- 10XFQPA safety factor.
- Risk quotients (RQs) exceed LOCs for effects on endangered mammals and endangered terrestrial plants.
- Closed cockpit application equipment required.
- Low soil adsorption, some potential to leach to ground water or run off to surface water.
- Needs to be soil-incorporated because of high losses through volatilization otherwise.
- Numerous data gaps.

#### (RED, 09/99)

#### Ethephon

- The most sensitive indicator of exposure to ethephon is the inhibition of red blood cell and plasma cholinesterase which occurs at low levels of exposure and may not be accompanied by clinical signs of toxicity until a threshold level of exposure is reached.
- Human studies have shown that humans may be more susceptible to the clinical toxicity of ethephon than experimental animals.
- The acute oral RfD for ethephon is 0.06 mg/kg-day, based on a LOAEL of 1.8 mg/kg-day and an uncertainty factor of 30. (Uncertainty factor is based on 10x for intraspecies variability and 3x for no NOAEL. There was no 10x for interspecies variability because the study was a human study).
- Data indicate that technical-grade ethephon is slightly toxic on an acute oral basis
  to bobwhite quail, and slightly toxic on a sub-acute dietary basis to bobwhite quail
  and mallard ducks.

## (TRED, 6/2006; EXTOXNET)

#### Fenoxaprop

- EPA has established the chronic RfD of 0.0025 mg/kg-day. This RfD is based on a rat reproductive toxicity study with a NOEL of 0.25 mg/kg-day. An uncertainty factor of 100 was used.
- Characterization of the carcinogenicity of fenoxaprop-ethyl has been referred to EPA Health Effects Division. For the interim, a worst case and protective risk assessment was carried out by use of a linear low dose extrapolation method (Q1\*) based on the increases in adrenal tumors in male mice. The Q1\* for the adrenal tumors is 9.1 x 10<sup>-2</sup>.

#### (Federal Register, 6/1998)

#### **Fluazifop**

- The chronic dietary endpoint for all populations is based on decreased spleen, testes, and epididymal weights in males and decreased uterine and pituitary weights in females observed in rats at the LOAEL of 5.8 mg/kg-day in males and 7.1 mg/kg-day in females. The NOAEL in this study was 0.74 mg/kg-day. An uncertainty factor of 100 was applied resulting in a cRfD of 0.0074 mg/kg-day.
- Fluazifop-p-butyl may be highly to moderately toxic to fish.
- Has been detected in a high percentage of well sampled (58%) in the PGWDB ground water survey, at concentrations as high as 20  $\mu$ g/L

#### (TRED, 9/2005; EXTOXNET 6/1996)

#### Fluometuron

- •Likely/possible carcinogen;  $Q_1 = 1.8 \times 10^{-2} \text{ mg/kg/day}$ .
- Preliminary EPA analysis calculated an aggregate cancer risk of 9.3 x 10<sup>-5</sup>
- Majority of the aggregate cancer risk is due to drinking water
- •EPA estimated the cancer risk from ground water exposure (using Sci-Gro modeling) to be approximately 9.1 x 10<sup>-5</sup>, and the cancer risk from exposure through surface water (using PRZM-EXAMS modeling) to be approximately 7 x 10<sup>-6</sup>. Both exceed the benchmark value of 1 x 10<sup>-6</sup>
- Has been detected in surface water and ground water monitoring

(No RED yet, but there are EFED and HED chapters in the EPA docket) Docket number EPA-HQ-OPP-2004-0372, documents 0008 and 0009)

#### Glufosinate

- There is no RED available for this product
- An acute reference dose (aRfD) of 0.50 mg/kg-day is based on a NOAEL of 50 mg/kg-day, based on based on a study in rats. An uncertainty factor of 100 was used.
- EPA has established a chronic RfD of 0.021 mg/kg-day. This RfD is derived from a NOAEL of 2.1 mg/kg-day, based on a rat study. An uncertainty factor of 100 was used.
- USEPA lacks sufficient water-related exposure data to complete a comprehensive drinking water exposure analysis and risk assessment for glufosinate ammonium. Modeling data is used.

#### (Federal Register, 8/1999)

#### Glyphosate

- RED facts notes that endangered plants and Houston toad may be at risk.
- RfD= 0.1 mg/kg-day based on a NOAEL of 10 mg/kg-day and a uncertainty factor of 100.
- Can cause eye and skin irritation.
- Federal Drinking Water Standard= 700 μg/L
- Some endangered species may be at risk from exposure to glyphosate (endangered plants, Houston toad).
- Glyphosate has a median half-life in soil of 13.9-140.6 days (depending on geographic location).

## (IRIS, TOXNET, USEPA RED 9/1993)

# Halosulfuron (methyl)

- The acute oral RfD (for females 13-50 years, infants, and children) is 0.5 mg/kg-day, based on a rabbit study with a NOAEL of 50 mg/kg-day and an uncertainty factor of 100. In the risk assessment, therefore, the acute RfD of 0.5 mg/kg-day is equal to the acute population-adjusted dose (aPAD).
- The chronic oral RfD (all populations) is 0.1 mg/kg-day, based on a NOAEL of 10 mg/kg-day with an uncertainty factor of 100.
- USEPA lacks sufficient water-related exposure data to complete a comprehensive drinking water exposure analysis and risk assessment for halosulfuron. Modeling data is used.

#### (Federal Register, 9/2000)

#### MCPA (4-chloro-2methyl phenoxy) acetic acid

- A developmental neurotoxicity study (DNT) required on MCPA 2-EHE for prenatal neurotoxicity due to clinical signs indicative of neurotoxicity in acute and subchronic studies.
- Highly toxic to plants
- EPA identified ecological risks of concern in terrestrial plants, terrestrial mammals and avian species.
- MCPA-acid is considered extremely mobile in laboratory batch equilibrium studies (high leaching potential; high potential for run-off to surface water).

#### (RED Fact Sheet, 09/04)

#### (Mecoprop) MCPP

- Oral RfD based on increased absolute and relative kidney weight a rat study, with a NOEL of 50 ppm (3 mg/kg-day) with an uncertainty factor of 3,000.
- Listed as a possible human carcinogen.
- MCPP may be teratogenic at high doses, based on rat studies.
- MCPP may be genotoxic at high doses, based on Salmonella bioassay studies.
- A study of people employed in the manufacture of phenoxy herbicides including mecoprop showed an association between these herbicides and cancer of soft tissues and non-Hodgkin's lymphoma. Not all studies, however, support this conclusion
- The duration of mecoprop's residual activity in soil is about two months.
- Acute oral LD<sub>50</sub> in rats:1,166 mg/kg body weight. Target organs are the kidney and liver.
- Target organs are the kidney and liver in long-term and cancer studies.
- Lowest known oral NOAEL 20 ppm (1.1 mg/kg-day), based on rat studies.
- Sources: IRIS; EXTOXNET 9/1995; EC Health & Consumer Protection Directorate

#### Metolachlor

- Was originally considered a Group C carcinogen (possible carcinogen). Peer Review later recommended a margin of exposure (MOE) approach for chronic risk assessment since there was no supportable mutagenicity concern and further metabolism data indicated that formation of the presumed carcinogen was actually very low.
- Some evidence of developmental toxicity in rats.
- Level of concern (LOC) is exceeded for risk to endangered species for birds.
- LOC is exceeded for risks to waterfowl ingesting short grass.
- LOCs are exceeded for endangered species and restricted use for small mammals ingesting short grass.
- Exceeds endangered species LOC for fish in shallow water.
- EPA expects risk to non-target plants.
- Moderately persistent to persistent in soil.
- Mobile to highly mobile; high leaching potential; high potential for run-off to surface water.
- Very high rate of detection in surface water samples (>80% of samples positive).
- Detected in ground water at a high rate (17% of wells sampled; in 20 states, 3 of which levels exceeded the lifetime Health Advisory of 100 ppb and 5 of which concentrations in well water exceed 10% of the Health Advisory Level).
- Among the top five pesticides found in surface water in mid-western corn belt.
- Labels will need ground water and surface water advisories.

(TRED Fact Sheet, 05/02)

Nonecas	
Napropamide	<ul> <li>Chronic LOCs were exceeded for mammals based on standard upper-end EECs.</li> </ul>
	For terrestrial and wetland/riparian plants, LOCs were exceeded for seedling
1	emergence in areas next to treated fields.
	<ul> <li>LOCs for acute endangered species risks for marine/estuarine mollusks were exceeded in several scenarios.</li> </ul>
	<ul> <li>LOC for adverse effects on marine/estuarine crustaceans was exceeded in one scenario.</li> </ul>
	<ul> <li>LOC for adverse effects on endangered vascular aquatic plants was exceeded in several scenarios.</li> </ul>
	<ul> <li>There were listed endangered or threatened wetland plant and terrestrial plant risks in several scenarios.</li> </ul>
	<ul> <li>Endangered species chronic mammalian LOCs were exceeded for several feed items at modeled rates.</li> </ul>
1	EPA notes the potential for indirect adverse effects on endangered and
	threatened species Persistent but not particularly mobile. Possible surface water contamination through run-off.
	<ul> <li>Endangered species dependent upon other plants and animals that may be adversely affected.</li> </ul>
(RED, 09/05)	
Norflurazon	Key subchronic and chronic effects include effects on blood cell counts, liver, and
	thyroid (suggesting possible endocrine effects).
	<ul> <li>Non-Q<sub>1</sub>* group C cancer classification (possible carcinogen).</li> </ul>
	Causes reproductive effects in birds.
	RQs exceed level of concern for chronic effects on endangered birds and
	endangered small mammals.
	Poses high risks to endangered terrestrial and aquatic plants.
	<ul> <li>Persistent and mobile in soil (high potential to leach; high potential to run off to surface water).</li> </ul>
	Desmethyl metabolite is also persistent and mobile.
	Surface water and ground water contamination advisories required on labels.
(TRED, 06/02)	and ground water contamination advisories required on labels.
Oryzalin	• Carcinogenic in rats, Q <sub>1</sub> * 1.3 x 10 <sup>-1</sup> mg/kg/day, causing mammary and thyroid
•	tumors; classified as a Group C carcinogen (possible human carcinogen)
	<ul> <li>Dietary cancer risk = 8.1 x 10<sup>-7</sup>; this does not include cancer risk from drinking</li> </ul>
	water.
	• Cancer risk to commercial applicators using a hand wand applicator (highest risk)
	= 2.6 x 10°; mitigation required
	High risk to terrestrial plants
	Moderately persistent in soil, but not highly mobile, degradates may leach
	• Has been detected in surface water samples at concentrations >1.0 μg/L.
(RED, 09/94)	- PO

### Oxadiazon Likely to be carcinogenic to humans. Q<sub>1</sub>\* is 7.11 x 10<sup>-2</sup> mg/kg/day. Significant increase in liver adenomas and/or carcinomas combined in males at 9.3 mg/kg/day. Endangered species LOCs for liquid and granular formulations of oxadiazon are exceeded for acute risks to birds, mammals, freshwater and estuarine fish and invertebrates, and aquatic vascular plants. Also assume that endangered terrestrial plants are at risk, but study is not complete. Persistent and stable under typical terrestrial environment conditions. (RED, 09/03) Paraquat Very persistent and could potentially be found in surface water systems associated with soil particles carried by erosion High acute risk, restricted use and endangered species LOCs are exceeded for At certain use rates, high acute risk, restricted use and endangered species LOCs are exceeded for mammals. Endangered species LOCs have been exceeded for chronic effects on birds, small mammals and for acute effects on semi-aquatic and terrestrial plants. Highly toxic by inhalation route (Toxicity Category I). Moderately toxic by the oral route (Category II) and slightly toxic by the dermal route (Category III). Can cause moderate to severe eye irritation (Category II) and minimal dermal irritation (Category IV). Subchronic toxicity tests in rats showed changes in the lungs. Dermal tests in rabbits resulted in scabbing and inflammation. When rats were exposed to respirable aerosols, they had lung changes and extensive sores and swelling in the larynx. A chronic toxicity study in dogs resulted in an increase in the severity and extent of chronic pneumonitis in mid-dose and high-dose animals. Does not hydrolyze or photodegrade in aqueous solutions. Resistant to microbial degradation under aerobic and anaerobic conditions. Primary route of environmental dissipation is adsorption to biological materials and soil clay particles. Could be found in surface water systems associated with soil particles carried by erosion, but is not expected to be a groundwater concern. Moderately toxic to non-endangered and endangered birds and mammals, nontarget terrestrial and semi-aquatic plants. Acutely toxic to birds and mammals immediately after application. RfD is 4.5 E-3 mg/kg-d, based on chronic pneumonitis in dogs (UF of 100, NOAEL of 0.45 mg/kg-d. (RED 9/1997, IRIS (RED, 08/97)

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#### Pendimethalin

- Classified as a Group C carcinogen (possible human carcinogen).
- Chronic risk quotients LOCs for fish exceed the LOC.
- May adversely affect endangered species of terrestrial and semi-aquatic plants, aquatic plants, and aquatic invertebrates, including mollusks. May also adversely affect endangered fish and birds. Some risks to non-target terrestrial and semiaquatic plants are expected.
- Laboratory studies and limited field study data show it is slightly to moderately persistent in aerobic soil environments.
- May contaminate surface water from spray drift.
- Has been detected in surface water samples at concentrations >1.0 μg/L.
- Detected at low levels in ground water samples
- Included on the EPA TRI list of PBT chemicals.

(RED Fact Sheet, 04/97)

#### **Prodiamine**

- Enhances hepatic metabolism and excretion of thyroid hormone.
- Used on turfgrass in large recreational areas such as golf courses, residential gardens, and agricultural crops.
- Nontoxic to mammals if ingested. Prodiamine may be more toxic to amphibians than mammals, but less toxic to amphibians than fish.
- Prodiamine is a root inhibitor belonging to the dinitroaniline chemical class.

(LSU Agricultural Center; Environmental Health Perspectives; pesticideinfo.org, JR Simplot MSDS, Michigan State University.)

#### Prometryn

- Triazine herbicide (same class as atrazine)
- Common degradates with atrazine
- Hexa- and pentachlorobenzene (HCB, PCB) impurities are oncogenic.
- Persistent in soil and water, mobile in sandy and alkaline soils (prohibited from use in these soils); potential to leach to ground water and runoff to surface water.
- Risk quotient (RQs) exceed LOC for risks to endangered mammals and freshwater invertebrates.

(RED, 09/95)

#### Propanoic acid

- Corrosive, causes severe skin and eye burns.
- Used in animal feed, as a grain preservative, calcium and sodium salt production, cellulose ester production, plastic dispersions, pharmaceuticals, and flavors and fragrances.
- High mobility in soil.
- Expected to volatilize from dry soil surfaces.

(HSDB Search Results for Propanioc Acid; RED 9/1991)

#### Pyrithiobacsodium

- RfD established as 0.587 mg/kg-d, based on a systemic NOAEL of 58.7 mg/kg-day (in male rats) with an uncertainty of 100.
- Group C carcinogen, based on liver adenomas, carcinomas and combined adenoma/carcinomas in the male mouse and rare kidney tubular adenomas, carcinomas and combined adenoma/carcinomas in male rats.
- Unit risk, Q1\* (mg/kg-day)<sup>-1</sup> is 1.05x 10<sup>-3</sup> (mg/kg-day)<sup>-1</sup> in human equivalents, based on male kidney tumors.
- 10X FQPA safety factor
- EECs for chronic exposure are 7.76 ppb for surface water, 0.778 ppb for groundwater.

## (Cornell University Cooperative Extension)

# Sodium chlorate

- Sodium and chlorate anions are expected to be very mobile
- Reports indicate that sodium chlorate can be persistent in the field from 6 months to 5 years.
- Chronic avian RQs exceed the LOC.
- LOC for endangered aquatic plants was exceeded for non-agricultural uses.
- Powerful oxidizing agent.
- May be irritating to the skin, eyes or respiratory tract when used as a pesticide.
- Drinking water guidelines: 800  $\mu$ g/L in California (as chlorate ion), 7  $\mu$ g/L in Maine (as chlorate ion).
- Remains in soil for 0.5-5 years.
- Soluble in water.
- Acute doses of >100 mg/kg are generally fatal to humans.
- Chronic RfD = 0.03 mg/kg-day.
- Thyroid toxicant producing thyroid gland follicular cell hypertrophy.
- Not considered to be carcinogenic at doses that do not alter thyroid hormone homeostasis.
- For infants <1 year of age, using the estimated highest annual average of drinking water concentrations, food and drinking water chronic estimates were above the Agency's level of concern; when 90<sup>th</sup> percentile and median annual average water concentrations were used, all population subgroups were below the LOC.
- Potential acute and chronic toxicity to birds, mammals, and endangered aquatic plants.
- Closed cockpit regulation for applicators.
- Prohibition on application in such a way that will contact people or animals directly.

## (HSDB Search Results for Sodium Colórate; RED 6/2006, RED, 07/06)

#### **Thidiazuron**

Thidiazuron is persistent and has intermediate mobility

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- Risk quotients exceed LOCs for non-endangered and endangered plants adjacent to treated sites and for semi-aquatic dicots.
- Chronic risk quotients for mammals exceed LOCs
- Persistent in soil.
- Photolysis is major route of transformation.
- Potential exceedances of the LOC for: 15 grams mammals foraging on short grass, broadleaf forage and small insects; and terrestrial and semi-aquatic plants.

#### (USEPA RED, 9/2005)

#### Triclopyr Common metabolite with chlorpyrifos (3,5,6-trichloro-2-pyridinol (TCP) Risk quotients exceed the following LOCs, even with the lower maximum use rates established in the RED: Chronic risk to mammals, acute risk to fish (BEE), acute risk to non-target plants. Triclopyr acid is somewhat persistent, and is mobile; therefore has a potential leach and run-off to surface water. The major degradate TCP is also persistent and mobile. (RED Fact Sheet, 09/97) Trifuralin Dinitroanaline herbicide. Group C carcinogen (possible human carcinogen) due to effects on bladder, kidneys, and thyroid; $Q_1 = 0.0077 \text{ mg/kg/day}$ Oncogenicity risk <10<sup>-5</sup> for commercial applicators, <10<sup>-7</sup> for residential handlers Acute RQs exceed endangered species LOCs for birds (chronic), endangered fish, endangered freshwater invertebrates. Was in Special Review (initiated 1979) because of nitrosamine impurity (a known carcinogen), which exceeded oncogenicity concerns Nitrosamine content required to be <0.5 ppm Fish display vertebral abnormalities, suggesting possible developmental effects. Very highly toxic to fish, high risk to semi-aquatic plants Moderately persistent, non-mobile. Included on the EPA TRI list of PBT chemicals. (RED, 08/04)

## **Appendix IV**

The maximum detected concentrations of the alternatives in surface water are provided in Table IV-1 for NAWQA Cycle I. The maximum detected concentrations in ground water are provided in Table IV-2 for NAWQA Cycle II.

Table IV-1: Maximum concentrations of OPP-proposed alternatives to the organic arsenical herbicides detected in surface water and ground water under NAWQA Cycle I (1991-2001).

OPP-Proposed	Maximum detected	concentration (μg/L)
alternative	Surface water	Ground water
2,4-D	15	14.8
atrazine	201	4.78
dicamba	1.14	1.46
diuron	14	5.53
EPTC	29.6	0.45
fluometuron	8.6	1.29
MCPA	19	Not detected
metolachlor	77.6	32.8
napropamide	0.767	0.07
norflurazon	1.24	29.2
oryzalin	1.8	0.08
pendimethalin	2.05	0.098
triclopyr	16	Not detected
trifluralin	0.17	0.014

<sup>--</sup> No groundwater data available

Table IV-2: Maximum concentrations of OPP-proposed alternatives to the organic arsenical herbicides detected in surface water and ground water under NAWQA Cycle II (2002-present).

OPP-Proposed	Maximum detected	concentration (μg/L)
alternative	Surface water	Ground water
2,4-D	8.7	1.4
atrazine	191	2.34
dicamba	1.8	0
diuron	9.2	0.92
EPTC	0.29	0.01
fluometuron	6.11	1.87
glufosinate	0.56	
glyphosate	9.72	0.16
metolachlor	14.3	16.1
napropamide	0.61	0.01
norflurazon	0.15	0.31
oryzalin	0.45	0.03
pendimethalin	42.0*	0.07
prometryn	0.3	
triclopyr	6.04	0.28
trifluralin	0.2	0.05

<sup>\*</sup>Next highest value is 1.1 µg/L

## Surface water

Detailed summaries of the NAWQA Cycle I (1991-2001) surface water monitoring data for each of the four major land use categories (agricultural, mixed, undeveloped, and urban) are provided in Tables IV-3 – IV-4, respectively. Table IV-5 provides and overall summary of the NAWQA Cycle II data for all the land use categories combined.

<sup>--</sup> no data

Table IV-3: Summary of surface water monitoring results under NAWQA Cycle I (1991-2001) for OPP-proposed alternatives in USGS-NAWQA Database (Agricultural Sites) (http://ca.water.usgs.gov/pnsp/ pestsw/Pest-SW\_2001\_table1\_ag.html).

OPP-Proposed alternative	MCL¹ (μg/L)	HAL² (μg/L)	Other available WQ criteria (µg/L)	Upper minimum reporting limit (µg/L)	No. of monitoring sites	No. of samples	Percent of detection	Max. detected conc. (μg/L)
2,4-D	70			0.16	48	1223	15.35	15*
Atrazine	3		17.5 <sup>3</sup> aquatic communities	0.007	76	1852	90.44	201*
Dicamba				0.110	48	1233	1.55	1.14
Diuron		10	2.4 <sup>4</sup> acute nonvascular plants	0.12	48	1235	13.04	14*
EPTC		200		0.002	78	1890	14.11	7.3
Fluometuron				0.060	48	1236	7.58	8.60*
MCPA				0.200	48	1233	1.40	0.920
Metolachlor		100		0.013	78	1887	82.74	77.6*
Napropamide				0.007	77	1858	3.25	0.767
Norflurazon		30		0.042	48	1235	3.6	1.24
Oryzalin				0.310	48	1236	0.49	1.80*
Pendimethalin		280 <sup>5</sup>	WHO: 17 <sup>6</sup> , NY: 50 <sup>7</sup>	0.022	78	1884	6.56	2.05
Triclopyr				0.250	48	1233	2.27	16.0*
Trifluralin		5		0.009	78	1889	13.34	0.17

<sup>\*</sup> Estimated concentrations based on monitoring results.

MCL (Maximum Contaminant Level) - The highest level of a contaminant allowed in drinking water, by USEPA.

<sup>&</sup>lt;sup>2</sup> HAL - EPA Lifetime Health Advisory Level.

<sup>&</sup>lt;sup>3</sup> Cited by USGS-NAWQA: USEPA, 2003. Atrazine MOA Ecological Subgroup-recommendations for aquatic community level of concern (LOC) and method to apply LOCs to monitoring data, Final Report, October 22, 2003: U.S. Environmental Protection Agency, Public Docket Number EPA-HQ-OPP-2003-0367-0007, accessed Jan. 24, 2006, at http://www.regulations.gov.

<sup>&</sup>lt;sup>4</sup> Cited by USGS-NAWQA: USEPA, 2003. Reregistration eligibility decision for diuron, list A, case 0046: USEPA, OPPTS, SRRD, accessed September 21, 2005, at http://www.epa.gov/oppsrrd1/REDs/diuron\_RED.pdf

<sup>&</sup>lt;sup>5</sup> Calculated by Environmental & Turf Services, Inc.

<sup>&</sup>lt;sup>6</sup> WHO water quality guideline (WHO, Second Consultation on Herbicides in Drinking-Water, Rome, 13-18 July 1987. Document ICP/CWS 012A(S) (1987).

<sup>&</sup>lt;sup>7</sup> The State of New York has an MCL of 50 μg/L for pendimethalin.

Table IV-4: Summary of surface water monitoring results (1991-2001) for OPP-proposed alternatives in USGS-NAWQA Database (Mixed Land Use) (http://ca.water.usgs.gov/pnsp/ pestsw/Pest-SW\_2001\_table1\_ag.html)

OPP-Proposed alternative	Upper minimum reporting limit (µg/L)	No. of monitoring sites	No. of samples	Percent of detection	Max. detected conc. (μg/L)
2,4-D	0.160	25	562	7.79	1.40
Atrazine	0.007	47	971	88.09	12.8
Dicamba	0.110	25	561	0.80	0.390
Diuron	0.120	25	557	8.66	4.15*
EPTC	0.002	47	1000	11.88	29.6*
Fluometuron	0.060	25	561	0.0	<0.035
MCPA	0.200	25	562	2.04	18.6*
Metolachlor	0.013	47	1023	71.37	9.10
Napropamide	0.007	46	1004	2.6	0.332
Norflurazon	0.042	25	561	0.09	0.040
Oryzalin	0.310	25	557	0.51	0.430
Pendimethalin	0.022	47	1020	6.72	0.144
Triclopyr	0.250	25	562	0.19	1.04
Trifluralin	0.009	47	1021	10.62	0.097

<sup>\*</sup> Estimated concentrations based on monitoring results.

Table IV-5: Summary of surface water monitoring results (1991-2001) for OPP-proposed alternatives in USGS-NAWQA Database (Undeveloped Land Use) (http://ca.water.usgs.gov/pnsp/ pestsw/Pest-SW\_2001\_table1\_ag.html)

OPP-Proposed alternative	Upper minimum reporting limit (µg/L)	No. of monitoring sites	No. of samples	Percent of detection	Max. detected conc. (μg/L)
2,4-D	0.160	1	19	0.0	< 0.150
Atrazine	0.007	4	59	60.23	0.085
Dicamba	0.110	1	19	0.0	< 0.035
Diuron	0.120	1	19	9.07	0.002
EPTC	0.002	4	60	1.64	0.004
Fluometuron	0.060	1	19	9.07	0.080
MCPA	0.200	1	19	5.62	0.020
Metolachlor	0.013	4	60	29.11	0.027
Napropamide	0.007	4	60	1.20	0.006
Norflurazon	0.042	1	19	9.07	0.170
Oryzalin	0.310	1	19	0.0	<0.310
Pendimethalin	0.022	4	60	0.0	<0.010
Triclopyr	0.250	1	19	0.0	<0.250
Trifluralin	0.009	4	60	0.0	< 0.009

<sup>\*</sup>Estimated concentrations based on monitoring results.

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Table IV-6: Summary of surface water monitoring results (1991-2001) for OPP-proposed alternatives in USGS-NAWQA Database (Urban Sites) (http://ca.water.usgs.gov/pnsp/ pestsw/Pest-SW\_2001\_table1\_ag.html)

OPP-Proposed alternative	Upper minimum reporting limit (µg/L)	No. of samples	Percent of detection	Max. detected conc. (μg/L)
2,4-D	0.15	573	18	5.5*
Atrazine	0.001	611	85	14.00
Dicamba	0.035	573	0.52	0.16
Diuron	0.02	574	21	11*
EPTC	0.002	611	4.6	0.04
Fluometuron	0.035	576	0.0	<mdl< td=""></mdl<>
MCPA	0.17	573	4.9	19*
Metolachlor	0.002	610	65	2,42
Napropamide	0.003	611	1.2	0.04
Norflurazon	0.024	576	0.17	0.04
Oryzalin	0.31	573	2.6	1.7*
Pendimethalin	0.004	611	16	0.37
Triclopyr	0.25	573	3.3	3.4*
Trifluralin	0.002	611	10	0.04

\* Estimated concentrations based on monitoring results.

MDL Method Detection Limit

Note: The number of monitoring sites for each compound was not available for the urban sites

Table IV-7. Summary of Surface Water Cycle II Monitoring Results for all Land Use Types.

OPP- Proposed alternative	Upper minimum reporting limit (ug/L)	No. of samples	Percent of detection	Max. detected conc. (ug/L)
2,4-D <sup>1</sup>	0.32	952	55.5	8.7
Atrazine <sup>2</sup>	0.09	5037	78.3	191
Dicamba <sup>1</sup>	0.64	950	11.7	1.8
Diuron <sup>1</sup>	0.13	953	53.0	9.2
EPTC <sup>2</sup>	0.3	3749	8.5	0.29
Fluometuron <sup>1</sup>	0.2	954	9.2	6.11
Glufosinate <sup>3</sup>	0.1	469	0.4	0.56
Glyphosate <sup>3</sup>	0.1	471	32.5	9.72
Metolachlor <sup>2</sup>	0.5	5071	63.5	14.3
Napropamide	0.04	3576	2.3	0.61
Norflurazon <sup>1</sup>	0.03	952	11.0	0.15
Oryzalin <sup>1</sup>	0.72	952	0.9	0.45
Pendimethalin <sup>2</sup>	0.3	5049	10.9	42.0
Prometryn <sup>3</sup>	0.05	1879	9.2	0.3
Triclopyr <sup>1</sup>	0.56	952	21.4	6.04
Trifluralin <sup>2</sup>	0.05	5049	11.6	0.2

<sup>&</sup>lt;sup>1</sup>HPLC methodology

#### **Ground water**

Ground water monitoring data from the NAWQA database indicate detections that exceed MRLs for 12 of the 14 OPP-proposed alternatives for which there is information in the database for Cycle I, as shown in Table IV-1 above.

Ground water monitoring for NAWQA Cycle I agricultural sites for OPP-proposed alternatives to the organic arsenical herbicides are presented in Table IV-8, including the frequency of detection and maximum concentration levels. In addition to the monitoring data available at the USGS NAWQA website, data for glyphosate and for fluazifop are available from EPA's Pesticide in Ground Water Database (PGWDB). Table IV-8 presents a summary of the results from both databases.

Tables IV-9 through IV-11 present ground water monitoring data for mixed, undeveloped, and urban land use sites for Cycle I. Atrazine also demonstrated a high frequency of detection in NAWQA Cycle I ground water samples for other land use sites (mixed, undeveloped, and urban) ranging from 13.4% to 32% of the samples (Tables IV-9 - IV-11). Detection frequencies were also significant (>5%) for metolachlor for the mixed land use and urban land use sites. Diuron was detected in >3% of the samples collected from urban land use sites.

<sup>&</sup>lt;sup>2</sup>GCMS methodology

<sup>&</sup>lt;sup>3</sup>Glufosinate, glyphosate, prometryn have no assigned methodology

Table IV-12 presents a summary of the available ground water monitoring data for the alternative compounds for Cycle II. The ground water monitoring data for Cycle II demonstrate that atrazine and metolachlor continue to have very high frequencies of detection, 31% and 12%, respectively. Diuron has been detected in approximately 4% of the Cycle II samples, with fluometuron and norflurazon being found in approximately 2% of the Cycle II samples. The frequency of detection for the alternatives has remained consistent between Cycle I and Cycle II for the majority of the alternative compounds.

Table IV-8: Summary of Ground Water Monitoring Results (1991-2001) for OPPproposed alternatives in the USGS-NAWQA and Pesticides in Ground Water Databases (Agricultural Sites http://ca.water.usgs.gov/pnsp/pestgw/Pest-GW\_2001\_Text.html)

OPP-Proposed alternative	MCL <sup>1</sup> (µg/L)	HAL <sup>2</sup> (µg/L)	Other available WQ criteria (µg/L)	Upper minimum reporting limit (µg/L)	No. of wells	Percent of detection	Max. detected conc. (ug/L)
2, 4-D	70			0.16	1218	0.58	4.54*
Atrazine	3			0.007	1438	41.9	4.78
Dicamba				0.11	1218	0.41	0.45*
Diuron		10		0.12	1224	3.84	5.53*
EPTC		200		0.002	1443	1.11	0.45
Fluometuron				0.06	1226	0.41	0.43
Fluazifop <sup>3</sup>				0.1	12	58	20.32
Glyphosate <sup>3</sup>	700		-	0.1	247	2.8	150
Metolachlor		100		0.013	1443	17.0	32.8*
Napropamide				0.007	1443	0.48	0.043
Norflurazon		30		0.042	1226	2.12	29.2*
Pendimethalin		280 <sup>4</sup>	WHO: 17 <sup>5</sup> NY: 50 <sup>6</sup>	0.022	1443	0.28	0.059
Trifluralin		5		0.009	1443	0.69	0.014

<sup>\*</sup> Estimated concentrations based on monitoring results.

<sup>&</sup>lt;sup>1</sup> MCL (Maximum Contaminant Level) - The highest level of a contaminant allowed in drinking water, by USEPA.

<sup>&</sup>lt;sup>2</sup> HAL - EPA Lifetime Health Advisory Level.

<sup>&</sup>lt;sup>3</sup> USEPA, Pesticides in Ground Water Database (PGWDB) 1971-1991.

<sup>&</sup>lt;sup>4</sup> Calculated by Environmental & Turf Services, Inc.

<sup>&</sup>lt;sup>5</sup> WHO water quality guideline (WHO, Second Consultation on Herbicides in Drinking-Water, Rome, 13-18 July 1987. Document ICP/CWS 012A(S) (1987).

<sup>&</sup>lt;sup>6</sup> The State of New York has an MCL of 50 μg/L for pendimethalin.

Table IV-9: Summary of Ground Water Monitoring Results (1991-2001) for OPP-proposed alternatives in the USGS-NAWQA and Pesticides in Ground Water Databases (Mixed Land Use http://ca.water.usgs.gov/pnsp/pestgw/Pest-GW\_2001\_Text.html

OPP-Proposed alternative	Upper minimum reporting limit (µg/L)	No. of wells	Percent of detection	Max. detected conc. (μg/L)
2, 4-D	0.16	1473	0.41	0.15
Atrazine	0.007	2712	18.6	2.8
Dicamba	0.11	1482	0.07	0.07
Diuron	0.12	1480	2.10	1.92
EPTC	0.002	2717	0.33	0.182
Fluometuron	0.06	1484	0.40	1.29
MCPA	0.2	1483	0.0	<rl< td=""></rl<>
Metolachlor	0.013	2717	5.04	2.62
Napropamide	0.007	2717	0.22	0.07
Norflurazon	0.042	1484	0.20	0.15
Oryzalin	0.31	1480	0.07	0.03
Pendimethalin	0.022	2717	0.04	0.098
Triclopyr	0.25	1476	0.0	<rl< td=""></rl<>
Trifluralin	0.009	2717	0.33	0.009

<sup>&</sup>lt;RL Less than maximum reporting limit

Table IV-10: Summary of Ground Water Monitoring Results (1991-2001) for OPP-proposed alternatives in the USGS-NAWQA and Pesticides in Ground Water Databases (Undeveloped Land Use http://ca.water.usgs.gov/pnsp/pestgw/Pest-GW\_2001\_Text.html

OPP-Proposed alternative	Upper minimum reporting limit (µg/L)	No. of wells	Percent of detection	Max. detected conc. (μg/L)
2, 4-D	0.16	46	0.0	<rl< td=""></rl<>
Atrazine	0.007	67	13.4	0.018
Dicamba	0.11	46	0.0	<rl< td=""></rl<>
Diuron	0.12	47	0.0	<rl< td=""></rl<>
EPTC	0.002	67	0.0	<rl< td=""></rl<>
Fluometuron	0.06	47	0.0	<rl< td=""></rl<>
MCPA	0.2	46	0.0	<rl< td=""></rl<>
Metolachlor	0.013	67	1.49	0.005
Napropamide	0.007	67	0.0	<rl< td=""></rl<>
Norflurazon	0.042	47	0.0	<rl< td=""></rl<>
Oryzalin	0.31	47	0.0	<rl< td=""></rl<>
Pendimethalin	0.022	67	0.0	<rl< td=""></rl<>
Triclopyr	0.25	47	0.0	<rl< td=""></rl<>
Trifluralin	0.009	67	1.49	0.004

<sup>&</sup>lt;RL Less than maximum reporting limit

Table IV-11: Summary of Ground Water Monitoring Results (1991-2001) for OPP-proposed alternatives in the USGS-NAWQA and Pesticides in Ground Water Databases (Urban Sites http://ca.water.usgs.gov/pnsp/pestgw/Pest-GW\_2001\_Text.html

OPP-Proposed alternative	Upper minimum reporting limit (µg/L)	No. of wells	Percent of detection	Max. detected conc. (μg/L)
2, 4-D	0.16	619	0.81	14.8*
Atrazine	0.007	833	32.0	4.2
Dicamba	0.11	619	0.48	1.46*
Diuron	0.12	618	3.24	2.0*
EPTC	0.002	834	0.72	0.02
Fluometuron	0.06	618	0.32	0.11
MCPA	0.2	619	0.0	<rl< td=""></rl<>
Metolachlor	0.013	835	8.98	2.09
Napropamide	0.007	834	0.0	<rl< td=""></rl<>
Norflurazon	0.042	619	0.16	0.44
Oryzalin	0.31	619	0.48	0.08
Pendimethalin	0.022	834	0.60	0.084
Triclopyr	0.25	619	0.0	<rl< td=""></rl<>
Trifluralin	0.009	834	0.60	0.014

Estimated concentrations based on monitoring results

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<sup>&</sup>lt;RL Less than maximum reporting limit</p>

Table IV-12. Summary of Ground Water Cycle II monitoring results for all land use types.

OPP- Proposed alternative	Upper minimum reporting limit (ug/L)	No. of samples	Percent of detection	Max. detected conc. (ug/L)
2,4-D <sup>1</sup>	0.04	2955	0.6	1.4
Atrazine <sup>2</sup>	0.04	10498	31.4	2.34
Dicamba <sup>1</sup>	0.04	2916	0	0
Diuron <sup>1</sup>	0.02	3894	3.9	0.92
EPTC <sup>2</sup>	0.02	7620	0.2	0.01
Fluometuron <sup>1</sup>	0.05	3048	2.2	1.87
Glyphosate <sup>3</sup>	0.1	1342	0.9	0.16
Metolachlor <sup>2</sup>	0.5	10465	12.1	16.1
Napropamide	0.04	6102	0.2	0.01
Norflurazon <sup>1</sup>	0.02	2964	2.0	0.31
Oryzalin <sup>1</sup>	0.14	2958	0.2	0.03
Pendimethalin <sup>2</sup>	0.11	10393	0.1	0.03
Triclopyr <sup>1</sup>	0.03	2955	0.4	0.28
Trifluralin <sup>2</sup>	0.05	10393	0.4	0.05

<sup>&</sup>lt;sup>1</sup>HPLC methodology <sup>2</sup>GCMS methodology <sup>3</sup>No assigned methodology