Minnesota Pollution Control Agency
Outline of Basis for Draft Proposed
Acetochlor and Metolachlor
Class 2 Water Quality Standards
January 17, 2006

Summary

Draft proposed aquatic life and recreation (Class 2) standards:

<table>
<thead>
<tr>
<th></th>
<th>Chronic, µg/L</th>
<th>Maximum, µg/L</th>
<th>Final Acute Value, µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetochlor</td>
<td>1.7</td>
<td>86</td>
<td>173</td>
</tr>
<tr>
<td>Metolachlor</td>
<td>23</td>
<td>271</td>
<td>543</td>
</tr>
</tbody>
</table>

Introduction

Acetochlor and metolachlor (including s-metolachlor) are both preemergence herbicides used to control grasses and some broadleaf weeds. About three to four million pounds of acetochlor and about one million pounds of metolachlor are applied in Minnesota each year, mainly on corn.

Chronic aquatic life and recreation (Class 2) standards fall into one of three categories: toxicity-based, human health-based and wildlife-based. For most pollutants, toxicity-based and human health-based criteria are determined, and the lower of the two is the adopted chronic standard. Wildlife is usually not at risk unless the pollutant is highly bioaccumulative; therefore, wildlife criteria are normally not determined for non-bioaccumulative pollutants. The proposed chronic standards for acetochlor and metolachlor are toxicity-based.

Toxicity Data and Protection Level Goals

Not surprisingly, toxicity data for the two herbicides acetochlor and metolachlor show that aquatic plants tend to be more sensitive to harmful effects than fish and aquatic invertebrates. The effect endpoints used in plant toxicity tests measure non-lethal impacts such as growth, loss of biomass and population changes. Thus, essentially all plant toxicity data is chronic, rather than acute for which mortality is the end point. The proposed chronic standards are based on the plant data.

Plant toxicity data is more difficult to interpret than animal data, and the Environmental Protection Agency (EPA) provides little guidance on how to use plant data in developing standards. For this reason, the Minnesota Pollution Control Agency (MPCA) felt it was important to spell out our protection-level goals for chronic standards based on plant data. These goals are consistent with ecological risk assessment guidance.

- Protect the overall integrity of the plant community from significant impacts. For example, avoid discernable or projected negative shifts in species composition, such as green algae species replaced by a blue-green algae, or a sensitive "desirable" macrophyte replaced by a "less desirable" macrophyte.
• Protect the most sensitive species tested if it is clear that the species is ecologically important in Minnesota; otherwise it is not necessary to totally protect the most sensitive species from any impact to provide a community level of protection.

• Target approximately a 20th percentile level of protection based on the body of chronic toxicity data for plants. We feel this can be achieved by selecting a 5th percentile median effect concentration (EC-50), or 20th percentile maximum acceptable toxic concentration (MATC) from the distributions.

The acute toxicity-based final acute values and maximum standards (FAV and MS) are derived from the limited aquatic animal data available for the two herbicides. The proposed standards (chronic, FAV and MS), the values used to arrive at the FAVs and MSs, and the human health-based criteria are shown in table 1.

Table 1. Final Acute Value, Maximum Standard and Human Health Criteria Calculations. Proposed Standards Are in Shaded Rows.

<table>
<thead>
<tr>
<th>Parameter or Proposed Standard*</th>
<th>Acetochlor µg/L</th>
<th>Metolachlor µg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aquatic-toxicity (TOX) Standards</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number of genus mean acute values (animal data)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Lowest genus mean acute value (GMAV)</td>
<td>1210</td>
<td>3800</td>
</tr>
<tr>
<td>Tier II method, adjustment factor (AF)</td>
<td>7.0</td>
<td>7.0</td>
</tr>
<tr>
<td>Final acute value (lowest GMAV divided by AF)</td>
<td>173</td>
<td>543</td>
</tr>
<tr>
<td>Maximum standard (final acute value divided by 2)</td>
<td>86</td>
<td>271</td>
</tr>
<tr>
<td>Acute to chronic ratio (Minn. R. 7050.0218, subp. 5)</td>
<td>55</td>
<td>55</td>
</tr>
<tr>
<td>Animal-based “chronic criterion ” (FAV / 55)</td>
<td>3.15</td>
<td>9.87</td>
</tr>
<tr>
<td><strong>Chronic standard, plant-based</strong></td>
<td>1.7</td>
<td>23</td>
</tr>
<tr>
<td><strong>Human health-based (HH) chronic criteria</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Reference dose (mg/kg/day)</td>
<td>Na</td>
<td>0.1</td>
</tr>
<tr>
<td>Cancer potency factor</td>
<td>0.0327 (mg/kg/day)(^1)</td>
<td>Na</td>
</tr>
<tr>
<td>BAF (all Class 2 waters)</td>
<td>43.40 l/kg</td>
<td>16.47 l/kg</td>
</tr>
<tr>
<td>Chronic (Class 2A, 2Bd)</td>
<td>6.5</td>
<td>561</td>
</tr>
<tr>
<td>Chronic (Class 2B, 2C, 2D)</td>
<td>16</td>
<td>2777</td>
</tr>
</tbody>
</table>

\(^{*}\)see Minn. R. ch. 7050 for methods for calculating TOX and HH criteria, and descriptions of use classes

**Analysis of Plant Data**

The MPCA reviewed the draft EPA atrazine criterion\(^1\) to obtain ideas for deriving standards for acetochlor and metolachlor. The atrazine criterion is helpful in framing an overall approach to assessing plant data, as reflected in the protection level goals stated above, but the criteria determination methods used by EPA for atrazine can not be used for acetochlor and metolachlor, because:

• There is far more plant data for atrazine, including an extensive set of micro- and mesocosm data from laboratory and field aquatic plant community studies, which

\(^1\) [http://www.epa.gov/waterscience/criteria/atrazine/index.htm](http://www.epa.gov/waterscience/criteria/atrazine/index.htm)
• Allowed EPA to predict 5th percentile plant community effect levels versus time from the mesocosm data set using a mathematical model.

The MPCA decided to use the EPA method for calculating “final acute values” as the basic approach to calculating the chronic standards. This method has been used by EPA since the late 1970s to calculate aquatic life criteria. The FAV method is a probability calculation of the 5th percentile (or other percentile) value from the distribution of acceptable toxicity data. It is typically used with acute data (median lethal concentrations, LC-50s) to calculate a final acute value. For the FAV calculation, the four values from the distribution of all values that most closely bracket the 5th percentile are used, which are almost always the lowest four because of limited data. The method can be used with chronic as well as acute data, which is what we are doing with the herbicide plant data. The resulting value is then called a “species chronic value” (SCV). Percentile values other than the 5th percentile can be calculated as well, which is what we do with the MATC data, as explained below.

For our analysis, aquatic plant data were divided into:
• EC-50 values – median effect concentration; the concentration that demonstrates nonlethal effects or impacts on half the test population.
• MATC values – maximum acceptable toxicant concentration; the mean of the lowest concentration showing a measurable effect (LOEC) and the highest test concentration showing no significant effect (NOEC). The MATC is comparable to an EC-20.
• No effect (NE) values – highest concentration tested had no significant effect.
• In a few cases, EC-50s were estimated from LOEC or NOEC concentrations using an EC-50 to MATC ratio, if no EC-50 was available for that species.

In general, the plant data for acetochlor and metolachlor show:
• The lowest to highest test results span about five orders of magnitude (e.g. toxicity values for acetochlor range from 0.088 to 35,000 µg/L).
• The relative results of toxicity tests (EC-50s, MATCs and NEs) across species often did not fall where expected (i.e., EC-50 > MATC > NE).
• The ratio between associated EC50s and MATCs is generally small, in the range of 1-4.
• The lowest values for both chemicals are dominated by two commonly tested sensitive species, Selenastrum capricornutum (green algae) and Lemna gibba (inflated duckweed).

Plant data were assessed as follows:
• Acceptable species-specific EC-50 and MATC values were assembled. If two or more EC-50s or MATCs are available for the same species, species geometric means are determined.
• We could not discern any consistent relationship between test results and the toxic endpoint used in the test (i.e., growth, growth rate, change in biomass, frond development, etc.).
• We could not discern any consistent relationship between test results and the duration of the test, which ranged from less than one day to 90 days (most are 3 to 14 day tests).
• Therefore, results for the same species were averaged together regardless of the chronic endpoint or test duration.
• 5th percentile SCVs from the EC-50 data sets were determined.
• 20th percentile SCVs from the MATC data sets were determined.
SCVs based on EC-50 and MATC data are shown in Table 2, along with the number of values in the database.

Table 2. Species Chronic Values from the Species-mean EC-50s and MATCs.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Acetochlor</th>
<th>Metolachlor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N Value</td>
<td>N Value</td>
</tr>
<tr>
<td>EC-50</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5th %tile</td>
<td>8 0.093</td>
<td>18 35.6</td>
</tr>
<tr>
<td>20th %tile</td>
<td>8 3.58</td>
<td>18 98.5</td>
</tr>
<tr>
<td>MATC</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20th %tile</td>
<td>8 1.74</td>
<td>9 11.1</td>
</tr>
<tr>
<td>5th %tile</td>
<td>8 0.004</td>
<td>9 0.56</td>
</tr>
</tbody>
</table>

The 5th percentile EC-50 for metolachlor and the 20th percentile MATC value for acetochlor in the shaded cells in Table 2 are the primary bases for the proposed standards. Other information is used to confirm or adjust the proposed chronic standards.

**Discussion of Proposed Chronic Standards**

As noted, two species commonly used in herbicide toxicity tests, *Selenastrum capricornutum*, and *Lemna gibba*, are very sensitive to both acetochlor and metolachlor. Chronic standards that would protect these two species from any impact at all times would need to be lower than the standards being proposed. *Selenastrum* is a very minor component in lake samples in Minnesota and is easily replaced by another genus of green algae, *Scenedesmus*. *Lemna gibba* does not occur in Minnesota; however, a related species of duckweed, *L. minor*, is very common. Data for metolachlor and other herbicides suggest that *L. minor* is not as sensitive as *L. gibba*. Therefore, neither of the two very sensitive species is considered to be "ecologically important" in Minnesota. The MPCA believes the proposed standards will protect the overall integrity of aquatic plant (and animal) communities.

Both herbicides appear to be mobile in most soils and moderately persistent in the environment, but they apparently do not bioaccumulate in fish and wildlife. Human health-based standards were calculated for both herbicides and they are less stringent than the proposed plant toxicity-based chronic standards (Table 1).

1. **Acetochlor**

The MPCA believes the 20th percentile MATC value of 1.7 µg/L from the plant data will be protective of Minnesota aquatic plant communities, and is the proposed chronic standard.

There are eight species-mean EC-50s and five species-mean MATCs for acetochlor. The SCV calculations are very sensitive to the number of toxicity values (N) used in the calculations, particularly when N is small. The MPCA is using an N of eight for both the MATC and EC-50 calculations. This is near the minimum number of values we like to have; an N of 15 – 30 is preferred. With the low N, calculated SCV values at the “tails” of the distribution, such as the 5th
percentile, are more vulnerable to distortion than values calculated more toward the center of the distribution, such as the 20th percentile. The large range in magnitude of the lowest four values, which are used to make the SCV calculations, can exacerbate the distortion (for example, 0.22 to 819 µg/L in the case of acetochlor MATCs). For these reasons the MPCA places more confidence in the 20th percentile MATC value than in the 5th percentile EC-50 value for acetochlor. The mesocosm studies are not very useful because more than half of the reported results were unable to show effects at the concentrations tested.

In conclusion, the proposed standard of 1.7 µg/L is (see Figure 1):
1. The 20th percentile of the available MATCs using an N of 8, including MATCs for *Selenastrum capricornutum* and *Lemna gibba*.
2. Higher than the MATCs and EC-50s for *S. capricornutum* and the MATC for *L. gibba*; the standard may not protect these two species from all harmful effects.
3. Below the EC-50s for *L. gibba*, and well below MATCs and EC-50s for the other species tested.
4. Well below the EC-50 of 47 µg/L for the nonnative African *Elodea*. This is the lowest EC-50 (or MATC) for the next most sensitive species after *L. gibba* and *S. capricornutum*.
5. Below the calculated aquatic animal-based chronic value of 3.6 µg/L (Table 1).
6. Below the lower of the two human health-based criteria, 6.5 µg/L.

2. Metolachlor (racemic and s-metolachlor)

The MPCA believes that the 5th percentile SCV from the aquatic plant EC-50 data of 36 µg/L is a reasonable “starting point” for the proposed chronic standard, but it must be adjusted lower based on the body of available toxicity data. The proposed standard of 23 µg/L will be protective of Minnesota aquatic plant communities.

The plant toxicity data set for metolachlor is far more robust than for acetochlor, in terms of number of species tested and available EC-50s (18 for metolachlor, 8 for Acetochlor). There are six MATCs for metolachlor. Because of the relatively large number of EC-50s, the MPCA places more confidence in the 5th percentile SCV calculation from the EC-50 data than in the 20th percentile MATC SCV. The MATC SCV of 11.1 µg/L, calculated using an N of 9 (6 MATCs supplemented with 3 LOECs), however provides some information on an appropriate standard in the context of all the data (Table 2).

The MPCA believes that the 5th percentile EC-50 value of 36 µg/L should be lowered based on the other toxicity information available for metolachlor. The proposed standard of 23 µg/L is based on the following assessment of that information (see Figure 2):
- A chronic test result of 41 µg/L is available for fathead minnow (Metolachlor 88:12). This chronic value divided by a “safety factor” of 2 is 21 µg/L.
- A relatively low EC-50 of 70 µg/L is available for coon tail (*Ceratophyllum demersum*), an important resident species. This EC-50 is the third lowest after *S. capricornutum* and *L. gibba*. An estimated MATC of 23 µg/L for coon tail can be determined by dividing the EC-50 of 70 µg/L by the mean of the five species-mean EC-50/MATC ratios (3.027).
• The midway point (average) between the 5th percentile EC-50 (36 µg/L) and the 20th percentile MATC (11 µg/L, N = 9) is 23.

In conclusion, the proposed standard of 23 µg/L is:
• Higher than the MATCs for *Selenastrum capricornutum* and *Lemna gibba*, but below the geometric mean EC-50s for these two sensitive species.
• Higher than an MATC of 6.9 µg/L for a diatom, *Navicula pelliculosa*. The MPCA suspects this MATC may be an outlier. It is 55 times lower than the EC-50 of 380 µg/L for this species. An EC-50/MATC ratio of 55 is many times larger than the typical ratio, which average about 3. We include it in the SCV calculation of the 20th percentile MATC because we can not confirm that it is an outlier. No explanation is provided in the original study as to why these data are atypical. *Navicula pelliculosa* is widely distributed in the United States. We are seeking information on the role this species plays in the diatom communities in Minnesota.
• Well below the MATC of 265 µg/L for the resident species *Lemna minor*, and all EC-50s for the other species tested.
• Below the lower of the two human health-based criteria of 561 µg/L.
• It is higher than the calculated animal-based chronic value of 9.87 µg/L, but the MPCA believes this is acceptable because this value is based on the conservative qualities of the tier II method combined with use of a conservative default acute to chronic ratio of 55.
Figure 1.

Plant Toxicity Data for Acetochlor
Circle = EC-50; Square = MATC; Triangle = No Effect; m = Mesocosm Data
Open Symbols = Data for S. capricornutum and L. gibba

Figure 2.

Plant Toxicity Data for Metolachlor
Circle = EC-50; Square = MATC; Triangle = No Effect; m = Mesocosm Data
Open Symbols are Data for S. capricornutum and L. gibba