

Environmental Fate of Metolachlor

Linda Rivard
Environmental Monitoring Branch
Department of Pesticide Regulation
1001 I Street
Sacramento, CA 95812
April 2003

This document reviews the environmental fate of metolachlor [2-chloro-N-(2-ethyl-6-methylphenyl)-N-(2-methoxy-1-methylethyl) acetamide]. Metolachlor is a chloroacetanilide herbicide that is available as an emulsifiable concentrate.

Chemical structure and primary degradation

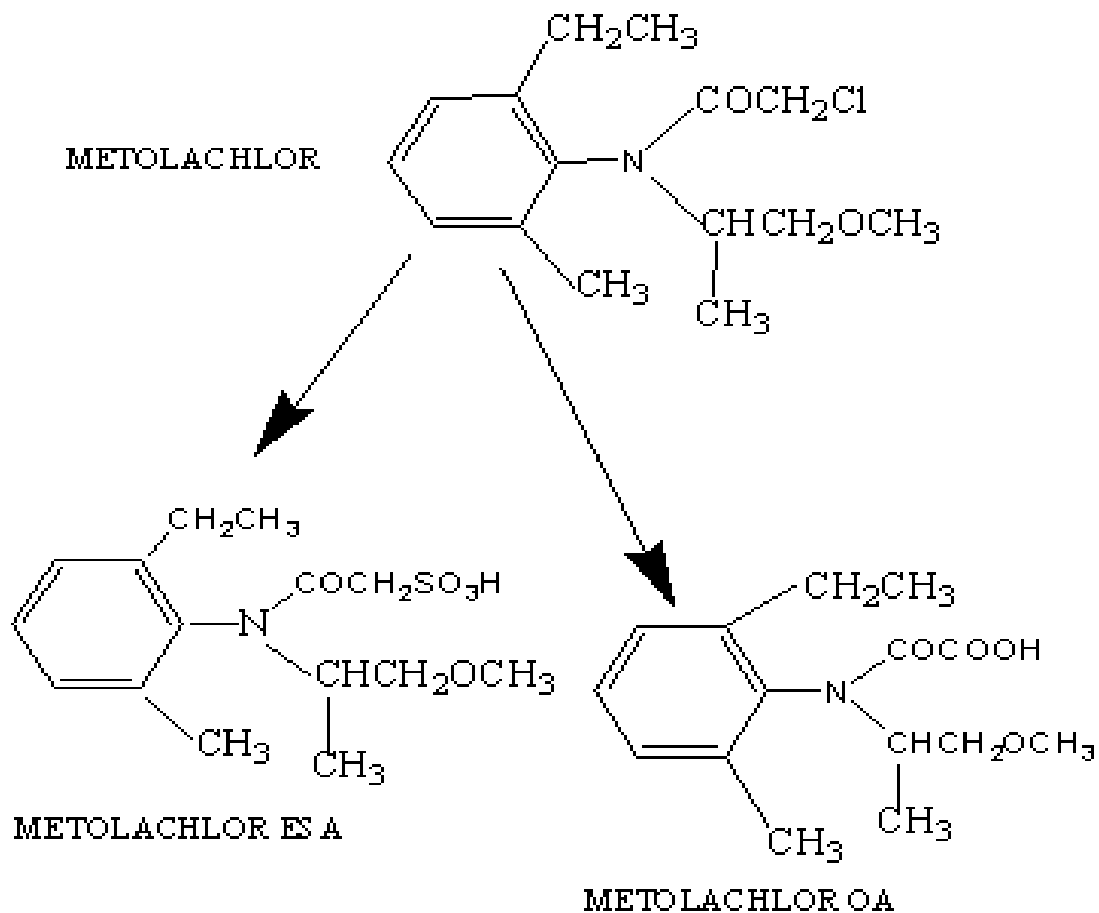


Table 1. Physical-Chemical Properties^a

Metolachlor is a member of the chloroacetanilide herbicide chemical family. Other members include acetochlor, alachlor, butachlor, butenachlor, delachlor, diethatyl, deimethachlor, metazachlor, pretilachlor, propachlor, propisochlor, prynachlor, terbuchlor, thenylchlor, and tylachlor. Metolachlor is a colorless and odorless liquid at room temperature.

Chemistry Abstracts Registry # (CAS #)	51218-45-2
Molecular formula	C ₁₅ H ₂₂ ClNO ₂
Molecular weight	283.46 g/mol
Water solubility	530 mg/L (20° C)
Vapor pressure	1.3 x 10 ⁻⁵ mmHg (20° C)
Henry's Law Constant 25° C	2.44 x 10 ⁻⁸ atm m ³ /mol ^e
Hydrolysis half-life	> 200 days ^f (30° C, pH 1-9)
Octanol-water coefficient (K _{ow} at 25° C)	794 ^d
Average soil adsorption coefficient (K _{oc})	200 ^d
Average field dissipation half-life (days)	114 ^f
Aerobic soil degradation half-life (days)	26 ^f
Anaerobic soil degradation half-life (days)	37 ^f
Soil Photolysis half-life (days) (sandy loam)	8-37 ^f
Aqueous Photolysis	> 30 ^f

Table 2. Ecotoxicology Table^a

Rainbow trout (96 hours)	LC ₅₀ 2.0 mg/kg
Carp (96 hours)	LC ₅₀ 4.9 mg/kg
Bluegill sunfish (96 hours)	LC ₅₀ 15.0 mg/kg
Channel catfish (96 hours)	LC ₅₀ 4.9 mg/L ^d
Earthworms in soil	LD ₅₀ 140 ppm ^d
Daphnia (48 hour)	LC ₅₀ 25.1 mg/L ^d
Bobwhite quail (oral)	LD ₅₀ 4640 mg/kg ^d
Mallard (oral)	LD ₅₀ >2510 mg/kg ^d

Table 3. Water Quality Criteria^a

Drinking water health advisory	0.525 mg/L
HAL (lifetime health advisory)	70 ppb ^g

^a Extoxnet, 2000a.

^b Extoxnet, 2000b.

^c World Health Organization, 1996.

^d Weed Science Society of America, 1994.

^e Ciba-Geigy Corporation, 1996.

^f Kollman and Segawa, 2000.

^g Environmental Protection Agency, 1997.

General Information, Characteristics and Mode of Action

Synthesized in 1972 by Ciba-Geigy Limited, Basel Switzerland (Weed Science Society of America, 1994), metolachlor was registered in 1977.

Metolachlor is a pre-emergent herbicide that is used to control certain broadleaf weed species, and annual grassy weeds (yellow nutsedge (*Cyperus esculentus*), barnyard grass (*Echinochloa crusgalli*), crabgrass (*Digitaria* spp.), fall panicum (*Panicum dichotomiflorum*), and foxtails (*Setaria* spp.)). Metolachlor is primarily used on corn, soybean, peanuts, sorghum, potatoes, cotton, safflower, and woody ornamentals (Exttoxnet, 2000b). When absorbed through the roots and shoots just above the seed of the target weeds, it acts as a growth inhibitor by suppressing synthesis of chlorophyll, proteins, fatty acids and lipids, isoprenoids (including gibberellins), and flavonoids (including anthocyanins).

Estimated usage of metolachlor in the United States is 60-65 million pounds active ingredient per year (Environmental Protection Agency, 1997). Over 125,000 pounds of active ingredient were applied in California in 2000 (California Department of Pesticide Regulation, 2003). It is or has been sold under the trade names Bicep, Codal, Cotoran multi, Dual, Dual 8E, Metelilachlor, Milocep, Ontrack 8E, Pennant, Pennant 5G, Primagram, and Primextra. It may be used in formulations with other pesticides such as atrazine, cyanazine, and fluometuron (Exttoxnet, 2000a).

Environmental Fate of Metolachlor

The degree of herbicide transport in the environment depends on several factors such as application rate, herbicide persistence and mobility, rainfall, topography, and climate (Lin et al., 1999). Pesticides in soil are subject to sorption as well as several biological and chemical degradation mechanisms. These involve chemical, microbial, and photodecomposition, which cause a decrease in pesticide concentrations in the soil. Pesticides may be transported to different parts of the environment by volatilization, wind and runoff erosion, and leaching. Transport by runoff and leaching may cause the contamination of surface and ground water.

K_{oc} is a measure of the tendency of a compound to partition into soil organic carbon from aqueous solution, and is generally inversely related to movement to ground water (Sanyal and Kulshrestha, 1999). Water solubility is also used as a measure of the relative likelihood of pesticides to be detected in ground water. Of the acetanilide herbicides, metolachlor appears to be the most persistent and has the potential to leach to ground water because of its relatively high water solubility (530 mg/L at 20° C) and low K_{oc} (200 mL/g).

Air

Generally very little metolachlor is lost to the atmosphere by volatilization, as is predicted by its low Henry's Law Constant of 2.44×10^{-8} atm m³/mol (Ciba-Geigy Corporation, 1996), and its low vapor pressure of 1.3×10^{-5} mm Hg (Exttoxnet, 2000a).

Soil

Pesticide mobility and fate in soil are influenced by sorption and degradation processes. The importance of these processes is determined in part by the physical and chemical properties of the pesticide, such as organic-carbon and mineral-surface sorption coefficients, aqueous solubility, and soil dissipation half-life (Savoca et al., 2000).

The breakdown of pesticides in the soil is affected by temperature, moisture, microbial activity, soil type, nitrification, oxygen concentration, sunlight, and amount of leaching (Exttoxnet, 2000a). Rainfall patterns and the timing/intensity of irrigation in relation to high rainfall intensities will also influence herbicide movement in or from soil.

Metolachlor is considered to be moderately persistent in different soil types (U.S. EPA, 1997), and has an average field dissipation half-life of 114 days (Kollman and Segawa, 2000).

Metolachlor is considered to moderately adsorb to soil. The adsorption of the pesticide increases with increased soil organic matter and clay content, and can slow its movement in soil.

Metolachlor's half-life in soil varies depending on soil type and environmental conditions, and is estimated to be between 15-132 days (USDA 1995, Exttoxnet, 2000a, and Kollman and Segawa, 1997).

One of the major breakdown pathways of metolachlor in the soil is by aerobic and anaerobic microorganisms. The transformation by soil microorganisms of metolachlor to its primary degradates (metolachlor ESA - ethane sulfonic acid and metolachlor OA - oxanilic acid) has been suggested to occur as a result of displacement of the chlorine atom of the parent compound by glutathione, followed by the formation of the ESA and OA degradates by different enzymatic pathways (Barbash et al., 1999).

In the laboratory a half-life of 67 days for aerobic microbial metabolism of metolachlor in sandy loam soil (at 25° C) has been reported resulting in the production of (2-ethyl-6-methylphenyl)(2-methoxy-1-methylethyl) amino oxo-acetic acid as the major degradate (WSSA, 1994). A laboratory half-life of 81 days was reported for anaerobic microbial metabolism, which produced the same degradate.

Photodegradation in soil- Sunlight can be another important degradation pathway of metolachlor in soil. This photodegradation can be a major contributor to dissipation in the field, particularly under prolonged lack of rainfall when metolachlor remains on the soil surface. It is estimated that about 50% of applied metolachlor degrades in eight days on sunlit soil (WSSA, 1994). However, if it is incorporated into the top two inches of soil, degradation by photolysis is minimal, about 6% degraded over a month (Exttoxnet, 2000a).

Leaching- Extensive leaching can occur in soils with low organic carbon content, and is greatest if soil texture is coarse (Exttoxnet, 2000a). Precipitation and/or irrigation can also move metolachlor very rapidly to ground water. High organic soils have less metolachlor movement when the organic matter content approaches 2.0%. In addition, leaching is inhibited by soils with high clay and/or silt content (Exttoxnet, 2000b).

Water

Hydrolysis is one of the major chemical transformation pathways of pesticides in aqueous solution, and the hydrolysis half-life of metolachlor is

estimated to be over 200 days (at 20° C) for a broad range of pH values (Exttoxnet, 2000a).

Photodegradation in water- It is possible that a majority of the soil-applied metolachlor reaching ground and surface waters through leaching and surface runoff is adsorbed on the mineral and organic constituents of the soil, which may influence photolysis in water in different ways. These materials may accelerate photodegradation by energy transfer reactions, photoinduced oxidation, or by efficient light scattering.

Hydroxylation, dehalogenation, oxoquinoline formation, and demethylation are the main processes observed during the photolysis of metolachlor, and the major degradation product formed is 4-(2-ethyl-6-methylphenyl)-5-methyl-3-morpholine (Mathew and Khan, 1996).

Contamination of water- Metolachlor has a very high potential to contaminate ground water since it is relatively mobile and persistent in soil.

Metolachlor has been detected under a variety of conditions in California surface water (CDPR, 2002a.).

A 1988 study of surface and ground water in the United States found metolachlor in 2091 of 4161 surface water samples, and in 13 of 596 groundwater samples. The 85th percentile of all non-zero samples was 12 µg/L for groundwater (WHO, 1996).

A multiple year study of well water across the United States (Holden et al., 1992) analyzed over six million private and domestic wells for a number of commonly used pesticides. Metolachlor was detected in 1% of wells (about 60,000) at concentrations ranging from 0.1-1.0 ppb (Exttoxnet, 2000a).

In a study of surface water samples in 1997, metolachlor was detected in 1644 samples (from 312 locations in 14 states) at a maximum concentration of 138 ppb. The high concentrations were probably the result of runoff during spring and summer applications to crops. (Exttoxnet, 2000a).

Metolachlor and atrazine were the most commonly detected pesticides in samples from agricultural areas in a study of surface water in Iowa. The amounts did not exceed U.S. EPA drinking water quality criteria, and these

levels generally have not been exceeded in other studies of shallow aquifers in the Midwest (Savoca et al., 2000).

Metolachlor degradates: Once in the soil, pesticides undergo degradation processes that give rise to a complex pattern of degradates, which can be transported to ground water and streams. Degradates can be more persistent and mobile than their parent compounds, which can lead to frequent detection and increased concentration in ground water. The U.S. EPA Office of Drinking Water has defined drinking water quality guidelines for many pesticides, but guidelines for pesticide degradates are relatively uncommon.

Metolachlor ethane sulfonic acid (ESA) and metolachlor oxanilic acid (OA) are the two most common degradates of metolachlor. Both degradates have been detected in California surface water (CDPR, 2002a) and California groundwater (CDPR, 2002b). A study of degradates in tile drain discharge from agricultural fields in central NY indicated that metolachlor ESA and OA can persist in agricultural soils for 3 or more years after application, and that metolachlor ESA concentrations in tile-drain discharge exceeded metolachlor OA by a factor ranging from 2 to 5 (Eckhardt et al., 1999).

Chloroacetanilide and triazine herbicide degradates are substantial components of the pesticide load in eastern Iowa streams. A 1996-1998 study by USGS National Water-Quality Assessment Program (Kalkhoff and Thurman, 1999) of 355 water samples from 12 stream sites in Eastern Iowa found metolachlor ESA in 99.7% of samples, metolachlor OA in 94.3% of samples and the parent compound in 54.1% of samples (based on a common reporting limit of 0.20 µg/L). This study also tested for acetochlor and alachlor, the triazine herbicides atrazine and cyanazine, and their degradates. Degradates constituted 93% of total pesticide concentration detected with metolachlor degradates accounting for 63%.

Another study of ground water samples containing chloroacetanilide herbicides (Kalkhoff et al., 1998) showed that ESA and OA degradates were present in almost 75% of the samples and were generally present 3-45 times more frequently than the parent compound. In addition 1 or more of the chloroacetanilide degradates were present in 100% of the stream samples. The ESA & OA degradates were found 2 to more than 100 times more frequently than the parent herbicides. The degradates accounted for more than 80% of the measured concentration of chloroacetanilide compounds in

surface water. These results demonstrate that the metolachlor ESA and OA degradates are frequently present in ground and surface water in substantial concentrations in the Midwest. It also identifies the importance of quantifying both parent compounds and degradates to fully understand the environmental fate and transport of herbicides in the hydrologic system.

Biota

Metolachlor is generally considered to be non-toxic to mammals, birds, and insects (including honeybees) (WSSA, 1994). Mallard ducks and bobwhite quail can tolerate exposures of greater than 10,000 mg/kg for five days, and studies have shown that metolachlor causes no significant adverse effects on soil microorganism and invertebrate populations from exaggerated metolachlor usage (Extoxnet, 2000b).

In cold and warm water fish (including rainbow trout, carp, and bluegill sunfish), metolachlor is considered to be moderately toxic. Very little of the pesticide is accumulated, and it is excreted rapidly when the fish are placed in clean water. Since residues found in fish are low it is not considered to pose a threat to human health (Extoxnet, 2000a).

Metolachlor may cause toxicity to aquatic organisms through non-point source pollution (Lin et al., 1999). In a study by Hall et al. (1999), metolachlor showed an average acute toxicity level of 53 µg/L based on acute laboratory studies and sensitivity to metolachlor was as follows: plants – 106 µg/L, benthos – 3,103 µg/L, and fish – 4,334 µg/L. Aquatic plant toxicity tests are frequently conducted in environmental risk assessments to determine the potential impacts of contaminants on primary producers, and wide differences in sensitivity can occur across phylogenetic groups. Fairchild et al. (1997) tested a species of unicellular green algae (*Selenastrum capricornicum*) and a floating vascular plant (*Lemna minor*) for sensitivity. Acetanilide herbicides exhibited high toxicity to both plant species over a variable range of concentrations.

Conclusion

Metolachlor is a widely used chloroacetanilide herbicide. It is a pre-emergent herbicide used to control annual broadleaf weeds and grasses in corn, soybean and other crops. It acts as a growth inhibitor in the target

weeds by preventing the synthesis of chlorophyll, proteins, fatty acids, and lipids.

Metolachlor has a relatively low Henry's Law Constant and low vapor pressure; consequently it is not expected to be found in air. It has the potential to leach into ground water due to relatively high water solubility and low K_{oc} , and has been widely detected in U.S. ground and surface water. Metolachlor is considered to be moderately persistent in soil and water with an average field dissipation half-life of 114 days, and a hydrolysis half-life of > 200 days.

Degradation of metolachlor in soil occurs mainly through microbial decomposition and photodegradation. Microbial degradation rates are affected by soil depth, organic carbon and dissolved oxygen concentrations, temperature, and size of microbial populations. For sandy soils a half-life of 67 days for aerobic microbial populations, and 81 days for anaerobic microbial populations was reported in the laboratory. Photodegradation is an important degradation pathway only when metolachlor is present on the soil surface. Fifty percent of surface-applied metolachlor can degrade in 8 days on sunlit soil, while only 6% degrades over one month in soils where metolachlor was incorporated into the surface layer.

In water the main photolysis processes are hydroxylation, dehalogenation, oxoquinoline formation and demethylation.

The major degradates of metolachlor are metolachlor ethane sulfonic acid (ESA), and metolachlor oxanilic acid (OA). These degradates are more persistent than the parent compound and are found in higher concentrations and more frequently in surface and ground water than metolachlor itself.

Metolachlor is not considered to be toxic to mammals, birds, and insects. Mallard ducks and bobwhite quail are able to tolerate high exposures over several days, and it is not thought to effect soil invertebrate and microbial populations.

In fish, metolachlor is considered to be moderately toxic to both cold and warm water species. It is considered to be toxic to some aquatic plants such as green algae and floating vascular plants.

References

- Arthur, Ellen L., Brenda S. Perkovich, Todd A. Anderson, and Joel R. Coats. 2000. Degradation of an atrazine and metolachlor herbicide mixture in pesticide-contaminated soils from two agrochemical dealerships in Iowa. *Water, Air, and Soil Pollution*. 119:75-90.
- Barbash, Jack E., and Elizabeth A. Resek. 1996. Pesticides in ground water. Pp. 406-410. Ann Arbor Press, Chelsea, MI.
- Barbash, Jack E., Gail P. Thelin, Dana W. Kolpin, and Robert Gilliom. 1999. Distribution of major herbicides in ground water of the United States. U.S. Geological Survey, Water-Resources Investigations Report 98-4245. Sacramento, CA.
- California Department of Pesticide Regulation, 2003. DPR Pesticide Use Report.
- California Department of Pesticide Regulation. 2002a. DPR Surface Water Database.
- California Department of Pesticide Regulation. 2002b. DPR Groundwater Database.
- Ciba-Geigy Corp. 1996. AI: Metolachlor product chemistry. EPA Reg. No. 100-587. Vol. 25 of 31.
- Düring, Rolf-A., and Hans E. Hummel. 1999. Herbicide and metabolite movement in different soils as studied by computer assisted microlysimeters. *Chemosphere*. 39:641-654.
- Eckhardt, David A.V., William M. Kappel, William F. Coon, and Patrick J. Phillips. 1999. Herbicides and their metabolism in Cayuga Lake and its tributaries, New York. U.S. Geological Survey Toxic Substances Hydrology Program—Proceedings of the Technical Meeting Charleston South Carolina March 8-12, 1999. Volume 2 of 3. Contamination of hydrologic systems and related ecosystems. Water-Resources Investigation Report 99-4018B.

Environmental Protection Agency: Office of Pesticide Programs. 1997. The acetanilide pesticides: alachlor, metolachlor, and acetochlor.

Exttoxnet: Extension Toxicology Network. 2000a. Pesticide information profile: metolachlor.

Exttoxnet: Extension Toxicology Network. 2000b. Metolachlor (Dual) herbicide profile 2/85.

Fairchild, J.F., D.S. Ruessler, P.S. Haverland, and A.R. Carlson. 1997. Comparative sensitivity of *Selenastrum capricornicum* and *Lemna minor* to sixteen herbicides. *Archives of Environmental Contamination and Toxicology*. 32:353-357.

Fava, L., P. Bottoni, A. Crobe, and E. Funari. 2000. Leaching properties of some degradation products of alachlor and metolachlor. *Chemosphere*. 41:1503-1508.

Hall, Lenwood W. Jr., Ronald D. Anderson, Jay Kilian, and Dennis P. Tierney. 1999. Concurrent exposure assessments of atrazine and metolachlor in the mainstem, major tributaries and small streams of the Chesapeake Bay Watershed: Indicators of ecological risk. *Environmental Monitoring and Assessment*. 59:155-190.

Holden, L.R., J.A. Graham, R.W. Whitman, W.J. Alexander, R.W. Pratt, S.K. Liddle, and L.L. Piper. 1992. Results of national alachlor well water survey. *Environmental Science and Technology*. 26(5): 935-943.

Kalkhoff, S.J., D.W. Kolpin, E.M. Thurman, I. Ferrer, and D. Barcelo. 1998. Degradation of chloroacetanilide herbicides: The prevalence of sulfonic and oxanilic acid metabolites in Iowa groundwater and surface waters. *Environmental Science and Technology*. 32(11): 1738-1740.

Kalkhoff, S.J., and E.M. Thurman. 1999. The occurrence of chloroacetanilide and triazine herbicide metabolites in streams in Eastern Iowa. Abstracts of the Seventh Symposium on the Chemistry and Fate of Modern Pesticides, Lawrence, KS, September 14-16, 1999.

Karuppiyah, Makesh, Girvin Liggans, and Gian Gupta. 1997. Effect of

river and wetland sediment on toxicity of metolachlor. *Ecotoxicology and Environmental Safety*. 36:180-182.

Kollman, W. and R. Segawa. 2000. Pest Chemistry Database. Environmental Hazards Assessment Program. California Department of Pesticide Regulation. Sacramento, CA.

Lin, Yaw-Jian, Makesh Karuppiah, Anugrah Shaw, and Gian Gupta. 1999. Effect of simulated sunlight on atrazine and metolachlor toxicity of surface waters. *Ecotoxicology and Environmental Safety*. 43:35-37.

Mathew, Regi, and Shahamat U. Khan. 1996. Photodegradation of metolachlor in water in the presence of soil mineral and organic constituents. *Journal of Agricultural Food Chemistry*. 44:3996-4000.

Muller, M.D., T. Poiger, and H. Buser. 2001. Isolation and identification of the metolachlor stereoisomers using high-performance liquid chromatography, polarimetric measurements, and enantioselective gas chromatography. *Journal of Agricultural Food and Chemistry*. 49 (1): 42-49.

Novartis. 2001. 1998 Annual Report. Available at: <http://www.info.novartis.com> (verified March 21, 2001).

Pesticide Action Network. 2001. Pesticide Database: Information about metolachlor, (S).

Phillips, Patrick J., David A. Eckhardt, E. Michael Thurman, and Stephen A. Terracciano. Ratios of metolachlor to its metabolites in ground water, tile drain discharge, and surface water in selected areas of New York State, in Morganwalp, D.W., and H.T. Buxton, eds. U.S. Geological Survey Toxic Substances Hydrology Program—Proceeding of the Technical Meeting, Charleston, South Carolina, March 8-12, 1999—Volume 2 of 3—Contamination of Hydrological Systems and Related Ecosystems: U.S. Geological Survey Water-Resources Investigations Report 99-4018B, p. 383-393.

Rice, P.J., T.A. Anderson, J.C. Anhalt, and J.R. Coats. 2000. Phytoremediation of atrazine and metolachlor contaminated water with submerged and floating aquatic plants. Abstract.

Sanyal, D., and G. Kulshrestha. 1999. Effects of repeated metolachlor applications on its persistence in field soil and degradation kinetics in mixed microbial cultures. *Biology of Fertile Soils*. 30:124-131.

Savoca, Mark E., Eric M. Sadorf, S. Mike Linhart, and Kymm K.B. Akers. 2000. Effects of land use and hydrogeology on the water quality of alluvial aquifers in Eastern Iowa and Southern Minnesota, 1997. U.S. Geological Survey, Water-Resources Investigations Report 99-4246. Iowa City, IA.

U.S. Department of Agriculture Alternative Crops and Systems Lab. 1995. ARS Pesticide Properties: Metolachlor.

U.S. EPA. 2000. Federal Register Document: Equivalency of pesticides metolachlor and S-metolachlor with respect to ground water contamination; Notice of availability and request of comment.

Weed Science Society of America. 1994. Herbicide Handbook 7th Edition, Champaign, IL pp. 197-200.

World Health Organization. 1996. Guideline for drinking-water quality, 2nd ed. Vol. 2. Health Criteria and other supporting information. Geneva, Switzerland. pp. 725-729.