ALACHLOR AND TWO DEGRADATES OF ALACHLOR IN GROUND AND SURFACE WATER, SOUTHWESTERN GEORGIA AND ADJACENT PARTS OF ALABAMA AND FLORIDA, 1993-2005

Elizabeth A. Frick and Melinda S. Dalton

AUTHORS: Hydrologists, U.S. Geological Survey, 3039 Amwiler Road, Suite 130, Peachtree Business Center, Atlanta, Georgia 30360-2824.
REFERENCE: *Proceedings of the 2007 Georgia Water Resources Conference*, held March 27–29, 2007, at The University of Georgia, Athens, Georgia.

Abstract. Ground- and surface-water samples have been collected in the Apalachicola–Chattahoochee–Flint River Basin (ACFB) and Georgia-Florida Coastal Plain (GAFL) study units since 1993 as part of the U.S. Geological Survey's National Water-Quality Assessment Program (NAWQA) program. This paper focuses on the use and occurrence of the herbicide alachlor and two degradates of alachlor in several ACFB and GAFL NAWQA ground- and surface-water sampling networks within agricultural areas in southwestern Georgia and adjacent parts of Alabama and Florida. Alachlor was analyzed during cycle I (1993–2001 water years) and to date in cycle II (2002–2005) of NAWQA. Two degradates of alachlor—alachlor ethane sulfonic acid (alachlor ESA) and alachlor oxanilic acid (alachlor OA)—were analyzed in a subset of cycle II samples collected during water year 2002 and during May 2004.

Although alachlor use in the study area declined from the 13th most used herbicide during 1992 to the 24th most used herbicide during 2002, alachlor was the third-most frequently detected pesticide in ground water for 1993–2005 behind the more frequently used herbicides atrazine and metolachlor. Alachlor was the only pesticide analyzed during this study that exceeded a U.S. Environmental Protection Agency maximum contaminant level standard (2 micrograms per liter) or health-advisory level in ground-water samples collected within the study area. When analyzed, alachlor ESA and alachlor OA were typically detected more frequently and at higher concentrations than alachlor.

INTRODUCTION

Ground- and surface-water samples have been collected, using standard U.S. Geological Survey (USGS) water-quality sampling field protocols (U.S. Geological Survey, variously dated), in the Apalachicola–Chattahoochee–Flint River Basin (ACFB) and Georgia-Florida Coastal Plain (GAFL) study units since 1993 as part of the USGS National Water-Quality Assessment Program (NAWQA) program (Fig. 1).

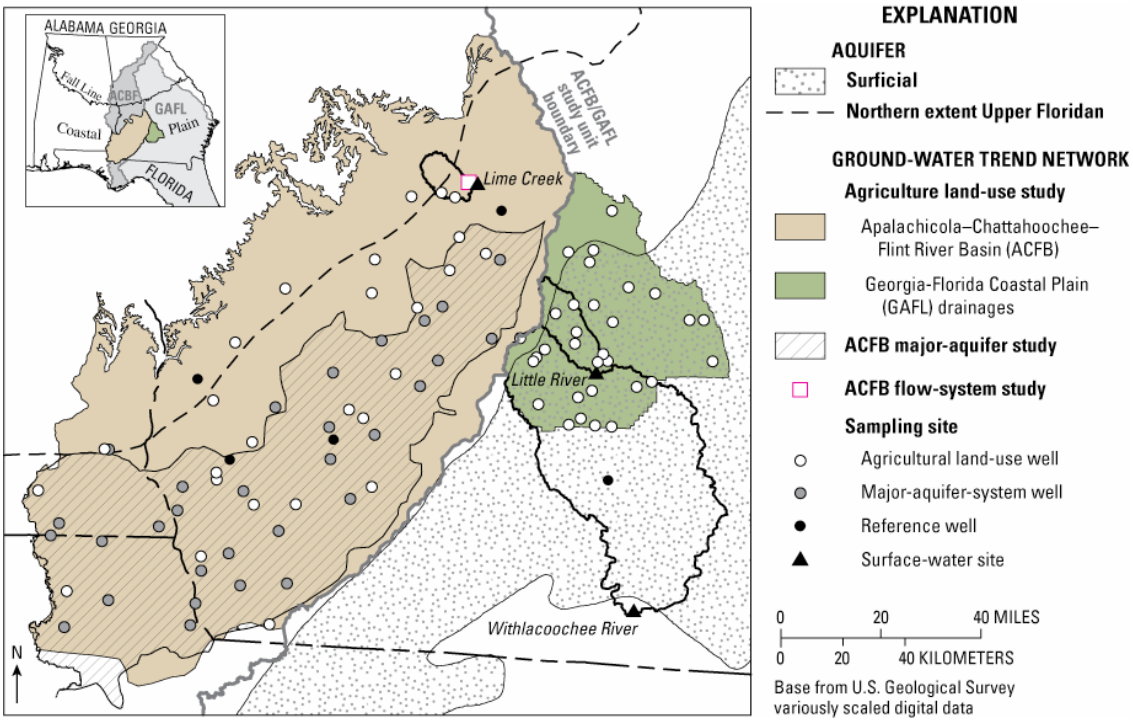

Figure 1. Location of wells and surface-water sites sampled by network type. [ACFB, Apalachicola–Chattahoochee–Flint River Basin; GAFL, Georgia-Florida Coastal Plain; MAS, major aquifer study; AgLUS, agricultural land-use study)

This paper focuses on the use and occurrence of the herbicide alachlor and two degradates of alachlor in several ACFB and GAFL NAWQA ground-water and surface-water sampling networks within agricultural areas in southwestern Georgia and adjacent parts of Alabama and Florida. Ground-water monitoring networks include domestic and low-capacity wells open to the Upper Floridan aquifer (UFA) as part of a major-aquifer study (MAS) in the ACFB; shallow monitoring wells drilled at the edge of agricultural fields open to the surficial aquifer in Agricultural land-use studies (AgLUS) in the ACFB and GAFL; reference wells in undeveloped locations within (ACFB) or near (GAFL) the AgLUS; and shallow monitoring wells, agricultural drains, and a tributary stream as part of a flow-path study (FPS). Surface-water monitoring at fixed sites include predominantly agricultural watersheds in the ACFB (Lime Creek) and the GAFL (Little River) that overlap the respective AgLUS. Additionally, surface water was also sampled at Withlachoochee River near Quitman, Georgia, within the GAFL, a large watershed with mixed land use downstream from the Little River watershed. Alachlor was analyzed during cycle I (1993–2001 water years) and to date in cycle II (2002–2005) of NAWQA. Two degradates of alachlor—alachlor ethane sulfonic acid (alachlor ESA) and alachlor oxanilic acid (alachlor OA)—were analyzed in a subset of cycle II samples collected during water year[1] 2002 and during May 2004.

Alachlor is an herbicide of interest because: (1) although its use in the study area declined from the 13th most used herbicide during 1992 to the 24th most used herbicide during 2002, it was the third-most frequently detected pesticide in ground water from 1993–2005 behind the more frequently used herbicides atrazine and metolachlor (Fig. 2) (Gianessi and Reigner, 2006); (2) it has a moderately low U.S. Environmental Protection Agency (USEPA) maximum contaminant level (MCL) of 2 micrograms per liter (µg/L) (U.S. Environmental Protection Agency, 2004); (3) it is classified as an oncogen; (4) it has moderate to high water solubility and relatively low soil-sorption coefficients and, therefore, can be relatively persistent in soil and mobile in ground water (Schnoebelen and others, 2003); and (5) when analyzed, two of its degradation products, alachlor ESA and alachlor OA, were typically detected more frequently and at higher concentrations than the parent compound in ground water and surface water. Alachlor degrades quickly in the unsaturated zone, but the degradation process slows under saturated conditions where there is generally less organic matter, more compaction, and low biotic activity (Thurman and others, 1996). Previous studies have summarized the occurrence of herbicides and some degradates in the ground and surface water in agricultural areas of the ACFB (Hippe and others, 1994; Frick and Crandall, 1995; Hippe and others, 1995; Hippe, 1997; Hippe and Garrett, 1997; Frick and others, 1998) and GAFL study units (Crandall, 1996; Hatzell, 1997; Berndt and others, 1998; Pittman and Berndt, 2003).

The predominant crop grown in the study area has shifted from corn during the 1960s through the 1970s, to soybeans during the early 1980s, to peanuts in the mid-1980s, to cotton from the mid-1990s to present (Fig. 3) (Gianessi and Reigner, 2006). Herbicide use changed during this time period, in part due to changes in the distribution of crops grown within the study area. During 1992, metolachlor—typically used on corn, peanuts, and soybeans—was the most heavily used herbicide. By 1997, the number of acres of cotton planted in the study area increased to about four times those of 1992 (Fig. 3), and fluometuron—commonly applied to cotton—became the most heavily used herbicide. By 2002, with the introduction of genetically modified cotton, glyphosate became the most heavily used herbicide, accounting for almost one-third of all herbicide use in the study areas (Gianessi and Reigner, 2006).

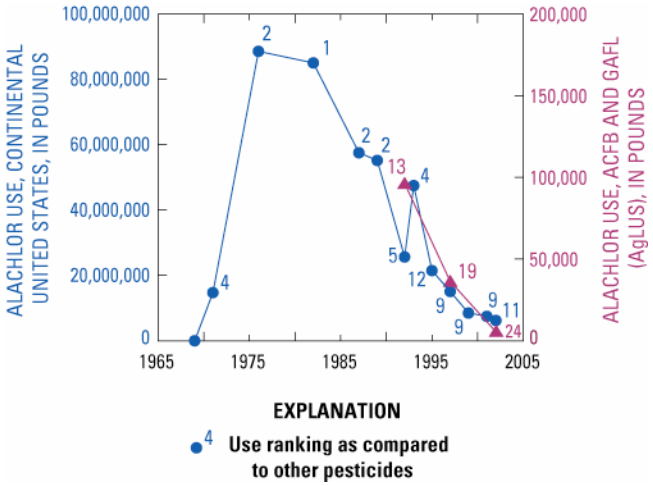

Figure 2. Estimated use of alachlor in the continental U.S. and the Apalachicola–Chattachoochee–Flint River Basin (ACFB) and Georgia-Florida Coastal Plain (GAFL) drainages agricultural land-use areas (AgLUS), 1968–2002.

[1]In USGS reports, the 12-month period October 1 through September 30, designated by the calendar year in which it ends and which includes 9 of the 12 months; therefore, the year ending September 30, 2006, is called water year 2006.

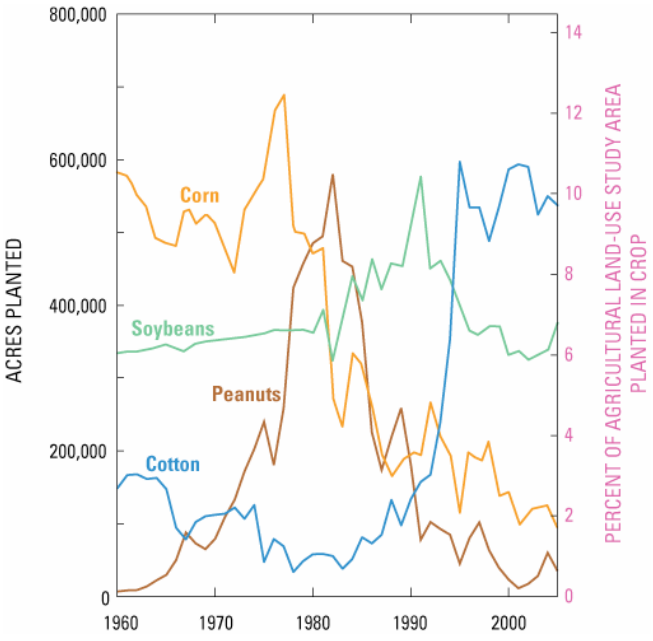

Figure 3. Changes in distribution of major crops grown in the Apalachicola–Chattahoochee–Flint River Basin and Georgia-Florida Coastal Plain agricultural land-use study areas, 1960–2005.

RESULTS AND DISCUSSION

Alachlor and alachlor degradate data collected as part of ACFB and GAFL ground- and surface-water sampling networks at various spatial and temporal scales (Fig. 4) provide information about the occurrence and persistence of alachlor in different parts of the hydrologic system. The frequency of alachlor detections decreased from cycle I to cycle II in the ACFB MAS, ACFB agricultural stream (Lime Creek), GAFL AgLUS, and the GAFL agricultural stream (Little River). These decreases in frequencies of detections correlate with a decrease in alachlor use from the same time period (Fig. 2). There were minimal differences between frequencies of detection or alachlor concentrations from cycle I to cycle II in ACFB AgLUS or in the GAFL mixed land-use stream (Withlachoochee River). The ACFB FPS was the only network resampled in cycle II that had a large increase in the detection frequency of alachlor; however, the highest alachlor concentrations measured in 1994–95 exceeded the USEPA MCL of 2 µg/L, whereas the highest concentration measured in 2004 was 1.3 µg/L. Alachlor is the only pesticide analyzed that exceeded its USEPA MCL or health-advisory level in ground-water samples collected within the study areas. Although not shown in Figure 4, there were no detections of any pesticides in samples collected from 1993–2005 from the ACFB or GAFL reference wells.

In the ACFB, the detection frequency of alachlor was higher during both cycle I (35 percent) and cycle II (24 percent) in low-capacity wells open to the underlying Upper Floridan aquifer (UFA) than in monitoring wells open to the surficial aquifer (14 and 16 percent) (Fig. 4A). Factors that may contribute to higher alachlor detection frequencies in wells open to the UFA compared to the surficial aquifer include: (1) larger recharge areas, higher hydraulic conductivities, and higher water use; and (2) water sampled from the UFA may have recharged the aquifer at a time when more crops were grown on which alachlor was commonly applied. No wells open to the UFA were sampled that underlie the GAFL agricultural study area.

From water year 1993–2001, alachlor was detected in less than 10 percent of ground- and surface-water samples collected. By water years 2002–2005, alachlor was no longer detected in the GAFL AgLUS or Little River and was only detected at low concentrations in 6 percent of Withlachoochee River samples (Fig. 4B). However, alachlor degradate data for all water-year 2002 ground- and surface-water samples collected from sites in or near the GAFL AgLUS show that more than a decade after alachlor was commonly used, degradates of alachlor remain in ground water. Although the parent compound alachlor was not detected in cycle II GAFL AgLUS samples, alachlor ESA was detected in 46 percent and alachlor OA was detected in 19 percent of the same water samples (Fig. 4B) at concentrations 2 to 3 orders of magnitude higher than the laboratory reporting limit of the parent compound. In GAFL surface-water samples, alachlor ESA was detected in 100 percent of surface-water samples collected January–May 2002 from the Little River and the concentration range was narrow (from 0.11 to 0.21 µg/L). This narrow range of concentrations indicates that the source of alachlor ESA to streamflow is baseflow. Alachlor ESA was detected in 35 percent of the samples collected from the Withlachoochee River, downstream from the Little River; however, alachlor ESA was detected in 100 percent of the Withlachoochee River samples from February–May 2002—the same time period that there were 100 percent detections of alachlor ESA from samples collected upstream at Little River. Alachlor OA was not detected in any of the GAFL surface-water samples in which it was analyzed.

Water year 2002 was an extremely dry year near the end of a multiyear drought. The Little River often goes dry each year; during water year 2002 the Agricultural Research Service recorded flow only in the Little River at Upper Ty Ty near Tifton, Georgia, for December 23, 2001, through May 12, 2002. During a dry year, such as water year 2002, the percentage of streamflow in Little River contributed by ground water is likely larger than in years with more precipitation and runoff. Therefore, it is likely that the alachlor and alachlor ESA and OA concentrations measured in Little and Withlachoochee Rivers during spring and summer 2002 are representative of concentrations in ground water near the end of the flowpath where ground water recharges streamflow.

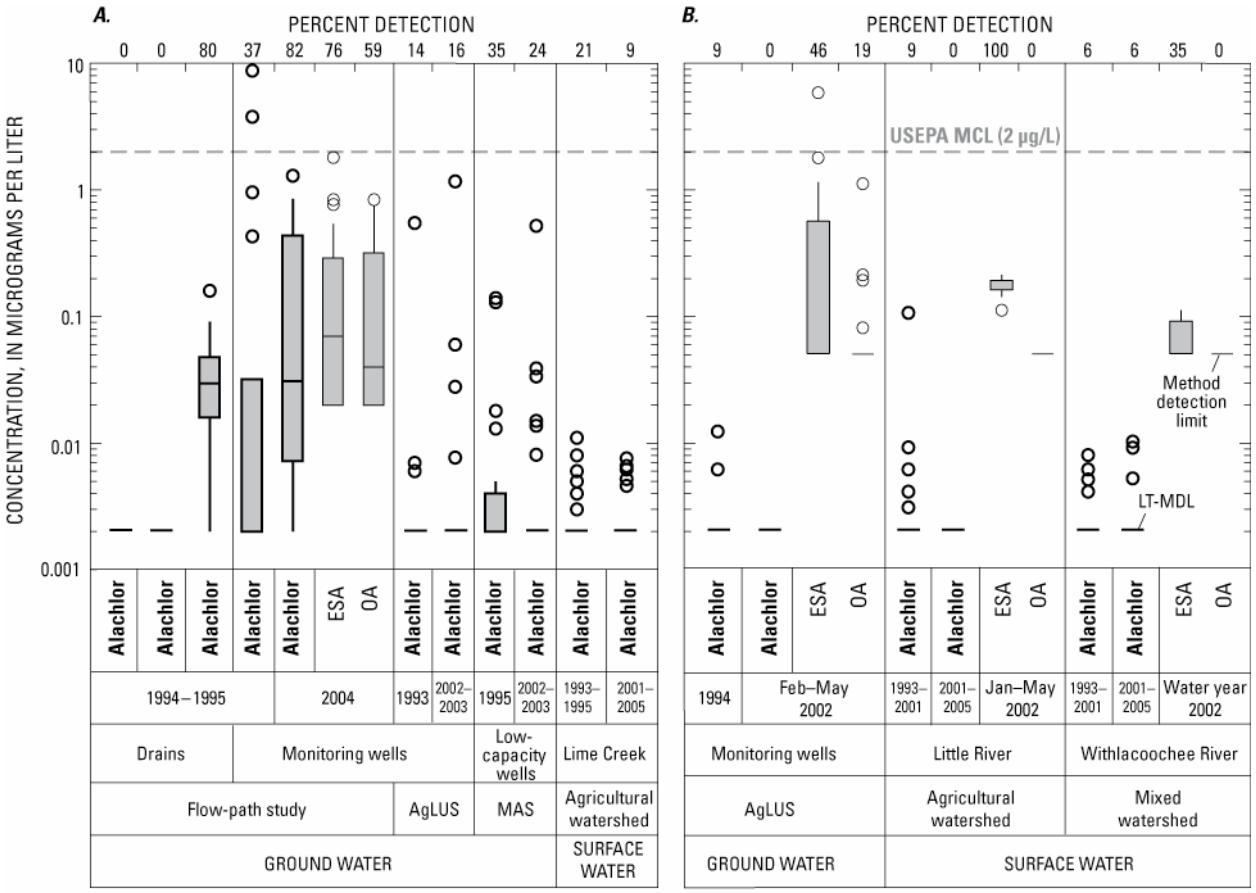

Figure 4. Concentrations of alachlor and two degradates in (*A*) Apalachicola–Chattahoochee–Flint River Basin and (*B*) Georgia-Florida Coastal Plain ground- and surface-water sampling networks in agricultural areas, 1993–2005. [percent detection, frequency of detection for compound analyzed; USEPA, U.S. Environmental Protection Agency; MCL, maximum contaminant level; µg/L, microgram per liter; LT-MDL, long-term method detection limit; AgLUS, agricultural land-use study; MAS, major aquifer study; ESA, alachlor ethane sulfonic acid; OA, alachlor oxanilic acid]

Most ground-water samples collected from the ACFB flow-system study during May 2004 have an estimated aquifer recharge age between 1970 and 1989, based on chlorofluorocarbon (CFC) and dissolved-gas data. These dates provide good predictors of relative alachlor and alachlor degradate concentrations—ground water with recharge dates prior to 1970 or after 1989 had the lowest alachlor concentrations. Concentrations of alachlor and alachlor ESA and OA degradates tended to be an order of magnitude higher in samples with recharge dates from 1973 through 1989, which corresponds to the highest use period for alachlor (Fig. 5).

The combination of a steep decline in the use of alachlor and continued occurrence of the herbicide degradates supports conclusions of other studies that alachlor ESA and alachlor OA degradates are relatively persistent and stable. The results of this study illustrate the importance of including degradate analysis in pesticide studies; without this inclusion, the concentration and movement of pesticides in ground water is substantially underestimated. Additionally, age-dating ground-water samples can substantially improve understanding of the origin of water sampled and the fate and transport of pesticides in ground- and surface-water systems.

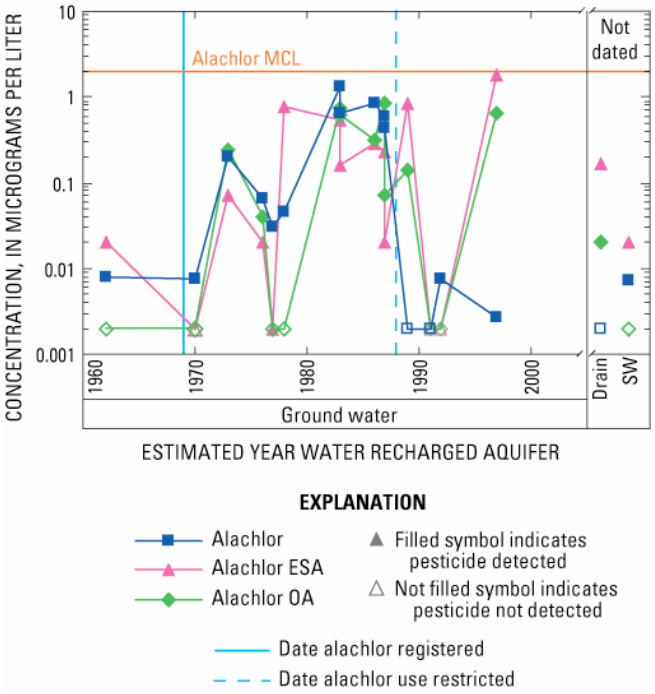

Figure 5. Concentrations of alachlor and two degradates and estimated year water recharged aquifer, Apalachicola–Chattahoochee–Flint River Basin flow-path study, May 2004. [ESA, alachlor ethane sulfonic acid; OA, alachlor oxanilic acid; SW, surface water]

LITERATURE CITED

Berndt, M.P., H.H Hatzell, C.A. Crandall, M. Turtora, J.R. Pittman, and E.T. Oaksford, 1998. Water quality in the Georgia-Florida Coastal Plain, Florida and Georgia, 1992–96. U.S. Geological Survey Circular 1151, 34 pp.

Crandall, C.A., 1996. Shallow ground-water quality in agricultural areas of south-central Georgia, 1994. U.S. Geological Survey Water Resources-Investigations Report 96-4083, 23 pp.

Frick, E.A., and C.A. Crandall, 1995. National Water Quality Assessment Program: Water quality in surficial aquifers in two agricultural areas in Georgia, Alabama, and Florida, *in* Hatcher, K.J. (ed.), Proceedings of the 1995 Georgia Water Resources Conference, Athens, Ga., Institute of Ecology, The University of Georgia, pp. 42–45.

Frick, E.A., D.J. Hippe, G.R. Buell, C.A. Couch, E.H. Hopkins, D.J. Wangsness, and J.W. Garrett, 1998. Water Quality in the Apalachicola–Chattahoochee–Flint River basin, Georgia, Alabama, and Florida, 1992–95. U.S. Geological Survey Circular 1164, ISBN 0-607-89340-0, 38 pp., accessed May 11, 2005, at *http://ga.water.usgs.gov/publications/cir1164* and *http://water.usgs.gov/pubs/circ/circ1164/*.

Gianessi, L.P., and N. Reigner, 2006. Pesticide use in U.S. crop production: 2002 with comparisons to 1992 & 1997: Fungicides and herbicides. Washington, D.C., CropLife Foundation, unpaginated, accessed May 20, 2006, at *http://www.croplifefoundation.org/Documents/PUD/NPUD%202002/Fung%20&%20Herb%202002%20Data%20Report.pdf*

Hatzell, H.H., 1997. Pesticides in surface water from three agricultural basins in south-central Georgia. U.S. Geological Survey Water Resources-Investigations Report 96-4196, 12 pp.

Hippe, D.J., 1997. Pesticide occurrence in the Upper Floridan aquifer in the Dougherty Plain and Marianna Lowlands districts, Southwest Georgia and adjacent areas of Alabama and Florida, *in* Hatcher, K.J. (ed.), Proceedings of the 1997 Georgia Water Resources Conference, Athens, Ga., Institute of Ecology, The University of Georgia, pp. 65-67, abstract accessed February 9, 2004, at *http://ga.water.usgs.gov/nawqa/publications/dan.pest.occur.97.html*

Hippe, D.J., and J.W. Garrett, 1997. Spatial distribution of dissolved pesticides in surface water of the Apalachicola–Chattahoochee–Flint River Basin, *in* Hatcher, K.J. (ed.), Proceedings of the 1997 Georgia Water Resources Conference, Athens, Ga., Institute of Ecology, The University of Georgia, pp. 410–419, accessed February 9, 2004, at *http://ga.water.usgs.gov/nawqa/publications/dan.spatial.gwrc.97.html*

Hippe, D.J., H.H. Hatzell, L.K. Ham, and P.S. Hardy, 1995. National Water Quality Assessment Program: Pesticide occurrence and temporal distribution in streams draining urban and agricultural basins in Georgia and Florida, 1993–94, *in* Hatcher, K.J. (ed.), Proceedings of the 1995 Georgia Water Resources Conference, Athens, Ga., Institute of Ecology, The University of Georgia, pp. 34–41.

Hippe, D.J., D.J. Wangsness, E.A. Frick, and J.W. Garrett, 1994. Water quality of the Apalachicola-Chattahoochee-Flint and Ocmulgee River basins related to flooding from tropical storm Alberto; pesticides in urban and agricultural watersheds; and nitrate and pesticides in ground water, Georgia, Alabama, and Florida. U.S. Geological Survey Water-Resources Investigations Report 94-4183, 36 pp.

Pittman, J.P., and M.P. Berndt, 2003. Occurrence of herbicide degradation compounds in streams and ground water in agricultural areas of southern Georgia, 2002, *in* Hatcher, K.J. (ed.), Proceedings of the 2003 Georgia Water Resources Conference, Athens, Ga., Institute of Ecology, The University of Georgia, 4 pp., accessed September 14, 2005, at *http://ga.water.usgs.gov/pubs/other/gwrc2003/pdf/Berndt-GWRC2003.pdf*

Schnoebelen, D.J., S.J. Lalkhoff, K.D. Becher, and E.M. Thurman, 2003. Water-quality assessment of the eastern Iowa basins: Selected pesticides and pesticide degradates in streams, 1996–98. U.S. Geological Survey Water-Resources Investigations Report 03-4075, 61 pp., accessed October 10, 2006, at *http://pubs.usgs.gov/wri/2003/wri034075/pdf/wrir03-4075.508.pdf*

Thurman, E.M., D.A. Goolsby, D.S. Aga, M.L. Pomes, and M.T. Meyer, 1996. Occurrence of alachlor and its sulfonated metabolite in rivers and reservoirs of the Midwestern United States: The importance of sulfonation in the transport of chloroacetanilide herbicides. Environmental Science and Technology, v. 30, pp. 569–574.

U.S. Environmental Protection Agency, 2004. 2004 Edition of the drinking water standards and health advisories. U.S. Environmental Protection Agency, EPA 822-R-04-005, 12 pp., accessed June 23, 2006, at *http://www.epa.gov/waterscience/criteria/drinking/standards/dwstandards.pdf*

U.S. Geological Survey, 1997–2006. National field manual for the collection of water-quality data. U.S. Geological Survey Techniques of Water-Resources Investigations, Book 9, Chapters A1–A9, variously paged, accessed September 12, 2006, at *http://water.usgs.gov/owq/Fieldprocedures.html*