

## Time-Related Analysis of Alachlor Concentrations in Florida Wells

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Cohen et al, 1986 reported alachlor detections in four states (Iowa, Nebraska, Pennsylvania, and Maryland) at concentrations between 1 and 10 µg/L (parts per billion). Alachlor is a herbicide used in corn, soybean, and peanut production. 2.4 million acres were treated in 1994 with alachlor and 6.6 million pounds were used (The Ground Water Gazette). Alachlor(2-chloro-2',6'-diethyl-N-(methoxymethyl) acetanilide is a herbicide widely used in the United States Both has been determined in the ground water (Aga et al.,1994). Alachlor has been classified as human carcinogen and its maximum contaminant level (MCL) was established at 2 µg/L by the United States Protection Agency (USEPA) in 1992. An evaluation of rural drinking water sources in the United States indicated that 97% is derived from underground sources, along with 55 % of all livestock water and 40 % of all irrigation water (Pepperman and Kuan, 1994). Ground water studies in Virginia by Gallagher et al (1996) indicated the presence of alachlor in 18 percent of the samples at levels mostly < 1 µg/L. Richards et al (1995) sampled nearly 35,000 wells in Ohio, Indiana, Illinois, West Virginia, and Kentucky. 1.1 percent of the wells were above 2 µg/L for alachlor in this survey. No information was given on the persistence of alachlor in well water that can be expected once contamination has been detected. The following observations are therefore being reported. Over 200 wells were sampled in Florida and 16 wells containing alachlor at levels near or over 2 µg/L were sampled since 1989 to present. Alachlor concentrations remained > 2 µg/L in all but four wells. One well which was initially < 2 µg/L went over that level in 1994. The mean of alachlor in all wells was 13 µg/L and 9 µg/L, in 1994 and 1995, respectively. All alachlor use in Florida was canceled before the 1991 use season but sampling periods did not indicate a discernable trend. As a group, the concentrations of the alachlor were not significantly different with time no matter how sampling intervals were analyzed.

### MATERIALS AND METHODS

In 1988, Department of Health (DH) found one well to contain over 10 µg/L alachlor. In early 1989, the Florida Department of Agriculture and Consumer Services (FDACS) sampled 100 wells for alachlor in Jackson County, and the Monsanto Laboratory (the registrant of alachlor) analyzed the samples. After alachlor was identified in Jackson

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County drinking water wells in the following counties were sampled: Santa Rosa (11), Escambia (4) Alachua (25) Levy (19) Marion (22) Walton (13), Okaloosa (6), Baker (8) Columbia (19) Holmes (16), Washington (6).

Initially 9 wells were  $> 2 \mu\text{g/L}$  and 6 more wells were found to contain alachlor at levels over or near  $2 \mu\text{g/L}$ , since 1990. All wells were sampled at least once per year. Wells containing alachlor over or near the MCL were carbon filtered by Monsanto and sampled quarterly through 1993. When no significant changes in the alachlor concentrations became apparent in 1993, wells were thereafter sampled annually. Presently, nineteen wells are being monitored by Monsanto. A description of the wells and the area immediately around the wells can be found in Table 1.

## RESULTS AND DISCUSSION

Twenty-five wells were positive for alachlor and 9 exceeded the MCL of  $2 \mu\text{g/L}$  of the 100 private wells sampled during the summer of 1989 in Jackson County. Two more wells with alachlor  $> 2 \mu\text{g/L}$  and 4 wells below  $2 \mu\text{g/L}$  but above  $1 \mu\text{g/L}$  have been added to the sampling network since 1990.

Table 1. Location by county and notes on the sampled wells<sup>a</sup>

Site	County	Notes
LY 02	Levy	New well installed in mixing and loading (M&L) site
MA 21	Marion	No M&L, but peanut washing operations
LY 04	Levy	M&L near well
MA 19 Fly P-b	Marion	Possible mixing and loading near well
MA 11 Fly P-q	Marion	Farm well for cattle, possible M&L
844003	Jackson	M&L near well
345002	Jackson	M&L near well, surface water infiltrating along well
944002	Jackson	Possible M&L near well
231 naf	Jackson	Possible M&L. Karst and slowly permeable subsoil
JA 29naf	Jackson	On NAF, karst. No M&L
JA 20naf	Jackson	No M&L. On NAF
484001	Jackson	No M&L. Poorly constructed well.
171500	Jackson	M&L near well
123500	Jackson	No apparent M&L activities near well
APS001	Jackson	Near 1235001, no M&L activities

<sup>a</sup>Wells in Jackson County, except 231, are 2 inch in diameter and about 70 ft deep. The 4-inch 231 well is cased till about 100 feet and 300 ft deep. The diameter and depth of the wells in other counties are variable.

Presently, fifteen wells are being monitored annually. The wells were sampled 4 times per year till 1993 and averaged for presentation and once per year since 1993 (Table 2). Two wells, 231 and 345002, indicated peaks during two cropping seasons following the 1991 cancellation. One well in Jackson County was a non-detect (ND), 4 wells were  $< 2 \mu\text{g/L}$  while 7 wells  $> 2 \mu\text{g/L}$ . Alachlor concentration in the well

identified as APS001 has increased gradually since 1989 and contained more than 2 µg/L in 1996. Nearby wells were sampled in 1996 but no alachlor was determined. Peanuts were grown near the 1235001 and APS001 wells in 1989, however the area has not been cultivated since 1989 and no mixing and loading activities have taken place near the 1235001 well. All wells on the North American Farms property (2 1, JA 20, and JA 29) showed significant peaks during the 1991 field season when the field was

Table 2. Annual alachlor concentrations in µg/L, (parts per billion) of Florida wells studied

Site	89	90	91	92	93	94	95	96
231	65.90	33.90	28.55	15.11	13.38	7.77	6.44	3.00
944002	8.83	3.60	7.21	8.11	14.45	5.72	45.1	9.50
1715001	1.30	0.65	0.90	1.44	1.78	1.30	0.58	0.50
345002	21.77	15.42	14.14	9.48	2.76	7.63	7.35	15.10
484001	4.05	3.27	3.24	3.77	2.61	2.34	2.64	1.10
JA52	ns <sup>a</sup>	ns <sup>a</sup>	0.92	2.1	0.81	1.00	0.20	nd <sup>a</sup>
JA20	28.40	17.80	22.19	18.04	22.35	19.40	24.19	15.60
JA29	ns <sup>a</sup>	4.32	6.03	4.15	4.22	3.99	3.79	ns <sup>a</sup>
1235001	6.41	2.26	2.07	2.95	2.10	0.57	0.26	nd <sup>a</sup>
APS001	0.62	0.81	ns <sup>a</sup>	1.26	1.97	2.87	ns <sup>a</sup>	5.90
844003	4.92	3.58	4.62	3.29	3.10	1.83	1.37	1.10
MA11	1.48	5.53	10.78	9.56	2.00	2.49	0.78	0.46
MA21	ns <sup>a</sup>	6.51	9.93	7.33	7.86	8.81	0.21	1.53
MA19	ns <sup>a</sup>	0.97	1.49	2.12	2.66	3.31	5.02	ns <sup>a</sup>
LY02	127.50	87.87	68.78	62.39	51.95	24.18	13.68	5.86
LY04	22.00	8.71	11.42	7.62	7.50	6.48	7.16	6.22
MEAN <sup>2</sup>	24.43	13.01	12.82	9.92	8.84	6.23	8.47	5.48

<sup>a</sup>ns - not sampled; nd - below minimum level of detection; <sup>2</sup>R=0.83\*

cropped with cotton and no alachlor was used. The alachlor concentrations in the 944002 well fluctuated with every cropping season. A sharp concentration peak was determined in 1995 could be related to the well's proximity to Alabama where alachlor is still used. This work considered only the situation of the wells near alachlor-use areas. Factors contributing to pesticide movement into the vadose zone such as rainfall, soils, and crop rotations were not considered in this analysis. The means of the data in Table 2 indicated a significant decline ( $r=0.83$ ) over time in the concentrations of alachlor in the wells. A regression equation can be expressed as follow:  $y = 11.15 -$

0.83 x.

The Z values (the number of standard errors from a predictive value) were calculated for the North American Farms wells (Table 3). The 2 values for the JA29 well data were significant and the indicated peaks were a departure from predicted values while the other wells did not indicate a significant departure from the predictive value.

Table 3. The significance of departure of actual and predicted alachlor concentrations (Z value) in three wells on North American Farms (NAF), Jackson County

SAMPLE #	DATE (m)	ACT. VAL ( $\mu\text{g/L}$ )	PRED. VAL ( $\mu\text{g/L}$ )	Sy.x	Z	A
JA20	4/20/91	26.9	21.4	17.84	.31	12
JA20	7/22/91	27.0	21.2	17.84	.32	12.6
NAF	4/20/91	30.5	32.4	11.31	-.17	6.8
NAF	7/22/91	37	29.8	11.31	.64	23.9
JA29	4/20/91	8.0	4.9	1.29	2.4	49.2 <sup>a</sup>
JA29	7/22/91	7.1	4.8	1.29	1.78	46.2 <sup>a</sup>

\* Actual value is significantly different from the predicted value at 95 percent confidence

The 345002 well indicated peaks during the 1991 and 1992 field seasons (Table 4). The determination of the Z value showed that the departure of the actual concentration of alachlor was statistically different from the predicted alachlor concentration in the wells for the two field seasons.

Table 4. Z value for the determination of the significance of departure of determined and predicted alachlor concentrations in the 344002 well.

WELL	DATE	ACT. VAL	PRED. VAL	Sy.x	Z
345002	7/22/91	16.0	6.57	6.82	1.38
345002	10/18/91	20.6	4.92	6.82	2.30
345002	8/04/92	11.2	0.58	6.82	1.73
345002	10/17/92	15.6	1.68	6.82	2.53

\* Significant departure at 5 percent level of predicted value from measured value.

In order to explain possible effects of the cancellation of the alachlor before the 1991 use season, a grouping of the data for the years 89 and 90, 91 and 92, and 93, 94, 95 was done (Table 5). The results indicated that no statistical validity could be obtained by managing the data in this manner.

Table 5. Analysis of Variance with all the sampling dates as the main effect.

SOURCE OF VARIATION (SAMPLING PERIODS 89-95)	# WELLS	F VALUE	SIGN. F =.05
ALL WELLS	16	1.216	0.261
JACKSON CO. WELLS	10	0.746	0.734
NAF (JACKSON CO.)	3	1.529	0.161

This work has resulted in a rule prohibiting the use within Florida of pesticide products containing alachlor (February, 1991). Thus, no alachlor applications were made in the Northern and Central Florida use areas as of 1991. In addition, the work created a modus operandi with the pesticide companies on drinking water wells contaminated at the MCL or Health Advisory Level (HAL) with pesticides. Monsanto agreed to filter drinking water wells in which the alachlor concentration was above 2 µg/L or exceeded the MCL and maintain filtration devices for at least two years after the concentration of alachlor in the wells dropped below 2µg/L. Monsanto continued to sample the wells in the network even though the concentrations dropped below the MCL and filtered wells subsequently found to be over the MCL for alachlor. These wells were taken into the routine yearly sampling program.

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