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PESTICIDE CONCENTRATION VARIATIONS CORRELATED WITH WELL BORE VOLUME REMOVAL IN SHALLOW COASTAL PLAIN GROUND WATER

Key Words: Pesticides, well bore volume, purging

Jeffrey M. Novak and Donald W. Watts

USDA-ARS
Coastal Plains Soil, Water, and Plant Research Center
2611 West Lucas Street
Florence, SC 29501-1242

ABSTRACT

The effects of well bore volume removal (V_n) on the concentration of alachlor [2-chloro-N-(2,6-diethylphenyl)-N-(methoxy methyl) acetamide] and prometon (6-methoxy-N,N'-bis(1-methylethyl)-1,3,5-triazine-2,4-diamine] in ground water obtained from three monitoring wells installed in the Coastal Plain region of North Carolina was investigated. Seasonal effects were also investigated by conducting the exercise in February and May. In the majority of cases, the lowest pesticide concentrations occurred in the initial well bore volume (V_1 = stagnant water). Removal of additional well bore volumes (V_2 to V_{10}) from two of the wells resulted in pesticide concentrations that did not vary substantially. This indicates that a

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representative aquifer sample was obtainable, in most cases from these wells, after removal of the initial well bore volume. In contrast, a third well required the purging of two well bore volumes before a stable alachlor concentration was achieved. Seasonal effects of bore volume removal vs. pesticide concentrations for the three wells were not significant ($P > 0.05$). It was concluded that a protocol for improved accuracy in pesticide analyses of ground water can be obtained by establishing a pesticide concentration-purging (well bore volume) relationship for each well.

INTRODUCTION

In a ground water monitoring study, development and evaluation of a sample collection method is a serious concern. An important issue in this method is the determination of a well purging protocol. Purging is necessary to remove stagnant well water to obtain ground water that is chemically representative of the aquifer (U.S. EPA, 1986). The literature suggests that purging can be accomplished by removing a given number of well bore volumes or by purging until a certain chemical parameter in the effluent has stabilized (Herzog et al., 1991). Reported number of well bore volumes to remove range from one to seven (Humenick et al., 1980; Gibb et al., 1981; Schuller et al., 1981; Unwin and Huis, 1983; Spalding et al., 1993). However, the actual number needed may not be constant for all situations because the purging requirement may be specific to site, system, season, or chemical parameter (Gibb et al., 1981).

The second school of thought regarding purging volumes advocates that the monitoring well should be purged until certain chemical parameters in the effluent

have stabilized. Commonly, such chemical parameters as temperature, pH, Eh, and specific conductance can be monitored (Herzog et al., 1991). This protocol was successfully applied by Wood (1976) who recommended that U.S. Geological Survey wells be purged until the effluent samples have a stable pH value. Zlotnik et al. (1995) also monitored for the stability of nitrate and atrazine in effluent pumped from ground water wells in Nebraska to determine suitability of a sample as representative of the ground water. This purging protocol is straight forward, although purging of large volumes of effluent may create disposal problems, especially if the effluent contains a hazardous waste.

A third more rigorous protocol was proposed by Lee and Jones (1983). This protocol recommends collecting effluent from one, four, six, and ten bore volumes, analyzing for the constituents of concern, and then determining in which sample the constituent has stabilized. Once this relationship is established, a sample can then be collected after removal of a specific number of well bore volumes. This protocol reduces excess purging and minimizes the potential of altering the chemistry of the sample by overpurging. Lee and Jones (1983) also suggest that the exercise should be repeated at least twice per year because water quality chemistry can change seasonally.

The water quality program at the USDA-ARS-Coastal Plains Research Center utilizes a large number (n=92) of shallow ground water monitoring wells to determine the behavior of nutrients and pesticides in the Coastal Plain. This program required a sample collection method that would provide a representative sample, however, would also be convenient and not produce excess effluent. In this study, the well

purging method recommended by Lee and Jones (1983) for three USDA-ARS shallow ground water monitoring wells has been evaluated. These wells were chosen because they were the only wells (n=3) out of 92 that contained measurable concentrations of pesticides (Novak et al., 1996). The objectives were: (1) to measure the concentration of alachlor and prometon in purge effluent removed successively from three monitoring wells and (2) to determine the necessary number of well bore volumes to remove where the pesticide concentration stabilized.

MATERIALS AND METHODS

Watershed Delineation, Pesticide Application, and Well Description

The monitoring wells are located in the Herrings Marsh Run watershed of Duplin Co., North Carolina. This watershed is located in the Cape Fear River basin and is part of the Middle Coastal Plain physiographic region. Two principal aquifers - a surficial and a Cretaceous - are described within the watershed (Coble et al., 1984). Soil parent materials in the watershed are marine and fluvial sediments containing porous sands and clays (Daniels et al., 1984). Row (corn, soybean, cotton) and vegetable (pepper, cucumber) crops are cultivated (54% of watershed land area) in the 2044-ha watershed. Alachlor is heavily (579 kg active ingredient.) used in the watershed for weed control in row crops, while prometon is used less frequently for weed control around buildings (C. Fountain, Duplin Co., North Carolina Extension Service, 1995, personal communication).

The three monitoring wells, referred to as wells A, B, and C, are located on three separate farms in the watershed and were among 92 installed in 1992 and 1993 as

TABLE 1

Characteristics of Sampled Wells and Aquifer

	Well		
Characteristic	A	B	C
Well depth (m)	7.38	7.31	3.05
Length of screen (m)	1.5	1.5	1.5
Depth to screen (m)	6.11	5.81	1.55
Inside radius of casing (m)	0.042	0.042	0.042
Depth to static water table (m)	1.84	2.01	1.78
Saturated thickness of aquifer (m)	10	10	10
Average pumping rate (L m^{-1})	1	1	1
Average recovery time (min)	27.9	5.6	2.9
Average drawdown (m)	6	0.5	0.2
Hydraulic conductivity (cm s^{-1})	2.9×10^{-5}	2.1×10^{-4}	8.0×10^{-5}
Transmissivity (m^2 d^{-1})	0.26	1.78	0.69

outlined by Stone et al. (1994). Wells A and B are located on agricultural field borders, while well C is located near an animal facility. Specific well physical characteristics are presented in Table 1. The wells were placed between depths of 3 and 8 m, which reflects the typical range for residential well depths within the watershed. Shallow residential drinking water wells are common because of the high water table depth (< 2 m). The typical range for the saturated thickness of the aquifer in this Coastal Plain region of North Carolina is 10-15 m (Dr. Ron Huffman, North Carolina State University, 1996, personnel communication). Transmissivity (T) for

the aquifer around each well was determined using the Jacob-time drawdown method as described by Heath (1984). For this determination, the depth of the saturated aquifer (b) and the well pumping rate were assumed to be 10 m and 1 L min^{-1}, respectively. Hydraulic conductivity (k) around each well was estimated using the equation T = k * b, assuming the b value was 10 m (Heath, 1984).

Sample Collection, Pesticide Extraction and Analyses

Initial well water table depths were measured using a water level meter (Testwell Instr., Georgetown, Ontario[1]). After recording the water table depths, the probe was removed and the initial bore volume of water (usually 8 to 12 L) was hand-pumped from each well using a PVC line equipped with a foot valve. The bore volume of water in the well was based on the initial water table height and the inside diameter of the PVC pipe. The average pumping rate from each well was 1 L min^{-1}. A water sample was collected (as described below) of the initial bore volume (referred to as V_1). The water table probe was rinsed with deionized water and placed back into each well corresponding to the initial water table depth. The recovery time for the water table to reach the initial depth was recorded. This process was repeated sequentially nine times for the February 1996 and 11 times for May 1996 samplings.

Each unfiltered water sample was collected in a 250-mL amber bottle, stored on ice, and transported back to the laboratory. The samples were filtered and extracted for dissolved alachlor and prometon using solid-phase extraction (SPE) and gas

[1] Mention of a trade mark, proprietary product, or vendor is for information only and does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture and does not imply its approval to the exclusion of other products or vendors that may also be suitable.

chromatographic (GC) techniques as outlined by Novak and Watts (1996) with a slight modification. Each sample was spiked with 1 mL of a 100 μg L^{-1} cyanazine (2-[[4-chloro-6-(ethylamino)-1,3,5-triazine-2yl]amino]-2-methyl-propanenitrile) as a correction for the incomplete recovery of alachlor ($\bar{x}$ = 94%, SD = 11) and prometon ($\bar{x}$ = 88%, SD = 14). Cyanazine is an appropriate internal standard because its recovery is close (recovery$\bar{x}$ = 98%, SD = 8) to 100% and has not been detected in these wells. A Varian 3600 CX GC (Walnut Creek, California) fitted with a Varian nitrogen/phosphorus detector and a Restek (Bellefonte, Pennsylvania) Rtx-35 column was used to separate and identify the compounds. Details of the column conditions, gas flows, injection volumes, and minimum detection limits are provided by Novak and Watts (1996).

Field and Laboratory Quality Control Protocols

Rigorous quality control protocols were used in the field and laboratory. All amber bottles were washed and then rinsed with pesticide-free methanol. Prior to sample collection, each amber bottle and cap was rinsed three times with purged ground water. Deionized water was used to flush the water level probe and was retained as a rinsate blank. Additionally, the V_5 sample was split into two portions to determine the reproducibility of the extraction procedure. During each batch extraction, SPE cartridges were tested for the presence of contaminants and for pesticide extraction efficiency using a 100 μg L^{-1} spiking solution containing the three pesticides. No pesticides were detected in the probe rinsate, indicating that the possibility of cross-contamination was minimal. Pesticide concentration comparisons between the V_5 split sample differed by less then 5% (relative variation), indicating excellent

reproducibility. Analytical accuracy was checked by analyzing replicates (n = 7) of a 100 $\mu g\ L^{-1}$ spiking solution containing the three pesticides mixed with ground water. This ground water was obtained from another monitoring well in the watershed that contained no measurable pesticides (detection limits between 0.1 to 0.35 $\mu g\ L^{-1}$ for the three pesticides). This source of ground water was used to insure that the matrix of the spiking solutions was chemically similar to that of the samples. The relative precision of seven replicate recoveries was ± 2 and 12% for alachlor and prometon, respectively.

Statistical Analyses

Pesticide concentration mean, standard deviation, standard error, 99% upper and lower confidence intervals for wells A, B, and C were determined using SigmaStat (SigmaStat Corp., San Rafael, California) software. The effects of bore volume removal on alachlor and prometon concentrations were considered negligible if the pesticide concentrations were within the 99% confidence interval. Seasonal effects were statistically evaluated, according to Zar (1974) using a *t*-test, by comparing the slopes computed from a linear regression analyses of February vs. May pesticide concentrations in the successive bore volume effluents.

RESULTS AND DISCUSSION

Well Characteristics

Characteristics of the three monitoring wells are shown in Table 1. Wells A and B were placed deeper into the soil to sample ground water at depths similar to most of the watershed residential drinking water wells. Well C was placed shallower to

evaluate the effects of nutrient and pesticide runoff from a turkey composting facility on very shallow ground water quality. The recovery time measured for these wells represents the average time for the static water level to reach the initial depth measured prior to purging. Well recovery time was calculated by computing an average from pooled February and May data because recovery times between months were similar (<10% relative variation). Drawdown was the average of the vertical distance that the static water table was lowered due to removal of one bore volume of water. Well A had a relatively slow recovery time and a deeper drawdown than wells B and C. Well B had a higher hydraulic conductivity and transmissivity value than wells A and C. These aquifer hydraulic parameters should be considered gross estimations since the values were calculated using an assumed saturated aquifer thickness and well pumping rate.

Well Pesticide Concentrations and Seasonal Effects

Variations in pesticide concentration between purgings were assumed to be affected mainly by aquifer properties rather than by well construction because the wells had similar casing composition, screening size, and sealing material. A total of V_{10} and V_{12} well bore volumes was purged during February and May, respectively, from the three wells (Table 2). Ground water samples from two additional well purges in May were obtained to insure that concentration trends noted in February were reproducible.

The influence of bore volume removal on the concentration of alachlor in well A was highly significant. Alachlor concentrations in the V_1 and V_2 effluent were low (5.10 and 8.73 $\mu g\ L^{-1}$) and were also outside the 99% confidence interval. Effluent

TABLE 2

Alachlor and Prometon Concentrations in Well Bore Volume Samples Removed Sequentially from Wells A, B, and C (all concentrations corrected for recovery)

	A		B		C	
	Alachlor		Alachlor		Prometon	
V_n	Feb	May	Feb	May	Feb	May
	$\mu g\ L^{-1}$					
1	7.91	5.10	1.51	1.16	2.19	2.08
2	8.73	8.14	2.03	1.76	2.07	1.46
3	9.72	9.19	1.77	1.74	2.25	1.42
4	10.28	8.92	2.24	1.66	2.03	1.61
5	10.79	10.86	1.88	1.72	2.05	1.34
6	11.97	12.12	1.83	1.71	1.91	1.61
7	12.25	12.24	1.90	1.67	2.07	1.59
8	12.23	11.44	1.99	1.92	2.21	1.58
9	10.37	13.37	1.88	1.90	2.08	1.49
10	11.35	13.39	2.32	1.82	2.00	1.48
11	*	11.68	*	1.77	*	1.91
12	*	12.70	*	1.75	*	1.91
$\bar{x}$	10.56	10.76	1.94	1.72	2.09	1.63
SD	1.47	2.48	0.23	0.19	0.10	0.23
SE	0.47	0.72	0.07	0.06	0.03	0.07
99% LC†	9.05	8.53	1.69	1.57	1.98	1.42
99% UC‡	12.07	12.98	2.17	1.92	2.19	1.83

† equals lower confidence (LC) and ‡ equals upper confidence (UC) concentration.

* not sampled

from subsequent bore volume purges had concentrations (12.25 and 13.39 $\mu g\ L^{-1}$) that increased dramatically, although the concentrations were still within the 99% confidence interval. The data indicate that ground water can be collected from well A after removal of two well bore volumes because alachlor concentrations had stabilized. Additional pumping of well A (past V_3) gave no improvement in accuracy.

The alachlor concentration vs. well bore volume response for well A is probably related to the deeper drawdown than the other two wells (Table 1). This means that the volume of ground water needed to supply the recharge was substantially larger than the other wells. Consequently, well A was drawing ground water from a radial zone far beyond the screened interval, which was nearly dry when the purging was complete. The inflow of ground water from a larger radial distance probably was alachlor enriched, which resulted in higher alachlor concentrations in the successive purges.

Well bore volume removal effects on the concentration of alachlor and prometon in wells B and C were not as dramatic as in well A (Table 2). However, alachlor and prometon concentrations in samples from the initial well purging (V_1) were outside the 99% confidence interval indicating a significant difference ($P = 0.01$). These findings support the importance of removing at least one bore volume prior to sample collection. The data also show that removal of additional well bore volumes (V_2 to V_{10}) was unnecessary since the alachlor and prometon concentrations stabilized after removal of the initial stagnant water. Additional well purging transported ground water that had near uniform concentrations of alachlor and prometon.

Seasonal effects were tested using linear regression for well bore volume removal

vs. pesticide concentration for the February and May sampling periods. Comparing the regression slopes with a *t*-test revealed no significant seasonal effect ($P > 0.05$). This finding is not unexpected since the slopes from the three wells for the February vs. May samplings were similar (A = 0.376 vs. 0.591; B = 0.038 vs. 0.0311; and C = 0.011 vs. 0.010).

CONCLUSIONS

Establishing a well purging protocol is essential to obtaining a representative aquifer sample. A minimum of one purge cycle should be completed prior to sample collection. The relationship of pesticide concentration vs. well bore volume removal is site specific. Therefore, a protocol consisting of removing a uniform set number of well bore volumes from a large population of wells over a large area may not be appropriate. The data obtained in this study agree with the overall finding in the literature that wells vary in their need for purging. Establishing the relationship between well volume removal vs. pesticide concentration for each well is desirable because it is a good step towards balancing cost and accuracy.

REFERENCES

Coble, R. W., Giese, G. L., and Elmers, J. L, "National Water Summary 1984-Hydrologic Events, Selected Water Quality Trends, and Ground-water Resources" U.S. Geol. Water Supply Papers 2275, pp. 9-34 (1984).

Daniels, R. B., Kleiss, H. J., Buol, S. W., Byrd, H. J., and Phillips, J. A., "Soil Systems in North Carolina" North Carolina State Univ. Bulletin 467 (1984).

Gibb, J. P., Schuller, R. M., and Griffin, R. A., "Procedure for the Collection of Representative Water Quality Data from Monitoring Wells" Cooperative Ground Water Report 7, Illinois State Water Survey and Illinois State Geological Survey , pp. 1-61 (1981).

Heath, R. C., "Basic Ground-water Hydrology" USGS Water-supply Paper 2220. USGS, Alexandria, Va. (1984).

Herzog, B., Pennino, J., and Nielson, G., In: "Practical Handbook of Ground Water Monitoring" D. M. Nielson (ed.), Lewis Publishers, Michigan, pp. 449-499 (1991).

Humenick, M. J., Turk, L. J., and Colchin, M. P., Ground Water, 18, 262-273 (1980).

Lee, G. F., and Jones, R. A., J. Water Pollution Control Fed., 55, 92-96 (1983).

Novak, J. M., and Watts, D. W., J. Environ. Sci. Health, B31, 1171-1187 (1996).

Novak, J. M., Watts, D. W., Stone, K. C., Johnson, M. H., Hunt, P. G., and Coffey, S. W., "Proceedings of the Watershed '96 Tech. Conf." Water Environ. Fed., Baltimore, Md., pp. 1016-1018 (1996).

Schuller, R. M., Gibb, J. P., and Griffin, R. A., Ground Water Monitor Rev., 1, 42-46 (1981).

Spalding, R. F., Burbach, M. E., Diffendal, R. F., Exner, M. E., and Papiernik, T. D., "Proceedings of Agric. Res. to Protect Water Quality Conf." Soil and Water Conservation Soc., Ankeny, IA, pp. 314-317 (1993).

Stone, K. C., Hunt, P. G., Novak, J. M., and Matheny, T. A., "Proceedings of 2nd Conf. on Environmentally Sound Agric." ASAE, Michigan, pp. 280-286 (1994).

Unwin, J. P., and Huis, D., "Proceedings of 3rd National Symp. on Aquifer Restoration and Ground Water Monitor" National Water Well Assoc., Dublin, OH, pp. 257-262 (1983).

U.S. EPA, "RCRA Ground-water Monitoring Technical Enforcement Guidance Document" U.S. Environmental Protection Agency, Office of Solid Waste and Emergency Response OSWER-9950.1 (1986).

Wood, W. W., "U.S. Geological Survey Techniques of Water Resources Investigations," pp. 1-24 (1976).

Zar, J. H, "Biostatistical Analyses" Prentice-Hall, Inc., New Jersey (1974).

Zlotnik, V. A., Burbach, M. E., Exner, M. E., and Spalding, R. F., J. Soil and Water Conser., 50, 95-101 (1995).

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