Bull. Environ. Contam. Toxicol. (1989) 43:159–164

Bulletin of Environmental Contamination and Toxicology

Distribution of Atrazine, Simazine, Alachlor, and Metolachlor in Soil Profiles in Connecticut

L. Q. Huang and C. R. Frink

The Connecticut Agricultural Experiment Station, 123 Huntington St., Box 1106, New Haven, Connecticut 06504-1106, USA

Contamination of ground water with toxic chemicals has been reported from every state in the US (Patrick et al. 1987). The sources include natural geological processes, waste disposal, spills and leaks, and application of chemicals to the soil. Numerous reports in the early 1980's of the systemic insecticide Temik (aldicarb) in ground water focused attention on the potential leaching of pesticides (Cohen et al. 1984). The discovery of the soil fumigant ethylene dibromide (EDB) in domestic and municipal wells in a number of states in 1983-84 provided additional evidence that some pesticides can indeed leach to ground water. In Connecticut, about 320 wells out of 1820 tested in the vicinity of tobacco fields were found to be contaminated with EDB (Frink and Hankin 1986) at concentrations exceeding 0.1 ppb. A smaller number also contained traces of another soil fumigant, 1,2-dichloropropane (1,2-DCP). A survey of 25 municipal ground water supplies (Frink and Hankin 1986) did not reveal the presence of compounds other than EDB and 1,2-DCP which are no longer in use.

Studies by Pignatello et al. (1989), however, showed that EDB may persist throughout the soil profile and continue to leach slowly to ground water for decades after application. Studies of the sorption of other organic compounds (Pignatello 1989) have shown that this phenomenon is not unique to EDB. Hence, there was a compelling need to determine what other chemicals might be present both in soil and in ground water at selected sites in an urbanized state such as Connecticut where pesticides are used in substantial amounts in both agricultural and residential areas (Frink 1987).

Accordingly, the Connecticut General Assembly mandated that a study of pesticide pollution of the ground

---

Send reprint requests to LQ Huang at the above address.

waters of the state be conducted by the Connecticut Department of Environmental Protection (DEP), in cooperation with the U.S. Geological Survey (USGS) and The Connecticut Agricultural Experiment Station (CAES). An interim report of the installation of the wells and the analyses of water samples during the first year of the study has been prepared by DEP (*Study of Pesticide Contamination in Connecticut's Ground Water, February 1988*) and a final report will be published by USGS at the completion of the 3-yr study.

The principal responsibility of CAES was to analyze soil samples for pesticides at selected sites and to prepare an interpretive report. In Massachusetts, Jenkins et al. (1988) found low concentrations of alachlor, metolachlor and atrazine in the upper 1 ft of soil and none in the profile below. However, our analyses of soil samples collected by USGS during 1987 using new and more sensitive analytical methods (Huang 1989) revealed the presence of these herbicides throughout the soil profile at a number of sites. These results have immediate and important implications for any study of the potential leaching of pesticides and hence are reported here.

MATERIALS AND METHODS

The first year of the study focused on aquifers in stratified drift in Connecticut's river valleys where the potential for leaching of pesticides is well documented by earlier studies with EDB. A total of 17 sites were selected by USGS, based primarily on accessibility of the site and the availability of records of applications of pesticides. Test holes and wells were installed at each site by USGS, and continuous soil cores were collected from the soil surface to the ground water. Representative sections of the cores were sampled for analyses for particle size and organic matter by CAES. Subsamples were collected in washed and hexane-rinsed bottles and frozen until analyzed for pesticides by CAES. Water samples were collected from the test wells and analyzed by USGS for the pesticides reported to have been used at the site. The sand, silt and clay content of samples from the soil cores were determined by the pipet method after treatment with hydrogen peroxide to remove organic matter (Black 1965a). Organic matter was determined by loss on ignition (Black 1965b).

The herbicides alachlor, metolachlor, atrazine, and simazine in the soil cores were analyzed as previously described (Huang 1989). Briefly, stable-labeled isotopes of ^{15}N, ^{13}C-alachlor and ^{2}H$_5$-atrazine were added to the soil samples as internal standards. After

1 hr of equilibration, the soil was slurried with 100 ml of MeOH/H_2O (9:1) and shaken by a wrist-action shaker for 2 hr. The herbicides were then isolated by a solid-phase extraction procedure and determined with a low resolution mass spectrometer coupled to a gas chromatograph (GC/MS) [Hewlett-Packard 5988A]. Quantitation was based on the amount and response of isotope-labeled herbicides added as internal standards which ensures that both good accuracy and precision are achieved (Huang 1989).

RESULTS AND DISCUSSION

One or more of the herbicides alachlor, atrazine, metolachlor and simazine were found in water from wells at five sites according to analyses by USGS (DEP, *Study of Pesticide Contamination in Connecticut's Ground Water, February 1988*). Four sites were agricultural corn fields and the fifth was a well located downgradient from experimental nursery plots at the Valley Laboratory of CAES at Windsor, CT. This site is the subject of ongoing investigations and will not be discussed further here.

Soil samples collected from the surface to the water table at the four remaining sites were analyzed, and typical results from two sites are shown in Tables 1 and 2. At both sites, the concentrations of atrazine and metolachlor are similar at each depth of soil despite the fact that metolachlor is about 20-fold more soluble in water than atrazine. The concentrations present in the soil at Franklin are higher than at Simsbury.

Table 1. Herbicides in Hinckley loamy sand at Simsbury. Simazine was not detected (<0.5 ppb).

Soil Properties			Herbicides, ppb		
Depth (ft)	Clay (%)	OM[a] (%)	Atrazine	Alachlor	Metolachlor
0-1.8	4.0	0.3	42.4	2.5	29.3
1.8-2.5	1.5	0.2	17.4	1.2	27.7
2.5-3.5	0.3	0.1	5.0	0.8	8.4
3.5-4.0	0.3	0.2	1.1	1.7	1.0
4.0-4.5	0.1	0.1	0.8	0.8	1.3
4.5-5.5	0.8	0.5	0.6	1.7	0.5
5.5-6.2	2.2	0.5	1.3	1.6	1.4
6.2-7.5	2.2	0.9	0.8	1.6	1.2

[a] Organic matter

Table 2. Herbicides in Ninigret sandy loam at Franklin. Alachlor was not detected (<0.5 ppb).

Soil Properties			Herbicides, ppb		
Depth (ft)	Clay (%)	OM (%)	Atrazine	Simazine	Metolachlor
0-0.9	3.6	11.4	900	6.9	846
0.9-2.5	5.0	3.4	21.7	nd[a]	5.4
2.5-3.0	3.9	1.3	26.4	nd	16.7
3.0-4.9	1.7	2.1	3.6	nd	2.5
4.9-5.9	1.4	2.1	1.7	nd	1.1
5.9-7.5	1.4	2.1	9.3	10.2	5.8

[a] nd = <0.5 ppb

Pesticides applied at Simsbury (Table 1) in the spring of 1986 and 1987 prior to sampling in 1987 were atrazine and metolachlor in the form of Bicep at the rate of about 2 qt per acre (Personal communication to C.R. Frink). The active ingredients (AI) in Bicep are 2.0 lb AI of atrazine and 2.5 lb AI of metolachlor per gal. At Franklin, Bicep was reported (Personal communication to C.R. Frink) to have been applied at the rate of 2 qt per acre yearly since 1985. Although the exact rates of application of Bicep at the two sites are not known, the results are consistent with the general expectation that less pesticide will be retained by sandy soils low in organic matter than by finer-textured soils or soils with higher organic matter content which tend to immobilize these compounds.

The results also show a distribution profile that is consistent with soil organic matter and clay content, particularly for atrazine and metolachlor, where the concentrations of the herbicides in the surface samples are much higher than those in the deeper samples. This distribution would also be expected since the herbicides are applied to the surface soil. Of greater importance is that the herbicides are detected continuously in the soil from the surface to the water table at 7.5 ft. Numerous studies have shown that microbial degradation is slower in subsoils (Cohen et al. 1984). Hence, the herbicide residues detected in deep soils in this study could be sources of leaching to ground water for many years.

The presence of alachlor at the site in Simsbury is attributed to its use in previous years since it is often used in mixtures with atrazine and metolachlor at similar rates. Though the concentration of alachlor in the soil is low, the residue is detected from the surface to the water table, showing the same leaching profile observed for atrazine and metolachlor. Simazine was also detected in soil at the Franklin site (Table 2), again apparently from its use prior to 1985.

The amounts of herbicides remaining in the soil are not trivial, particularly at the Franklin site. Numerical integration of the curve relating concentration and depth shows that the amounts still remaining in the profile are the equivalent of 3.5 lb AI per acre of atrazine and 3.2 lb AI per acre of metolachlor. The corresponding amounts at the Simsbury site are about 0.39 lb AI per acre of atrazine and 0.34 lb AI per acre of metolachlor.

This study strongly supports the earlier suggestion by Cohen et al. (1984) that herbicides retained throughout the soil profile following application constitute a potential for continued leaching to ground water.

Acknowledgments. We thank the Water Resources Division, USGS, Hartford, CT for supplying the soil samples.

REFERENCES

Black CA (1965a) Methods of soil analysis I. Physical and mineralogical properties including statistics of measurement and sampling. American Society of Agronomy, Madison, WI

Black CA (1965b) Methods of soil analysis II. Chemical and microbiological properties. American Society of Agronomy, Madison, WI

Cohen SZ, Creeger SM, Carsel RF, Enfield CG (1984) Potential for pesticide contamination of groundwater from agricultural uses. pp. 297-325. In: Kruger RF, Sieber JN (eds) Treatment and Disposal of Pesticide Wastes. ACS Symposium Series 259, Am Chem Soc, Washington, DC

Frink CR (1987) Uses of pesticides in Connecticut. Conn Agr Exp Sta Bull 848, 11p

Frink CR, Hankin L (1986) Pesticides in ground water in Connecticut. Conn Agr Exp Sta Bull 839, 10p

Huang LQ (1989) Simultaneous determination of alachlor, metolachlor, atrazine, and simazine in water and soil by isotope dilution gas chromatography/mass spectrometry. J Assoc Off Anal Chem 72:349-354

Jenkins J, Stone CT, Bowes J (1988) Alachlor monitoring of soil and ground water in two cornfields in western Massachusetts. In: Agricultural Impacts on Ground Water Conference, March 21-23, 1988, Des Moines, Iowa, p 443-474

Patrick R, Ford E, Quarles J (1987) Groundwater contamination in the United States, 2nd ed. Univ. of Pennsylvania Press, Philadelphia, PA

Pignatello, JJ (1989) Sorption dynamics of organic compounds in soils and sediments. In: Sawhney BL, Brown K (eds) Reactions and Movement of Organic Chemicals in Soils. Soil Sci Soc Amer Special Publ 22, Madison, WI (in press)

Pignatello JJ, Frink CR, Marin PA, Droste EX (1989) Field observed ethylene dibromide in an aquifer after two decades. J Contam Hydrol (in press)

Received October 8, 1988; accepted April 7, 1989.