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Landscape Care Pesticide Residues in Residential Drinking Water Wells

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The migration of agricultural pesticides to ground and surface waters is recognized as a potential problem. In 1990 the USEPA acknowledged this and reported on well waters from 1300 community water systems and rural domestic wells (USEPA 1990). They estimated that 10.4% of community water systems and 4.2% of rural domestic wells contained pesticides or pesticide degradates. This survey overrepresented agricultural areas with high use of pesticides. There are, however, useages of pesticides in settings other than agricultural settings. Surveys have shown that as many as fifty percent of American households have used pesticides on their landscapes (Templeton, et. al. 1998; Aspelin, 1997). This use includes treatments by homeowners in addition to those applications by licensed lawn and tree care companies. Although some pesticides, such as atrazine, are not used to a great extent by the commercial, home, and garden sectors of the pesticide market, other pesticides are used at rates which rival those applied in agricultural settings. For example, 31-36 million pounds of 2,4-D was applied in agricultural settings in 1995, but, an additional 17-22 million pounds were applied in non-agricultural settings. Similarly for chlorpyrifos the numbers are 9-13 million pounds in agriculture, 11-17 million pounds elsewhere (Aspelin 1997). Clearly, if protection of groundwater from pesticides is a goal, the contribution of landscape chemicals to the problem can not be ignored.

There have been many studies of pesticide residues in groundwater. These studies include surveys at the state-wide level (Wade et. al. 1998), watershed basin level (Grady and Mullaney 1998), and nationwide level (Kolpin et. al. 1998). Although these surveys may include residential areas, they tend to focus on agricultural settings and shallow groundwater wells. Other studies may focus on residential areas with an agricultural past, such as studies showing the presence of EDB in drinking water wells (Pignatello et. al. 1990, Mayer et. al. 1991). There are few studies which focus on landscape-care pesticide residues in residential drinking water wells. In fact, in a report to the legislature the Connecticut Department of Environmental Protection (1991) states “that most pesticides in use are not tested for...we have little or no information on pesticides other than EDB in drinking water wells”.

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This paper reports on a survey of water from 53 residential drinking wells in a single town in Connecticut. The town is a residential community which relies on groundwater for its potable water source. Although the actual usage of pesticides by all homeowners of the town is not known, 66% of the homeowners participating in this survey reported at least intermittent pesticide use. Each water sample was analyzed for 19 pesticide residues (herbicides, insecticides and fungicides) including some of those commonly used in residential landscape care. This study, therefore, provides an insight into the potential contamination of groundwater from residential usage of pesticides.

MATERIALS AND METHODS

All of the solvents used, including methanol, methylene chloride, hydrochloric acid, glacial acetic acid, iso-octane, and isopropanol were of pesticide grade from J.T. Baker (Phillipsburg, NJ). The 6 mL C-18 and SPE-500 solid phase extraction cartridges and 75 mL reservoirs were also obtained from Baker. Pesticide standards were prepared from authentic material provided by the various manufacturers or from the EPA repository (Research Triangle Park, NC).

One liter water samples were collected in precleaned glass bottles with Teflon lined caps from each well at a tap located prior to any water treatment system. Sample collection was performed in a manner which allowed spiked samples and blanks to be included without laboratory identification of either the blank or spike prior to analysis. Samples were kept under refrigeration until analysis. All analyses on a sample were completed within 1 week of sampling. Subsamples were taken from each bottle for processing via two solid phase extraction (SPE) procedures. Laboratory fortified samples were prepared immediately prior to analysis by addition of analytical standards dissolved in methanol at the mg/L level to a 200-250 mL subsample of well water (or distilled water) to generate fortified samples at concentrations ranging from 0.125-40 µg/L (depending on compound and procedure). These fortified samples were analyzed at a rate of one fortified sample per four well samples. All concentrations reported were corrected for recovery through the use of the fortified samples analyzed concurrent with that sample batch.

The first SPE procedure used 250 mL of sample acidified with 0.2 mL concentrated HCl. A J. T. Baker C-18 SPE cartridge was conditioned with 10 mL methanol, followed by 20 mL distilled-deionized (DI-DI) water, and 5 mL of acidified water (0.2 mL of concentrated HCl to 250 mL of DI-DI water). The sample was then passed through the cartridge. The cartridge was dried and eluted with sufficient methanol to fill exactly a 2 mL volumetric flask containing 0.3 mL acidified water. This eluate was used for liquid chromatography (LC) based analyses. The second SPE procedure utilized a J. T. Baker C-500 cartridge conditioned with 15 mL methanol and 7.5 mL DI-DI water followed by 200 mL

of sample. The cartridge was dried and eluted with sufficient 80/20 methylene chloride/methanol to generate 2.0 mL of extract. This extract was used for gas chromatographic / mass spectrometric analysis (GC/MS).

Five acidic herbicides (dicamba, MCPA, MCPP, 2,4-D, and 2,4-DP) were determined by high performance liquid chromatography with ultraviolet detection (HPLC-UV). A Perkin-Elmer (Norwalk, CT) Integral 4000 HPLC was used with the following chromatographic conditions: 20 µl injection, a Supelcosil (Supelco, Bellefonte, PA) LC-18 25cm x 4.6mm column with a 5µm particle size, UV detection monitoring the 280nm channel, 30 °C column temperature, isocratic elution at 0.8 mL/min with a mobile phase composed of 55/45, methanol/DI-DI water containing 1% glacial acetic acid. The instrument was calibrated with solutions of the five herbicides at four concentration levels.

Carbaryl was determined using HPLC-MS on a Hewlett-Packard (Wilmington, DE) 1090 LC interfaced to a Hewlett-Packard 5988 MS with an Analytica of Branford (Branford, CT) electrospray source using a Supelcosil LC-8 15cm x 2.1mm column with a 3 µm particle size. A mobile phase flow rate of 0.2 mL/min was used with the following gradient: initial 30/70 methanol/DI-DI water; from 5-15 min a linear gradient to 45/55; from 15-45 min a linear gradient to 60/40; from 45-50 min a linear gradient to 80/20 which was held for 2 minutes. The MS was operated in the selective ion mode, monitoring 3 ions ($[M+H]^+$, $[M+Na]^+$, and a fragment) for both carbaryl and 4-bromo-3,5-dimethylphenyl N-methyl carbamate which was used as an internal standard and added prior to SPE. The three ions of each compound were summed for quantitation.

The remaining pesticide residues (see Table 1) were analyzed using a Varian (Sugar Land, TX) 3800 GC interfaced to a Varian Saturn 2000 MS ion trap, with a J+W Scientific (Folsom, CA) DB-608 30m x .32mm GC column with a .5µm film thickness and He as the carrier gas. Samples were analyzed using a splitless 2 µl injection with a temperature program as follows 100 °C for 2 min, 5 °C/min to 260 °C and hold for 5 min. The MS was scanned from 106 - 450 daltons. Three ions were monitored for each pesticide with the most intense ion (or summed cluster for chlorinated compounds) used for quantitation. Response factors for each pesticide were developed through the analysis of pesticide standards at four concentrations. These response factors were updated on each date that samples were analyzed. Total chlordane was estimated as the sum of three monitored compounds, α-chlordane, γ-chlordane, and trans-nonachlor.

RESULTS AND DISCUSSION

The town selected for this study is a small (19.3 sq. mile, 8000 population), residential community in South-Central Connecticut. The town has a few farms and is zoned in two acre lots. Most homes in the town are serviced by private

drinking water wells. Soils in the area consist of till or stratified drift over a metamorphic bedrock (Mazzaferro et. al. 1979). Many residences in the town use commercial lawn and tree care companies in addition to those homeowners who apply pesticides themselves (in our survey 66% of the homeowners reported at least some use of pesticides with about half of those reports indicating regular use of pesticides). The town is, therefore, useful as a model town to investigate if residential applications of pesticides are contaminating homeowners groundwater.

Table 1. List of Pesticides Analyzed and Method Detection Limits (MDL).

Pesticide	Type	Analysis Method	MDL (µg/L)
dicamba	H	HPLC/UV	5.0
2,4-D	H	HPLC/UV	2.5
MCPA	H	HPLC/UV	2.5
2,4-DP	H	HPLC/UV	2.5
MCPP	H	HPLC/UV	2.5
carbaryl	I	HPLC/MS	0.10
trifluralin	H	GC/MS	0.02
diazinon	I	GC/MS	0.01
lindane	I	GC/MS	0.02
chlorothalonil	F	GC/MS	0.07
dacthal (DCPA)	H	GC/MS	0.02
chlorpyrifos	I	GC/MS	0.02
malathion	I	GC/MS	0.12
dicofol	I	GC/MS	0.13
isofenfos	I	GC/MS	0.13
DDE	I	GC/MS	0.07
DDT	I	GC/MS	0.16
methoxychlor	I	GC/MS	0.15
chlordane (total)	I	GC/MS	.05

Pesticide Type: H-Herbicide, I-Insecticide, F-Fungicide

Table 1 lists the pesticide residues analyzed in this study along with the detection limits. The limits are based on a signal to noise ratio greater than three for laboratory fortified samples taken through the entire procedure. The limits are, therefore, method detection limits, not instrumental detection limits, as they account for concentration factors and recovery of analyte. These pesticide residues include compounds currently applied by homeowners and lawn care professionals, as well as a few older pesticides which have been shown to be persistent in the environment (Bennett et. al. 1974). It can be seen from this table that the analytical method has a great influence on the method detection limits.

The analytical procedures used in this study were checked by the use of our laboratory fortified samples, laboratory blanks, and two samples spiked by the local water company and provided to the laboratory as blinds. The recovery of

pesticides from the laboratory fortified samples is shown in Table 2 along with the values we determined for the two spiked blind samples. Although the recovery of pesticide residues from fortified samples was less than ideal for some pesticides (i.e. dicofol at 18% recovery), it was fairly consistent, allowing us to correct for analyte recovery in the data. Our results for the two samples provided as blind spikes were reasonable when we consider that the sample concentrations were set for our least sensitive procedure, the analysis of acid herbicides via HPLCK/UV. The GC/MS procedure is 10 to 100 times more sensitive. Therefore, the concentration of pesticides in the blind spike was out of the calibration range used for the GC/MS. This data is supported by the fact that there is more error in the blind spike with the higher concentration. Also the acid herbicides and dacthal were provided as methyl esters which required an additional reaction procedure prior to the SPE. This additional procedure was developed after we had determined the sample to be the blind-spike, and was performed on a second subsample taken from the stored refrigerated sample.

Table 2. Average recovery of laboratory fortified samples and reported concentration for blind spikes. Blind A (all pesticides at 25 µg/L) and Blind B (all pesticides at 50 µg/L).

Pesticide	Average Recovery %	Blind A, µg/L	Blind B, µg/L
dicamba[1]	115	14	15
2,4-D[1]	130	15	47
MCPA[1]	130	22	50
2,4-DP[1]	130	*	*
MCPP[1]	101	38	75
carbaryl	108	23	50
trifluralin	36	37	126
diazinon	57	20	64
lindane	72	19	62
chlorothalonil	124	38	126
dacthal (DCPA)[1]	67	19	59
chlorpyrifos	40	21	69
malathion	51	24	124
dicofol	18	29	100
isofenfos	53	29	84
DDE	27	22	51
DDT	24	29	77
methoxychlor	31	44	191
chlordane (technical)[2]	28	27	76

1. Spiked as the methyl ester (see text).

2. Provided as the technical mix. Our quantitation was of the sum of three individual isomers (α–, γ–, and trans-nonachlor). A multiplication factor of 5 was used to convert this sum to a concentration in terms of technical chlordane.

*Compound not present in blind spike

Six of the 53 wells in our survey were found to be contaminated with at least one pesticide residue. This frequency of pesticide occurrence is less than that reported for the surficial aquifers in the Connecticut, Housatonic and Thames River basins (80% in agricultural areas, 60% in urban areas, and 48% in undeveloped areas) (Grady and Mullaney 1998), and shallow groundwaters throughout the United States (56% agricultural areas, 46% urban areas) (Kolpin et al 1998). Several factors could account for this lower frequency of detection. First, these studies focused on different groups of pesticides which would be expected to have different use patterns. Second, both of the previous studies examined shallow groundwater wells, not the deeper wells into bedrock which are used for the present study. The third possibility could be that for several of the pesticides in this study the method detection limit was simply not low enough for pesticides to be found (although these limits are sufficient to meet drinking water criteria). This third possibility is quite likely as Kolpin et. al. (1998) has shown that the frequency of detection is inversely proportional to the detection limit. As can be seen in Table 3, the average concentrations of the pesticides found is just above the most sensitive detection limits in this study (see Table 1). If some of the other pesticides were also present at this level they would not have been found. It should be noted that these pesticide concentrations do not exceed any maximum contaminant levels (MCL) for drinking water or reference dose (RFD) (assuming a 50 Kg person and 2 Liters of water consumed per day) as set by the United States Environmental Protection Agency.

Table 3. Concentrations of pesticides detected and regulatory limits in parts per billion (µg/L).

Pesticide	N[1]	Conc. (µg/L)[2]	MCL[3](µg/L)	RFD[4] (µg/L)
diazinon	5	0.02	a	2.3
dacthal (DCPA)	4	0.03	a	12500
trifluralin	3	0.04	a	4700
lindane	1	0.06	0.2	7.5
chlorpyrifos	1	0.06	a	75
chlordane	1	0.22	2	1.5

1. Number of wells with the pesticide
2. Average concentration in the N wells
3. Maximum Concentration Level- Data taken from the Extension Toxicology Network, Pesticide Information Profiles, Files archived and maintained at Oregon State University.
a- data not available
4. Reference Dose - Data taken from the Extension Toxicology Network, Pesticide Information Profiles, Files archived and maintained at Oregon State University. Reference dose converted to concentration by assuming a 50 Kg person and a 2 Liter per day water consumption.

It is more difficult to determine the source of the pesticide residues in these drinking water wells. The physical properties of the pesticides would seem to indicate that they should not migrate to a deep underground aquifer, though the presence of pesticide residues in shallow wells as reported by others does show some potential for transport (Grady and Mullaney 1998, Kolpin et. al. 1998, Wade et. al. 1998). The wells with pesticide residues detected did not cluster together in a single geographic region of town. This indicates that the pesticides found were likely not the result of a single large scale contamination of the groundwater. All of the wells with pesticides found were drilled into the bedrock and most wells were 30 or more years old. The bedrock in this area is a fractured metamorphic rock. Several hypotheses for the source of these pesticides may be advanced. There could be faults in the well casings allowing surface water into the wells. There could be large fractures in the bedrock which result in relatively fast flow of groundwater and recharge from the surface. It is also possible that the long term usage of these pesticides has allowed the pesticides to leach into the groundwater source despite their unfavorable physical characteristics. The scope of this study did not allow us to determine the mechanism by which these wells are being contaminated.

Five of the six wells with pesticide occurrences were resampled to confirm the presence of pesticide residues. This resample occurred approximately two months after the initial sampling. Although all five still had low levels of pesticides, the mix of pesticides found had changed. Diazinon was no longer detected while dacthal was found in all five resampled wells and trifluralin was found in two of the five wells at approximately the same average concentration as previously observed. There are several possible explanations for these data: 1) These data could be related to a different seasonal use pattern with a quick transport of contaminants from the surface. 2) They could be the result of differences in rainfall and groundwater recharge prior to sampling. 3) They could result from the high variability seen in analytical measurements at concentrations extremely close to the limits of detection, or, other errors in sampling and analysis. Many more samples are needed to test the various hypotheses.

These results show the presence of landscape care pesticides in deep groundwater wells from a residential suburban community. Although only a small percentage of the wells were found to have pesticide residues, and, the concentrations found were below levels of concern, these findings do indicate that pesticides can potentially contaminate the deep groundwater used by homeowners. To illuminate fully the scope of the contamination further research is necessary. First, a more widespread regionwide set of samples would allow us to determine how typical these results are for a community. Secondly, a smaller subset of wells should be monitored on a regular basis. This would allow us to determine if there is a seasonal aspect to the pesticide occurrences. In any case, this research does show the potential for contamination of drinking water, and therefore

supports the idea that land management practices which reduce pesticide use should be instigated when possible to reduce that potential contamination.

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