AN ABSTRACT OF THE THESIS OF

Lance O. Gatchell for the degree of Master of Science in Bioresource Engineering presented on June 6, 1996. Title: Monitoring Potential Groundwater Contamination due to Agricultural Production in Lane County, OR.

Abstract approved: _____

John S. Selker

Preventing groundwater contamination due to NO_3 and pesticide leaching requires identifying agricultural systems that give rise to elevated recharge concentrations. This is most conclusively accomplished through direct sampling of groundwater recharge concentrations below the root zone.

To determine an adequate sampling strategy, a study was conducted to investigate optimum separation distance for subsurface samplers. Soil cores were collected on five farms in Lane County, Oregon at 1 m depth and soil water was analyzed for NO_3 concentration. Semivariogram analysis indicated NO_3 concentrations autocorrelated to a range of 75 m on two greater than 1 ha fields, 40 m on two smaller fields, and random on one field. We conclude that a separation distance of 75 m may be justified when installing two or more lysimeters under fields greater than 1 ha in size, and 40 m in smaller fields. However, the variability not due to spatial structure ranged from 33% to 100% by inspection of the semivariogram nugget to sill ratios, and depending on the accuracy required, sample separation may thus not be justified.

Although pesticides are regulated to prevent leaching, their movement into aquifers remains an international public health concern. This is partially due to soil

macropores being very difficult to incorporate into pesticide leaching prediction models due to their heterogeneous and ephemeral nature. Given the unreliability of models, in-situ screening for pesticide leaching is necessary for predicting future groundwater contamination. Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine], Simazine [2-chloro-4, 6-BIS(ethylamino)-s-triazine], and Terbacil [5-chloro-6-methyl-3-butyluracil] leaching were assayed for in percolate collected in wick lysimeters installed at 1 m depth on six farms in Lane County, Oregon. Atrazine and Simazine were analyzed using immuno-assay, and Terbacil using gas chromatography. Twenty-one month flow weighted concentrations of Terbacil were 32.4, 18, and 80 ppb; below the drinking water standard of 90 ppb. Atrazine was not detected over the drinking water standard of 3 ppb. Simazine was detected at 3.56 ppb, slightly over the 3.5 ppb drinking water standard. From this study, pesticide leaching does not appear to be a serious threat in this area.

Monitoring Potential Groundwater Contamination due to Agricultural Production in Lane County, Oregon.

by

Lance O. Gatchell

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Dean of Graduate School

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Lance O. Gatchell

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1. GENERAL INTRODUCTION

Preventing groundwater contamination due to nitrogen fertilizer and pesticide leaching requires identifying agricultural systems that give rise to elevated recharge concentrations. This is most conclusively accomplished through direct sampling of groundwater recharge NO_3 concentrations below the root zone. Spatial structure of NO_3 concentration in recharge dictates minimum separation distance between samples for independent results. The study reported in chapter 2 was conducted to determine optimum separation distance for wick pan lysimeters as determined by the range of spatial autocorrelation of below root zone NO_3 concentrations. Secondarily, we investigated the resampling requirements (number of samples required when resampling) to estimate the mean NO_3 concentration.

Although pesticides are regulated to prevent leaching, their movement into aquifers remains a public health concern. This is partially due to soil macropores being very difficult to incorporate into pesticide leaching prediction models due to their heterogeneous and ephemeral nature. Given the unreliability of models, in-situ screening for pesticide leaching is necessary for predicting future groundwater contamination. In the study reported in chapter 3, leachate sampling for pesticide concentrations in groundwater recharge was investigated below agricultural production in Lane County, Oregon.

Chapter 2

Spatial Variability of Nitrate in Groundwater Recharge under Horticultural Crops

Lance O. Gatchell and John S. Selker

ABSTRACT

Preventing groundwater contamination due to nitrogen fertilizer leaching requires identifying agricultural systems that give rise to elevated recharge concentrations. This is conclusively accomplished through direct sampling of soil water NO_3 concentrations below the root zone. Spatial structure of NO_3 concentration in leachate dictates minimum separation distance between samples for independent results. This study was conducted to determine the optimum separation distance for wick pan lysimeters as determined by the range of spatial autocorrelation of below root zone NO_3 concentrations. Secondarily, we investigated the resampling requirements (number of samples required when resampling) to estimate the mean NO_3 concentration. Soil cores were collected on five different size production farms in Lane County, Oregon at 1 m depth and soil pore water was analyzed for NO_3 concentration. Semivariogram analysis indicated NO_3 concentrations were autocorrelated to a range of 75 m on two fields with areas greater than 1 ha, 40 m on two smaller area fields and random on one field. We concluded that for fields in the southern Willamette Valley a separation distance of 75 m between each wick lysimeter is justified when installing two or more lysimeters in fields greater than 1 ha in size. In smaller fields, a separation distance of 40 m provides statistical independence. However, investigation of nugget to sill ratios indicated that from 33% to 100% of the variability was not due to spatial structure. Therefore, depending on the field considered, separation of two wick lysimeters may not be reasonable given the added cost of installation at large separation distances.

INTRODUCTION

Nitrate contamination of groundwater due to leaching of agricultural fertilizer is widespread (Bergstrom and Brink, 1984; CAST, 1985; Commission of the European Communities, 1991; Owens et al., 1992; Barry et al., 1993; Jemison and Fox, 1994; Owens, et al. 1994; Owens et al., 1995; Meek et al., 1995). Contamination often results from agricultural management practices chosen to maximize crop yields. Excess fertilizer application often provides an economic return by assuring maximum crop growth with a relatively low cost (Jemison and Fox, 1994). Greater than 10 ppm NO_3-N in drinking water poses a potential public health threat of methemoglobinemia, particularly for infants consuming the water, which has led to designation of maximum contaminant level (MCL) at this level (Comly, 1945; U.S. Public Health Service, 1962; Swaan, 1975; CAST, 1985; Keeny, 1986). High NO_3 water also potentially increases cancer risk due to NO_3-N transformance to nitrosamimes which are known carcinogens (Wolf and Wasserman, 1972; Swaan, 1975; Weisenburger, 1993). Presently, agricultural managers and scientists are working to prevent groundwater contamination by monitoring agricultural leachate. Leachate monitoring can help managers determine the magnitude of contamination as well as the effectiveness of adjusting fertilizer application rates, and other management alternatives such as irrigation scheduling and cover cropping.

Leachate monitoring requires the use of sampling devices and strategies that accurately measure NO_3 flux (water volume and nitrate concentration) below the root

zone. Sampling alternatives include the use of soil cores, vacuum suction samplers, and lysimeters. The most suitable below root zone monitoring device in many conditions is a wick lysimeter due to its ability to directly measure NO_3 flux (Holder et al., 1991; Boll et al., 1992; Polletika et al., 1992; Knutson and Selker, 1994; Steenhuis et al., 1995). Some bias has been noted between methods which obtain resident soil water concentrations vs. flux concentrations (Brandi-Dorhn et al., 1996), although the effect on observed NO_3 concentration has been minimal. Designing a sampling strategy to determine the field average nitrate flux in groundwater recharge requires sampling a representative elementary volume (REV), a sufficient number of REV's to cover the area in question, and separation distance between samples which yield independent results (Folorunso and Rolston, 1984; Parkin et al., 1987; Rice and Bowman, 1988; Starr et al., 1992; Parkin, 1993; Cambardella et al., 1994). Aspects of sampling strategy are always constrained by financial resources.

Of critical importance in leachate monitoring is determining the separation distance for samples required for independent results. This is important because nitrate flux below the root zone may be patchy with significant variation over the field scale. Assessing mean NO_3 flux may require monitoring in a spatially distributed manner. The heterogeneity of NO_3 flux is influenced by intrinsically variable physical, chemical and biological soil properties (Wagonet and Rao, 1983). Extrinsic factors such as fertilizer application and plant uptake also create spatial variability in NO_3 flux. Separation distance required for independent sampling of NO_3 flux is based on the structure of NO_3 spatial variability, which can be defined with geostatistics (Clark, 1979; Oliver, 1987).

Geostatistics, originally developed for use in the mining industry (Matheron, 1963), is commonly used for characterizing spatial structure of natural phenomenon (Robertson, 1987; Martinez-Cobb and Cuenca, 1992), and characterizing spatial structure of soil properties (Haan, 1977; Vierra, 1983; Wagonet and Rao, 1983; Rao and Wagonet, 1985; Hamlett, et al., 1986; Parkin, 1993; Cambardella, 1994). The aspect of geostatistics most essential for determining sample separation distance is the semivariogram. Semivariograms plot the relationship between semivariance of sample value pairs and their separation distance. Semivariance, $\gamma(h)$, is commonly estimated as:

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} [z(i) - z(i+h)]^2 \tag{1}$$

where h is the measurement distance between points, z(i) is the measured value (e.g. NO_3) at location i and z(i+h) is the value at another location a distance h away. N(h) is the number of sample pairs, separated by distance h (Clark, 1979). The distance, h, is called the *lag*. The *sill* of a semivariogram is the semivariance at which semivariance no longer increases with lag. The *range* of a semivariogram is the lag distance at which semivariance is no longer increasing. The *nugget* of a semivariogram is the semivariance at the minimum lag distance (h=0). The nugget shows that variation exists at distances less than the minimum lag (sampling error and position independent variability). The *range* is the value sought for determining sample separation distance. Pairs of samples far enough apart that they are beyond the range of the semivariogram are independent of

each other which minimizes redundancy. For further geostatistics discussion, see Clark (1979), or Oliver (1987).

Previous studies of NO_3 spatial variability addressed the root zone (e.g. Robertson, 1987; Bramley and White, 1991; Cambardella et al., 1994; Cahn et al., 1994). These studies differ in their semivariogram estimations of range from less than 5 m to over 150 m. Some show no spatial structure of NO_3 (i.e. NO_3 concentrations appear to be purely random). For example, Tabor et al. (1985) examined NO_3 concentrations in 2.5 cm diameter soil cores to a depth of between 15 and 20 cm (49 samples in a 360 by 360 m plot) and found a range of 150 m. Robertson (1987) found NO_3 had a semivariogram range of about 10 m on a 1-50 m scale on a native Michigan grassland. Van Meirvenne and Hoffman (1989), using 247 samples to a 1 m depth in loamy sand (1 ha) cropped in potatoes, found the NO_3 range of autocorrelation increased during the winter. Ranges reported were 9.5, 25 and 34 m in October, February and April, respectively. Bramley and White (1991), using composites of two 5 cm diameter soil cores at 10 sites to a 24 cm depth in 3 cm layers on a 625 m^2 area, reported nitrate had a 12 m range (slightly extrapolative given the small sample number and area). Cambardella et al. (1994), in a watershed study of well to poorly drained loam soils (using 6 and 8 cm diameter soil cores from 0-15 cm depth), found NO_3 had a 150 m range on a no-till 6.25 ha field, and no definable range (random) on a 10 ha tilled field. Cahn et al., (1994) examined the 0-15 cm layer of silty loam and silty clay loam soils in a 3.3 ha field cropped with a corn-soybean rotation. They found a NO_3 range of autocorrelation of less than 5 m. Mohanty and Kanwar, (1994) investigated NO_3 variability using 3.2 cm diameter soil cores on a

1390 m^2 area. They found no range of autocorrelation, but noted a decrease in CV with depth, suggesting more uniformity of nitrate concentrations lower in the profile.

A students t-test can be employed to assess variability (but not spatial structure) by elucidating the number of samples required in resampling to estimate the mean within some acceptable level of accuracy (Snedecor, 1967; Dahiya et al., 1984a; Bowman, 1991). This test assumes random sampling, spatial independence, and normal distribution. The resampling requirement is based on the number of samples originally collected and the CV of the original data. The equation used to estimate number of samples required is:

$$N = \{[t/E]CV(\%)\}^2 \qquad (2)$$

where t is the students t value at some probability (e.g. 0.01). The parameter E is the allowable error, or inversely degree of precision in estimating the mean (e.g. 10%). CV(%) is defined as the standard deviation of the mean divided by the mean given in percent (Snedecor, 1967). Although this method assumes a normal distribution, it is robust to non-normality (Wulff, 1995, personal communication). Using a natural log transform of the data makes E a multiplicative rather than additive error in equation 2, and thus N calculated from ln-transformed data cannot be compared to N from untransformed data. Estimating the number of samples required to estimate the mean with this formula allows for comparison between fields, and is useful for comparing required number of samples between different studies (Van Meirvenne and Hoffman, 1989; Bowman, 1991).

Researchers have reported CV's of NO_3 in surface soils. Dahiya et al. (1984a) examined the 0-30, 30-60, and 60-90 cm depths on a 10 ha field, and found NO_3 had CV's of 23%, 29%, and 29% for the three depths, respectively. Dahiya et al. (1984b) constructed semivariograms of the same data, and found NO_3 had no definable range of autocorrelation. Bowman (1991) investigated 2 cm diameter cores at 0-10 cm and 10-20 cm depths, and found the CV for NO_3 concentration ranged between 18.7% and 30%. Their closest spacing was 30 m, and ranges of autocorrelation may have existed at shorter distances.

The objectives of this study were: (1) to determine optimum spacing for wick lysimeters as determined by the range of spatial autocorrelation of NO_3 concentrations below the root zone; (2) to investigate possible lack of correlation between values of NO_3 concentration in soil cores and wick lysimeter collections from the same fields at the same times; and (3) to investigate the CV's of data sets for resampling requirements to estimate the mean using a students t-test. Based on literature review we hypothesized that spatial structure of NO_3 may exist, and tested this using soil cores below the root zone at known locations.

MATERIALS AND METHODS

Study Area

Our study was conducted on five farms in Lane County, Oregon between January, and April, 1995. The farms were located in the Willamette River alluvial valley, which is extensively used for agricultural production of grass seed, mint, orchard, dairy and row crops. The water table in the valley is 3-4 m below the surface during the summer, and perched in places during the winter due to clay deposits. The soils we studied were loams, and each series is listed in Table 2.1. The farms chosen were part of an already established wick lysimeter study looking at NO_3 leaching under agricultural production in Lane County, Oregon (Shelby, 1995).

Procedures

Computer generated sample locations evenly distributed them in each of 10 distance classes to optimize construction of semivariograms according to Warrick and Myers, (1987). Forty locations were sampled on each site (except Mint #3). Sixteen of these locations were centered on a 4 x 4 grid, and 24 were generated according to Warrick and Myers, (1987) (Figure 2.1). This method promotes the possibility of a well defined semivariogram (Warrick and Myers, 1987).

Table 2.1. Summary of Sampling.

| Farm Site	Soil Series	Sampling Month	Sampling Area (m^2)	Number of Samples	Core Length (cm)	Minimum Lag (m)	Maximum Lag (m)
Organic #2 (Fenugreek)	Awbrig Silty Clay Loam	February	5376	40	30	2	106
Row Crop #2 (beets)	Newburg Loam	April	2304	40	15	2	58.6
Row Crop #3 (wheat)	Malabon Silty Clay Loam	February	7800	40	32	2	118
Mint #3 (pepermint)	Newburg Fine Sandy Loam	January	40600	21	29	14	206
Mint #4 (pepermint)	Malabon Silty Clay Loam	March	24000	40	25	4	236
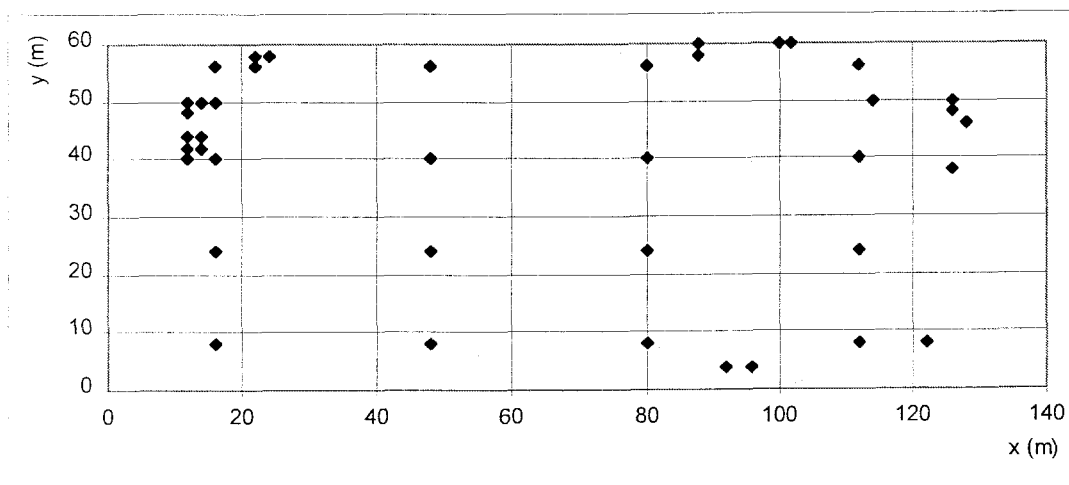
Figure 2.1 Example of sample locations (Row Crop #3) generated according to Warrick and Myers, (1987)

The site referred to as Mint #3 had a different sampling and analysis protocol than the other four in this study, as it was carried out prior to the establishment of the final

sampling procedure. Fifty-one locations were chosen in a nested grid pattern. Twenty locations were chosen at selected intersections on a 20 m grid, and 31 were chosen inside one 20 x 20 m block of that grid on a 2 m grid. The samples inside the 20 x 20 m block were averaged to represented one sample in the middle of the block. Mint #3 was treated as 21 samples rather than the original 51 samples

Wick lysimeters consisted of a collection vessel, vessel support box, fiberglass wicks, and access tubes. They were installed under undisturbed soil accessed from a 1 m x 10 m x 2 m deep trench. The collection vessel was a 60 liter High Density Polyethylene (HDPE) container 24 x 78 x 32 cm. An HDPE tube allowed pumping collected water samples to the surface after installation. High density polyethylene was used due to it's lack of chemical adsorption (Topp and Smith, 1992). The collection vessel was placed inside a fiberglass box (33 x 87 x 62 cm) for support. The top of each box was fitted with a 2700 cm^2 stainless steel plate to support wicks and catch percolating water. Wicks were chosen to match soil matrix potential according to Knutson and Selker (1994) (see Shelby, 1995 for details). All holes were sealed to prevent water leaking into the support box.

Soil samples were obtained using a 1.75 cm diameter soil core sampler. Three soil cores within 1 m^2 at each location were composited, and a 50 g subsample was taken. For comparison of soil core sampling with wick lysimeter sampling, the lysimeters were sampled at the time of soil core collection after a rainfall event (except Row Crop #2). The soil cores were taken from 1 m depth downward to a length equivalent to that of water in the lysimeters at the time of sampling using an estimated soil water content of

20% (e.g. 2 cm depth in the lysimeters = 10 cm long soil core). Soil core length ranged from 10 to 30 cm (Table 2.1). The subsamples were placed in sealed plastic bags and put on ice within 20 minutes of sampling. The soil cores were stored in a 1 $^{\circ}$C. refrigerator for no more than 24 hours before the water was extracted.

Water was extracted from the soil samples using a 20 minute shaking in water procedure (Bremner, 1965). A soil subsample (approximately 25 g) was placed in a clean, weighed HDPE container with approximately 50 ml of cold water. Exact weights were measured with a balance and noted. The solution was cooled in a freezer to near freezing and then shaken for 20 minutes. Large soil particles were allowed to settle for 8 hrs in a 3 $^{\circ}$C cold room, leaving a turbid solution. Three mL of solution was removed with a syringe, and centrifuged for five minutes at 12000 rpm in a Sorvall MC 12V micro-centrifuge to clear the solution in preparation for ion-chromatography. The clear solution was analyzed on a Dionex 2000i ion-chromatograph (IC) for NO_3 concentration. The remaining solution and settled soil in HDPE containers were oven dried for at least 48 hours at 45 $^{\circ}$C. to oven dry the soil, and weighed. The dilution factor from adding water was calculated and multiplied by the IC results to give the original soil water NO_3 concentration.

Data Analysis

Semivariograms were constructed using GEO-EAS, a United States Environmental Protection Agency software package (Englund and Sparks, 1991). We standardized semivariograms by dividing the semivariance by sample variance. We

tested for robustness by removing outliers, and by natural log (ln) transforming the data and then recalculating semivariograms. Recalculated semivariograms were inspected for changes from original semivariograms. We observed distances up to one-third the maximum lag distance to visually interpret the range of spatial autocorrelation (J. Jones, 1996, personal communication). The sill and nugget were also determined by visual interpretation, and their ratio was used to determine the fraction of the overall variability in the data that was due to spatial structure versus pure randomness.

For the students t-test the data was assumed spatially independent, random, and normally distributed. Sample mean, CV, skewness (g_1), kurtosis (g_2), and the normal probability plot correlation coefficient (r) were calculated. The normal distribution has a g_1 statistic of zero and a g_2 statistic of 3 (Snedecor, 1967). The value of r to consider a sample set normally distributed at the 5% critical value is 0.972 for 40 observations, 0.971 for 39 observations, and 0.952 for 21 observations (Filliben, 1974). Skewed data sets were natural log transformed to test the fit to the lognormal distribution. For inspection of the raw data, histograms were prepared.

The CV from untransformed data was used to estimate the resampling requirements to determine the mean within different desired precisions (equation 2). The students t value used was for a 90% confidence and 39 degrees of freedom (except Mint #3 where 20 degrees of freedom was used) (Snedecor, 1967).

RESULTS
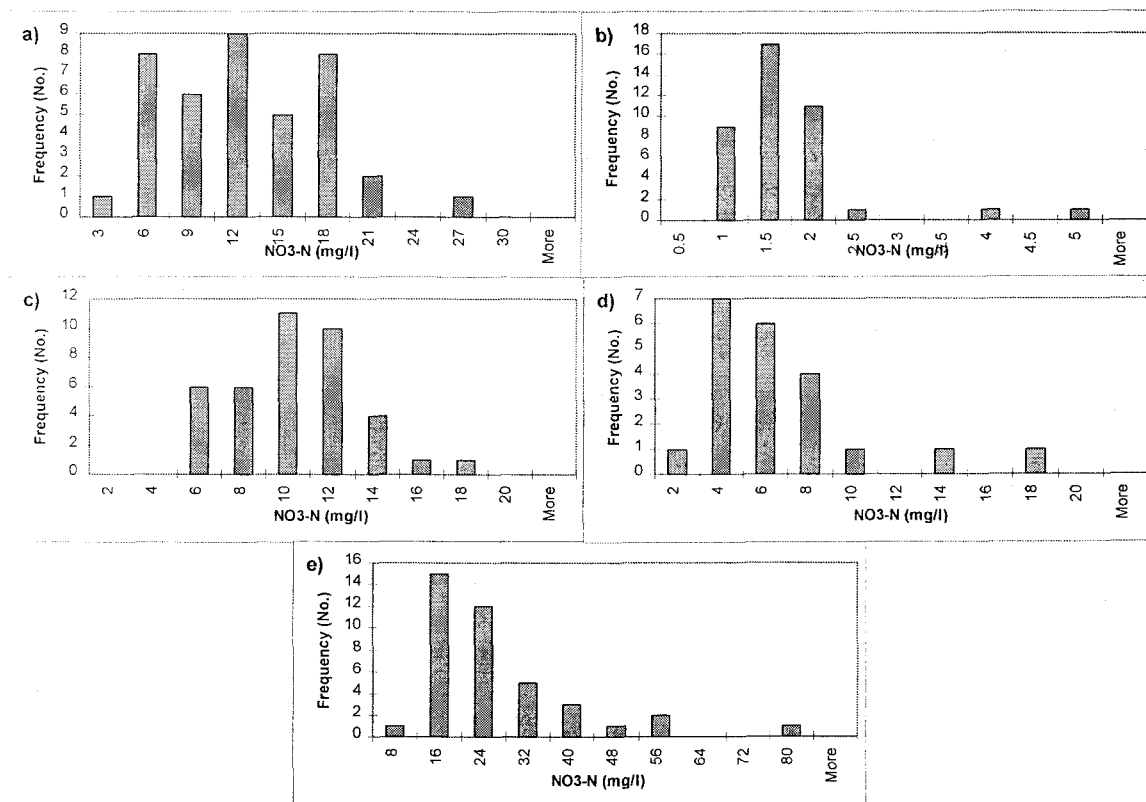
Figure 2.2. Histograms of nitrate concentrations for a) Organic #2, b) Row Crop #2, c) Row Crop #3, d) Mint #3, e) Mint #4. Note the different scales.

Histograms showed data was skewed to the right in all cases with outliers occuring as sample values with much higher nitrate concentrations than the bulk of the data (Figure 2.2). The various study sites had significantly different ranges of NO_3 concentrations, from 1 to 5 mg/l to 2 to 80 mg/l.

Semivariograms had ranges of autocorrelation from 0 to 75 m (Figure 2.3). Row Crop #2 appeared to have a 0 m range for original, outliers removed, and ln-transformed

data. The semivariogram obtained for Row Crop #2 changed shape markedly when outliers were removed and data was ln-transformed. Row Crop #3 had a range of 40 m, was determined to have no outliers to remove, and was not altered in shape significantly by ln-transformation. Mint #3 appeared to have a range of 75 m for original, outliers removed, and ln-transformed data, although the shape of the semivariogram changed with the adjustments in data. Mint #4 also appeared to have ranges of 75 m for all three adjusted data sets, but had less slope, and greater nugget than Mint #3. Organic #2 exhibited random ranges for the original and ln-transformed data, but appeared to have a range of 40 m when the outliers were removed (Figure 2.3).

Semivariograms had sill to nugget ratios ranging from 0.33 (one third of spatial variability due to randomness) to 1.0 (pure randomness). Row Crop #2 had a nugget to sill ratio of 0. Row Crop #3 had a nugget to sill ratio of 0.56. Mint #3 had a nugget to sill ratio of 0.33 using the Ln-transformed data. Mint #4 had a nugget to sill ratio of 0.5 using the Ln-transformed data. Organic #2 had a ratio of 0.33 using the outliers removed semivariogram.

Figure 2.3. Standardized semivariograms of original data (O), outliers removed (OR), and Ln-transformed (LN) for each of the five study sites; Row Crop #2 (A-C), Row Crop #3 (D-E), Mint #3 (F-H), Mint #4 (I-K), and Organic #2 (L-N).

Standardized Semivariance

Lag Distance (m)
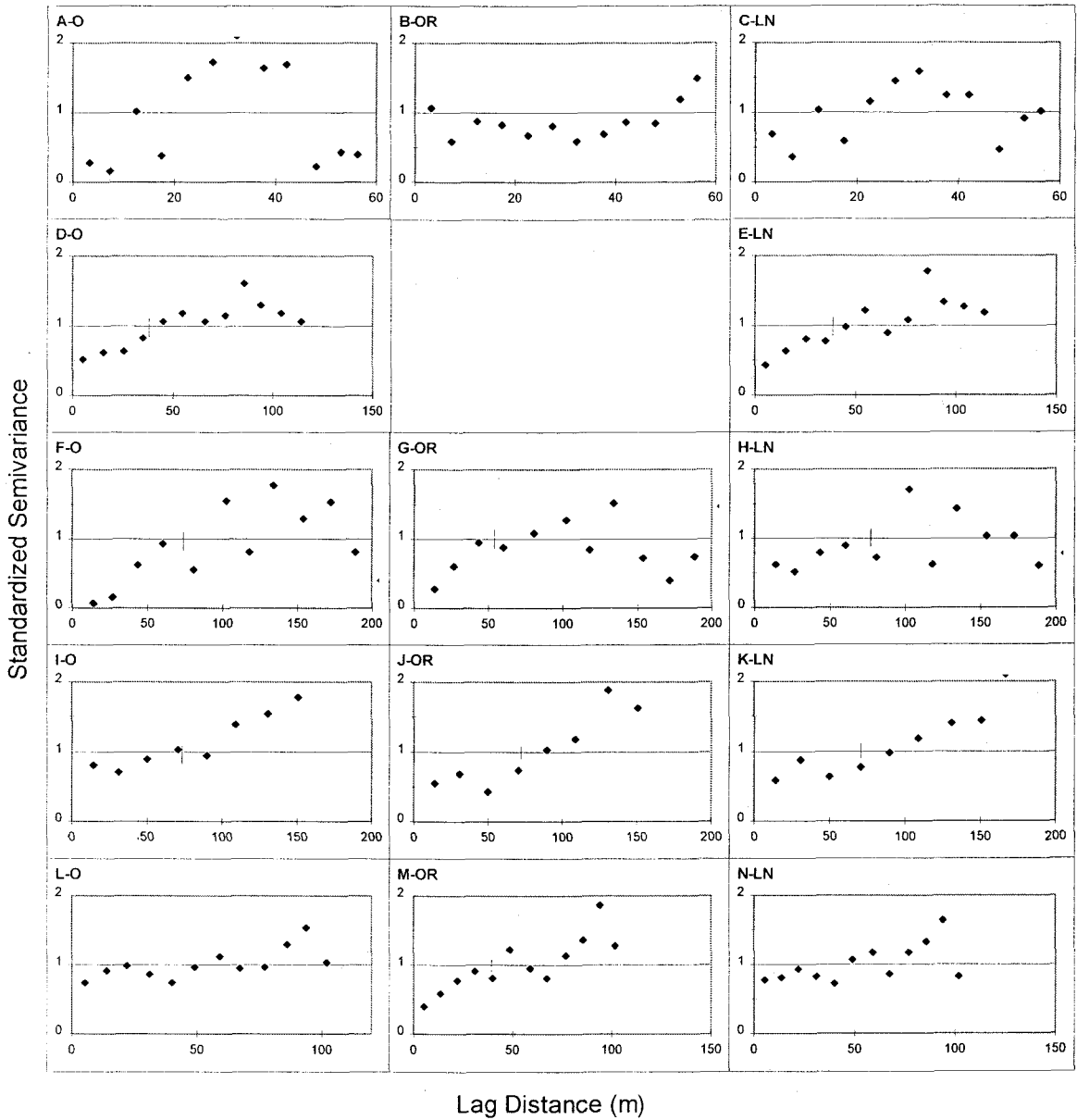
Results of comparison between wick lysimeters and mean soil core nitrate concentrations indicate no correlation between soil average and lysimeter results (Table 2.2). Organic #2 had much lower mean nitrate concentration from the soil cores than both lysimeters. Row Crop #3 had higher concentrations from soil cores than lysimeters. Mint #3 soil cores mean had similar low concentrations to the lysimeters. Mint #4 concentrations from the soil cores were much higher than in lysimeters. The lysimeter results for Organic #2 differed by a factor of two, and for Mint #4 by a factor of five.

Table 2.2. NO_3-N concentrations in lysimeters and soil cores at time of soil sampling.

	Organic #2	Row Crop #3	Mint #3	Mint #4
Soil Average	11	10	3	22
Lysimeter 1	32	6	1	2
Lysimeter 2	16	4	2	10

For the data sets on each of the five study sites the sample mean, CV, range of values, skewness and kurtosis were calculated (Table 2.3). The mean nitrate concentrations from the soil cores ranged from 1.44 mg/l to 22 mg/l. The CV's ranged from 31% to 64% for the untransformed data. Considering the consistency of the distribution of the data to the normal distribution Row Crop #3 was most consistent. By Filliben probability plot correlation coefficient test for normality Organic #2 and Row Crop #3 data were accepted as normal distributions. Mint #3 and Mint #4 data were accepted as ln-normal distributions. Row Crop #2 data could not be accepted as normal or ln-normal, but was nearer to fit a ln-normal distribution than normal.

Table 2.3. Mean (m), coefficient of variation (CV), range of values, skewness (g_1), kurtosis (g_2), and probability plot correlation coefficient (r) for each of the five field sites, and the log-transformed statistics for Row Crop #2, Mint #3, and Mint #4.

Farm	m (mg/l)	CV (%)	range	g_1	g_2	r
Original Data						
Organic #2	11.0	48	2.5-27	0.57	3.3	0.976
Row Crop #2	1.44	52	0.52-4.7	2.7	11.5	0.883
Row Crop #3	9.50	31	4-17	0.35	2.8	0.991
Mint #3	5.59	62	1.6-16	1.8	5.7	0.881
Mint #4	22.0	64	7-65	1.7	6.3	0.903
Ln-transformed Data						
Row Crop #2	2.42	29		1.39	6.40	0.962
Mint #3	4.93	25		0.63	3.33	0.992
Mint #4	19.9	19		0.34	2.68	0.989

Numbers of samples required in resampling calculated according to equation 2 ranged from less than 20 to more than 50 for a 15% degree of precision in estimating the mean (Figure 2.4). For Mint #4 the number of samples required would be more than 100 if less than 10% error was necessary. If a degree of precision less than 20% is not necessary, then no more than 30 samples would be required for any of the sites (Figure 2.4). Mint #3 and Mint #4 had similar CVs, largest areas, and most intensive resampling requirements. Row Crop #3 had the smallest area, smallest CV, and least intensive resampling requirements.

Figure 2.4. Chart of sample size required to estimate the mean vs. degree of precision required according to $N = \{[t/E]CV(\%)\}^{\wedge}2$ using an α-level of 0.1.
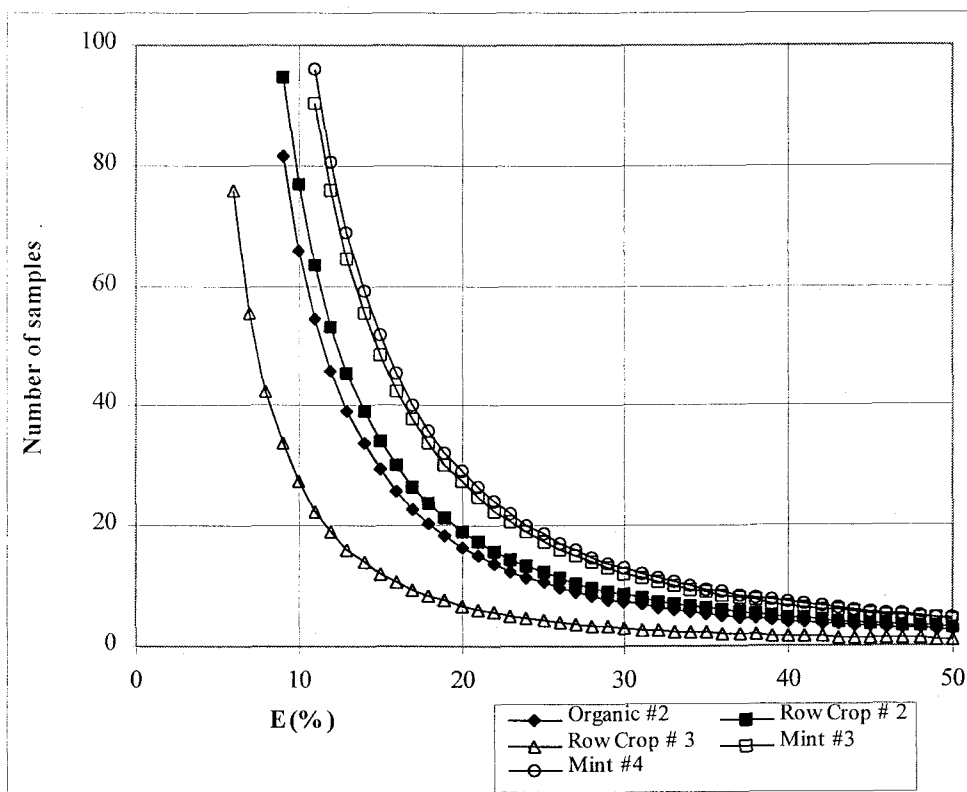
DISCUSSION

Ranges of spatial autocorrelation of NO_3 observed at the 1 m depth were consistent with surface soil studies in that they were related to size of field investigated, and that they fell within the range of ranges previously noted. Previous studies noted ranges of spatial autocorrelation from zero (Mohatany and Kanwar, 1994; Dahiya et al., 1984b) to over 150 m (Tabor et al., 1985; Cambradella et al., 1994). We observed smaller areas had shorter ranges. Our smallest area (2304 m^2) showed zero spatial autocorrelation, our two medium size areas (5,376 m^2 and 7,800 m^2) had ranges of 40 m, and our largest two areas (24,000 m^2 and 40,600 m^2) had ranges of 75 m. These results are consistent with Tabor, et al. (1985) and Cambardella et al., (1994) who noted 150 m ranges on 129,600 m^2 and 62,500 m^2 areas, respectively. Further, Bramely and White (1991) noted a 12 m range on a 625 m^2 area. In contrast, Cahn et al., (1994) found a less than 5 m range on a 33,000 m^2 area.

In order to make correlations between size of area and range of NO_3 autocorrelation, more controlled research is needed. Our goal, however, was to determine the optimum separation distance for wick lysimeter samplers. From our studies and others, it is obvious smaller areas need less separation distance for wick lysimeter samplers to obtain independent samples. This is likely due to larger areas having more variability in soil type, slope, and crop growth. Our results indicate that samplers need separation of 40 m in less than 1 ha, and 75 m in more than 1 ha agricultural areas in some cases. However, the nugget to sill ratio on the two greater than 1 ha area fields were 0.33 and 0.5. This suggests that sampling without the 75 m separation distance on

this size field one may obtain one-third to one-half the accuracy as that obtained with the separation distance. The smaller two fields, Organic #2 and Row Crop #3, had nugget to sill ratios of 0.33 and 0.56, respectively, also indicating that a similar loss of accuracy can be expected without the 40 m separation distance. However, this semivariogram analysis came from particular fields, and one is not guaranteed to obtain the same results on other fields, particularly given the intrinsic variability in soils.

Results to determine the number of samples required in resampling to estimate the mean nitrate concentration below agricultural production from soil cores (Fig. 2.4) indicated higher variability than in other studies of a similar nature. For example, we had CV's ranging from 31% to 64% as compared to Bowman (1991) who found CV's from 18.7% to 30%, and Dahiya et al. (1984) from 23% to 29%. Dahiya et al. (1984) and Bowman (1991) had results less variable than ours, perhaps due to the smaller area of their plots, which were 900 m^2 and 706.5 m^2, respectively. Our lowest CV of 31% is from a 7800 m^2 area, and our highest CV's were 62% from a 40,600 m^2 and 64% from a 24,000 m^2 area. The fact that our largest plots had the highest is expected since larger areas span greater range in the sources of variability such as soil type, slope, and crop growth.

In conclusion, we have successfully determined separation distances for wick lysimeters to theoretically obtain independent samples. If the sampling is in a greater than 1 ha field then 75 m separation between samplers may give independent results. If the field is smaller than 1 ha, then a separation distance of 40 m may give independent

results. Also, even though this study was not intended to determine resampling

requirements, our results indicate that larger area fields have higher variability.

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Chapter 3

Terbacil, Simazine and Atrazine Movement into Wick Lysimeters under Agricultural Production in Lane County, Oregon.

Lance O. Gatchell and John S. Selker

ABSTRACT

Pesticide movement into aquifers used for drinking water is an international

public health threat. Given the unreliability of models, (due to unpredictable macropore

effects among others) in-situ screening for pesticide leaching is necessary for predicting

future groundwater contamination. In this study, leachate sampling for pesticide

concentrations in groundwater recharge was conducted for 21 months with wick

lysimeters installed on six farms in Lane County, Oregon. Of the 21 pesticides used by

farmers in this study, Atrazine [2-chloro-4-(ethylamino)-6-(isopropylamino)-s-triazine],

Simazine [2-chloro-4, 6-BIS(ethylamino)-s-triazine], and Terbacil [5-chloro-6-methyl-3-

butyluracil] were considered most likely to leach, and were screened for leaching. We

analyzed Atrazine and Simazine using immuno-assay test kits, and Terbacil using gas

chromatography. Twenty-one month flow weighted concentrations of Terbacil found at 1

m depth in wick lysimeters were 32.4, 18, and 80 ppb, below the drinking water standard

of 90 ppb. Atrazine was detected, but not over the drinking water standard of 3 ppb.

Simazine was detected one month at 3.56 ppb, slightly over the 3.5 ppb drinking water

standard. A one year flow weighted Terbacil sample concentration was 108 ppb, and

coincided with the one farm that applied the herbicide in the fall. Further research is

needed to determine possible leaching of Terbacil on other farms that applied the

herbicide in the fall. Screening for Diuron (another likely to leach herbicide with a 14

ppb drinking water standard) should also be conducted.

INTRODUCTION

Groundwater contamination due to leaching of agricultural chemicals poses a threat to public health, and is widespread (CEC, 1991; CAST, 1985; Hallberg, 1988). Pesticides, previously thought to be immobile, have been found rapidly leaching to groundwater (Gish et al., 1991; Kladivko et al., 1991; Smith et al., 1990). Pesticide leaching is most likely when water soluble, stable chemicals are applied on sandy soils and then subjected to high rainfall or irrigation regimes (Kladivko et al., 1991). However, leaching is also affected by preferential flow, and several studies have shown that it is the causal mechanism that leads to unexpected pesticide contamination of groundwater (Thomas and Phillips, 1979; Sposito, et al., 1986). Preferential flow leaching is often due to macropores (Shipitalo, et al., 1994). Macropore flow is much faster than matrix flow, and thus pesticides move quickly to subsurface environments. Here they can persist and accumulate due to cooler temperatures and lack of microbial activity (Wagonet and Houston, 1990; Dobbins et al., 1992). Although preferential flow is know to occur, it is very difficult to incorporate into pesticide leaching prediction models due to its heterogeneous and ephemeral nature. Given the unreliability of models, in-situ screening for pesticide leaching is necessary for predicting future groundwater contamination.

Leachate monitoring requires the use of sampling devices and strategies that accurately measure contaminant flux below the root zone. Sampling alternatives include the use of soil cores, vacuum suction samplers, and lysimeters. The most suitable below root zone monitoring device in many conditions is a wick lysimeter due to its ability to

directly measure flux (Holder et al., 1991; Boll et al., 1992; Polletika et al., 1992; Knutson and Selker, 1994; Steenhuis et al., 1995).

Of numerous pesticides applied in Western Oregon, Simazine, Atrazine and Terbacil are most likely to leach (Jenkins, 1995, personal communication). Terbacil is considered leachable in sandy soil, but not under clayey conditions (Marriage, et al., 1977; Gardiner et al., 1969). However, due to its persistance Terbacil is a prime candidate for leaching in macropores which occur in structured clayey soils. Simazine and Atrazine are used widely to kill weeds, and commonly detected in groundwater (see Ritter, 1986). Terbacil is know to be harmful to intolerant crops up to two years after application (Marriage et al., 1977). The drinking water standards for these herbicides are 90 ppb for Terbacil, 3 ppb for Atrazine, and 3.5 ppb for Simazine (USEPA, 1989).

The objective of this study was to screen for Simazine, Atrazine and Terbacil leaching at 1 m depth in agricultural soils of Lane County, Oregon. Leaching was not expected since all pesticides were applied according to label instructions.

METHODS

This study was conducted from November, 1993 to July, 1995 on six farms in Lane County, OR. The study area was in the Willamette river alluvial valley, which is extensively used for agricultural production of grass seed, mint, orchard, dairy and row crops. The water table is 3-4 m below the surface during the summer, and perched in places during the winter due to clay deposits. The soils were loams, and each series is listed in Table 3.1. The six farms represented three herbicide application practices;

Terbacil applied to mint, Atrazine applied to row crops, and Simazine applied to

Blueberries.

Twelve farmers were surveyed in the summer of 1993 to determine which

pesticides they used and when pesticides were applied. Terbacil, Atrazine and Simazine

were selected for pesticide screening by the following criteria: (1) toxicity (MCL = 0 to

100 ppb); (2) USEPA guidelines for potential leaching to groundwater (Table 3.2)

(USEPA, 1988a; USEPA, 1988b) and, ultimately, (3) recommendation by a professional

agricultural chemist (Jenkins, J., 1995, personal communication). Several other

chemicals were applied to the surveyed farms that were not investigated due to lack of

leaching potential. Additional applied pesticides are listed in Table 3.3 with some aquifer

contamination potential characteristics. Although Diuron is likely to leach it was not

investigated in this study due to oversight.

Table 3.1. Farms site, soil series, chemical tested, and dates for the study.

Farm	Soil series	Chemical	Dates tested
Mint #1	Newburg loam	Terbacil	November '93 - July '95
Mint #3	Newburg fine sandy loam	Terbacil	November '93 - July '95
Mint #4	Malabon silty clay loam	Terbacil	November '93 - July '95
Row Crop #2	Newburg loam	Atrazine	April '94 - May '95
Row Crop #4	Malabon silty clay loam	Atrazine	April '94 - May '95
Blueberry #2	Newburg fine sandy loam	Simazine	April '94 - May '95

Table 3.2. Physical and chemical pesticide characteristics influencing leaching potential.

Pesticide Characteristic	Value or Range
Water Solubility	Greater than 30 ppm
K_d	Less than 5, usually less than 1
K_{oc}	Less than 300 - 500
Speciation	Negatively charged fully or partially at ambient pH
Hydrolysis half-life	Greater than 25 weeks
Photolysis half-life	Greater than 1 week
Field Dissipation half-life	Greater than 3 weeks

Table 3.3. Pesticides applied by farmers in this study and some aquifer contamination risk rating characteristics (USEPA, 1988b; USEPA, 1989).

Common Name	Water Solubility (ppm @ 20 °C.)	Aerobic Soil Half-Life (weeks)	Drinking Water Standard (ppb)
EPTC	3700	6.7	not available
Cycloate	75	4.3	not available
Pyrazon	400	21	not available
Ethofumesate	110	4.3	not available
Fonofos	13	11-16	10
Acephate	6.5×10^5	3	not available
Bromoxynil	0.08	1	not available
Oxyflourfen	0.1	120-130	not available
Paraquat	1.0×10^6	> 2	30
Propiconazole	110	10	not available
Chlorothalinol	1.2	1-4	not available
Myclobutanil	142	8	not available
Iprodione	13	3-8	not available
Diuron	42	17	14
Atrazine	33	21	3
Simazine	3.5	16	3.5
Terbacil	710	52	90

Two wick lysimeters per field were installed at a depth of one meter. Wick lysimeters consisted of a collection vessel, vessel support box, fiberglass wicks, and access tubes. They were installed beneath undisturbed soil, accessed from a 1 x 10 x 2 m deep trench. The collection vessel was a 60 L High Density Polyethylene (HDPE) container. High density polyethylene was chosen for it's demonstrated resistance to chemical adsorption (Topp and Smith, 1992). The collection vessel was placed inside a fiberglass box (33 x 87 x 62 cm) for support. The top of each box was fitted with a 2700 cm^2 stainless steel plate to support wicks and catch infiltrating water. Wicks were chosen to match soil matrix potential according to Knutson and Selker, (1994). An HDPE tube from the lysimeters to the soil surface allowed access for water sampling. The support box was sealed to prevent leaking.

Terbacil

Survey results showed Terbacil was applied by farmers according to label requirements to three mint fields to control weeds. On Mint #1 1.69.5 kg/ha was applied in February of 1994 and 1995. On Mint #3 2.25 kg/ha were applied in January of 1994 and 1995. On Mint #4 2.25 kg/ha were applied annually in 1994 and 1995 split between May and September.

Monthly Terbacil samples collected between November 1994 and July 1995 were mixed quarterly based on observed flow to obtain flux weighted quarterly samples. November 1993 to October 1994 annual flow weighted samples were obtained from samples stored in a -20 °C freezer where they had been stored since collection. Water

samples were analyzed by the Oregon State University Agricultural Chemistry Laboratory. Samples were extracted with Dichloromethane, heated to approximately 5 cm^3, then to dryness with no heat, and analyzed with a gas chromatagraph specific to Nitrogen detection (Pease, 1968). Total sample volume was always greater than 125 ml for Terbacil analysis as required for reliable detection.

Atrazine and Simazine

Atrazine and Simazine were applied by farmers according to label directions. Row Crop #2 had 0.985 l/ha applied as tradename Bicep on May 10, 1994. Row Crop #4 had Atrazine applied on February 1994 although the rate was not reported. The standard maximaum application rate for Atrazine is 0.856 l/ha provided that none was applied prior to emergence of the crop. Blueberry #2 had Simazine applied "according to the label rate" (farmer survey) in the spring of 1994. Recommended Simazine application rate for blueberries is 2.47 to 4.94 kg/ha.

Water samples used for Atrazine and Simazine were frozen immediately following collection @ -20 $^{\circ}$C. Samples were thawed overnight at room temperature, and analyzed with using an immuno-assay procedure (Ohmicron Inc., 1995) using a Hach DR/2000 Direct Reading Spectrophotometer.

RESULTS

Terbacil was generally detected below the root zone at concentrations below the 90 ppb drinking water standard. Volume weighted concentrations for 21 months ranged from 18 to 80 ppb (Table 3.4). Only the yearly sample of November 1993 to October 1994 on Mint #4 was above the drinking water standard.

Table 3.4. Farm site, date, depth volume, and Terbacil concentrations collected in wick lysimeters.

Farm site	Date	Depth volume (cm.)	Concentration (μg/l)
Mint #1	'93 Nov. - '94 Oct.	9.6	21.6
	'94 Nov. - '95 Jan.	7.4	38
	'95 Feb. - '95 Apr.	4.3	12.2
	'95 May - '95 July	2.6	49.5
aggregate	'93 Nov. - '95 July	23.9	**32.4**
Mint #3	'93 Nov. - '94 Oct.	122.5	14.3
	'94 Nov. - '95 Jan.	68.7	10
	'95 Feb. - '95 Apr.	38.3	2
	'95 May - '95 July	53.4	27.5
aggregate	'93 Nov. - '95 July	282.9	**18.0**
Mint #4	'93 Nov. - '94 Oct.	263.2	108.7
	'94 Nov. - '95 Jan.	88.5	40
	'95 Feb. - '95 Apr.	54.8	16
	'95 May - '95 July	12.8	41.1
aggregate	'93 Nov. - '95 July	419.3	**80.0**

Atrazine screening detected no concentrations over the drinking water standard, while Simazine screening detected one month's leachate was 3.56 ppb, slightly above the 3.5 ppb drinking water standard. Simazine and Atrazine detected in wick lysimeter

collected leachate samples were only at concentrations greater than 1 ppb in four samples (Table 3.5).

Table 3.5. Simazine and Atrazine concentrations detected in Wick Lysimeter collected percolate.

Farm site	Sampling date	Chemical	Concentration (ppb)
Row Crop #2	June 1994	Atrazine	0.25
	July 1994	Atrazine	0.89
	July 1994	Atrazine	0.34
	October 1994	Atrazine	1.51
	January 1995	Atrazine	0.12
	February 1995	Atrazine	0.15
	March 1995	Atrazine	0.12
	April 1995	Atrazine	0.13
Blueberry #2	July 1994	Simazine	3.56
	August 1994	Simazine	1.79
	September 1994	Simazine	1.14
	November 1995	Simazine	0.20
	January 1995	Simazine	0.11
	May 1995	Simazine	0.736
Row Crop #4	August 1994	Atrazine	0.34
	October 1994	Atrazine	0.25
	January 1995	Atrazine	1.23
	April 1995	Atrazine	0.11

DISCUSSION

Results of this study show leaching of Atrazine, Simazine, and Terbacil is occurring at detectable levels at 1 m depth in Lane County, OR. Terbacil and Simazine were sampled at levels slightly above legal limits for drinking water (USEPA, 1989). Pesticide leaching does not appear to be a serious threat on the farms investigated.

Terbacil is an extremely persistent herbicide (Marraige et al., 1977), and thus remains potentially leachable until heavy rains in the fall result in saturated flow conditions, the ideal for macropore leaching. The higher concentrations found under Mint #4 relative to other Mint farms coincided with this farm being the only mint field on which Terbacil was applied in the fall. Also, it is notable that a loam (Mint #1) had higher concentrations sampled than a sandy loam (Mint #3) even though more Terbacil was applied.

To compare our results of pesticides detected to what might be expected we used a plug flow model of infiltration. The model was based on retardation factors (Rf) of 0.31 for Atrazine and Simazine, and on Rf = 0.3 for Terbacil. Velocity was calculated as total volume collected in lysimeters divided by time of collection. Volumetric water content at field capacity used for soils was 0.48. Half lives of 3, 3 and 52 weeks were used for Atrazine, Simazine and Terbacil, respectively. Applied masses were from farmer survey results when available, or standard minimum application rates.

Results of the plug flow model estimation indicated that mass of annually applied Atrazine and Simazine leached to 1 m depth were 4.2% for Row Crop #2, 5.6% for Row Crop #4, and 15% for Blueberry #2. These results were higher than the wick lysimeter collection estimated herbicide mass losses which were 0.08% for Row Crop #2, 0.02% for Row Crop #4, and 0.2% for Blueberry #2. The results compare to Southwick et al. (1995) who noted percentage mass of applied Atrazine leached to subsurface drains was 0.6 to 1.2% in the summer, and 0.4 to 2.0% in the winter. Hall et al. (1989), using three pan lysimeters in 1984 found a percent loss of Atrazine of 0.19, <0.01, and 0.03% under a

conventional till field, and a percent loss of Atrazine under a no-till field of 0.79, 0.86, and 0.15%. They also investigated Simazine leaching in the same two fields and found 0.18, 0.01, and 0.03% loss under the conventional till and 0.06, 1.76, and 0.17% lost under the no-till field in the three lysimeters. Hall et al. (1989), in 1985 noted Atrazine leaching was greater than in 1984 at 0.85, and 0.75% under a the conventional till field, and 0.21, 1.02, and 9.6% under the no-till field. Simazine leaching in 1985 was 1.5, and 1.63% under the conventional till and 0.81, 8.36, and 0.96% under the no-till fiield.

Measured mass losses of Terbacil under the three mint fields were 0.3, 1.32, and 85.8% for Mint #1, Mint #3, and Mint #4, respectively. Measured losses were highly variable due to the variability in volume collected in wick lysimeters. Calculated losses using the plug flow method were very high, probably due to the long half-life of 52 weeks and fast travel times calculated from variable volumes collected. Calculated losses were 48, 83, and 96% of applied mass for Mint#1, Mint #3, and Mint #4, respectively. No references giving subsurface percentage mass losses of Terbacil were found to compare these results to.

This study was intended as a screening to investigate possible pesticide leaching at the 1 m depth. The results are not necessarily indicative of average field concentrations at the 1 m depth given the limited sampling area, and variability in volumes collected by wick lysimeters. It should also be noted that actual groundwater concentrations would be expected to be below those observed here due to sorption, degradation and dilution that would be expected to occur between the 1 m depth of our sampling and the well screen of a supply system. Further research should include testing

for Diuron in leachate below farms where it is applied due to its high aquifer

contamination potential.

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4. GENERAL CONCLUSION

In the study to determine optimum separation distance for vadose zone samplers using geostatistical analysis we have successfully determined separation distances. If the sampling is in a greater than 1 ha field then 75 m separation between samplers may give independent results. If the field is smaller than 1 ha, then a separation distance of 40 m may give independent results. However, investigation of nugget to sill ratios indicated that 33% to 100% of the variability was not due to spatial structure. Therefore, depending on the accuracy required, sample separation may not be justified.

Results of the pesticide leaching study indicate that below root zone leaching of Atrazine, Simazine, and Terbacil is occurring at detectable levels in Lane County, Oregon. For individual months, Terbacil and Simazine were sampled at levels above legal limits for drinking water (USEPA, 1989). When averaged over time, leachate concentration are consistently below drinking water standards. Aquifer contamination due to these pesticides does not appear to be a serious threat under the farms investigated.

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