MINNESOTA DEPARTMENT OF AGRICULTURE
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Analysis of the Co-occurrence Of Nitrate-Nitrogen and Pesticides In Minnesota Groundwater

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(Revised)

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Executive Summary

Public concern over the impacts of pesticides on groundwater has resulted in significant interest in analyzing home drinking water samples for commonly used pesticides. The very high cost of analyzing water samples for pesticides makes it difficult for most homeowners to afford such an analysis. Local community health service agencies typically offer low cost analysis of water for nitrate-nitrogen and coliform bacteria although not for pesticides. Accordingly many homeowners have had water samples tested for nitrate and bacteria. When bacteria or nitrate are found in their wells they wonder whether they should test their water for other chemicals such as pesticides. When informed of the high cost of such a sample test they typically ask if there is a link between high nitrates or bacteria with other chemicals like pesticides. Unfortunately very little work has been done to research such a link.

This report investigates the link between pesticides and nitrate-nitrogen in groundwater samples collected from around the state of Minnesota. Pesticide and nitrate data from samples collected at monitoring wells and domestic drinking water wells were compared to determine whether such a link exists. Results of this analysis indicate that it is not possible to predict the concentration of pesticides in a well from the concentration of nitrate in that same well. However, it appears that mobile pesticides are more likely to be detected in a well when nitrate-nitrogen concentrations increase beyond natural background levels. Data analyzed for this report shows much higher probabilities of detecting a pesticide when nitrate-nitrogen levels rise above 3.0 parts-per-million. When levels of nitrate go above 10.0 parts-per-million the likelihood of detecting a pesticide increases even more. Different aquifer types have different actual percentages of wells containing pesticides at various nitrate ranges, although the general shape of the relationship across nitrate ranges is similar for all aquifer types. Whether it would be useful for a homeowner to spend the money to analyze a sample from a well for pesticides when nitrate in that well is high may depend on additional information. Local geologic conditions and the types of pesticides used in the surrounding area are two of the most important pieces of extra information needed. Details of the results from this investigation, including general conclusions, may be found in the body of this report.

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Introduction

Groundwater impacts from the application of pesticides and fertilizers have been well documented for more than two decades. Public concern over these impacts has resulted in significant interest in analyzing home drinking water samples for nitrate as well as pesticides. Typically homeowners contact local health or environmental agencies and find that a sample for nitrate-nitrogen and coliform bacteria is relatively inexpensive and simple to collect and choose to do so. After receipt of a lab result showing elevated levels of nitrate-nitrogen in their well water many homeowners make a follow-up call to their local government or agriculture agency seeking analysis of a water sample for pesticides. Unfortunately, what homeowners discover is that analysis of pesticides in water samples is quite expensive, perhaps costing hundreds or even thousands of dollars. The cost differential between pesticide and nitrogen analysis in water samples has led to a relative plethora of nitrate-nitrogen results. This availability of nitrate-nitrogen sample results has led to the question of whether the level or detection of pesticide compounds may be predicted from knowledge of the nitrate level. Homeowners may also ask whether they should be concerned about pesticides when they have a high nitrate result; inquiring as to the link between mutual detection of the two compounds. As pesticide analysis is expensive, it would be advantageous to know how pesticide concentrations relate to nitrate concentrations in groundwater and whether nitrate-N could be a useful predictor of pesticide concentration or detection.

Water quality professionals have frequently suggested that a link between the concentration of nitrate-nitrogen and pesticides in groundwater may indeed exist in certain situations. Research has found that measurable links between nitrate and pesticide levels in groundwater is likely the result of geologic conditions, land use practices near well sites, and the chemical characteristics of the pesticides applied in the area (Burow, et.al. 1998, Bertrand, 2005). Several researchers have investigated the association of nitrogen and pesticides and report a very weak or non-existent relationship between the concentration of nitrate-nitrogen and specific pesticides (see Table 1).

Table 1. A selection of publications reporting analysis of pesticide versus nitrate-nitrogen relationship in groundwater.

Source*	**Remarks**
Rupert, M.G.	Weak non-predictive relationship.
Gosselin, D.C.	Spearman test indicated an association. Strength of association increased as NO3 increased
Goody, D.C.	NO3-N concentration and pesticide detection showed no clear relationship.
Goodman, P.	No correlation between pesticides and nitrate was seen throughout Kentucky.
Burow, K.R.; et.al.	Varies by land use; not correlated in some cases although correlated in others.
Bertrand, L.	Significant differences in spatial and temporal relationships
Welhan, J and Merrick, M.	“No useful bivariate relationships between atrazine and nitrate were found.”
Dawson, B.J.M.	“No correlation was found between nitrate concentration and pesticide occurrence…”
Spalding, R.F.	Very weak correlation between atrazine and nitrate concentrations

*references cited are located at the end of this report.

No reliable prediction of pesticide concentration based on the concentration of nitrate-nitrogen in water samples has been suggested. Few researchers have investigated in detail whether there is a probabilistic link between high nitrate concentrations and the detection of pesticides, although much work has been suggestive of such a link.

This report has been developed in response to the aforementioned public interest in possible relationships between nitrate-nitrogen and pesticides in groundwater. The report investigates relationships between nitrate-nitrogen concentration and pesticide concentration and detection in groundwater quality data collected by the Minnesota Department of Agriculture (MDA). Data from the MDA Central Sands Groundwater Monitoring Network, the original MDA groundwater monitoring network and an older study by the Minnesota Department of Health on private drinking water wells were used for the comparison. Various nitrate ranges were imposed on the data for investigating the details of any possible relationships between pesticides and nitrate-nitrogen in Minnesota groundwater. The usefulness of this evaluation lies in the possibility of using nitrate-nitrogen results (an inexpensive analysis) as an index value that would suggest the need for pesticide analysis (a very expensive analytical procedure) of water samples.

Pesticide and Nitrate-Nitrogen Relationships in MDA data.

Figure 1 is a graph of NO3-N versus total pesticide concentration in samples collected simultaneously from the MDA Central Sands Network monitoring wells. A regression line fit to the data shows an obvious positive slope. The slope of the line is statistically significant with an associated p-value of << 0.01. Spearman rank correlation analysis also shows a positive relationship between pesticide and nitrate concentration in groundwater. However, as evidenced by the low regression R^2, predicting an exact concentration of total pesticides from the NO3-N concentration would be unreliable.

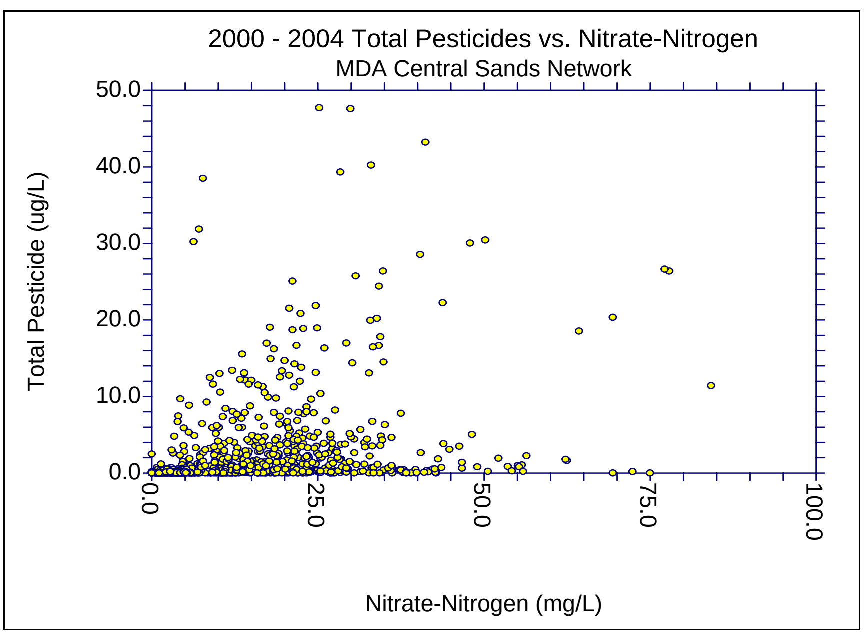

Figure 1. Pesticide versus nitrate-nitrogen concentration from MDA central sand plain wells. Data collected between January 2000 and October 2004.

Although total pesticide compared with nitrate-nitrogen concentrations demonstrate no well-defined predictive relationship, individual pesticides may not behave the same. Regression analysis conducted on individual pesticides and their breakdown products, however, produced results similar to total pesticides (see Table 2). To further evaluate the relationship between nitrate and pesticides a Spearman rank correlation analysis was conducted on the same set of data. The correlation analysis shows that pesticides and NO3-N exhibit a weak positive correlation. Results for the Spearman rank correlation analysis are included in Table 2.

Table 2. Regression and Spearman rank correlation analyses of pesticides versus nitrate-nitrogen concentration in central sands network sample results.

Compound	Slope	Intercept	R-squared	Spearman's R CI*
Total Acetochlor	0.03	-0.28	0.10	0.14 – 0.27
Total Alachlor	0.03	-0.01	0.05	0.19 – 0.32
Total Atrazine	0.006	0.18	0.03	0.24 – 0.37
Total Dimethenamide	0.003	-0.02	0.04	0.11 – 0.24
Total Metolachlor	0.05	0.41	0.03	0.17 – 0.30
Total Metribuzin	0.03	0.31	0.03	0.17 – 0.30
Total Pesticide	0.14	0.69	0.09	0.37 – 0.48

*CI is the Fischer's Z 95% confidence interval of Spearman's rank correlation coefficient. If the entire interval does not include zero then the data show a tendency toward correlation. A larger absolute value of R means higher correlation with a maximum of 1.0

The weak positive correlation exhibited between NO3-N and pesticide concentrations, coupled with the positive regression slopes, suggests that there may be an increase in the probability of detecting a pesticide as NO3-N concentration increases. To facilitate the analysis of this possibility NO3-N sample results were divided into four concentration ranges and compared with pesticide detections. The NO3-N ranges utilized were as follows:

less than detectable or ND;
0.1 ppm to 3.0 ppm (a range associated with natural sources);
3.1 ppm to 10.0 ppm (elevated but not exceeding a standard);
Greater than 10.0 ppm (exceedence of health standard)

Figure 2 graphically represents sample results for the various NO3-N ranges. Each NO3-N category has a different number of samples associated with it (see Figure 2 and Table 3) requiring greater care when interpreting statistical analysis results.

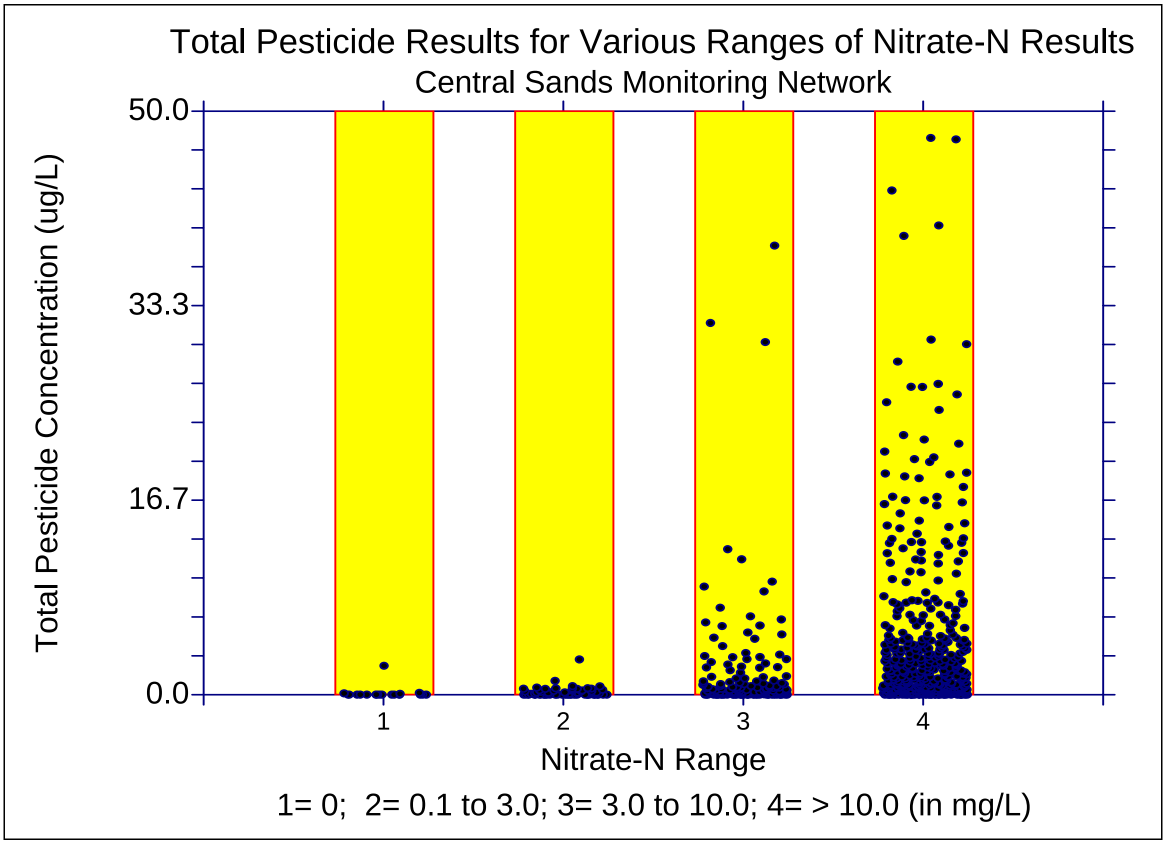

Figure 2. Total pesticide concentrations in samples collected from MDA central sands groundwater monitoring wells based on 4 ranges of associated levels of nitrate-nitrogen sample results.

The largest numbers of samples from the central sands wells have NO3-N concentrations exceeding 10.0 parts-per-million. This is not surprising given the shallow sand aquifer conditions and the purposeful similarity among the network's well sites. Summary statistics for total pesticide concentration for each NO3-N category is located in Table 3. There is no statistically significant difference between the total pesticide concentrations of NO3-N groups 1 and 2. There is, however, a large and statistically significant difference in total pesticide concentration between groups 3 and 4. Groups 3 and 4 also show significant differences when compared to groups 1 or 2. A similar analysis conducted on the probability of pesticide detection for each group returned identical results (see Figure 3).

Table 3. Summary statistics of total pesticide results from samples collected during 2000 through 2004 from the MDA central sands network.

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	21	4	0.13	ND	ND	0.14	2.48
0.1 – 3.0 ppm	78	35	0.19	ND	0.29	0.53	3.01
3.1 – 10.0 ppm	205	155	1.49	0.20	0.86	3.49	38.48
> 10.0 ppm	516	461	3.91	1.15	4.23	12.16	47.71

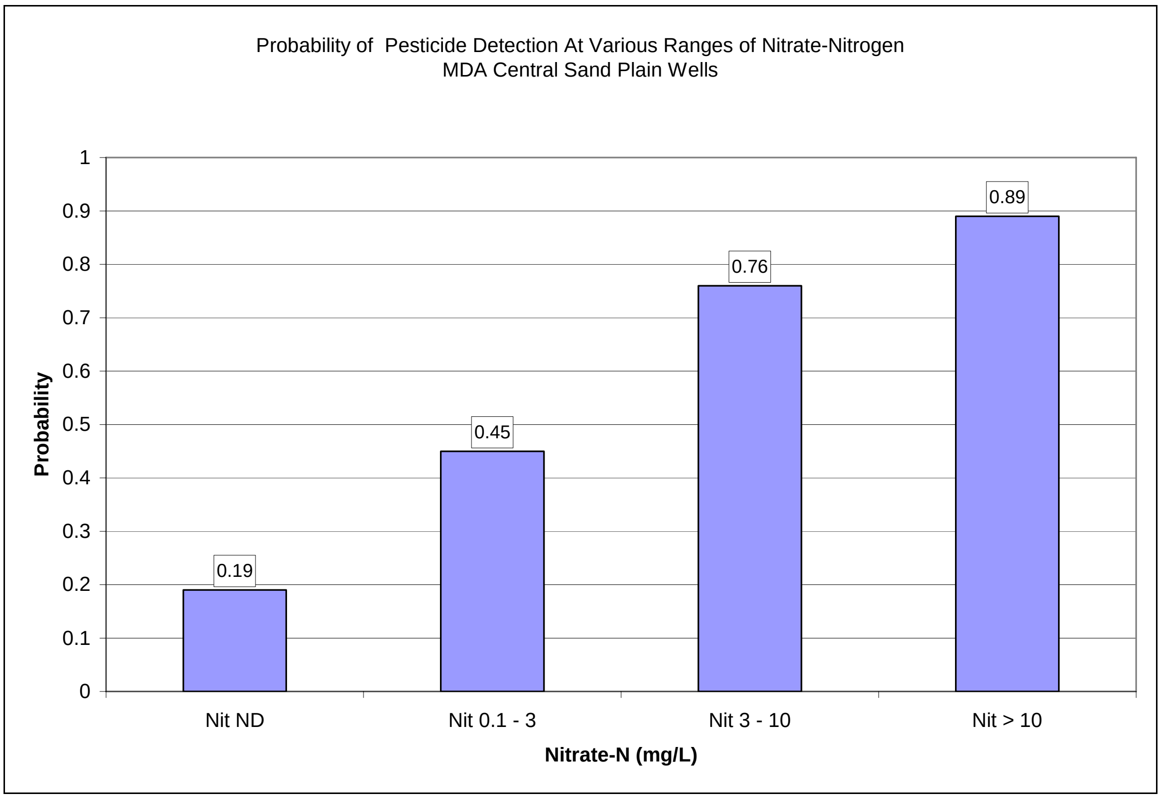

Figure 3. Probability of detecting a pesticide at various ranges of nitrate-nitrogen in MDA central sand plain wells.

To broaden the scope of this assessment, data collected from the MDA's original groundwater monitoring network[1] (1985 – 1996) was similarly analyzed. The original network data was collected from aquifers not represented in the current central sand network thus providing an opportunity to investigate whether the tendencies seen in the central sands data is also present in data from other aquifers in the state. Figure 4 is constructed utilizing data from all the wells in the original MDA network, and is similar in shape to the central sands data. The difference in the probability is likely due to the mixing of samples from several aquifers in the original network, while the central sands network represents sand plain wells only.

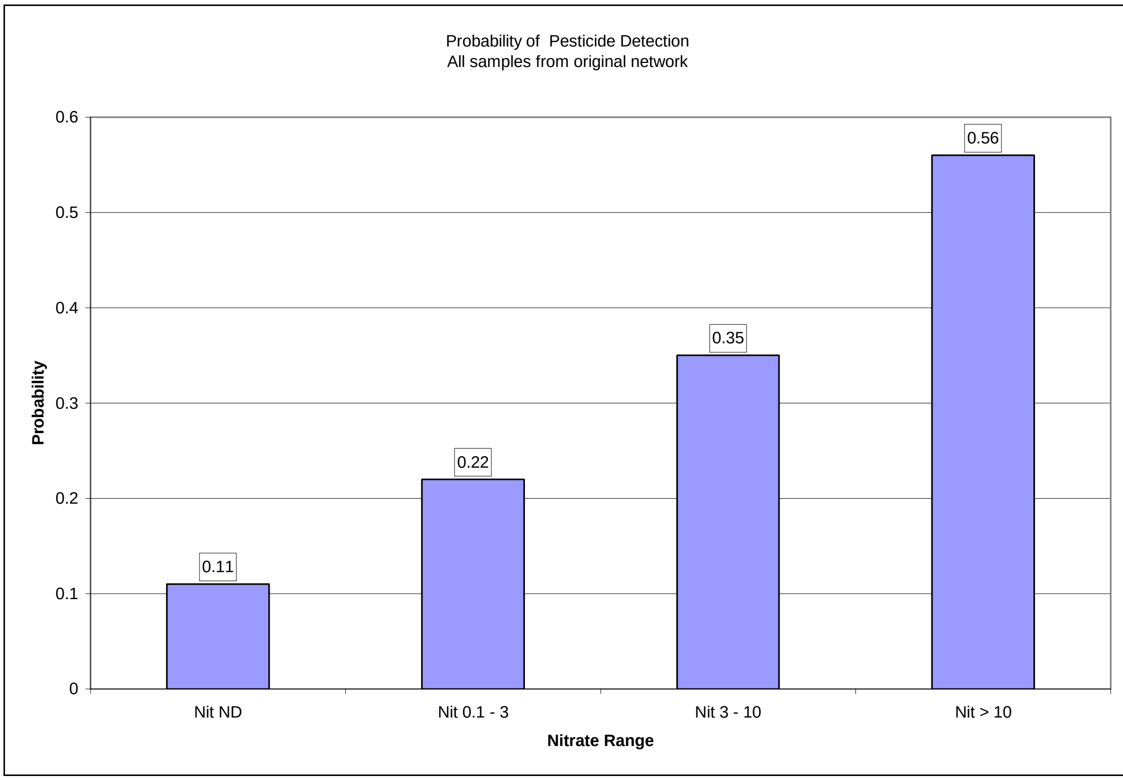

Figure 4. Probability of detecting a pesticide at various nitrate-nitrogen levels in samples from original MDA monitoring network.

Laboratory results of samples collected from sand plain wells installed in conditions similar the central sands network was investigated for similarities to the central sands data. Although the probability values are less than the central sands the overall appearance is strikingly similar to the chart from current central sands data (Figure 5). Figure 5 and Table 4 shows charts and summary statistics for data from each major aquifer type from the original network and reveals the similarity between the data. In each case it was much more likely to detect a pesticide in wells with elevated nitrate-nitrogen concentrations.

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[1] MDA's original monitoring network was begun in late 1985 and continued for 10 years. It was closed down and replaced by the regional network concept of which the central sands network was the initial effort.

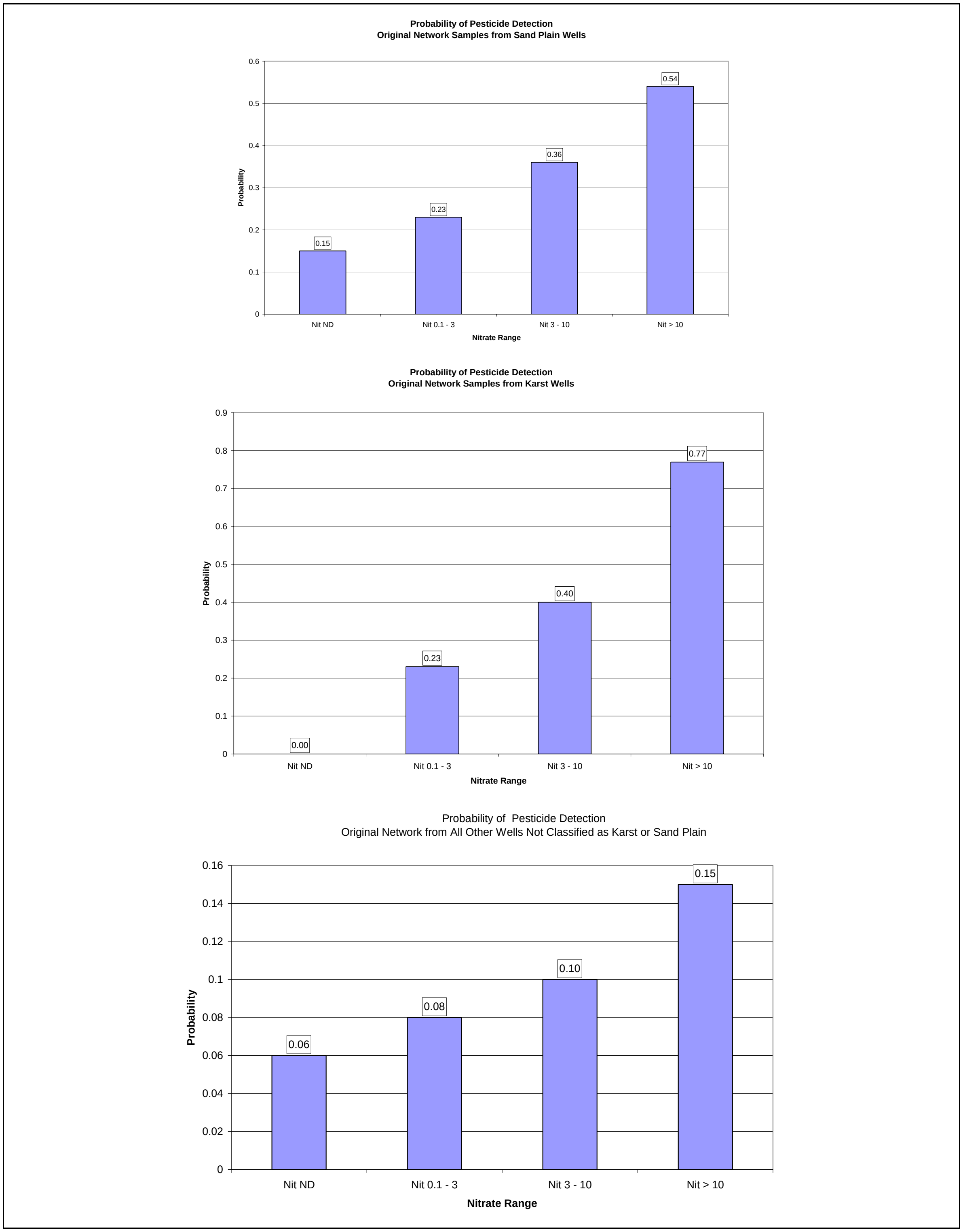

Figure 5. Probability of pesticide detection at various levels of nitrate-nitrogen in different aquifer classes from original MDA groundwater monitoring network.

Table 4. Summary statistics of total pesticide results for samples collected from various aquifers during monitoring of the original MDA network.

Sand Plain Wells

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	474	70	0.38	ND	ND	2.10	7.89
0.1 – 3.0 ppm	153	35	0.82	ND	ND	2.17	50.21
3.1 – 10.0 ppm	415	149	0.97	ND	2.12	2.57	13.47
> 10.0 ppm	646	351	1.29	0.77	2.24	2.75	20.95

Karst Wells

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	57	0	ND	ND	ND	ND	ND
0.1 – 3.0 ppm	31	7	0.43	ND	ND	2.16	2.80
3.1 – 10.0 ppm	133	53	0.74	ND	1.60	2.17	3.10
> 10.0 ppm	116	89	1.89	2.19	2.60	3.30	4.75

All Other Wells Not Classed as Karst or Sand Plain

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	188	11	0.13	ND	ND	ND	4.1
0.1 – 3.0 ppm	12	1	0.25	ND	ND	1.90	2.71
3.1 – 10.0 ppm	41	4	0.18	ND	ND	0.87	2.20
> 10.0 ppm	33	5	0.25	ND	ND	1.07	2.31

All the data discussed to this point was collected from very shallow monitoring wells or carefully selected karst bedrock drinking water wells. In 1986 the Minnesota Department of Health (MDH) conducted a relatively comprehensive study of pesticide impacts to private drinking water wells (Klaseus and Hines, 1989). Two-hundred twenty five wells were sampled from several different aquifer types and different geographic regions across the state. As this remains the most complete set of pesticide data collected from private wells in Minnesota to date, it is being utilized here to investigate whether drinking water well results are similar to those from specifically constructed monitoring wells. Unlike specifically constructed monitoring wells many drinking water wells may be quite deep within the aquifer and may represent sources of pesticides other than field application. The 1986 MDH study purposely targeted worst-case conditions, resulting in a somewhat biased data set. The following data needs to be evaluated in that context.

Clearly the most outstanding feature of the MDH data is how closely it mirrors data from monitoring wells (Figure 6 and Table 5). Although collected more than a decade apart and from wells that are constructed to dissimilar standards, the tendency in the two data sets is remarkably similar. All pesticide detection results show an increase in frequency of detection with increasing nitrate concentration range, regardless of the aquifer in which the well was constructed.

The most remarkable aspect of this analysis is that regardless of aquifer, type of well, depth of well or well use, the pesticide and nitrate-nitrogen relationship stays the same. The magnitudes present in the relationship may vary, however the general characteristics of the relationship do not. One possible explanation for this result is that nitrate and soluble pesticides both leach into groundwater in areas which are geologically sensitive to contamination from activities at the ground surface. United States Geological Survey researchers (Nolan, et. al., 2002), among others, have shown results supporting this possibility. They further suggest that simple geologic sensitivity, or susceptibility, based on well-drained soils overlying coarse-grained deposits, remains the most predictive measure of groundwater impacts due to activities at the surface of the land. The physical and chemical characteristics of pesticides used in the vicinity of a specific well dictate whether they are capable of leaching downward to groundwater in a geologically sensitive area. Geologic sensitivity coupled with pesticide chemistry will largely determine the true susceptibility of the groundwater in a specific area to pesticide impacts. Analysis of land use, pesticide use, pesticide chemistry and geologic sensitivity information represents the most effective way to determine whether to sample a well for pesticides based on its level of nitrate-N. The first two nitrate ranges from karst aquifer wells are represented by very few samples making it difficult to establish a good estimate of the probability for these ranges. Care should therefore be exercised when drawing conclusions for the overall tendencies across all ranges for this data set.

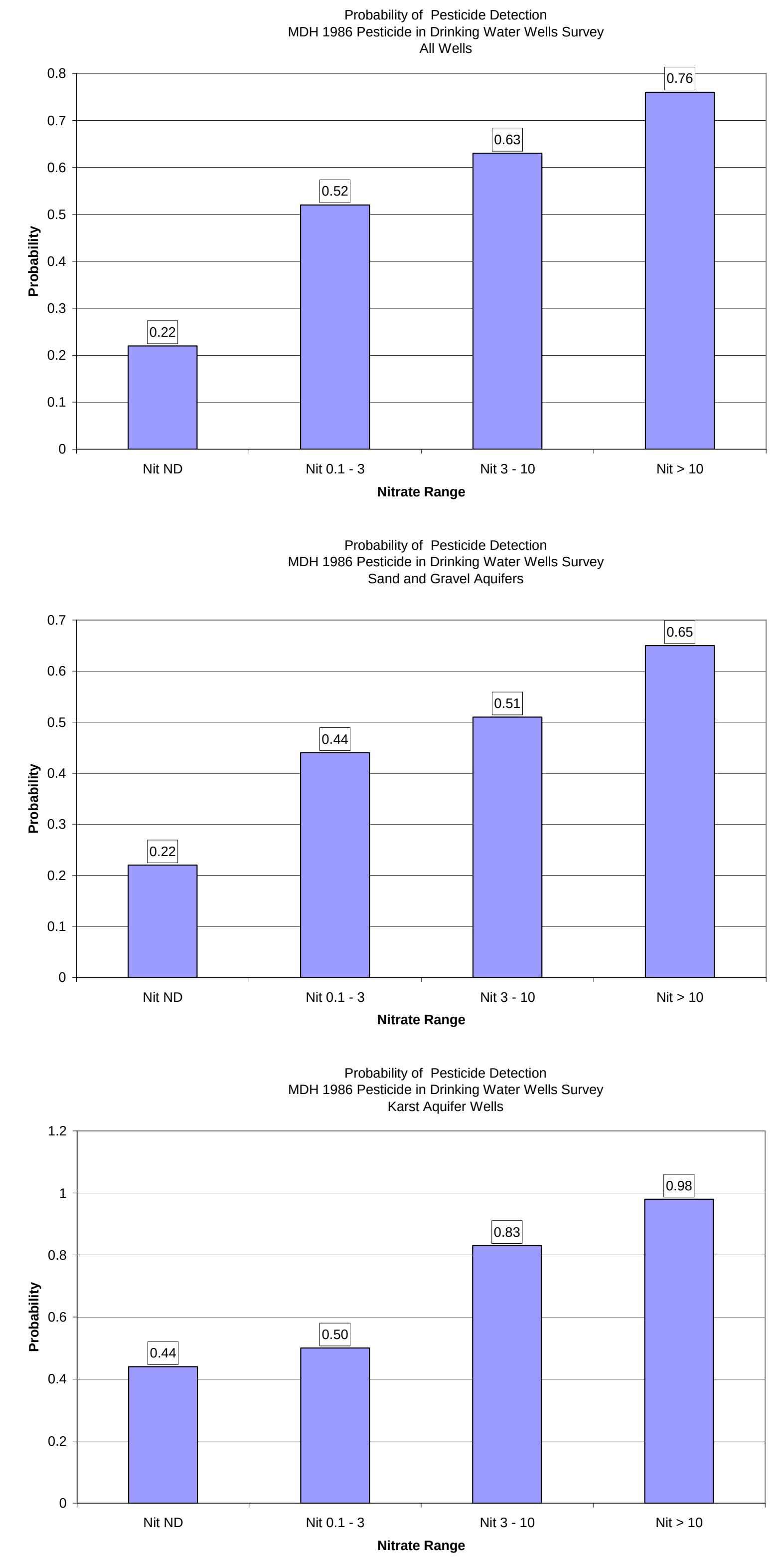

Figure 6. Probability of pesticide detection at various levels of nitrate-nitrogen in different aquifer classes from original 1986 MDH drinking water well survey.

Table 5. Summary statistics of total pesticide results for samples collected from various aquifers during sampling of the MDH Drinking Water Survey.

All Wells

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	72	16	0.04	ND	ND	0.04	1.3
0.1 – 3.0 ppm	25	13	0.10	0.01	0.14	0.41	0.64
3.1 – 10.0 ppm	59	37	0.20	0.03	0.16	0.34	4.53
> 10.0 ppm	137	104	0.87	0.09	0.49	2.21	18.42

Sand and Gravel Aquifer Wells

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	48	10	0.05	ND	ND	0.14	1.3
0.1 – 3.0 ppm	18	8	0.12	ND	0.15	0.59	0.64
3.1 – 10.0 ppm	37	19	0.12	0.01	0.15	0.33	1.36
> 10.0 ppm	85	55	0.42	0.05	0.32	0.96	8.85

Karst Aquifer Wells

Nitrate-N Range	Number of Samples Within Nitrate-N Range	Number of samples in Nitrate-N Range with Pesticide Detections	Mean Total Pesticide Concentration (ug/L)	Median Total Pesticide Concentration (ug/L)	75th %-ile Total Pesticide Concentration (ug/L)	90th %-ile Total Pesticide Concentration (ug/L)	Maximum Total Pesticide Concentration (ug/L)
Not Detected	9	4	0.01	ND	0.03	0.05	0.05
0.1 – 3.0 ppm	4	2	0.05	0.04	0.11	0.13	0.13
3.1 – 10.0 ppm	18	15	0.39	0.07	0.23	1.37	4.53
> 10.0 ppm	45	44	1.51	0.23	0.75	4.77	18.42

Conclusions

Results of the data analysis conducted here indicate a stronger likelihood of detecting a pesticide when nitrate-nitrogen concentrations in a well are elevated. In particular when nitrate-nitrogen exceeds 3.0 mg/L it is much more likely that pesticides may also be detected. The strength of this relationship increases as nitrate-nitrogen concentration increases. This relationship, however, does not hold for every well, nor should it be expected to. Decisions on whether the nitrate-nitrogen result from a specific well warrants collecting a pesticide sample require additional information, most notably the geologic vulnerability of the aquifer to contamination from the ground surface. Information on soil organic matter, pesticide use, and the chemistry of the pesticides used would also prove valuable.

Based on historical MDA monitoring information, nitrate-nitrogen concentration in a water sample is a rough indicator, not an absolute predictor, of the pesticide concentrations in the same sample. However, pesticides and nitrate-nitrogen do behave differently in the environment and the concentration of one cannot be predicted based on the concentration of the other. For example, a certain value of nitrate-nitrogen in a water sample tells very little about the concentration of a specific pesticide such as atrazine, in that same water sample.

Based on this analysis and reports from other similar assessments, it would be inadvisable to use nitrate-nitrogen concentration alone as a substitute for pesticide sample analysis. However, there is a general correlation between nitrate-nitrogen and total pesticides. At elevated nitrate-nitrogen levels, it may be reasonable for homeowners to test water samples from wells for pesticides following a nitrate-nitrogen detection of greater than 10.0 mg/L. Conducting the same analysis for samples with nitrate-nitrogen results between 3.0 and 10.0 mg/L may depend on other supporting information, such as that mentioned above. The availability of relatively inexpensive water analysis tools, such as pesticide immunoassay screens, may provide the homeowner with alternatives to expensive laboratory analysis. However, results from an immunoassay screen showing pesticide detections may need to be verified by more accurate laboratory analysis to determine the identity and precise concentration of specific pesticides.

For more information on the MDA monitoring program, annual monitoring results, pesticide immunoassay screens, and available commercial laboratories refer to the MDA web site at http://www.mda.state.mn.us/waterland.htm.

References

Bertrand, L. 2005. Development and validation of a probabilistic methodology aiming at integration of data from different sources, for the evaluation of groundwater pollution by plant protection products. PhD Dissertation. Department of Geography, Université Catholique de Louvain, Unité de Genie Rural.

Burow, K.R., Et. al. 1998. Occurrence of Nitrate and Pesticides in Ground Water Beneath Three Agricultural Land-Use Settings in the Eastern San Joaquin Valley, California, 1993 – 1995. USGS-WRI Report 97-284.

Dawson, B.J.M. 2001. Shallow Ground-Water Quality Beneath Rice Areas in the Sacramento Valley, California, 1997. USGS-WRI Report 01-4000.

Goody, D.C., et. al. 2005. Pesticide Pollution of the Triassic Sandstone aquifer of South Yorkshire. Q. J. of Engineering Geology and Hydrogeology. Vol. 38, no. 1:53-63.

Goodman, P., et. al. 2000. Results of Monitoring Pesticides, Nitrate, and MTBE; Kentucky Division of Water Ambient Groundwater Monitoring Program. Proceedings of the Kentucky Water Resources Annual Symposium.

Gosselin, D.C. et.al. 1996. Domestic Well Water Quality in Rural Nebraska. Nebraska Department of Health.

Klaseus, T.G., and Hines, J.W. 1989. Pesticides and Groundwater: A Survey of Selected Private Wells in Minnesota. Minnesota Department of Health.

Nolan, B.T., et.al. 2002. Probability of Nitrate Contamination of Recently Recharged Ground Waters in the Conterminous United States. ES&T v.36.n10, p. 2138-2145.

Rupert, M.G. 1998. Probability of Detecting Atrazine/Desethylatrazine and Elevated Concentrations of Nitrate (NO2+NO3-N) in Ground Water in the Idaho Part fi the Upper Snake River Basin. USGS-WRI Report 98-4203.

Spalding, R.F., et.al. 2003. Herbicide Loading to Shallow Ground Water beneath Nebraska's Management Systems Evaluation Area. J. Environ. Qual. 32:84-91.

Welhan, J, and Merrick, M. Statewide Network Data Analysis and Kriging Projed – Final Report. 2002. Idaho State University.