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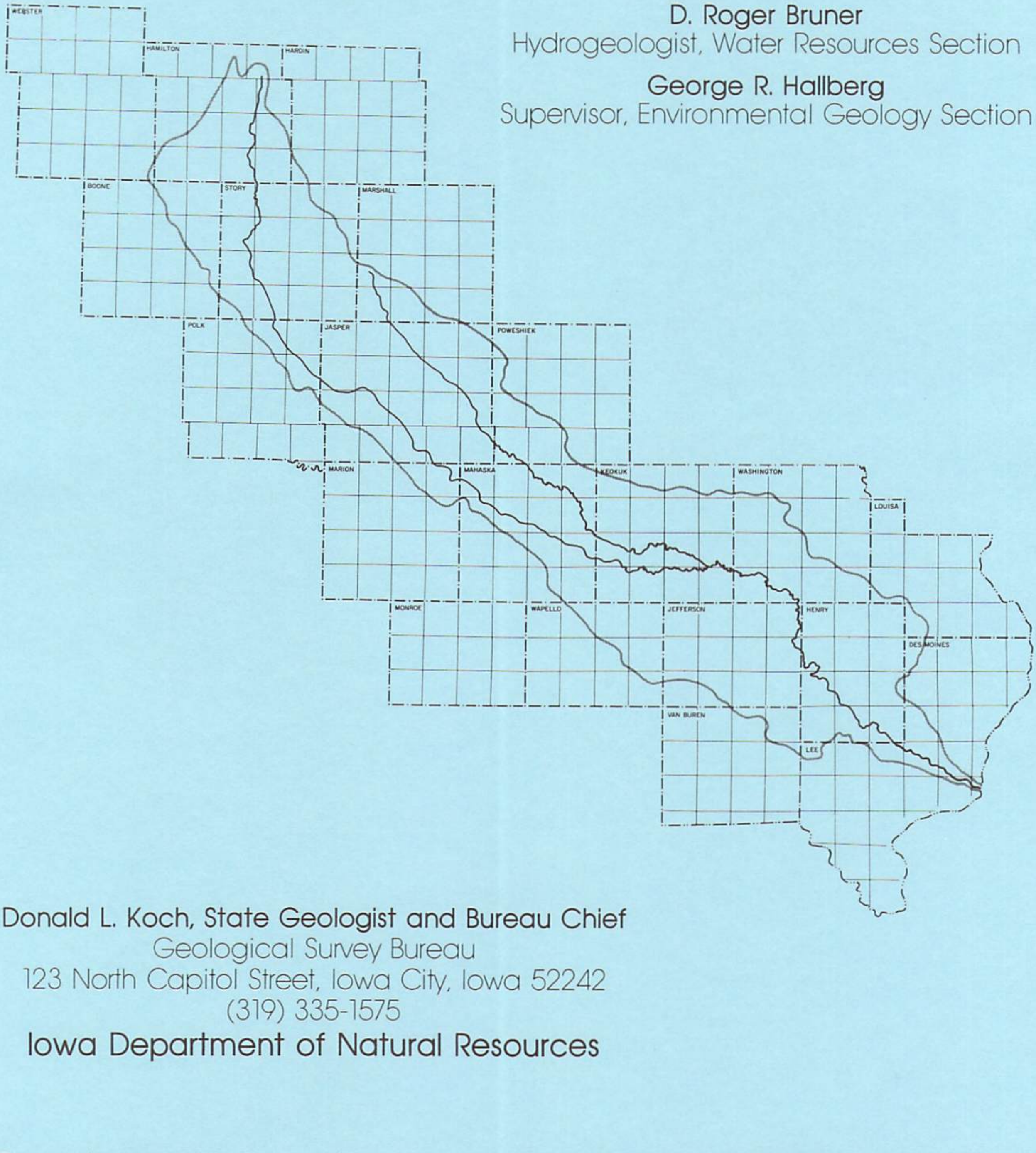
AN OVERVIEW OF GROUNDWATER QUALITY IN THE SKUNK RIVER BASIN



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The publication of this document has been supported through a cooperative agreement with the USDA-Soil Conservation Service (68-6114-5-2056), as part of the Skunk River Basin Study (P.L. 83-566, 68 Stat. 666 (16U.S.C. 10667)).

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EXECUTIVE SUMMARY

Geologic and groundwater quality information were reviewed by the Iowa Department of Natural Resources-Geological Survey Bureau (IDNR-GSB) in a cooperative agreement with the United States Department of Agriculture-Soil Conservation Service (USDA-SCS) as part of an effort by the USDA-SCS to develop an integrated soil and water conservation plan for the Skunk River basin. The basin covers all or part of 21 counties, from north-central Iowa to the Mississippi River in the southeast corner of Iowa. The bedrock and Quaternary geology are variable across the basin. Unlike other portions of Iowa, there is not a continuous bedrock aquifer through the region that produces adequate quantities of good quality water. Hence, adequate quanities of good quality groundwater are deficient in much of the basin. Deeper aquifer sources in the basin are often highly mineralized and some exhibit natural quality problems with radionucleides.

The population, in much of the Skunk River basin, relies on shallow groundwater sources for their drinking water supplies; 50% of all private wells analyzed in the basin were less than 50 feet deep. Deeper sources are generally unavailable to many people in the basin. Many public water-supplies utilize surface water for all or part of their drinking water supplies. This dependance on shallow groundwater and or surfacewater makes the southern portions of the basin, in particular, vulnerable to increasing water contamination problems.

Nitrate (NO3) analyses from private water supplies were reviewed to determine if contamination of the groundwater supplies has occurred or could occur. These data showed a general trend of decreasing nitrate concentration in the groundwater with increasing well depth, as has been shown in other areas of Iowa. Wells in the Skunk River basin that were less than 100 feet deep had significantly higher nitrate concentrations than deeper wells. 'Shallow Bedrock' areas(areas with less than 50 feet of glacial materials covering bedrock) and `Deep Bedrock' areas both showed the general trend of decreasing nitrate concentrations with depth. However, the data from Shallow Bedrock areas show (statistically) significantly greater nitrate concentrations than Deep Bedrock areas, especially in the shallower wells. While data are limited, pesticide residues are also present in shallow wells, coexisting with high nitrate concentrations.

While the median nitrate concentrations on the shallow groundwater are lower than in northeast Iowa, the percentage of wells over the recommended drinking water standard are about the same; 17%. Water quality is much more variable than in northeast Iowa, likely because of the differences in the geology, soils, and agricultural land-use between the two areas.

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INTRODUCTION

The United States Department of Agriculture-Soil Conservation Service (USDA-SCS) is assessing the informational and natural resources needs of selected major river basins, to develop an integrated soil and water conservation plan for each basin. This report on the Skunk River basin is part of a cooperative agreement between the USDA-SCS and the Iowa Department of Natural Resources-Geological Survey Bureau (IDNR-GSB) designed to address some of these information needs for planning purposes. The Skunk River basin stretches from north-central Iowa to the southeast corner of the State, north of Keokuk, where the Skunk River joins the Mississippi River (see figure 1), and covers all or part of 21 Iowa counties. Geologic and groundwater quality data, focusing on nitrate (NO_3) analyses from private water supplies and depth to bedrock, were studied to determine if any contamination of the groundwater supplies has occured which may be related to surficial activities, as in other parts of Iowa. Figure 2 shows the basin boundaries, counties, and the various towns that were used as sample centers for the statistical analysis of the nitrate analyses from private wells in the study area.

GEOLOGY AND WATER RESOURCES

There are five major sources of water used within the basin. One source of water used by several communities is the surface water of the Skunk River, its tributaries, and related reservoirs and impoundments. Various aquifers, provide groundwater to wells for the majority of residents in the basin. There are four primary groups of aquifers: alluvial aquifers, buried channel aquifers, various bedrock aquifers, and drift aquifers.

The alluvial aquifers, associated with the Skunk River and tributaries, provides part of the water used within the basin. The alluvial aquifer consists of river-deposited sand and gravel, in the floodplain and adjacent terraces. Figure 3 shows the general extent of the alluvial aquifers within the basin. This map was constructed from topographic maps and soil survey data for the counties in the basin.

Buried-channel aquifers are comprised of sand and gravel which was deposited in pre-existing stream valleys that were later covered by glacial drift. Figure 3 shows the known (and inferred) location of major buried channel aquifers in the study area. This figure is based on well log information,

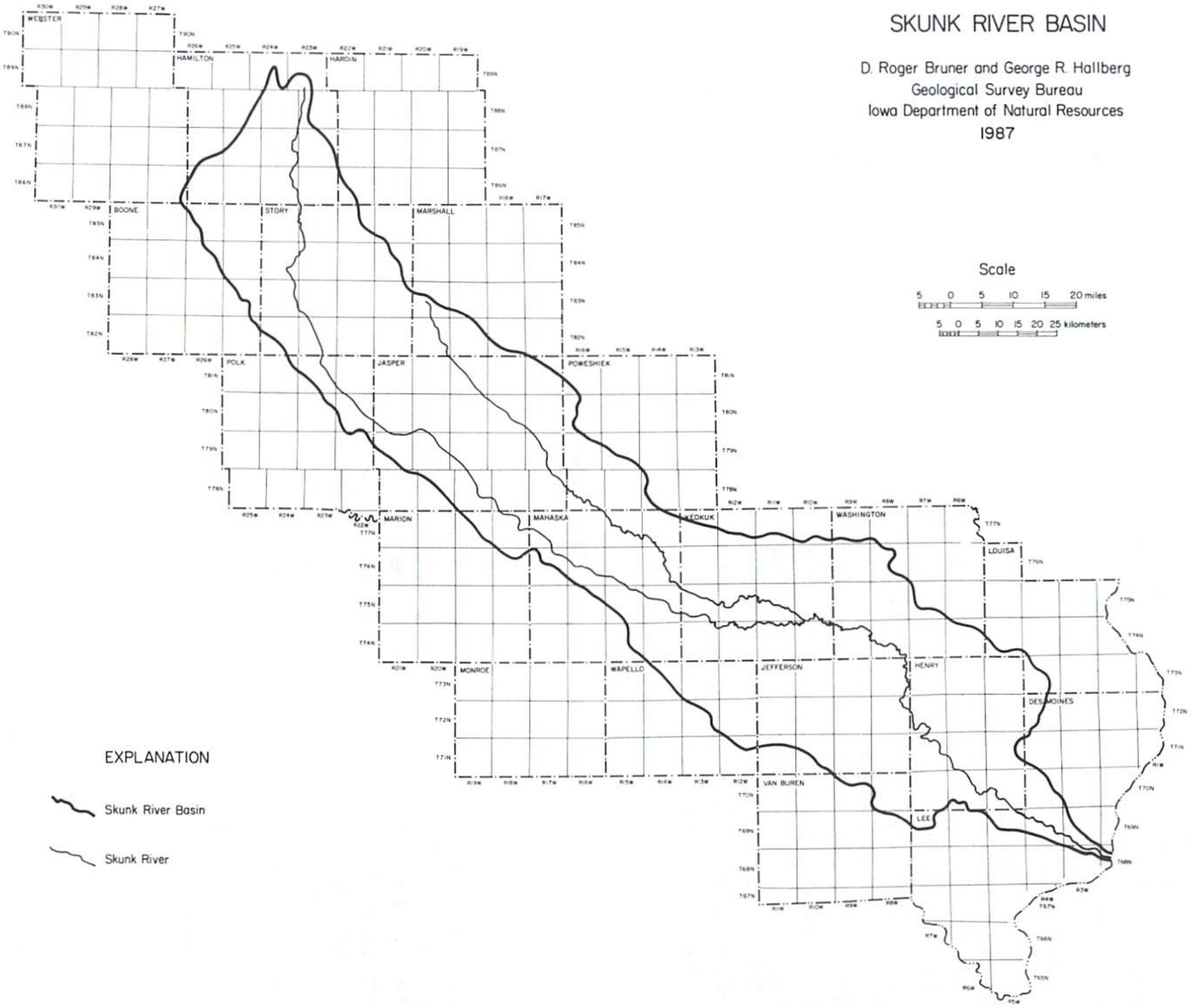


Figure 1. Location of the Skunk River and the basin boundary.

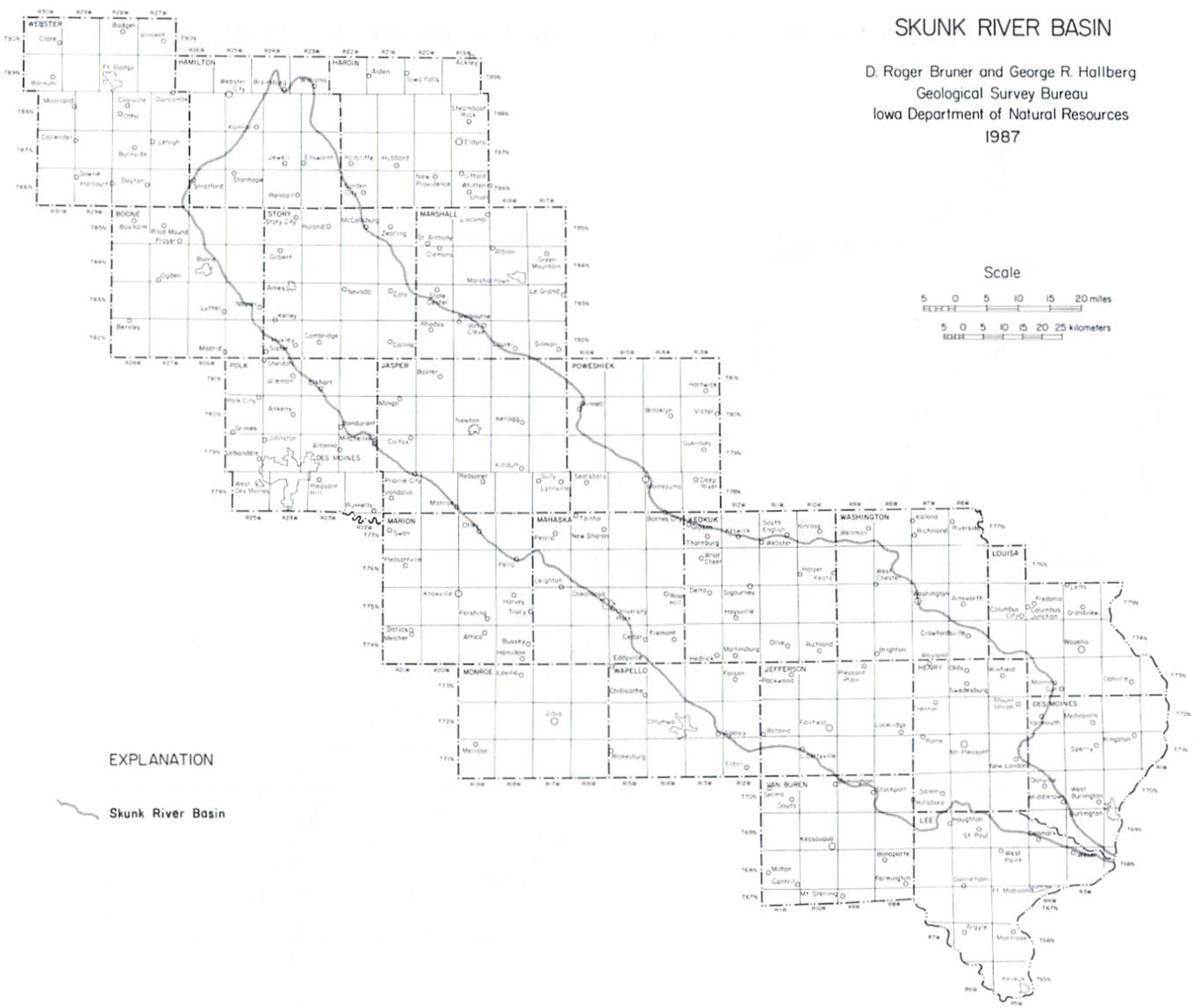


Figure 2. Cities and towns in and around the Skunk River basin.

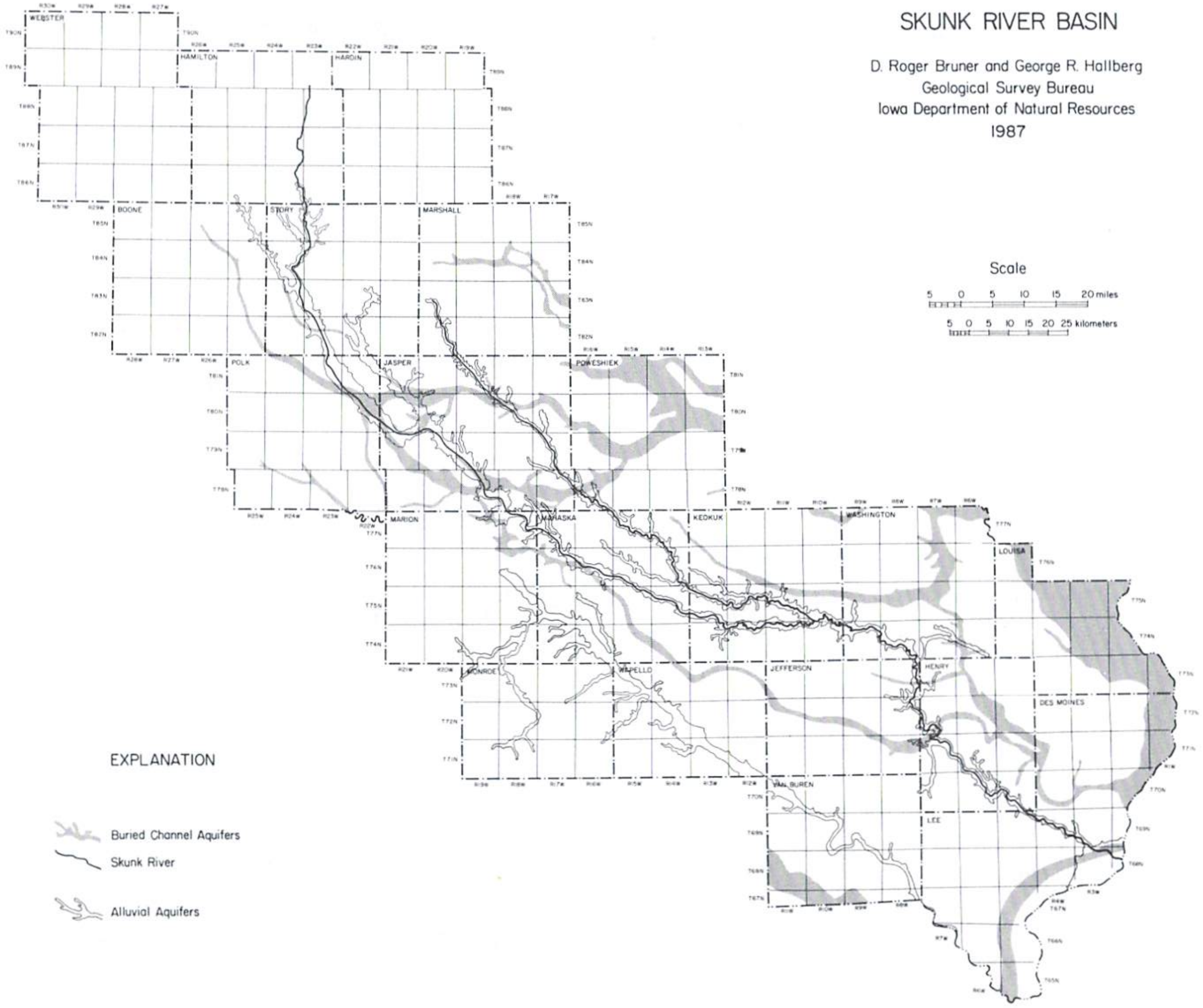


Figure 3. Alluvial and buried channel aquifers in the Skunk River basin.

bedrock topography, and various water atlases for this area(Buckmiller et al.,1985, Coble and Roberts, 1965). These major buried-channel aquifers occur within buried valleys in the bedrock surface.

With few exceptions all of the major consolidated rock aquifers of Iowa underlie the basin. The major rock aquifers, which provide large quantities of good quality water in east-central and northeast Iowa are relatively deeply buried in the Skunk River basin. However, the water quality in these aquifers is naturally degraded in this area, in contrast to other parts of the state, and because of their greater depth, it becomes more costly to drill wells into them. The upper-most bedrock (i.e. the first rock unit beneath the land surface) in the basin is comprised of Mississippian or Pennsylvanian rock units. The Skunk River basin does not have a bedrock aquifer that provides a consistent source for an adequate quantity and quality of groundwater. The Pennsylvanian-aged rocks have a few sandstone channels that provide a reliable water source for local areas, but in most of the basin the Pennsylvanian rocks are comprised of thinly bedded siltstones, shales, and coal, that do not provide an adequate quantity or quality of water. Mississippian rocks, in the southern portions of the basin, are also quite variable . Water quality in these rocks are also variable. At depth the groundwater in these units is often of poor quality, as will be discussed. (Additional information is available from the GSB water atlases cited previously and from Miscellaneous Map Series of the major bedrock aquifers in the state: Mississippian aquifer, Horick and Steinhiber, 1973, Silurian-Devonian aquifer, Horick, 1984, and Jordan aquifer, Horick and Steinhilber, 1978, and the following Water Atlases, North-Central, Buchmiller et al., 1985, Central, Twenter and Coble, 1965, East-Central, Wahl et al., 1978, and Southeast Iowa, Coble and Roberts, 1971.)

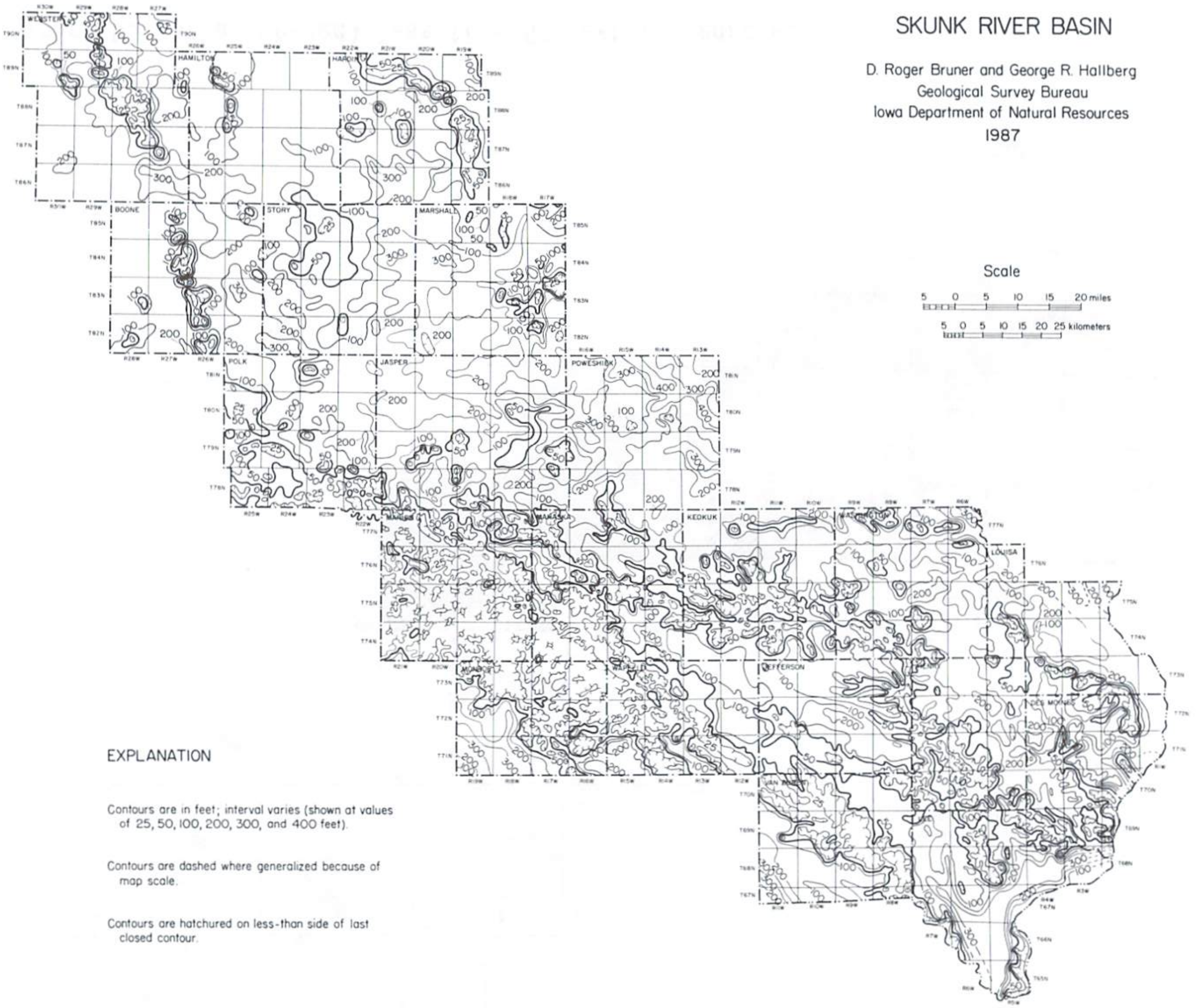
Because of the uncertainties with the groundwater quality and quantity from the bedrock units many wells are not finished in any of these sources, but tap relatively small, discontinuous sand and/or gravel bodies in the unconsolidated glacial materials that overlie the bedrock. This source of groundwater was not mapped because of its highly variable and discontinuous nature. This diffuse source, which can often provide adequate quantities of water to most private rural wells (i.e. 2-10 gallons per minute) is referred to as the 'drift aquifer.' Data from the drift aquifer and the buried-channel aquifers are often combined and summarized as the Pleistocene aquifer.

To characterize the susceptibility of the basin's bedrock aquifers to contamination from man's activities, the depth to bedrock was mapped in detail. The methods used are based on those outlined by Hallberg and Hoyer (1982). The data used to compile these maps include: all GSB well and core logs (approximately 6000), quarry and outcrop records for locations in the basin or bordering it, and compilation of all soil-mapping units which encountered bedrock within the solum (from modern SCS-Iowa Cooperative Soil Survey reports). The complete depth-to-bedrock map is shown in figure 4. A summary map showing the areas where bedrock is less than 50 feet from the surface is shown in figure 5. The depth to bedrock is essentially derived by mapping the thickness of the unlithified, Quaternary deposits over the bedrock. Outside of stream valleys these deposits are dominated by relatively fine-textured glacial deposits, which tend to act as an aquitard, slowing groundwater recharge to aquifers below. Soil groups within the Skunk River basin change from those associated with the Des Moines Lobe physiographic region in the northern part of the basin to those soils that evolved on the Southern Iowa Drift Plain physiographic region found in the southern part of the basin. As many Iowa studies have shown, when an aquifer is covered by less than 50 feet of Quaternary materials (i.e. where glacial deposits are less than 50 feet thick) it may be very susceptible to contamination (Hallberg and Hoyer, 1982; Hallberg et al., 1983a,b, 1984; Libra et al., 1985; Mitchem et al., 1986). However, where it has a mantle of more than 50 feet of Quaternary deposits (and/or an equivalent thickness of a shale aquitard is present) the aquifer typically shows little contamination from nitrate or other man-made chemicals (unless unusual local conditions are involved). Hence, Figure 5 is also an important tool for analyzing the distribution of the water-quality data. As in past studies (Hallberg and Hoyer 1982), geologic data for the basin will be grouped into two categories, based on the thickness of Quaternary deposits, for comparison: 1. 'Shallow bedrock' areas, which have Quaternary deposits less than 50 feet thick; and 2. 'Deep bedrock' areas, which have deposits greater than or equal to 50 feet thick, varying in this region to greater than 400 feet in thickness.

Regional Groundwater Quality

The GSB maintains a copy of the data, for Iowa, from the United States Geological Survey (USGS) groundwater data base, WATSTORE. This data base contains several thousand water analyses for wells in Iowa and includes important information on water source, aquifer type, location, and, in some cases, on well construction. These data are primarily from public water supplies (i.e. municipal wells) and have been collected over the past 50 years. Hence, not all of the data is contemporary.

Seven chemical parameters were selected from the 44 available on the WATSTORE database to describe the general ground-



SKUNK RIVER BASIN

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Scale

EXPLANATION

Contours are in feet; interval varies (shown at values of 25, 50, 100, 200, 300, and 400 feet).

Contours are dashed where generalized because of map scale.

Contours are hatchured on less-than side of last closed contour.

Figure 4. Depth to bedrock. Contour at 25, 50 (heavy line) and 100 feet; subsequent contour interval 100 feet.

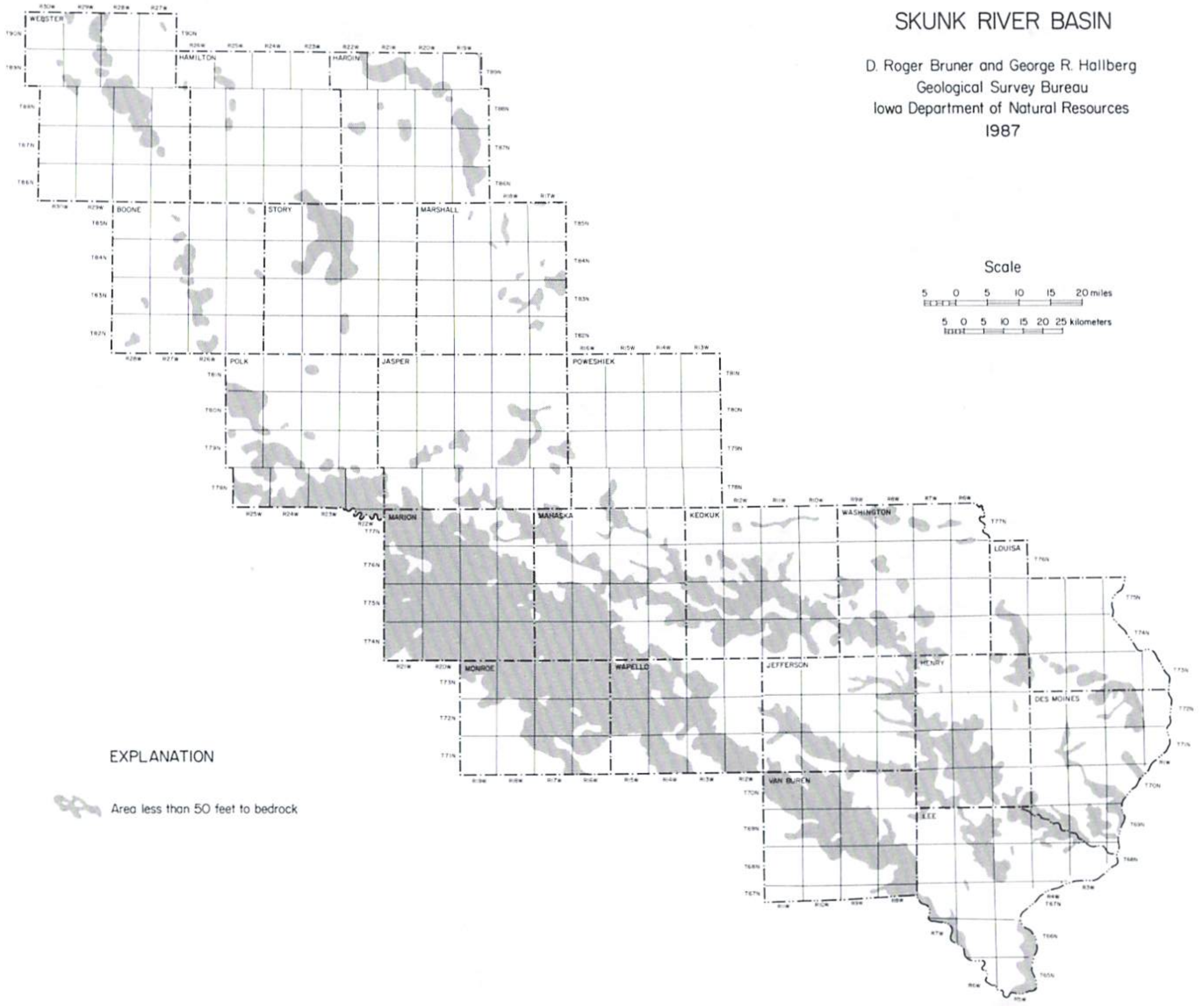

Figure 5. Area (shaded) less than 50 feet to bedrock.

water quality in the regional aquifers that occur in the study area. Total dissolved solids (TDS), total hardness, sulfate (SO_4), chloride (Cl), total iron (Fe), radium 226 (Ra226), and gross alpha radiation data were retrieved from the database for water samples taken from wells in the study area. This data was analyzed statistically and summarized using computerized statistical programs available to the GSB.

The groundwater quality of the different aquifers varies over the basin. Table 1 discusses the significance of the general water quality parameters studied and table 2 shows the average concentrations in the different aquifers that are used in the basin. Also shown is the first and third quartiles for these parameters, which provides an indication of the variability of the water quality in the specified aquifer. Total dissolved solids (TDS) is an indicator parameter of the overall water quality. Generally, as TDS increases, overall water quality decreases. A maximum level of 500 mg/l is set as an aesthetic standard for adequate water quality (see table 1) . This secondary standard for water quality is generally exceeded in groundwater from the bedrock and Pleistocene aquifer sources in the study area. The Silurian aquifer appears to have excellent water quality. This is somewhat misleading because it is used in only a small portion of the basin along the north-eastern border. The quality rapidly deteriorates towards the south and southwest, but there is only limited data from the rest of the basin. Other than alluvial aquifers, which are geographically restricted, most of the relatively shallow and therefore economical sources for private wells provide water that is generally high in TDS, sulfates, and iron. Deeper sources usually have these problems and have higher concentrations of radionucleides, as well. Therefore, as noted previously, many private wells tap the first available water source. Many towns use surface water sources (such as reservoirs) and/or alluvial aquifers where possible.

While these data provide an overview of the natural chemistry of the region's groundwater, they do not provide an adequate overview of current concerns with man-made contaminants in the relatively shallow groundwater system that is most often used by rural residents in the basin. The private-well water analyses described below, provides a better insight into these regional problems.

UHL Water Quality Data From Private Wells

The major water quality data set which provides a better overview of the shallow groundwater contamination concerns in the basin was provided by the University Hygienic Laboratory (UHL) in Iowa City. The data set is from private water samples, analyzed for nitrate and bacteria, and includes over

TABLE 1. Significance of Selected Chemical Constituents of Water.

Constituent	Maximum Recommended Concentration	Significance
Total Dissolved Solids (TDS)	500 mg/l	This refers to all the material in water that is in solution. Amounts over 2000 mg/l will have a laxative effect on most persons. Amounts up to 1000 mg/l are generally considered acceptable for drinking purposes if no other water is available.
Hardness		Hardness, together with chemical parameters, affects the lathering ability of soap. Hardness is primarily related to dissolved calcium and magnesium; and is reported in terms of an equivalent amount of calcium carbonate. Water becomes objectionable for domestic use when the hardness exceeds 100 mg/l however, this can be easily remedied by using a water softener.
Sulfate (SO_4)	250 mg/l	Commonly has a laxative effect when the concentration is 600 to 1000 mg/l, particularly when combined with magnesium or sodium. The effect is much less when combined with calcium. This laxative effect is commonly noted by newcomers, but they become acclimated to the

		water in a short time. The effect is noticeable in almost all persons when concentrations exceed 750 mg/l. Sulfate combined with calcium forms a hard scale in boilers and water heaters.
Chloride (Cl)	250 mg/l	Large amounts combined with sodium impart a salty taste.
Iron (Fe)	0.3 mg/l	Objectionable as it causes red and brown staining of clothing and porcelain. High concentrations affect the color and taste of beverages.
Radionucleides		
Radium (radium-226 and radium-228)	5 pCi/l	The effect and significance of low concentrations of radium on public water supplies isn't fully known. However, the EPA takes the position that any dose of ionizing radiation has a potential to produce deleterious effects on human health and that the effect will be proportional to the dose received.
Gross Alpha Activity	15 pCi/l	

9600 analyses. These samples were submitted from 1980 to 1985, inclusive . Well depth and location information is provided by the individual sending the sample. The control on location and well depth is variable, and locations are limited to rural route mailing addresses. Prior studies have found that about 70-80 per cent of well-depths reported by owners are reasonably accurate. This data may be biased for two reasons: first, people often submit samples when there is a known or suspected problem with their well; secondly, residential well construction and maintenance is more

Table 2. Median $\frac{\text{1st Quartile}}{\text{3rd Quartile}}$ Values for Selected Water Quality Parameters in the Different Aquifers in the Skunk River Basin (results in mg/l unless noted)

AQUIFER	TDS		TOTAL HARDNESS[1]		SO_4		Cl^-		TOTAL Fe		Ra^{226} [2]		GROSS α [2]	
Alluvial	376	$\frac{243}{532}$	300	$\frac{192}{420}$	66	$\frac{32}{120}$	10	$\frac{5}{21}$	0.32	$\frac{0.06}{2.80}$	0.4	$\frac{0.2}{0.5}$	2.1	$\frac{0.7}{4.2}$
Pleistocene	547	$\frac{421}{747}$	410	$\frac{330}{550}$	107	$\frac{51}{220}$	10	$\frac{4}{21}$	1.30	$\frac{0.20}{3.38}$	0.5	$\frac{0.2}{1.2}$	2.0	$\frac{0.8}{4.0}$
Cretaceous	985	$\frac{467}{1510}$	570	$\frac{360}{852}$	335	$\frac{83}{749}$	6	$\frac{2}{15}$	1.90	$\frac{0.70}{5.83}$	2.3	$\frac{1.3}{3.7}$	4.6	$\frac{2.0}{9.9}$
Pennsylvanian	1036	$\frac{543}{2555}$	370	$\frac{200}{705}$	520	$\frac{132}{1300}$	20	$\frac{5}{95}$	1.49	$\frac{0.58}{5.35}$	2.3	$\frac{1.0}{5.7}$	11.0	$\frac{4.4}{20.0}$
Mississippian	589	$\frac{422}{1270}$	420	$\frac{347}{620}$	160	$\frac{42}{692}$	7	$\frac{2}{30}$	1.60	$\frac{0.60}{3.71}$	2.5	$\frac{1.4}{4.7}$	4.1	$\frac{1.6}{11.8}$
Devonian	454	$\frac{339}{963}$	366	$\frac{276}{593}$	76	$\frac{28}{515}$	6	$\frac{2}{14}$	0.87	$\frac{0.30}{2.35}$	2.4	$\frac{1.4}{3.7}$	2.0	$\frac{0.8}{5.3}$
Silurian	364	$\frac{296}{471}$	312	$\frac{268}{384}$	33	$\frac{16}{68}$	5	$\frac{2}{12}$	0.56	$\frac{1.11}{1.60}$	2.8	$\frac{1.2}{4.5}$	1.3	$\frac{0.6}{2.9}$
Ordovician	863	$\frac{441}{1260}$	380	$\frac{294}{610}$	350	$\frac{84}{590}$	36	$\frac{7}{120}$	0.70	$\frac{0.12}{1.60}$	5.3	$\frac{3.0}{8.6}$	12.5	$\frac{4.0}{21.0}$
Cambrian	558	$\frac{357}{1161}$	344	$\frac{282}{450}$	191	$\frac{44}{523}$	20	$\frac{6}{65}$	0.44	$\frac{0.20}{1.50}$	4.8	$\frac{3.2}{7.1}$	9.4	$\frac{3.4}{17.0}$
PreCambrian	898	$\frac{702}{1782}$	420	$\frac{290}{770}$	521	$\frac{145}{963}$	53	$\frac{8}{213}$	3.60	$\frac{0.14}{9.15}$	3.5*	$\frac{1.7}{5.6}$	4.3*	$\frac{1.5}{11.4}$

1) mg/l as $CaCO_3$
2) pCi/l
*) <30 observations

variable than for municipal wells. However, rural residents are increasingly being required to have their wells tested as part of mortgage agreements, and the growing concern with water-quality has prompted more precautionary sampling. Other recent studies in Iowa have shown that the very large sample size (N=9631) generally compensates for these biases, and these data should indeed be a reasonable representation of the overall water quality, at least for nitrate.

Each UHL data record consists of the county number, and rural route mailing address, well depth, nitrate concentration, bacteria classification and lab ID number. The nitrate analysis used has a lower detection limit of 5 mg/l. Samples with concentrations of <5 mg/l were assigned the value of 2 mg/l for ease of numerical and statistical manipulations. These data were analyzed using the Statistical Analysis System (SAS), which is a set of statistical analysis computer programs. The data were grouped by different variables and analyzed by one of several parametric and non-parametric statistical procedures. The methods for spatial analysis used in this report were devised by Hallberg and Hoyer (1982). The samples were grouped by rural route mailing addresses into 'sample centers'. These 'sample-centers' were then classified into 'Shallow' or 'Deep' bedrock categories by comparing them to the dominant setting in their area (i.e. most areas greater than or less than 50 feet to bedrock).

Bacteria Data. The bacterial data was correlated with several other well construction and water quality parameters in an attempt to ascertain its relative importance to the water quality in the Skunk River Basin. There was no apparent relationship between bacterial data and well depth, nitrate concentration or thickness of Quaternary deposits that overlie the bedrock. This seemingly random distribution of bacterial concentrations indicates that a regional pattern probably does not exist and suggests that site-specific bacterial problems overwhelm any bacterial problems related to geologic setting or regional hydrogeologic patterns of contamination. (Past GSB studies have shown that many bacterial 'problems' are related to either sampling errors or the local water storage/ water supply system.)

Nitrate Data Analysis. The statistical analysis of the UHL nitrate data indicates a relationship between nitrate concentration and well depth. The nitrate data from the study area is summarized by well depth class in table 3. There are two obvious trends in the data presented. First, the number of analyses for each well depth class decreases with increasing depth. This indicates that there are many more shallow wells than deep wells in the study area. Second, the mean and

Table 3. Comparison of Nitrate Concentration Distribution by Well Depth.

Well Depth Class (ft)	N	NO_3 Concentration		Kruskal-Wallis Test With Next Lower Class	
		Mean	Medium	DF	Significance
0-49	4772	38.6	9	1	1.34
50-99	1525	39.9	7	1	262.57
100-149	914	12.4	2	1	10.07
150-199	697	7.2	2	1	2.50
200-249	586	6.2	2	1	3.12
250-299	385	3.4	2	1	0.34
300-399	455	7.8	2	1	1.47
400-499	138	3.1	2	1	2.00
≥ 500	159	3.9	2	-	-

Critical value of χ^2 at $\alpha = .025$; $\chi^2 = 5.02$

median nitrate concentration also decreases with depth. This indicates that the deeper wells tend to have lower nitrate concentrations. The trend of decreasing nitrate concentration with depth is seen in nearly all of the data in Iowa (e.g., Hallberg and Hoyer, 1982; Hallberg, 1986). This concentration-depth relationship is shown graphically in figure 6. A Kruskal-Wallis analysis (a non-parametric statistical test) was used to interpret the distribution of the nitrate concentration in each well depth class comparing it with the data in the succeeding well depth class. This tested the hypothesis that the distribution of nitrate concentrations were the same and therefore could have come from the same population. If the two depth classes had significantly different nitrate concentrations, for a specified level of significance, the calculated test statistic in the Kruskal-Wallis analysis would exceed a predetermined value, and the depth classes could be separated, from a statistical view, based on the nitrate concentrations. From the results presented in table 3, the first two well-depth classes, down to a total depth of 99 feet are not significantly different in their nitrate concentration and cannot be statistically separated from one another. This is expressed in the results of the Kruskal-Wallis test and by simple observation of the mean and median nitrate concentrations for those classes, which are nearly the same. There is a distinct difference between the second and third depth class. Nitrate concentrations in wells from 50 to 99 feet deep are much higher than those in wells that are 100 to 149 feet deep. This is also show by the Kruskal-Wallis test and by noting the mean and median nitrate concentrations. There is a less obvious, but still statistically significant decrease in nitrate concentrations between the third and fourth well depth class. The rest of the well depth classes show no significant change in the nitrate concentration distributions. This would indicate that the distribution of nitrate concentrations for wells greater than 150 feet would not be significantly different from one class to another and that as a group, the nitrate concentration is much lower in these wells than wells less than 150 feet deep.

There is also a trend in the number of wells from each well-depth class. The number of wells with sample analyses decrease substantially with depth and mirror the fact that private wells are usually drilled to the first, and therefore the shallowest, geologic unit that will provide an acceptable quantity of water for the intended use. As noted previously, the deeper groundwater in this area is often unreliable, and the natural quality is often not good. Therefore, shallow sources tend to be used even when the quality is marginal. A shallower well is also a simple matter of economics -- deeper wells are more expensive to drill and maintain. Over 65% of all the wells sampled were less than 100 feet deep and 75% of all the wells were less than 150 feet deep.

Both the median and mean nitrate concentrations are given on all the tables. Nitrate data are not normally (Gaussian) distributed (see Hallberg and Hoyer, 1982). Hence, the usual summary statistic, the mean (or the true arithmatic average), is not wholly appropriate. The median (the value of the 50th percentile) may provide a more appropriate indication of the 'average' value. The median may also be influenced by the skewed distributions with a large mode at the low (<5 mg/l) nitrate concentration. Thus, the median does not always provide as much information about the distribution for a qualitative comparison among the data in skewed distributions. Hence, both values (as well as other descriptive statistics) are given. To illustrate this point, Figure 7 shows the relationship between the mean and median nitrate concentrations for all wells and for wells less than 100 feet deep, for each county. In the 'all wells' grouping, most of

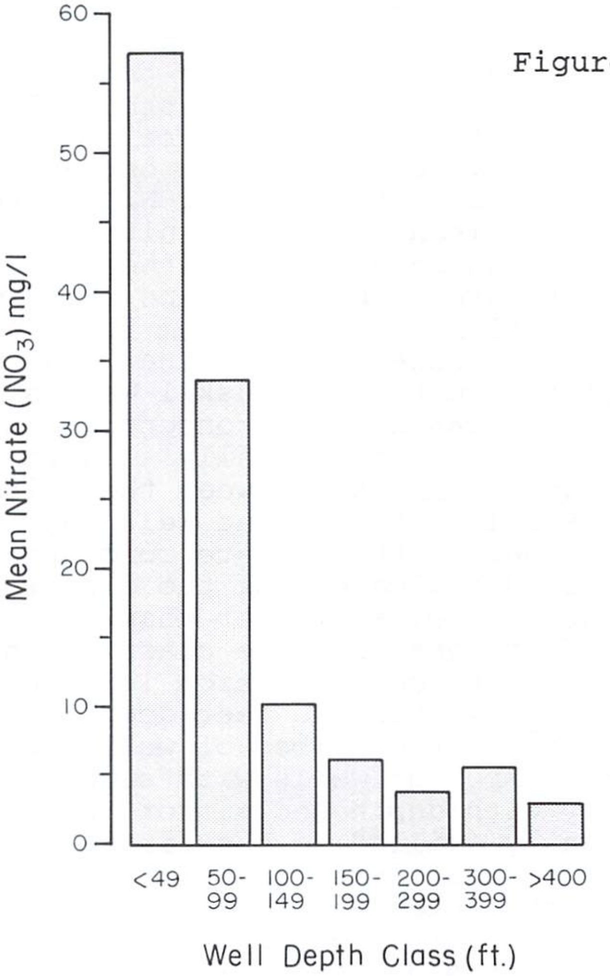

Figure 6. Histogram of mean nitrate (NO_3) concentration versus well depth classes.

the medians are <5 mg/l, (assigned a value of 2 for statistical analysis) even though the means may equal 30 or 40 mg/l. However, this difference is less important for the shallow wells which show the most prevalent nitrate contamination. For these wells, the median more often has a more meaningful value and the mean is more consistently 2 to 2.5 times greater than the median.

Nitrates and Depth to Bedrock

Other studies (Hallberg et al., 1982) have correlated local differences in nitrate contamination trends with the depth to the bedrock, particularly in areas where the bedrock is the major aquifer. The depth to bedrock is equal to the thickness of glacial materials that mantle the bedrock, and generally serve as an aquitard. The influence of little or no Quaternary materials covering the bedrock was also tested in the Skunk River Basin. As noted, the mailing centers were assigned to either of two classes based on the prevailing depth to bedrock in their area (figures 4 and 5). Those mailing centers that are located in areas of bedrock outcrop or having less than about 50 feet of Quaternary materials over bedrock were classified as 'Shallow bedrock', all others were classified as 'Deep bedrock'. A summary of the aggregate nitrate data, for the Shallow and Deep bedrock areas is given on table 5. A Kruskal-Wallis test was run to compare the nitrate distribution between the Shallow and Deep areas. The test produced a chi squared of 117.3, a highly significant difference in the distribution at the 0.025 confidence level. This demonstrates that wells constructed in areas that are shallow to bedrock tend to produce groundwater with greater nitrate concentrations than do wells with thick glacial drift deposits. Table 4 also lists the per cent of analyses exceeding both the maximum contaminant level (MCL) and 0.5, or 50%,

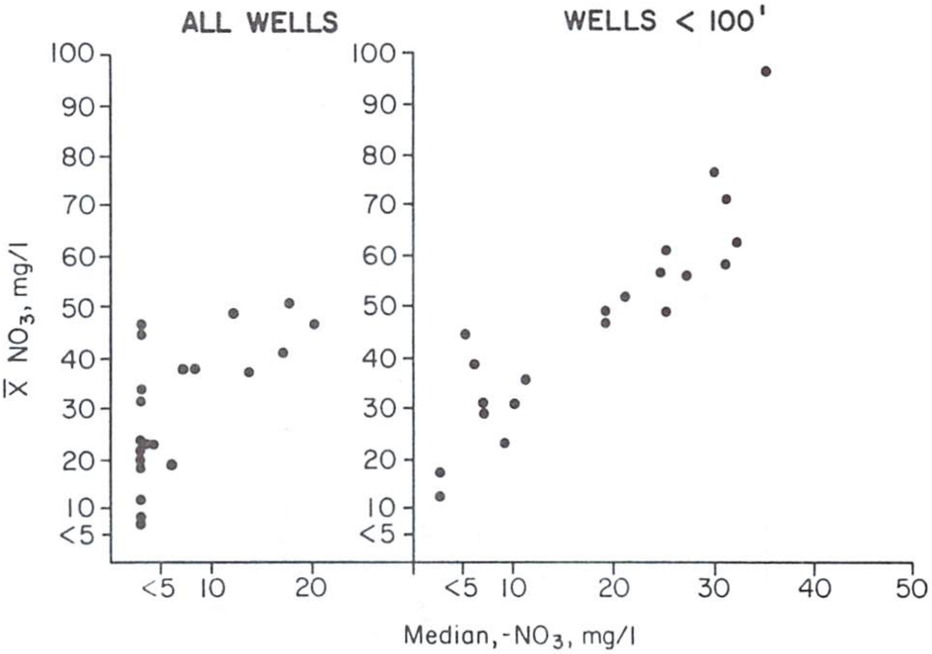

Figure 7. Mean versus median nitrate (NO_3) concentrations per county for all well data and for only wells less than 100 feet deep.

Table 4. Comparison of Nitrate Concentration Between Shallow Bedrock and Deep Bedrock Areas.

	SHALLOW						DEEP					
Well Depth Clast (ft)	N	%	Md (mg/1)	$\overline{X}$(mg/1)	% 1/2 MCL	% MCL	N	%	Md (mg/1)	$\overline{X}$(mg/1)	% 1/2 MCL	% MCL
0-49	2121	51.2	14	45.6	42.0	27.3	2651	48.3	6	33.1	32.9	20.9
50-99	719	17.4	12	48.2	40.1	28.4	806	14.7	2	32.5	30.9	19.6
100-149	373	9.0	2	12.5	12.6	7.0	541	9.9	2	12.4	10.9	4.6
150-199	277	6.7	2	7.1	7.2	4.7	420	7.7	2	7.3	6.2	3.6
200-249	230	5.6	2	5.6	5.2	2.2	356	6.5	2	6.6	5.6	3.1
250-299	143	3.5	2	4.5	1.4	1.4	242	4.4	2	2.7	0.4	0
300-399	203	4.9	2	6.6	5.4	3.0	252	4.6	2	8.7	2.4	1.6
400-499	41	1.0	2	3.2	4.9	0	97	1.8	2	3.1	2.1	0
$\geq$ 500	36	0.9	2	5.9	5.6	5.6	123	2.2	2	3.3	1.6	0.8
Basin	4143	100.2	2	34.2	30.8	20.2	5488	100.1	2	23.6	22.5	14.0

Table 5. Nitrate Concentration and Well Depth by County.

COUNTY	ALL WELLS						WELLS <100 FT.						WELLS >100 FT.					
	Well Depth		NO_3				Well Depth		NO_3				Well Depth		NO_3			
	Md	$\overline{X}$	Md	$\overline{X}$	% >1/2 MCL	%>MCL	Md	$\overline{X}$	Md	$\overline{X}$	% >1/2 MCL	%>MCL	Md	$\overline{X}$	Md	$\overline{X}$	% >1/2 MCL	%>MCL
Boone	96	165	2	21.5	16.7	11.1	60	57	2	30.6	24.5	16.7	233	278	2	2.7	0.0	0.0
Des Moines	120	159	2	19.6	18.5	10.2	40	48	2	26.2	25.6	15.6	180	234	2	10.3	8.7	2.9
Hamilton	170	212	2	11.8	11.1	5.7	60	57	2	21.5	22.8	11.8	234	274	2	3.6	1.2	1.2
Hardin	130	152	2	20.8	9.3	4.1	68	63	2	10.9	13.3	6.0	160	194	2	4.1	4.1	2.1
Henry	100	139	2	45.0	34.3	23.3	48	49	21	67.6	48.5	34.3	205	220	2	8.4	11.3	6.0
Jasper	55	121	2	30.5	26.2	17.7	40	43	12	41.3	36.1	25.3	215	238	2	5.5	3.4	1.7
Jefferson	45	72	20	46.4	47.9	29.6	40	46	23	49.7	51.0	31.9	209	225	2	17.0	21.4	14.3
Keokuk	80	147	7	38.4	32.2	22.8	40	45	16	52.1	44.3	31.9	180	266	2	11.8	8.8	5.7
Lee	80	145	8	37.8	37.2	25.5	40	44	29	54.0	54.5	38.7	240	260	2	8.6	6.3	3.6
Louisa	80	99	2	23.1	28.0	20.4	30	46	2	29.6	38.0	27.9	135	173	2	8.6	5.8	3.6
Mahaska	75	116	2	46.8	32.1	21.8	40	41	18	62.7	45.9	31.8	180	106	2	17.7	7.0	3.5
Marion	40	93	12	49.0	40.2	26.7	30	34	25	64.5	52.2	35.3	180	206	2	5.8	13.5	2.7
Marshall	100	129	2	20	25.0	11.0	44	49	10	28.1	35.9	17.6	180	207	2	5.6	5.8	2.3
Monroe	27	40	17	40.7	43.1	27.5	25	31	18	41.5	44.0	28.0	- - - Insignificant number of wells - - -					
Polk	65	164	6	18.5	26.1	8.8	50	54	9	21.5	31.2	11.5	350	413	2	7.3	6.8	2.7
Poweshiek	130	168	2	34.7	28.6	19.1	40	39	17	51.4	43.9	29.9	250	286	2	7.8	4.0	3.5
Story	165	204	2	7.1	5.7	4.1	60	57	2	8.5	7.8	5.8	200	251	2	4.7	2.2	1.3
Van Buren	40	79	17.5	50.6	43.9	28.1	35	37	21	56.0	48.6	31.5	210	279	2	12.0	10.0	6.7
Wapello	40	100	13.5	37.0	38.1	23.9	33	38	19	42.8	43.9	28.1	198	369	2	4.2	5.0	0.0
Washington	120	151	2	23.6	23.8	16.0	55	54	2	32.7	33.9	24.4	175	212	2	11.1	9.9	6.0
Webster	90	165	2	24.1	20.9	14.3	60	59	2	34.7	30.1	22.7	220	285	2	5.0	4.2	1.5
Basin	144	90	2	28.1	26.1	16.7	42	48	9	38.9	36.5	24.2	200	243	2	7.8	6.3	3.3

of the MCL for nitrate.(The nitrate MCL is set at 45 mg/l as nitrate). The listing of 0.5 MCL is used as an indicator of analyses that show significant contamination and that may seasonally exceed the MCL (suggested from prior studies).

A few similarities exist between the two areas. There is a general decrease in nitrate concentration with well depth in both areas. Along with this is a general decrease in per cent of analyses that exceed the MCL and those that are greater than 0.5 MCL. As with the total basin data the number of total well analyses also decrease with depth.

There are a few important differences between the two groups, however. The nitrate concentration in the two shallowest well depth classes is somewhat greater in the Shallow Bedrock areas than in the Deep Bedrock areas. In a similar fashion, the per cent of analyses that exceed both 0.5 MCL and the MCL is substantially higher in these well depth classes in the Shallow Bedrock areas. Note that even with the limitations on location data, the majority of wells in at least the first well depth class (0-49 feet) and many in the second class would not be drilled into bedrock in the Deep Bedrock areas (i.e., by definition, where the bedrock is greater than 50 feet deep).

The Shallow Bedrock areas have consistently higher percentages of analyses that exceed both of the 0.5 MCL and MCL in almost all of the well depth classes. This is reflected in the basin-wide figures for these categories (Table 4). The Shallow Bedrock areas, over the basin, exhibit a mean nitrate concentration about 10 mg/l greater, and 6% to 8% more analyses that exceed the MCL and 0.5 MCL than the Deep Bedrock areas. These trends are most pronouced for wells less than 150 feet deep.

County Aggregate Data

The data were also summarized by counties within the basin to see if there were geographic trends. A different system for segregating the data was required because only some of the counties had Shallow Bedrock areas located within their borders. Also all of the well-depth classes were not represented in every county. To evaluate the difference between shallow and deep wells, the large statistical difference in nitrate concentration distribution between the 50 to 99 foot and 100 to 149 foot well depth class was used to segregate the data. These data individual counties and the basin as a whole are presented in table 5.

The nitrate concentration in wells less than 100 feet deep is consistently greater than in the deeper wells for each county in the basin. The per cent of analyses that exceed either 0.5 MCL or the MCL for nitrate also follow this trend.

The mean well depth, for wells less than 100 feet deep, is about 48 feet. The mean nitrate concentration for these wells exceeds 80% of the MCL. Only two counties do not have more than 20% of their analyses exceeding 0.5 the MCL for nitrate. Over 50% of the analyses for wells less than 100 feet deep in Marion and Jefferson counties exceed 0.5 MCL for nitrate. In this same group of wells, over half of the counties have more than 25% of all analyses exceeding the MCL for nitrate. Conversely, for wells greater than or equal to 100 feet, only one county had more than 10 % of nitrate analyses exceeding the MCL. This deeper class of wells also averages about 200 feet in depth. An interesting point in this grouping is that Monroe county had only two analyses between 1980 to 1985, from wells greater than or equal to 100 feet, which again emphasizes the dependance on shallow wells, particularly in the southern portion of the basin.

Geographic Trends in Nitrate Contamination. Geographic trends in the nitrate data can be summarized by plotting the mean and median county nitrate concentrations and percentages exceeding the nitrate MCL on maps. Figure 8 shows the median nitrate concentrations for the counties in the Skunk River Basin. Figure 9 shows the median nitrate concentration for wells less than 100 feet deep. There is a distinct difference between the counties in the northern half of the basin and those in the southern half. Figure 10 shows the geographic distribution of the percentage of all analyses exceeding the MCL for nitrate. This plot also indicates the differences between those counties in the northern and southern portions of the basin. Figure 11, which shows the mean well depth by county, reveals the same pattern as figures 9 and 10; the southern portion of the basin is dominated (by necessity) by shallower wells which show greater nitrate contamination.

A comparison of these maps and figures 4 and 5, showing the depth to bedrock, also illustrates the general relationship between Shallow Bedrock regions, the use of shallow wells, and increasing percentages of analyses that exceed the MCL for nitrate in these Shallow bedrock-shallow well areas. Figure 12 relates the median nitrate concentrations for all wells, of each 'sample center' (i.e., each rural route, aggregated to the towns shown on figure 2), to the Shallow Bedrock regions, of figure 5. Note the relationship of low nitrate values in the Deep Bedrock regions (primarily in the north) and the higher nitrate concentration in and around the Shallow Bedrock regions.

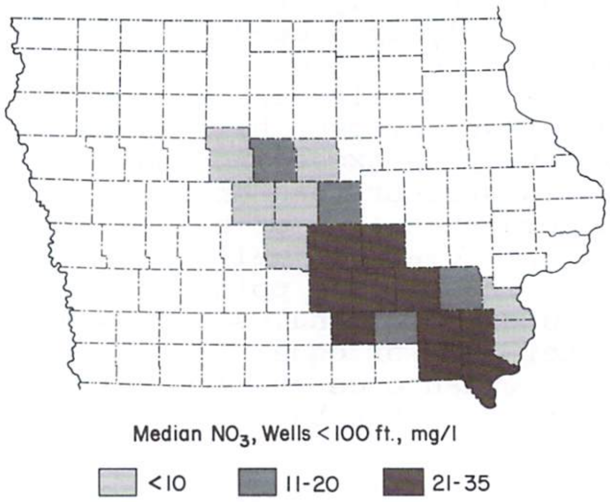

Figure 8. Median nitrate concentrations, for all wells in a county.

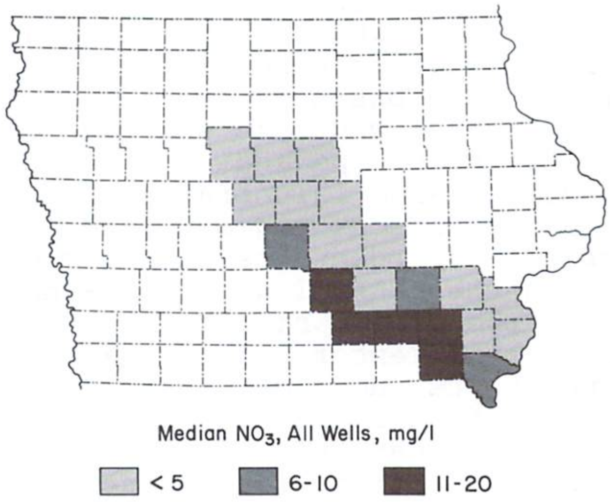

Figure 9. Median nitrate concentrations, for all wells <100 feet deep in each county.

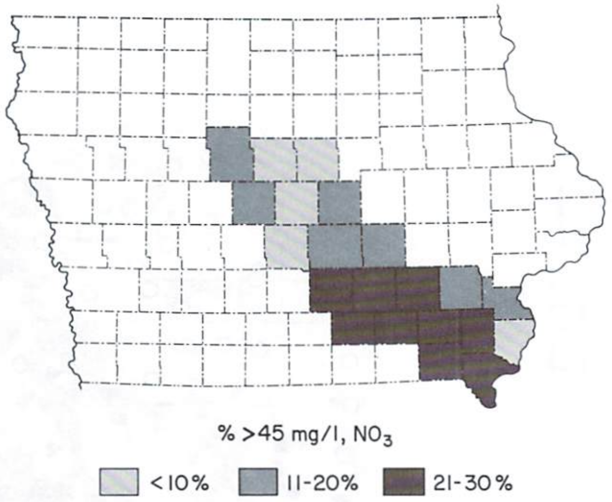

Figure 10. Percent of all analyses exceeding the nitrate MCL (45 mg/l NO_3).

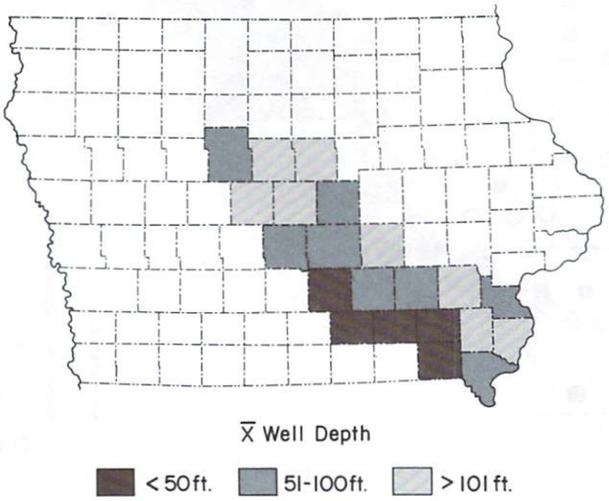

Figure 11. Mean well depth for all wells in a county.

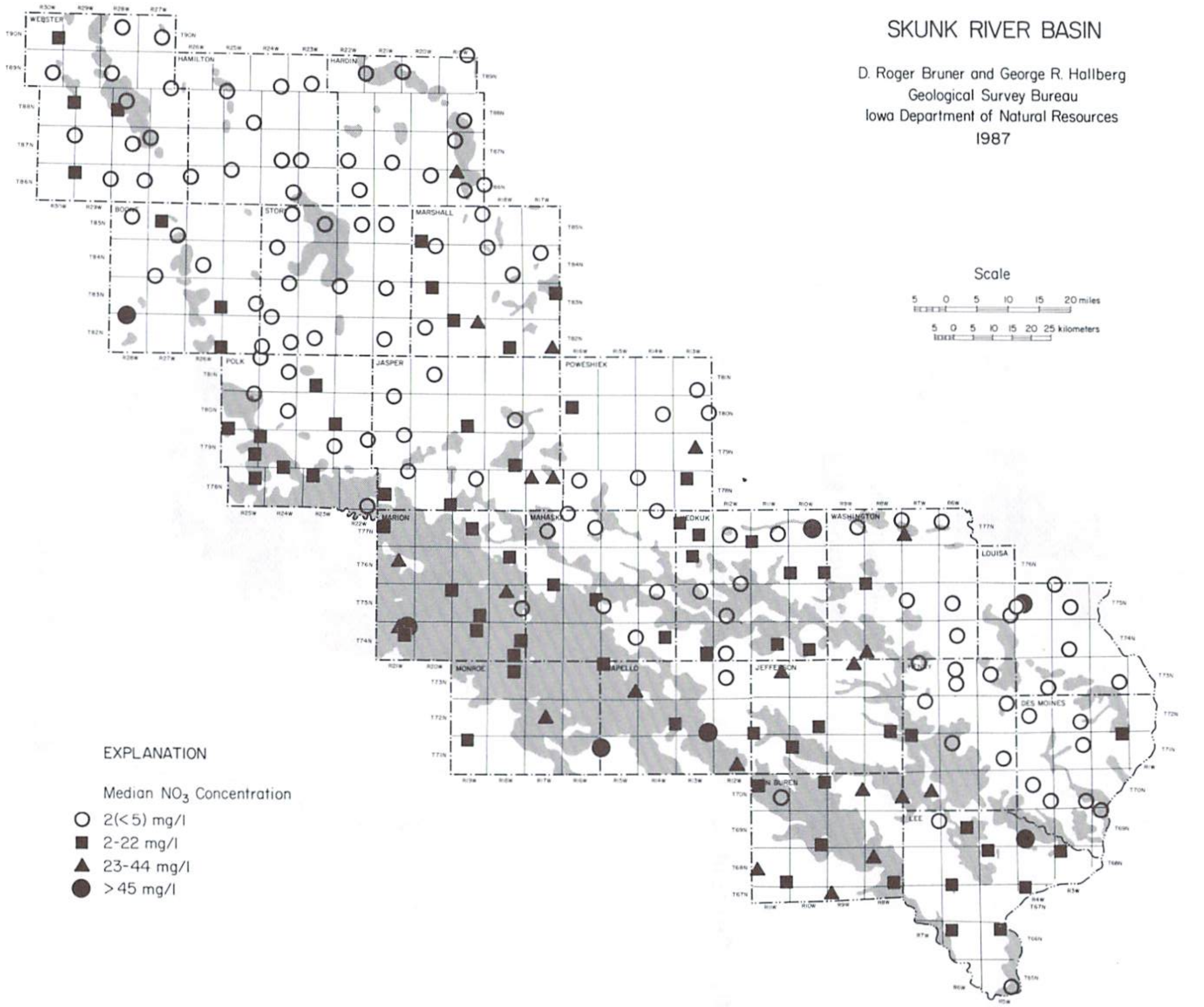

Figure 12. Median nitrate concentration for each sampling center and areas (shaded) less than 50 feet to bedrock.

NITRATES, SURFACE WATER, AND GROUNDWATER

In Iowa, and other humid areas, groundwater discharges into the major streams, providing perennial flow. This is why streams continue to flow even after many weeks without runoff-producing rain events. This interconnection between groundwater and surface water also affects the surface-water quality.

As previously noted, a number of municipal and public water supplies use surface water in the Skunk River basin. In the past, a great deal of money and energy has been expended in resolving various surface water quality problems. Great strides have been made in Iowa, and the nation as a whole, in developing municipal wastewater treatment facilities and working with industry to control point-source pollution discharges into streams and lakes. However, even where waste treatment effects have been essentially eliminated, high nitrate loads have continued or increased in many streams. This is where the interconnection between groundwater and surface water again plays a role. The high nitrate concentrations that appear in these streams are related to periods of increased discharge from shallow groundwater into the streams. The nitrate is mobilized by water infiltrating through the soil, recharging shallow groundwater, which in turn, discharges into surface water. This is illustated in figure 13, which shows the discharge of the Skunk River(Q) and the NO_3-N concentration(N) of the water over time. Note that as the discharge of the river increases, the NO_3-N concentration is either stable or actually decreases. This is because the overland-runoff water that forms these stream discharge peaks is quite low in NO_3-N. Nitrate is actually formed in the soil by nitrification (oxidation) of ammonium or organic nitrogen and therefore is unavailable to overland flow. Hence, nitrate in the soil is picked up in the water moving down through the soil (i.e. groundwater), but not over it (i.e. surface runoff). Figure 13 shows that the peak NO_3-N concentration occurs as river discharge recedes. This recession after a peak discharge event is a period of enhanced groundwater discharge in streams (from tile-lines, and other shallow groundwater movement). Thus, after the runoff-water peak has rapidly moved down stream, the slower moving groundwater, recharged by the rain which generated the event (and bank storage, etc.) moves through the soil, mobilizing nitrate, and discharges into the stream producing the increases in nitrate concentration.

The timing of nitrate concentration fluctuations is related to seasonal recharge and not to the timing of seasonal agricultural practices. This is why nitrate concentrations in streams (and shallow wells) increase during spring recharge events, often several weeks before fertilizers are applied. Monitoring of the Skunk River (Fig. 13)

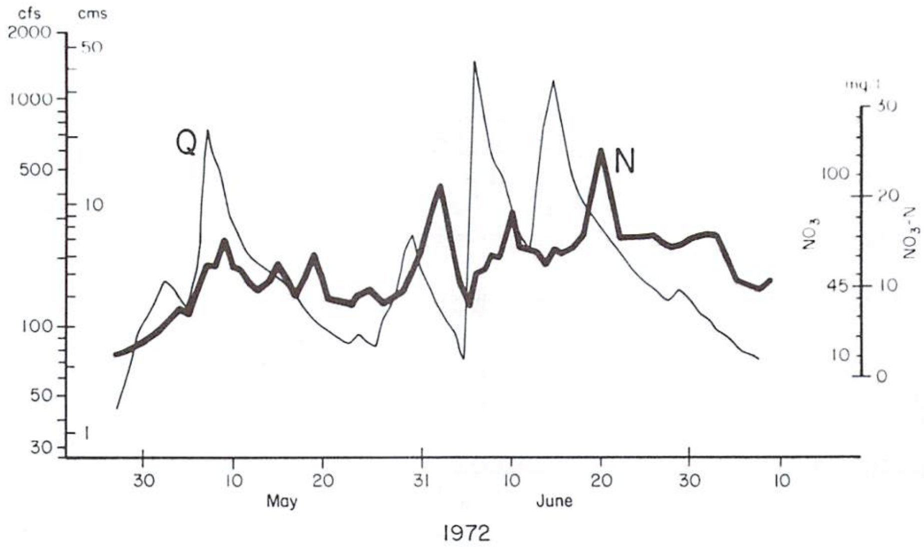

Figure 13. Nitrate concentrations (N) and discharge (Q) from Skunk River near Ames (after Johnson and Baker, 1973; Baker and Johnson, 1977).

also revealed that about 20 to 25 lbs-N/ac (soluble NO3 and NH4) were discharged out of the basin during 1972 (Johnson and Baker, 1973). This illustrates some of the economic concerns with nitrogen losses.

PESTICIDES AND OTHER SYNTHETIC ORGANIC CHEMICALS(SOC)

The Skunk River basin area has very limited analytical data on the occurrence of pesticides and other synthetic or volatile organic chemicals in water supplies. Various studies by Richard et al.(1975), Kelley (1985), data from the STORET database, and unpublished monitoring results from UHL, USGS, GSB, and the Environmental Protection Division-DNR (formerly the Iowa Department of Water, Air, and Waste Management) provide some information on the occurence of these contaminants for this region of the state (also see Kelley et al., 1986 for an overview).

As early as 1974, Richard et al. (1975) documented the occurrence of atrazine in alluvial aquifers suppling the cities of Des Moines, Marshalltown, and Oskaloosa. Trace residues ranging from 0.01 to 0.07 ug/l were detected in

Table 6. Range of pesticide concentrations and SOC/VOCs detected in water supplies in the Skunk River study area.

	alachlor (Lasso)	atrazine (AAtrex)	cyanazine (Bladex)	metolachlor (Dual)	metribuzin (Secor/Lexone)
			ug/l		
Skunk River	0.04-6.3	0.05-12.0	0.08-5.3	0.55-1.7	0.11-1.3
Tributary Streams		42.0			
Water-Supply Reservoirs	0.41	0.90-1.8	0.70-1.6		
Alluvial-Aquifer wells	0.20-1.0	0.01-0.90	0.80	0.18	0.05
Pleistocene and Bedrock Aquifer Wells		0.12-0.22			

SOC/VOCs From Public Water Supply Wells

Di-N-octyl phthalate - 60.0 ug/l

Styrene - 1.0 ug/l

these raw and finished (treated) water supplies. The remainder of the groundwater data discussed here was collected between 1982 and 1986. Five common herbicides have been detected, atrazine being the most common. Concentrations ranged from 0.1 to 0.9 ug/l. These data are summarized on table 6. Somewhat higher concentrations have been found in

Table 7. Comparison of well depths and nitrate concentrations between wells with and without, detectable pesticides.

ALLUVIAL AQUIFER WELLS

with pesticides			with no pesticides		
N	Depth (feet)	NO_3 (mg/l)	N	Depth (feet)	NO_3 (mg/L)
5	28-37 (Avg. 31)	3.6-30.6	5	33-70 (Avg. 53)	<0.1-81.0
PLEISTOCENE AND BEDROCK AQUIFER WELLS					
2	36-140 (Avg. 83)	0.5-14.5	30	38-548 (Avg. 150)	<0.1-9.5

the 1980s and are compatable with other findings in Iowa, that suggest pesticide residues in groundwater maybe increasing (see Kelley et al., 1986; Hallberg et al., 1985, Hallberg, 1986), but there are too few data in this region to be definitive.

The gerneral characteristics of the sampled wells are given in Table 7. Generalizations are difficult to make with limited data. However, the results do follow the same trend as seen elsewhere in the State. The wells where pesticides were detected are generally shallower than wells with no detections. Only 2 of 32 (6%) Pleistocene and Bedrock aquifer wells showed pesticide detections, but 50% of the Alluvial aquifer wells showed pesticide residues. Two wells showed other organic chemicals, as shown on Table 6, but these were also from relatively shallow wells.

Because reliable quantities of high-quality groundwater have always been more difficult to develop in this portion of Iowa than in many other areas of the state, surface water from streams or reservoirs are often used for public drinking water. Limited data on pesticide occurrence from these sources are also shown on Table 6; these data are from Richard and others (1975), STORET, and other unpublished UHL data. Maximum concentrations of the common herbicides are generally greater than in groundwater, because overland flow into surfacewaters typically carries greater concentrations of pesticides than does water infiltrating through the soil. However, average concentrations may appear similar because the groundwater baseflow sustains the stream discharge, and during these periods the pesticide residues likely come from the groundwater flux into the stream. In addition to the common, 'modern' herbicides, shown on Table 6, Richard et al., (1975) and the UHL also detected residues of dieldrin, DDT, and DDE in these waters during the 1970s (1973-1977). In the Skunk River and in reserviors, the reported concentrations were: dieldrin, 0.003-0.076 ug/l; DDT, 0.004-0.016 ug/l; and DDE, 0.001-1.86 ug/l. In tributary streams the reported concentrations were dieldrin, 0.07 ug/l; and DDE, 3.9 ug/l.

During 1979-1982, approximately 50% of the monthly samples from the Skunk River at Oskaloosa showed detectable residues of 'modern' herbicides (Table 6). About 60% of those samples with detectable residues showed the presence of two or more herbicides.

Currently, all municipal water-supplies are being sampled to analyze for a variety of pesticides, synthetic organic chemicals, and volatile organic chemicals. This sampling will provide a broad overview of the occurrence of some man-made contaminants in finished water-supplies in Iowa.

COMPARISON OF THE SKUNK RIVER BASIN WITH NORTHEAST IOWA

The data from the Skunk River basin supplement past studies and are illustrative of the water-quality problems being documented throughout Iowa. The regional contamination of shallow groundwater by nitrates, and locally by other synthetic chemicals, is clearly apparent in the various data presented. More detailed studies in northeastern and northwestern Iowa have shown that the degree of regional contamination of groundwater by nitrates and pesticides has significantly increased over the past 20 to 30 years from non-point sources. This is, in large part, from the widespread, increased usage of chemical fertilizers and pesticides. There was insufficient data, to clearly illustrate these temporal changes in the Skunk River basin, but many public water-supply records in the basin show increasing nitrate concentrations since the 1950's and 60's (WATSTORE and UHL data).

Table 8. Comparison of nitrate and well depth data (% of all wells in depth class), by geologic region, between the Skunk River basin and data from Northeastern Iowa, analyzed by Hallberg and Hoyer (1982). (Nitrate values in mg/l).

SKUNK RIVER BASIN
(1981 - 1985)

WELL DEPTH (feet)	SHALLOW		DEEP		KARST		TOTAL	
	MEDIAN NITRATE	% OF WELLS	MEDIAN NITRATE	% OF WELLS	MEDIAN NITRATE	% OF WELLS	MEDIAN NITRATE	% OF WELLS
≤49	14	51	6	48	NA	0	9	50
50-99	12	17	2	15	NA	0	7	16
100-149	2	9	2	10	NA	0	2	9
150-499	2	22	2	25	NA	0	2	23
>500	2	1	2	2	NA	0	2	2
% in region >45 mg/l	20%		14%		NA		17%	

NORTHEASTERN IOWA
(1977 - 1980)

WELL DEPTH (feet)	SHALLOW		DEEP		KARST		TOTAL	
	MEDIAN NITRATE	% OF WELLS	MEDIAN NITRATE	% OF WELLS	MEDIAN NITRATE	% OF WELLS	MEDIAN NITRATE	% OF WELLS
≤49	26	11	33	19	28	7	28	13
50-99	19	21	6	22	34	23	18	22
100-149	16	23	2	22	23	30	7	24
150-499	5	41	2	35	3	38	2	38
>500	2	4	2	2	2	2	2	3
% in region >45 mg/l	19%		15%		25%		18%	

The data from the basin do show some important contrasts with other areas. Table 8 compares the UHL data sets from the Skunk River basin and from northeastern (NE) Iowa (from Hallberg and Hoyer, 1982). There are two major differences: 1. the median nitrate concentrations in the shallow groundwater from wells in the Skunk River basin are significantly lower than in NE Iowa, and 2. the percentages of very shallow wells used in the basin are much greater than in NE Iowa. Also note that there is no real difference in the percentage of wells exceeding the nitrate MCL; 17% in the Skunk River basin and 18% in NE Iowa. These values are both below the state wide average of about 22-25%. For the percentage of those exceeding 0.5 MCL, there is a slightly greater difference; 26% in the Skunk River basin, 30% in NE Iowa.

The similarities in the percentage of samples with high concentrations of nitrate and the significant difference in median concentrations point out that the data from the basin are more skewed and more variable than in NE Iowa. This is also illustrated by the greater difference between the mean and median nitrate concentrations. The means average 2-2.5 times greater than the medians in the basin, but only 1.2-1.5 times greater than the medians in NE Iowa. This variability is apparent not only statistically but spatially as well.

The implications of these differences are complex. The median (50th percentile) values are smaller which indicate that there is a greater proportion of shallow wells in the basin with low nitrate concentrations, and hence, potentially less exposure of the residents to high nitrate (and possibly pesticides) in the drinking water (pesticide contamination tends to parallel nitrate contamination, as well). However, there are nearly equal proportions of high nitrate problems. Similar to NE Iowa, contamination was most apparent to depths of 100 feet, but statistically significant to 150 feet.

The potentially lower exposure is offset by the much greater usage of shallow wells in the Skunk River basin. About 50% of all the wells sampled in the Skunk River basin were less than 50 feet deep, and 66% less than 100 feet deep. In contrast, only 13% of the wells in NE Iowa were less than 50 feet deep, and only 35% less than 100 feet deep. These trends essentially offset one another, while the median nitrate concentrations are about 3 times lower, the use of wells less than 50 feet deep is nearly 4 times greater. The dependance of the population on shallow groundwater in the Skunk River basin make them particularly susceptible to groundwater contamination problems.

The greater variability of nitrate concentration data in the basin may be related to various factors. There are some fundamental differences in the geology and soils of the region which likely contribute. In the NE Iowa region, limestone/carbonate aquifers underlie the Quaternary deposits over broad areas, often covering more than one county. In the Skunk River basin conditions are much more variable with a mix of local to regional aquitards (e.g. shales) which may affect recharge even to shallow portions of the groundwater system. There are also more extensive upland areas of poorly drained soils, or areas with impeded shallow subsoil drainage in the basin, than in NE Iowa. The northern portion of the basin occurs on the young glacial deposits of the Des Moines lobe--the Clarion-Nicollet-Webster soils. Closed, minor depressions, poor drainage, and moderate to high organic matter content of soils are common. Much of the southern portions of the basin has a thin loess mantle, which overlie old buried soils, on broad, low-relief upland divides. The buried-soils are an impediment to the downward movement of water. This creates some extensive areas of poor drainage when combined with the broad, low-relief landscape. These conditions are conducive to denitrification and locally lateral movement of soil water and retardation of recharge.

Another factor may be the difference in the style of agriculture in the basin. At least in the southern and southwestern portions of the area, row crop agriculture, with attendant chemical use is not as extensive as in much of the northeast-quarter of the state. These differences though, are not as pronounced as the physical differences.

These factors may likely play a role in the greater variability of the nitrate concentration data. However, as noted by Thompson et al., (1986) and Kelly et al., (1986) in some areas where denitrification removes the nitrate from the groundwater, pesticides (or other synthetic chemicals) may still have leached into groundwater/drinking-water supplies.

CONCLUSIONS

Deep bedrock aquifers in the Skunk River basin have many natural water-quality problems, as well as quantity problems. Thus, the majority of residents in the area, particularly the southern two-thirds of the basin, have depended upon shallow groundwater, and/or surfacewater for their water-supplies. This makes the primary water supplies of the basin particularly susceptible to increased water contamination problems in the future.

Acknowledgements

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