

WATER QUALITY AS RELATED TO
POSSIBLE HEAVY METAL ADDITIONS
IN SURFACE AND GROUND WATER IN THE
SPRINGFIELD AND JOPLIN AREAS, MISSOURI

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ABSTRACT

Some 165 seasonal water samples were collected and analyzed for heavy metals from surface and subsurface sources in a one hundred mile area around Springfield and Joplin, Missouri, respectively. Joplin is in a former large zinc mining district. Springfield is 72 miles east.

Locally, cadmium, lead, zinc and iron exceed acceptable PHS standards for drinking water, but the majority of water samples are well within the established limits. Yet, ten percent of the water wells sampled in the Springfield area and twenty-five percent of those sampled in the Joplin area approached or exceeded the PHS limits of the one or more heavy metals for drinking water. High zinc values are related to known zinc-lead mineralization in both areas. Average cadmium values are slightly higher in Joplin, copper content is similar for both areas, and lead content is slightly higher near Joplin. Surface waters in Joplin are 17 times higher in average zinc content than in Springfield, though shallow wells for both areas are similar in zinc content. Iron is higher and more variable in Joplin. Mercury, in very low quantity in both areas, is somewhat higher in the Springfield area. Some seasonal variation occurs in the heavy metal content in both areas. Alternate sources of water are suggested for those areas having heavy metal content in excess of PHS standards. Effects on living systems within areas containing anomalous heavy metal content are unknown.

INTRODUCTION AND OBJECTIVES

Springfield is a large population center in southwest Missouri and on the eastern fringe of the world renown Tri-State mining district. Water supplies for this city are derived mainly from underground sources in a carbonate terrain. Joplin, Missouri, lies 72 miles to the west. It is in the area of the main mining district which was once the world's largest producer of zinc. Lead, copper and cadmium were produced as by-products of the mining operation. Joplin and the cities around it represent medium size population centers within the district. Water for domestic and industrial use is derived from surface and subsurface sources in this highly mineralized area.

The Springfield-Joplin areas lie within the continental climatic regime of central North America. Average annual precipitation is approximately 40 inches with extremes of 14 and 61 inches recorded. Heaviest precipitation occurs during the spring and early summer. Late July and August are typically hot and dry. The coldest months are December through February, and heaviest snowfalls typically occur in late winter. The average annual temperature is approximately 14 degrees centigrade.

Both Springfield and Joplin are located within the Springfield Plateau ground-water province. The surface waters associated with the two cities belong to two different river basins. The similar geographic but contrasting geologic conditions make these areas especially suitable for an investigation

of water quality changes which might occur through possible heavy metal additions from strongly or weakly mineralized country rocks, or other rocks which might contain the elements of interest. The porous and permeable character of the area's pseudolateritic soil, carbonate bedrock and extensively brecciated sedimentary rocks have resulted in broad access for movement of ground water (fig. 1).

Springfield: Springfield, Missouri, has a population of 120,000 and is the largest city in the southwestern part of the state. It has experienced a rapid growth in population and industry, and a resultant increased demand for both domestic and industrial waters. Several primary sources and some secondary and tertiary water sources are currently meeting the needs of the city. Fullbright Spring and Reservoir, and a deep well in the northern part of the city are the primary sources. To the south, the Park View Wells and Orchard Crest Well are also used as primary sources of water. McDaniel Lake and Valley Mills Reservoir, both north of the city, are secondary sources. Tertiary sources of water supply include Fellows Lake, north of the city, and three raw wells. Lake Springfield, south of the city, is used mainly as a cooling water supply for a thermal-electric plant and also as a recreational lake.

Waters for city use are treated at the Fullbright treatment plant or at the main well sites. These waters are then distributed throughout the city in the water main system. Continuous water quality tests are conducted by city staff members to determine manganese, mercury, nitrate, orthophosphate, iron, nitrogen, dissolved oxygen, bacteria, coliform and algae plus physical tests.

Beyond the city water distribution system of Springfield, homeowners and light industry obtain their water supplies from shallow, (Mississippian, Ordovician, Roubidoux or younger), and deep aquifers (Cambro-Ordovician) (fig. 3).

Joplin: Joplin, Missouri, is the largest city within the mining area and has a population of approximately 40,000. Much of the water supply for the City of Joplin comes from Shoal Creek from which it is pumped to a central treatment plant and distributed through the city mains to the various users.

Webb City and adjacent Cartersville, with approximately 8,000 people, are northeast of Joplin and share a common water supply. This comes from several wells in the city from which it is distributed to users through city mains. The small towns of Cal Junction, Oronogo and Duenweg have their independent water systems of wells and distribution networks. All of the above city wells obtain their water from the deep aquifer units.

Outside of the city distribution nets, individual owners obtain their water from the shallow aquifers. Several small industries of Joplin use municipal water supplies. The majority, however, use ground water from wells.

No large lakes are present in the Joplin area, but several open pits and underground openings left from mining operations are partially filled with water. These are generally less than 5 acres in extent and they may be in excess of 20 feet deep. Small, shallow farm ponds are moderately abundant in agricultural areas. These are generally 1 to 2 acres or smaller and less than 20 feet deep.

The two areas investigated were purposefully located in or near the large Tri-State mining district. Although the big ore bodies are mined out, there is enough mineralization left in pillars, walls, and country rocks to have an important effect on the quality of the ground waters of the area.

Zinc sulfide was the major mineral mined in the Tri-State mining district, but lead and copper sulfides were also present. Iron sulfides in the form of marcasite and pyrite and some iron bearing carbonates are also common in the sedimentary rocks in the district and in the non-mineralized formations. The main mineralization was essentially restricted to the Mississippian rocks. Recent work has confirmed the presence of surface trace contents of mercury near the ore zones in faulted areas (Hansuld, 1970).

Investigations to date have omitted the study of cadmium and mercury contents of the water and only rarely indicated lead and copper contents. Therefore, an investigation of the heavy metals in the waters of the area was warranted. In the light of recent studies related to toxicity, these elements could be important local pollutants of the surface and ground waters.

By comparison, only very spotty and rare sulfide mineralization is known in the Springfield area. What little is known occurs in a similar stratigraphic setting to that of the Joplin area. Consequently, it was expected that heavy metal addition to surface and ground waters in the Springfield area may be of differing magnitude from that of Joplin as far as natural pollution is concerned.

Previous Work: Bolter's studies (1969, et seq.) of surface waters in the "New Lead Belt" of Missouri is somewhat similar to this study, but relates more to addition of lead, zinc and other metals to surface waters as a direct result of deeper underground mining and surface milling practices. He did not investigate mercury, cadmium or the ground water regime. Beckman and Hinchey (1944) studied the chemical composition of the major springs of the state, but related mainly to the major elements. Feder et al. (1969) published a thorough and well documented report on the water resources of the Joplin area. The heavy metals, except zinc and rarely copper and lead, were not included. The results on zinc distribution gave impetus to this investigation. More recently, Miesch and his team (1970, et seq.) have undertaken and almost completed a state-wide reconnaissance of the trace element content of soils, vegetation and waters. Their study gives an excellent general view of the distribution of these elements. However, the variability of heavy metal contents over relatively short distances in ground and surface waters indicates that more detailed surveys are required if one is to identify patterns and possible additions of heavy metal to the ground water. While not investigated in this study, Marienfeld's work on trace elements in water and other trace substances in the environment has direct bearing on this study. Hopefully, the results of this study and perhaps an expansion of it, may be used to confirm or deny the long term health effects of such trace substances. Wixson et al. (1970 et seq.) are currently carrying out such a study

in the New Lead Belt. While the geological and ground water conditions are quite different from the Joplin-Springfield areas, the results should prove useful for the latter study.

Geologic Setting: Both Springfield and Joplin are situated within a relatively simple geologic environment. Essentially flat-lying beds of Mississippian and Pennsylvanian age are the main sedimentary rocks exposed. Locally, Ordovician strata crop out in the deeper stream valleys east and south of Springfield (fig. 1). An inlier of Ordovician rock crosses U.S. Highway I-44 midway between the two cities and is associated with a northwesterly trending fault zone. Up to 1,800 feet of Paleozoic sediments occur above the irregular surface of the Precambrian basement.

While all the strata are nearly horizontal, they have been cut by faults of general westerly to northwesterly trend. Displacements range to 150 feet. A prominent fault zone of southwest trend, and displacements up to 300 feet, is exposed south of Joplin and extends into Oklahoma. A series of broad gentle folds of westerly to northwesterly trend also occur in the region. These pitch generally northwest. The most pronounced is the Joplin anticline which roughly parallels an east-west fault south of I-44 then turns northwesterly and extends into Kansas. It is asymmetric with a steeper west limb.

Base metal sulfide mineralization occurs in the Mississippian rocks, mainly in the Keokuk and Warsaw formations. Some mineralization, but non-commercial, has been noted in the Cotter, Jefferson City, Roubidoux and Gasconade formations of

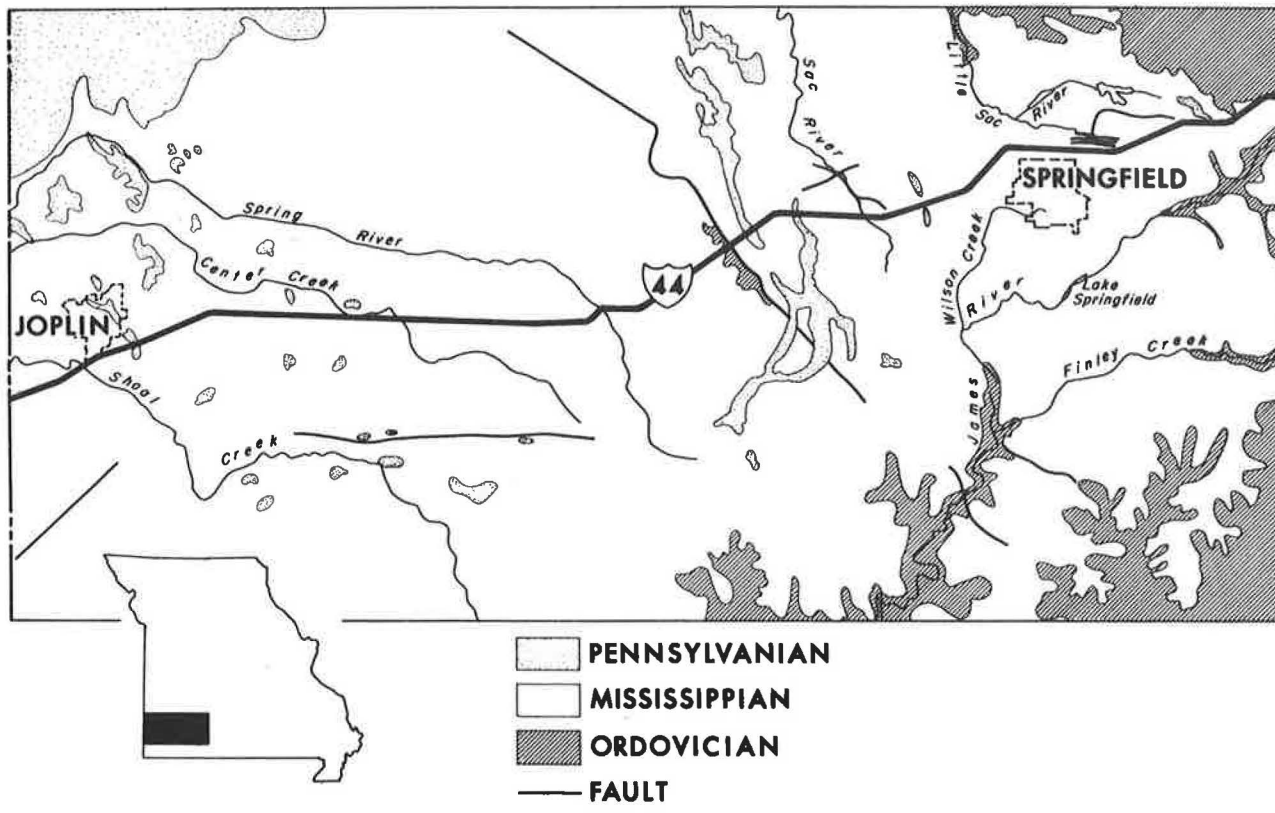


Figure 1. Index map to the Springfield-Joplin areas, Missouri.

Ordovician age. Essentially no mineralization has been observed in the older formations in this area.

Ground Water: Two major aquifer zones are available for water production. In this report the Mississippian strata and their included aquifers are titled the shallow aquifers and the Cambro-Ordovician strata, the deep aquifers in the Joplin area. These two units are hydrostatically separated with the piezometric surface of the shallow aquifer higher than that of the deep aquifer. Because of the relatively thin Mississippian section in the Springfield area, the shallow aquifers include the Mississippian strata and part of the underlying Ordovician rocks down through the Roubidoux sandstone.

Recharge areas for the deep aquifers lie outside of the area except for local seepage in the Joplin area through the Northview and Chattanooga formations and the surface Keokuk units in the Springfield area. The shallow aquifers are locally recharged and often quite directly from the percolation of surface waters. In some areas of the mining district, local drainage discharges directly into abandoned mine workings during periods of rainfall. Some of the open pit lakes are probably hydrostatically connected to the shallow aquifer system. Springs in both areas discharge from Mississippian strata.

Objectives: The primary research objective of this study was to determine the possible heavy metal addition to surface and ground waters in the Springfield-Joplin areas, Missouri, in respect to mercury, cadmium, lead, zinc, copper and iron, and to ascertain distribution patterns of these elements in the water supplies of these expanding population centers of the state.

A second objective was to relate the possible water quality changes produced by these elements to seasonal variation and to the source or source rocks in the area.

In conjunction with the above objectives, the hydrogen-ion concentration, alkalinity, conductance, temperature and turbidity were determined for each water sample.

The third objective was to suggest alternate water sources for those areas which show heavy metal contents in excess of those considered safe by the Public Health Service.

The study of the effect of the anomalous heavy metal content on the living systems within the area was not part of the research project. It is unknown, but the abundant data now available suggests this as a potentially productive future research area that should be considered for detailed study.

STATEMENT OF THE PROBLEM

The major population centers of southwest Missouri are centered about the cities of Springfield and Joplin. Water supplies for these large and rapidly expanding population centers are mainly from ground water. Here hundreds of water wells penetrate the bedrock to obtain water for both domestic and industrial uses. Significant geologic differences, as well as many similarities, exist for sources of ground water between these two separated cities.

Joplin lies within the Tri-State zinc mining district, at one time premier world producer of this metal with by-products of lead, copper and cadmium. Trace contents of mercury have recently been identified in the soils of the district (Hansuld, 1970). Sources of the domestic and industrial waters for Joplin are from surface waters and from wells which cut into the mineralized Mississippian rocks and into the older non-mineralized Cambrian and Ordovician rocks (fig. 2).

Major minerals in the Joplin area include sphalerite (ZnS), galena (PbS), with much less amounts of chalcopyrite ($CuFeS_2$), other sulfides (Hagni, 1962), and oxidation products. Among the minor sulfides, greenockite (CdS) has been identified. These minerals occur as disseminations in the host jasperoid and dolomite, as open-space fillings of fractures, as cement of rock fragments, and lining of druses, vugs and cavities in the Mississippian host rocks. Figure 2 illustrates the relative amount of sulfide mineral production from these rocks and the number of water wells sampled per 100 feet of depth in these host units. The largest number of sampled water wells

cut the zones of Mississippian rocks which are commonly mineralized in the mining areas. It is expected that such a stratigraphic location should have an addition of heavy metals to the waters from these zones. Additions which result and the systematic or random pattern produced in the aquifers is part of the basic research problem in the Joplin area. Little or no mineralization is known in the lower part of the section. Accordingly, it should be expected that these units should show a correspondingly lower heavy metal content in the recoverable well waters. The research was to confirm or deny this postulate.

Springfield lies 72 miles east of Joplin, Missouri, and has a population of about 120,000. Only minor quantities of introduced metallic minerals have been noted in the rocks of the Springfield area, but locally small mining activity was recorded. Figure 3 is the stratigraphic column for this area. The question is whether the waters from this area have a lesser heavy metal content than the Joplin area or not. As another part of the problem, do waters from the deeper aquifers, from which much of the city's water is obtained, have lesser heavy metal content? Or finally, because of industrial activity in the area, do the surface waters receive natural and/or man-made heavy metal additions within the studied area?

In summary, since the climatic conditions and the country rocks are practically the same, the problems resolve themselves to the similarities and differences in the heavy metal contents and sources in the Joplin and Springfield water supplies and whether the time of the year for sampling changes

the results? If heavy metal content is higher in either area than the PHS standards, what other available water sources can be readily and economically substituted to make these waters safer for human consumption.

METHOD OF INVESTIGATION

Circular areas of about 100 square miles were outlined centering around both Joplin and Springfield for sampling of water sources. Based on a study of the water well log library of the Missouri Geological Survey and Water Resources, specific localities were selected for collection of water well samples within these circular areas. Samples were selected to include all major surface waters, major springs, shallow and deep aquifers, mine waters in abandoned open cuts, and wells that penetrate extensively brecciated sedimentary rocks. Wells for which standard water analyses were already available were also sampled.

Sampling: Field collection procedures for each of the types of water followed those outlined by Brown, et al., (1970). At each site and for each sample the water was filtered and determinations made for temperature, pH, alkalinity, and conductance. Visual turbidity was also recorded. The water sample was acidified to inhibit precipitation of heavy metals on the walls of the plastic containers prior to chemical analysis in the laboratory.

Water samples were collected from over 113 sampled sites in the Springfield area. These include 71 water well, 8 spring, 3 lake, and 31 stream samples. At least 71 sample sites were sampled twice and 56 sampled three times during the year and one-half of the study from mid-1971 to the end of 1972.

For the Joplin area 10 samples were collected from deep wells, 24 from shallow wells, 12 from streams, 3 from springs

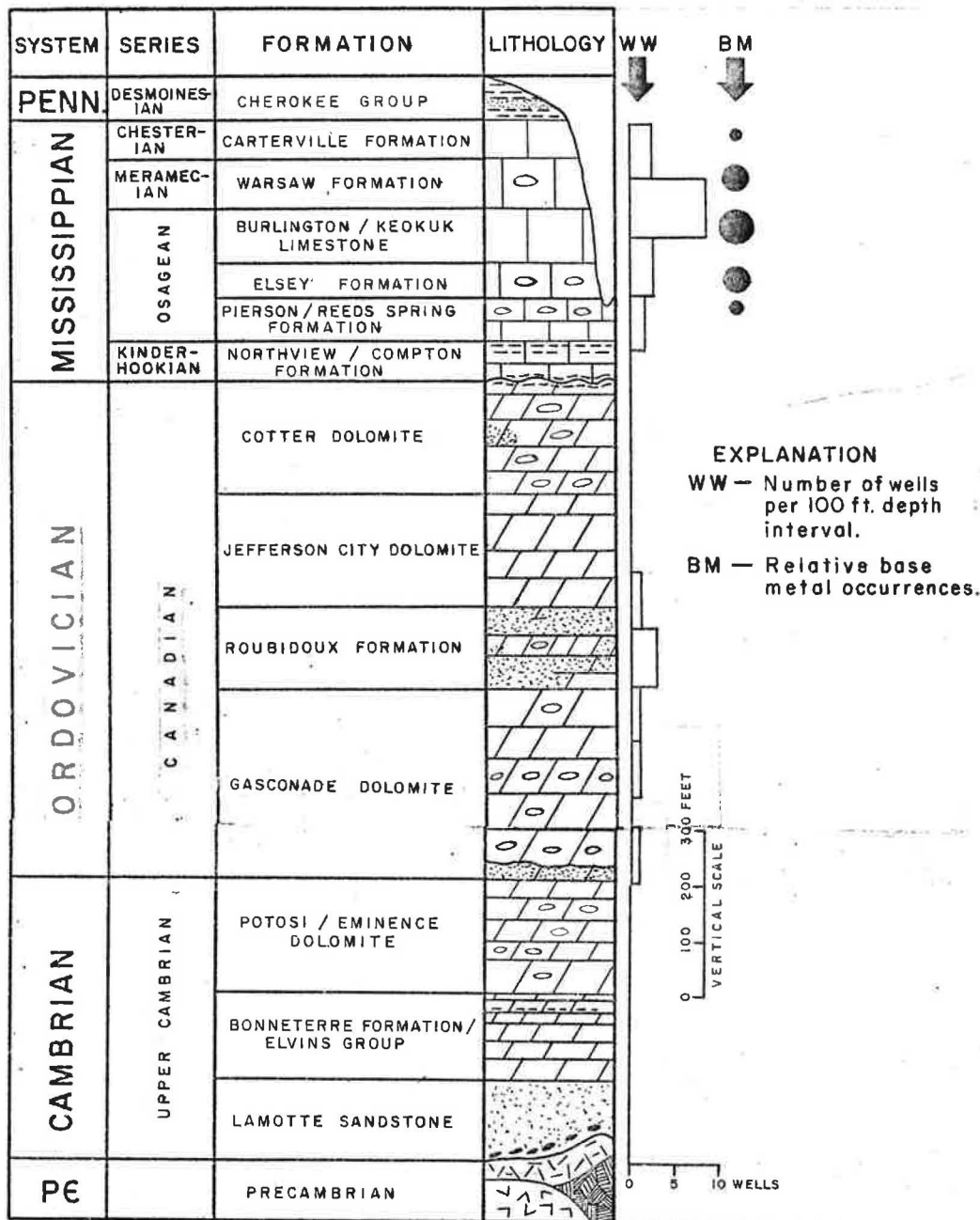


Figure 2. Stratigraphic column of the Joplin area showing relative frequency of base metal occurrences in the section and number of water wells sampled per 100 feet of depth.

and 3 from open pit lakes during the dry fall and early winter of 1971. A second set of samples was obtained during the wet spring and early summer of 1972.

In both the Springfield and Joplin areas stream water samples were collected near the banks at public access points and road crossings. The location of all samples is shown on figures 4 and 12 for each area respectively. Samples were collected during low flow conditions in the fall and again in the spring near bankfull stage when surface runoff was significant. Spring samples were much more turbid than fall samples.

Lakes in the Joplin area are actually filling formerly operated mine open pits. The Springfield lakes are man-made. In both areas, samples were collected near shore at a point of easy access. Samples from springs were collected as near the resurgence as possible. Well samples were taken as near the well head as permitted. The large city wells were sampled at access points at the well head. Most home site wells have submersible pumps and a surge tank at or close to the well head, and the great majority of such wells have no access until after the surge tank. In a few cases the nearest access for a sample was an outside faucet or kitchen faucet. A few have water softeners in the line and no way to sample ahead of the softener. In every case of sampling, however, the water flowed sufficiently long to purge the lines of standing water. In many cases this might not have been long enough to completely clear the surge tank.

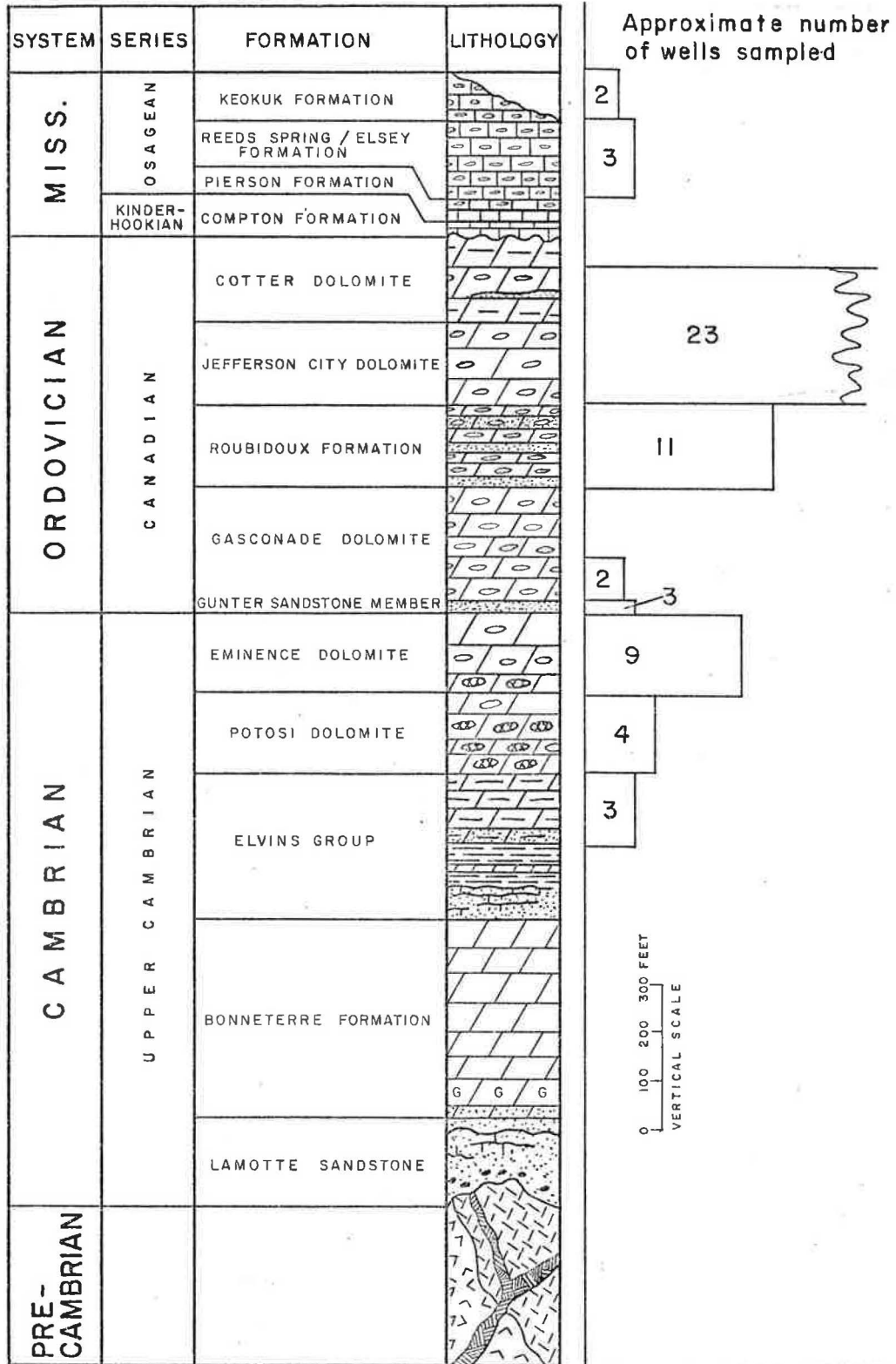


Figure 3. Stratigraphic column of the Springfield area showing number and stratigraphic portion of the wells sampled.

Chemical Analyses: Water samples were returned to the geochemical laboratory of the University where they were analyzed by atomic absorption spectrophotometers and according to methods carefully designed and checked by the United States Geological Survey (Brown, et al., 1970). These methods with slight modifications have been used in our laboratories for analyses of thousands of samples of water from the New Lead Belt (Bolter, 1969). Mercury analyses followed the potassium permanganate procedure of the Environmental Protection Agency (1972). A brief summary of the method is included in the Appendix.

The instrument used was a Perkin-Elmer Model 303 atomic absorption spectrometer with an x-y recorder. Chemical standards were supplied by Fisher Scientific Company. Analytical results were obtained for copper, lead, zinc, cadmium, mercury and iron.

Results of the individual metal analyses were plotted on base maps prepared for each of the areas. Separate maps were prepared for each element showing deep well, shallow well, springs, and surface water sample sites and chemical values. These maps permit ready visual observation of distribution of the heavy metal content. Two maps show the location of water samples having heavy metal values which exceed the PHS standards.

Average analyses and standard deviations were calculated for samples analyzed. Because of the more complex geology and the large scale epigenetic zinc-lead-copper mineralization in

the Joplin area, several types of statistical analyses of the analytical results by computer were included. Results of the analyses are summarized in the body of the report.

RESULTS

Results of chemical analyses of the surface, shallow and deep well waters of the Springfield and Joplin areas are summarized in this section. An overview of the total number of samples analyzed and their means, standard deviations and ranges are discussed in this introductory section. Details on individual metals are included in subsequent sections.

Ratios of the means for zinc in water samples collected in Springfield in the moderately dry fall, dry spring and wet late summer for surface waters are 0.7:1:1. Maxima and minima metal zinc contents are also similar. Lead in the surface waters, while low in content, has a different mean ratio of 1:0.4:^{0.3}~~0.2~~. Mean ratios for copper are 1:1.5:0.3, and for cadmium 1:1.6:0.6, not too different from the zinc mean values.

Deep wells which generally show the least variability of heavy metal values for individual water samples have mean ratios for the fall, spring and late summer periods for zinc of 1:1.1:3.2; lead, 1:1.8:1.6; copper, 1:1.9:2.6; and cadmium, 1:1.1:0.4. The greater variability is from the dry spring to the late wet summer.

Normally the shallow well environment has the greatest variability among individual samples. Ratios for the heavy metals means for the fall, spring and late summer from the shallow well sample groups are: Lead, 1:1.7:0.9; copper, 1:1.4:1; cadmium, not determined; zinc, 1:1.5:1.2; mercury, 1:10:2; and iron, 1:1.8:3.2. The variability is not as great as would be expected when one compares the maxima and minima or ranges of the metal values. Zinc content, for example,

varies from $\leq 1-8500$ ppb. Iron also shows a rather wide range of values. While a fairly wide range of values is present for copper, lead and zinc, the total metal content in the waters is generally low and of less significance. Mercury values were all less than one part per billion.

In the Joplin area only fall and spring sample collections were made, hence ratios cannot be compared directly with those of Springfield. As a generalization, however, the means for all water samples of copper, lead, zinc and cadmium increase in the fall samples as in Springfield. Iron slightly decreases in the fall. Table 1 summarizes the means and standard deviations for the various metals, sample environments and collection seasons in the Springfield area and Table 2 for the Joplin area.

Surface water mean values for zinc are about one-thirtieth that of the shallow wells in Springfield and about one-tenth that of the deep wells. In Joplin, on the other hand, the surface water zinc mean contents are about one-half those of the shallow wells and 15 times those of the deep wells. These suggest major additions of zinc to the surface and shallow underground waters of the Joplin area. The mean values for cadmium are three times as high for the shallow well-surface waters as for the deep wells in the Joplin area. Copper and lead means are not significantly different for surface waters and deep wells, but are 3 and 1.5 times as great, respectively, in the shallow well environment as in the deep wells.

In the surface waters, Center Creek has very high zinc values compared to the other streams. This creek is on the down dip side of the district. Springs located up dip and along

	Seasons*																							
	Mean	S.D.	Max.	Min.	Mean	S.D.	Max.	Min.	Mean	S.D.	Max.	Min.	Mean	S.D.	Max.	Min.	Mean	S.D.	Max.	Min.	Mean	S.D.	Max.	Min.
Surface Waters	1-6.47	12.63	70	0	2.8	5.6	31	.01	.74	.69	3	.1	24.4	25.5	125	2.5	poor data				no data			
	2-2.8	1.5	5.7	.5	4.16	1.82	7.3	.01	1.22	1.59	5	0	34.7	41.03	140	5	.18	.19	.6	0	47.6	39.9	135	2
	3-.17	.36	1	0	.94	1.05	3	0	.11	.3	.9	0	34.7	27.05	123	6	.01	.01	.03	0	41.2	60.5	170	1.5
Shallow Wells (<500')																								
	1-3.03	2.94	11.25	.75	6.7	7.06	29	0	0	0	0	0	1318.5	1756.9	8500	90	.01	.02	.05	0	20.7	20.6	55	1
	2-5	3.55	15	1	9.27	4.95	19	2	1.66	1.19	5	.01	875.7	890.7	3250	90	.1	.12	.35	0	37.8	18.4	70	10
	3-2.94	8.15	32	0	6.11	5.08	17	1.2	.84	2.84	11	0	1070	699.7	2130	149	.02	.03	.1	0	67.6	92.6	348	3
Deep Wells (>500')																								
	1-1.51	1.69	6.25	.01	2.45	3.98	18.5	.01	.95	1.87	8	0	165.7	299.4	770	.5	.07	.15	.77	0	43.9	102.8	455	0
	2-2.67	2.41	8	0	4.8	4.11	14	.01	1.06	2.54	10	0	185	268.6	900	.01	.11	.12	.35	0	25.1	44	160	0
	3-2.45	3.97	12	0	6.3	4.8	15	1	.35	.58	1.5	0	537.5	533.4	1425	25	.03	.03	.08	0	10.7	12.3	35	1
	Lead				Copper				Cadmium				Zinc				Mercury				Iron			

*1=fall & winter (dry) S.D.=Standard Deviation
 2=spring (dry)
 3=late summer (very wet)

Table 1. Means, standard deviations and ranges of heavy metal contents (ppb) in waters of the Springfield area, Missouri.

Water Samples	Cu	Pb	Zn	Cd	Fe
All Samples	(M)* 4.7 (S.D.)** 7.5	2.9 3.0	576 804	1.4 2.7	76.5 212
Fall Samples	(M) 6.3 (S.D.) 6.8	4.2 3.2	707 978	1.7 2.5	72 192
Spring Samples	(M) 3.2 (S.D.) 7.8	1.5 3.0	459 598	1.0 2.9	81 231
Surface Samples	(M) 1.4 (S.D.) 1.4	2.7 3.6	542 670	1.6 3.8	19 22
Shallow Well Samples	(M) 8.2 (S.D.) 9.1	3.2 3.9	932 948	1.7 2.4	95 297
Deep Well Samples	(M) 2.7 (S.D.) 6.5	2.4 1.9	37 54	0.5 0.7	112 157

*M=mean

**S.D.=standard deviation

Table 2. Means and standard deviations in ppb for Cu, Pb, Zn, Cd and Fe, Joplin area, Missouri.

Shoal Creek show lower zinc values. Turkey Creek, also in the main mining area, has higher values in copper and iron as compared to Center Creek, but it is lower in zinc values.

Heavy Metal Contents in Water of Springfield Area

As already noted, the domestic and much of the industrial water supply for the City of Springfield is derived from deep wells cut into the Cambrian-Ordovician rock units of the area. Residences in the greater Springfield area obtain their water supplies mainly from shallow water wells in the Mississippian and uppermost Ordovician rocks of the area. Some local deeper wells penetrate the older Cambrian-Ordovician rock units.

Concentrations of lead, zinc, copper, cadmium, mercury and iron; alkalinity; temperature; and the pH of water samples were determined for water samples collected during the dry fall-winter season, and from one to two times more in the dry spring and wet late summer of the year. Sample sites included shallow and deep wells, springs, streams and lakes in an area slightly over 113 square miles centered on the City of Springfield, Missouri.

Water sample locations are shown in figure 4. The type of water sample, i.e., shallow well, deep well, surface stream, spring or lake, is indicated by special symbols on the map. Separate maps show the high mercury, cadmium, zinc, lead, copper and iron values at the sample sites and for the type of water sample (figs. 5, 6, 7, 8, 9 and 10). All heavy metal values are expressed in the parts per billion (ppb) range for each sample site. Those sites where chemical analyses of heavy

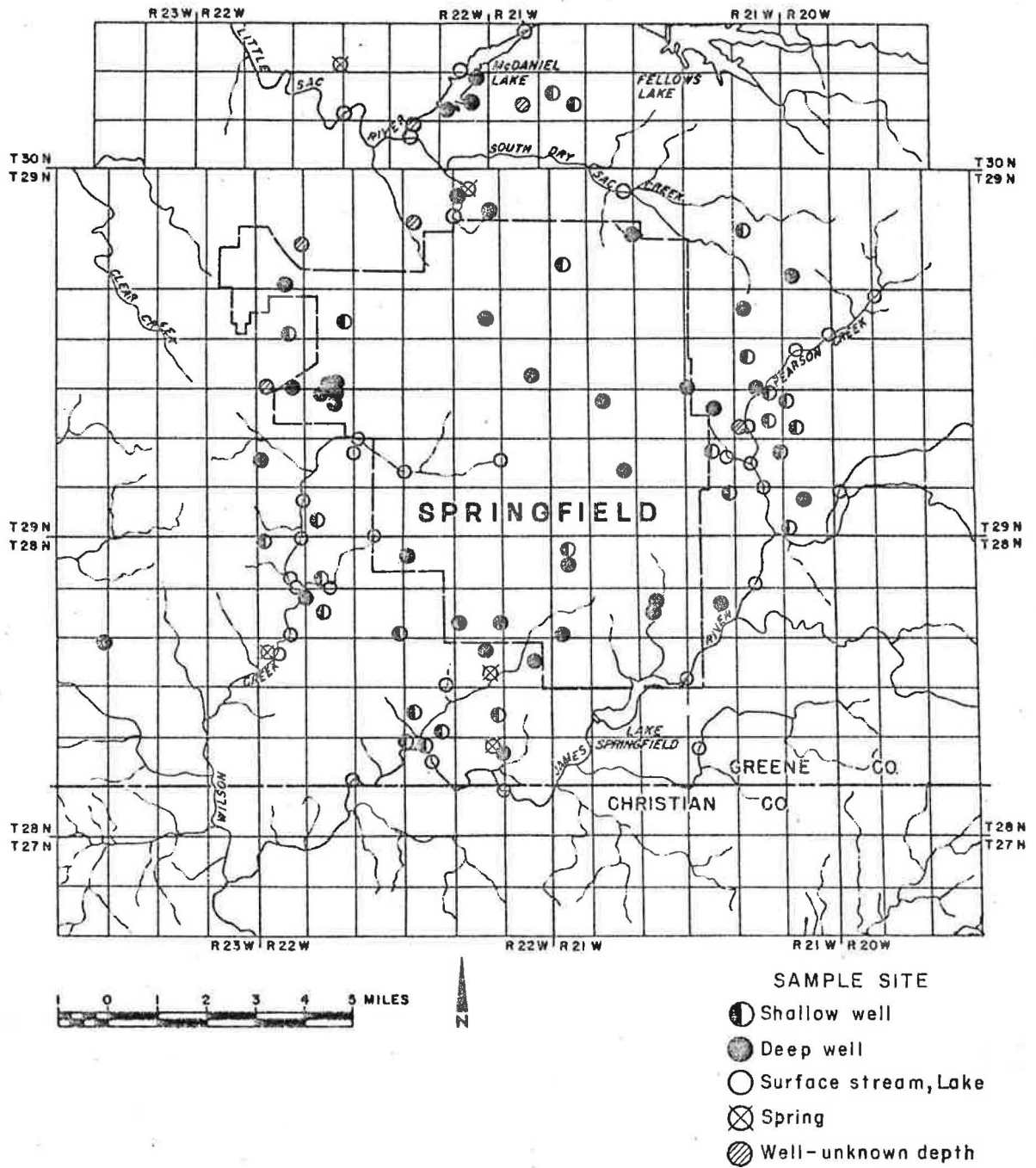


Figure 4. Location and types of water samples in the Springfield area, Missouri.

elements exceed or closely approach the Public Health Service standards (PHS) are shown in figure 11.

The results of the sampling and analytical results for the Springfield area are summarized below. A concluding paragraph indicates areas of concern for water quality and alternative water sources.

Mercury Content: The maximum range in mercury content from all sample sites in the Springfield area is from 0.01 to 0.77 ppb. This range is well within the acceptable Public Health Service standards. The large majority of the water samples range from 0.10-0.77 ppb. There appears to be little difference in mercury content in respect to whether the water sample came from surface waters, springs, deep or shallow wells. No consistent geographic distribution pattern is visible for mercury content in the low ranges detected in the waters of this area. (See figure 5)

Cadmium: Cadmium content in the Springfield water samples ranges from almost non-detectable to 11 ppb. In at least two cases, the PHS standards are exceeded. One of the samples is from a shallow well east of the city. The other water sample is almost 11 miles due west in a deep well just outside the city limits (fig. 6).

Most of the deep wells within the city limits contain only very small quantities of cadmium, and fall well below the upper PHS standard. Outside the city limits, almost twice as many samples from wells, springs and surface waters fall within the 1-9 ppb range, as in the 0.1-0.99 range. The higher range cadmium values are mainly from surface waters and shallow aquifers.

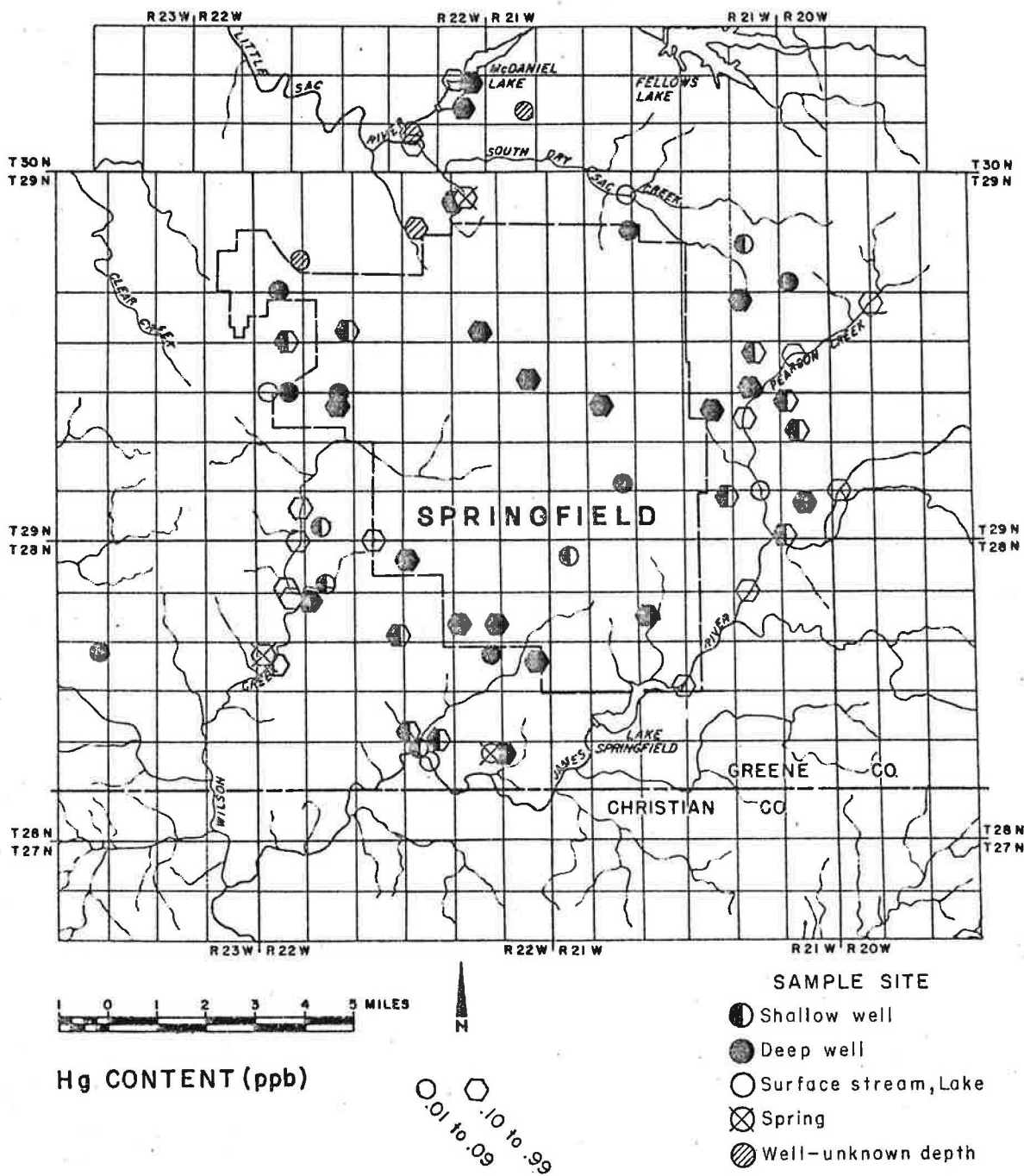


Figure 5. High mercury content in water samples from the Springfield area, Missouri.

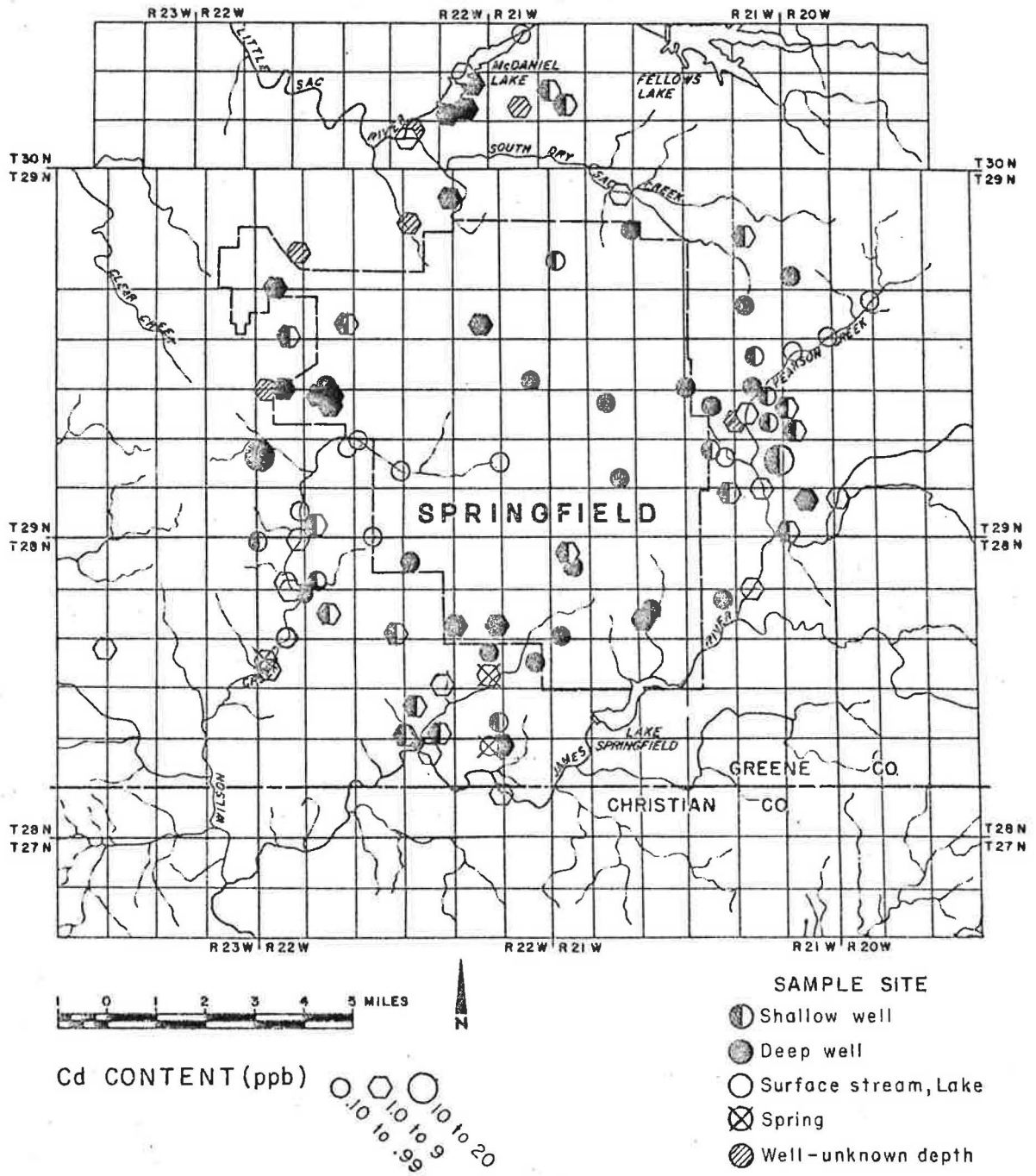


Figure 6. High cadmium content in water samples from the Springfield area, Missouri.

While no distinctive geographic distribution patterns are obvious, samples from the Little Sac River drainage north of Springfield do show slightly higher cadmium values. Cadmium values from Pearson Creek east, and Wilson Creek west of the city are approximately the same and somewhat higher than other parts of the overall area. Deeper well waters are conspicuously lower in cadmium content than surface and shallow aquifer beds within the drainage basin of Wilson Creek.

Zinc: Zinc content in the waters of the Springfield area ranges from the detectable limit (1 ppb) to 8500 ppb. At least one shallow well water sample site east of Springfield exceeds the PHS standards of 5,000 ppb. Cadmium content for this same sample site also exceeds the PHS standards.

Water samples from two shallow wells within the city limits have zinc values in the 1,000-5,000 ppb range. East of the city a rather distinctive pattern of relatively high zinc values occurs in the Pearson Creek area. Here water samples are mainly from shallow wells and some from deep wells. Zinc values for these sites generally fall within the 500-10,000 ppb range. Some old shallow mine workings for lead and zinc are known in the Pearson Creek area (Fellows, 1970) and may well account for these anomalous zinc values. Surface water samples have much lower zinc content in this area and generally fall in the range of 1-100 ppb.

North of Springfield and just east of McDaniel Lake, four wells, mainly shallow, have zinc values in the range of 500-5,000 ppb. Another area of similar zinc values occurs

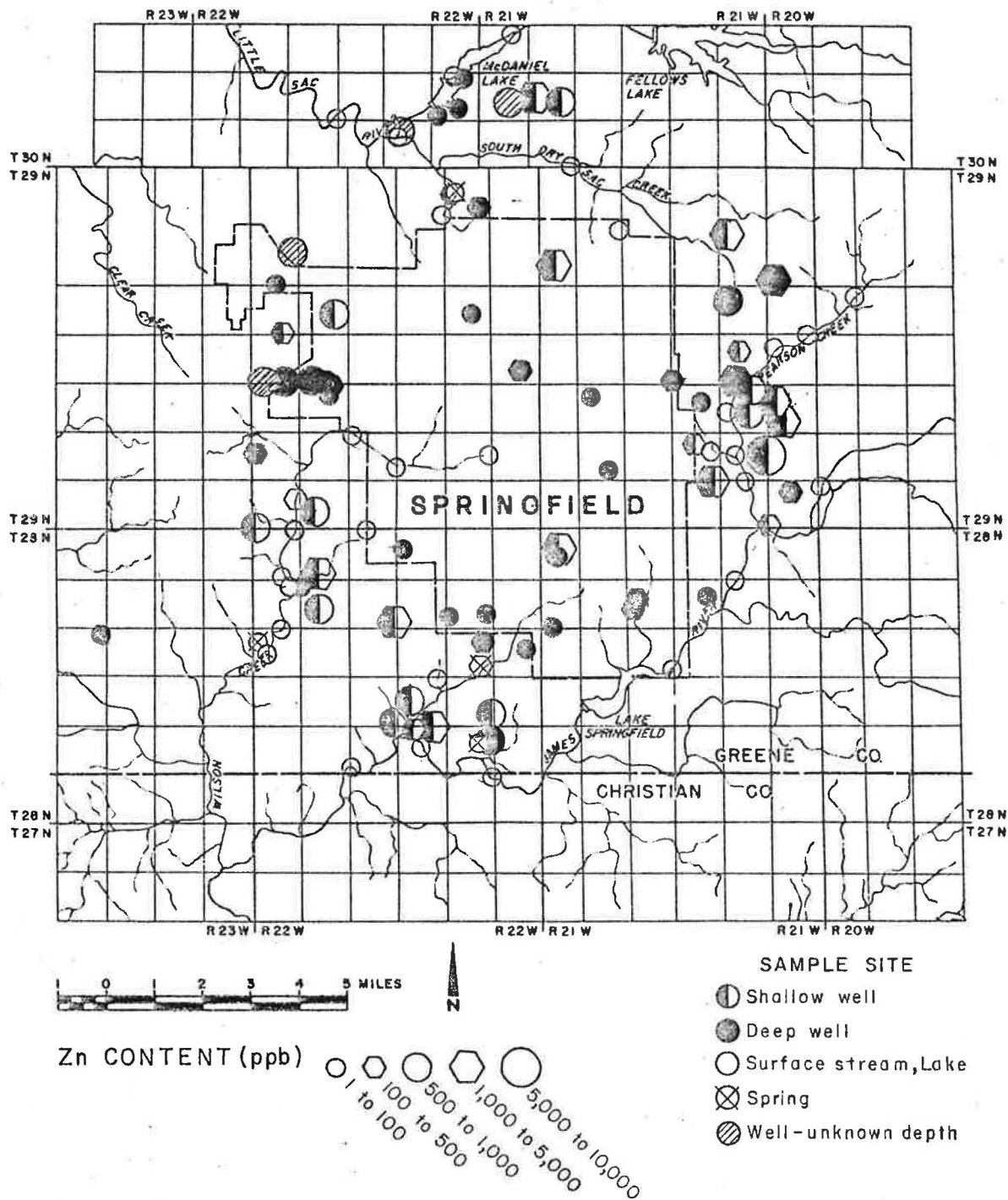


Figure 7. High zinc content in water samples from the Springfield area, Missouri.

in water from shallow and deep wells on the western and southwestern border of Springfield (fig. 7).

Surface and spring waters of the Springfield area show relatively low zinc values.

Copper: Maximum copper content in the water samples from this area range from 20-30 ppb. These values are far below the upper limit of the PHS standards of 1,000 ppb. Both deep and shallow water well samples within the city limits essentially fall in the range of 1-10 ppb (fig. 8). Surface water samples show a similar trend throughout the area.

The highest copper content range is from 20-30 ppb and occurs in water well samples from the west side of the city. These same samples also show higher zinc values. Somewhat similar higher copper values occur in water from well sites south of McDaniel Lake and from two well sites south of Springfield (fig. 8).

Surface waters show a fairly narrow and low range of copper content both inside and outside the city limits. These copper values of 1-10 ppb continue downstream with little change. An exception occurs along Wilson Creek where the 1-10 ppb copper range decreases southward to less than 1 ppb in a distance of two miles.

Lead: Within the city limits of Springfield all water well samples fall well within the PHS standards for lead content. Variations in lead content do exist, however. One shallow well in the northwest part of the city has lead content in the range of 10-20 ppb. Three miles to the southeast, water from

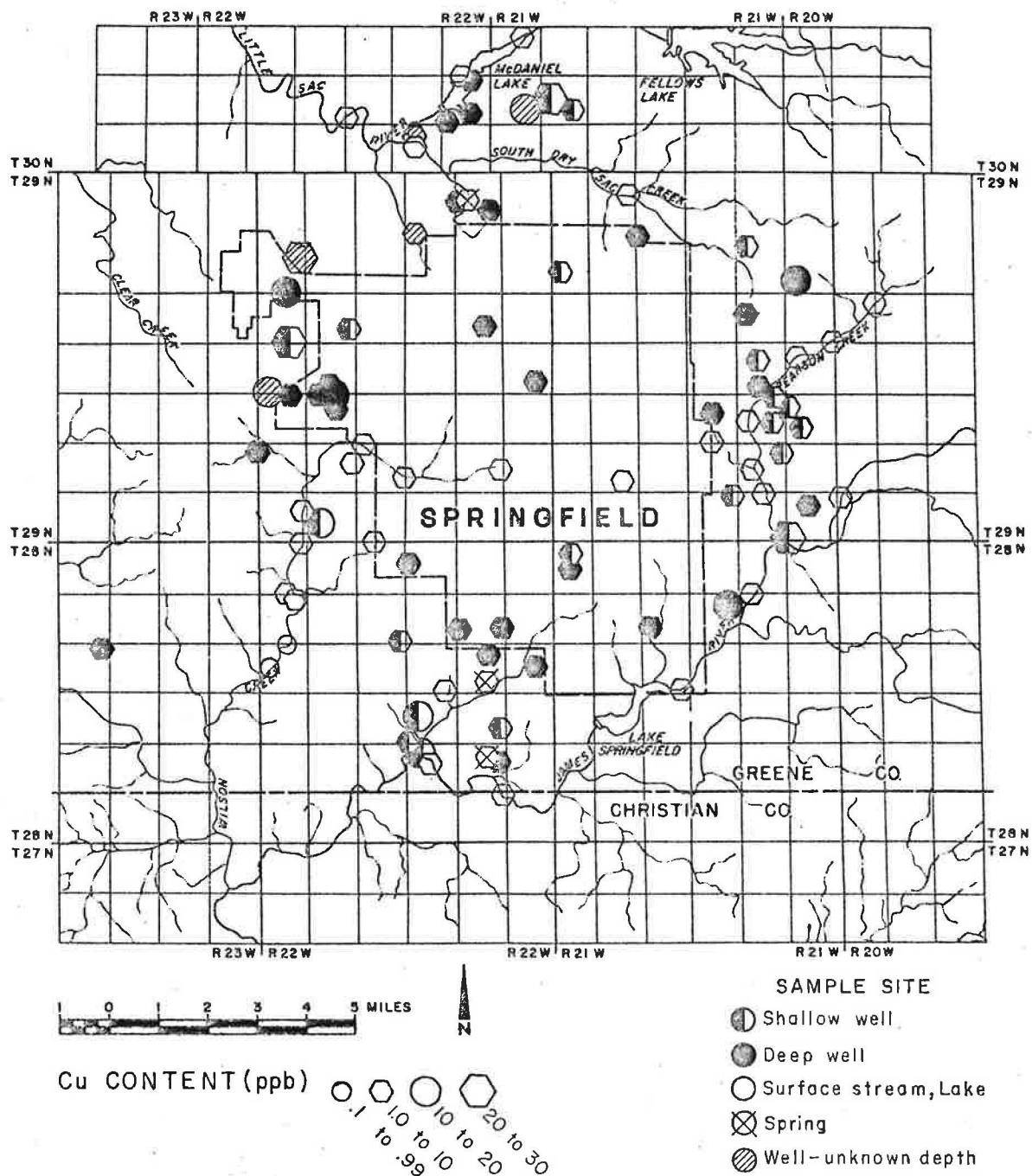


Figure 8. High copper content in water samples from the Springfield area, Missouri.

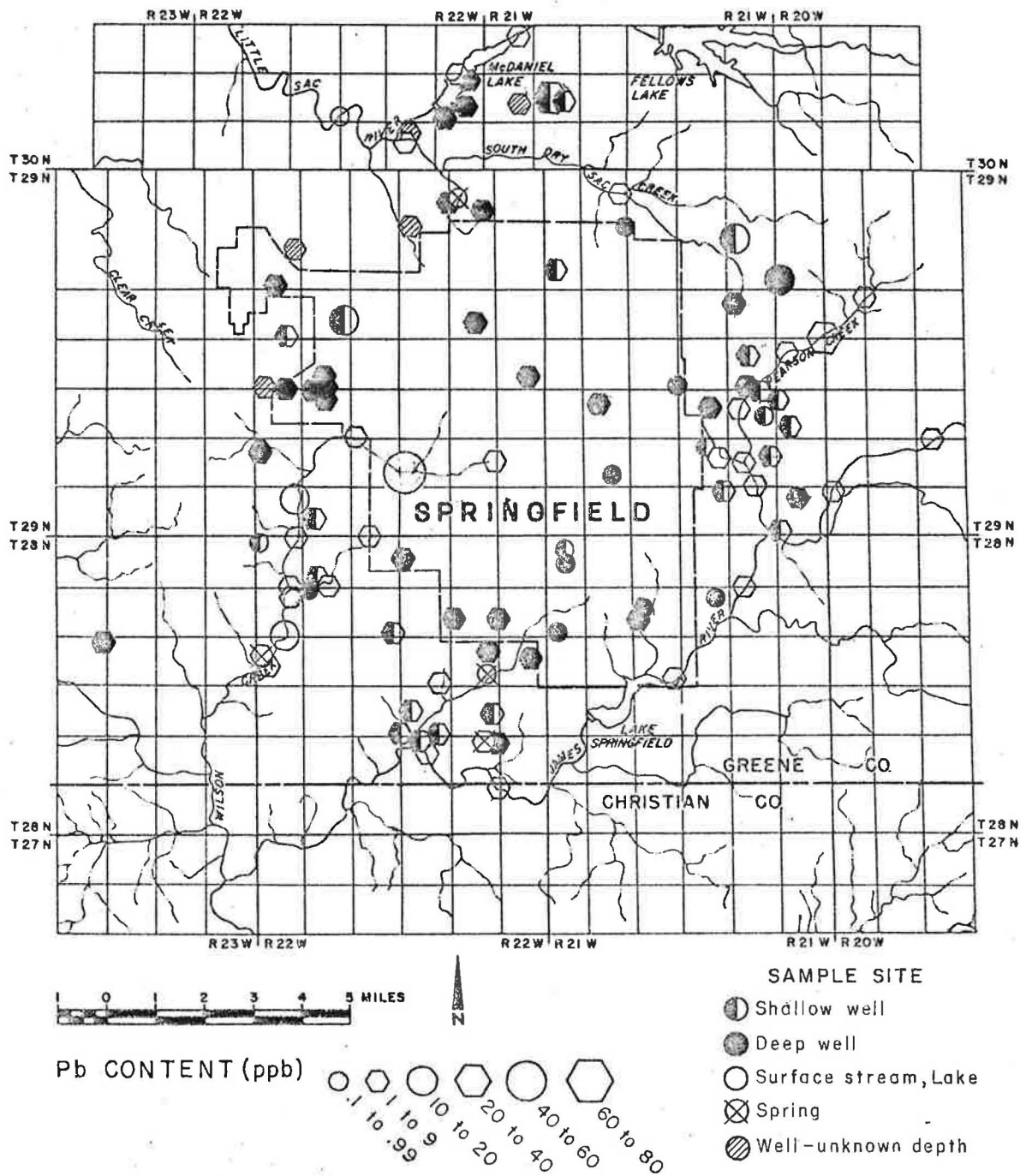


Figure 9. High lead content in water samples from the Springfield area, Missouri.

a stream within the city exceeds 50 ppb lead. Other than these higher lead values, all well and surface water samples within the city show 9 ppb or less of lead content.

While the lead content of water samples has less conspicuous highs than does zinc, the lead content of water samples does have similar distribution characteristics. In the vicinity of Pearson Creek, lead values rise to 20-40 ppb for a surface water sample. Shallow and deep wells, and surface waters generally contain less than 10 ppb lead content. The upper six miles of the surface waters of Wilson Creek show lead values of 20-40 ppb. Lower values of 1-9 ppb also occur along parts of this stream.

Lead values are somewhat higher in the two shallow and one deep wells just southeast of McDaniel Lake north of Springfield. These same wells also yielded higher zinc and copper values.

Iron: In the western part of Springfield city, all iron values for water samples fall within the 1-50 ppb range except for one shallow well (fig. 10). Indeed, the lowest iron content area includes the deep wells within the city limits which supply water to Springfield.

In the Pearson Creek area east of the city, the majority of shallow well water samples range from 50-100 ppb in iron content. These same sample sites generally contained higher values for the other heavy metals.

On the west side of the city in the upper 5-8 miles of Wilson Creek, five of seven water samples fall within the 100-200 ppb range for iron. Similar iron values occur in the

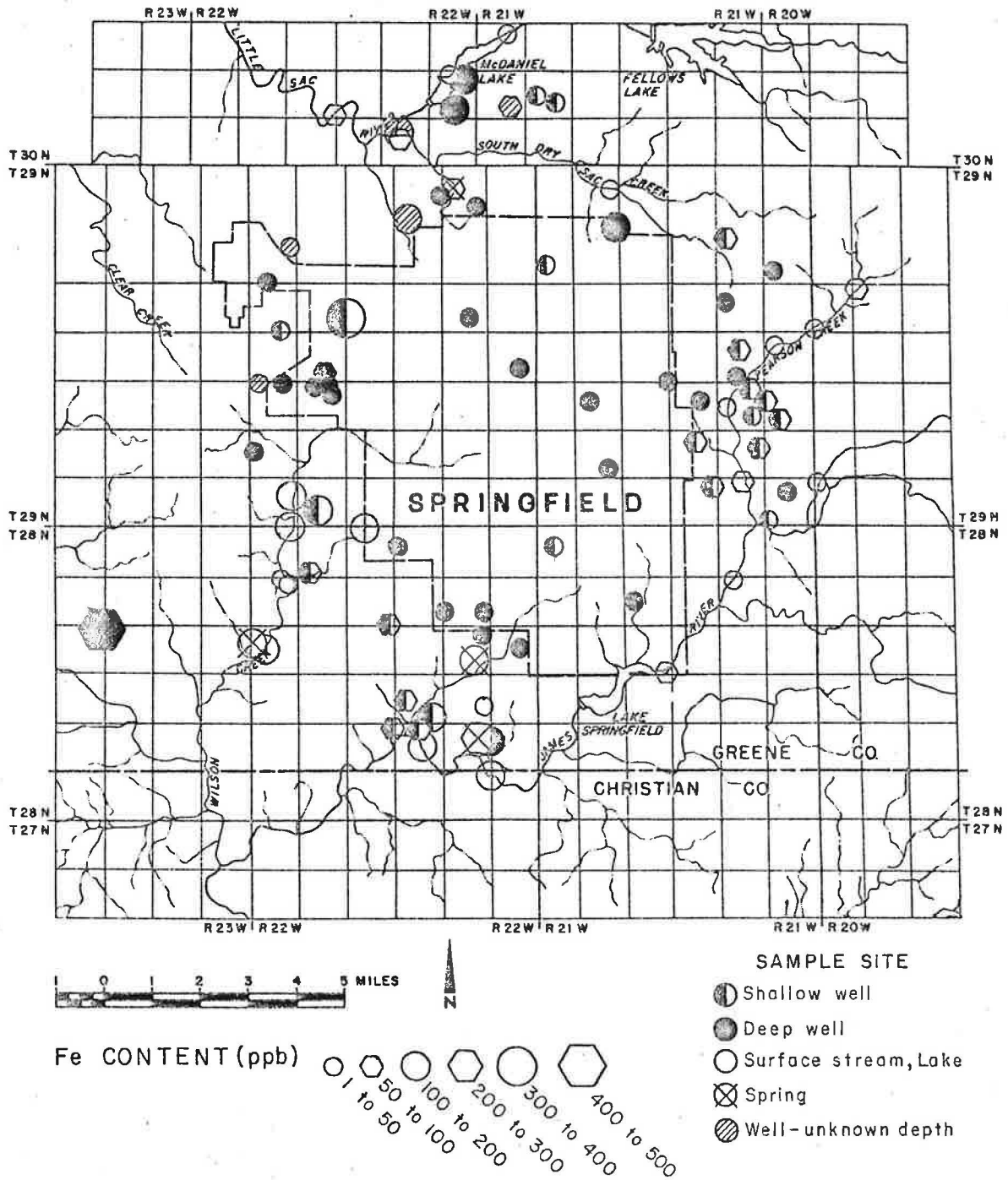


Figure 10. High iron content in water samples from the Springfield area, Missouri.

James River area south of Springfield and in two springs in this same area (fig. 10).

The highest iron content in the Springfield area comes from a well about five miles southwest of Springfield. A range of 400-500 ppb of iron content is indicated for this water sample. This is the only water sample which exceeded the PHS standards for iron in drinking water.

PHS Water Quality Standards: Eight sample sites in Springfield or its near environs showed heavy metal content near or in excess of the established PHS standards (fig. 11). Two sample sites had excess cadmium, one had lead, one had zinc, and another excess iron. Both zinc and cadmium contents exceeded the PHS standards in a shallow well east of Springfield near Pearson Creek. In the north-central part of the city a deep well had cadmium values just below the upper PHS drinking water standards for cadmium content.

Heavy Metal Contents in the Waters of the Joplin Area

In the Joplin area the concentrations were determined for lead, zinc, copper, cadmium, mercury and iron; the bicarbonate content; the temperature; and the pH of 51 water samples. These were collected once during the dry fall and again collected during the rainy spring seasons. Samples were from deep (Cambro-Ordovician formations) and shallow (Mississippian formations) wells and springs, streams and lakes within an area of about 113 miles square centered on the City of Joplin, Missouri, (fig. 12). All three lakes sampled were former open pit mines. Analytical procedures and instruments were the same as those used for the Springfield water samples.

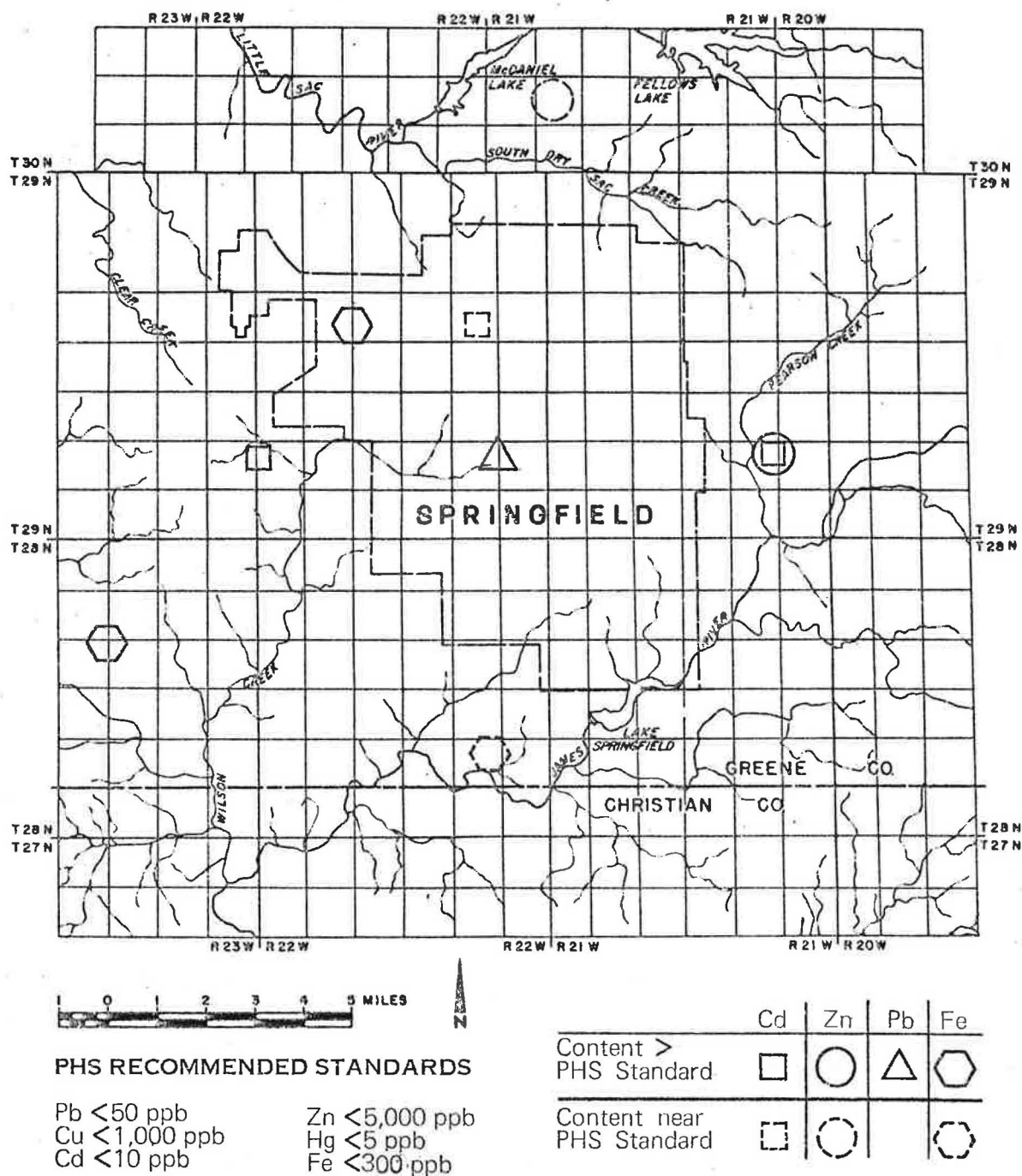


Figure 11. Water samples from the Springfield, Missouri, area with heavy metal content near to or in excess of PHS standards for drinking water.

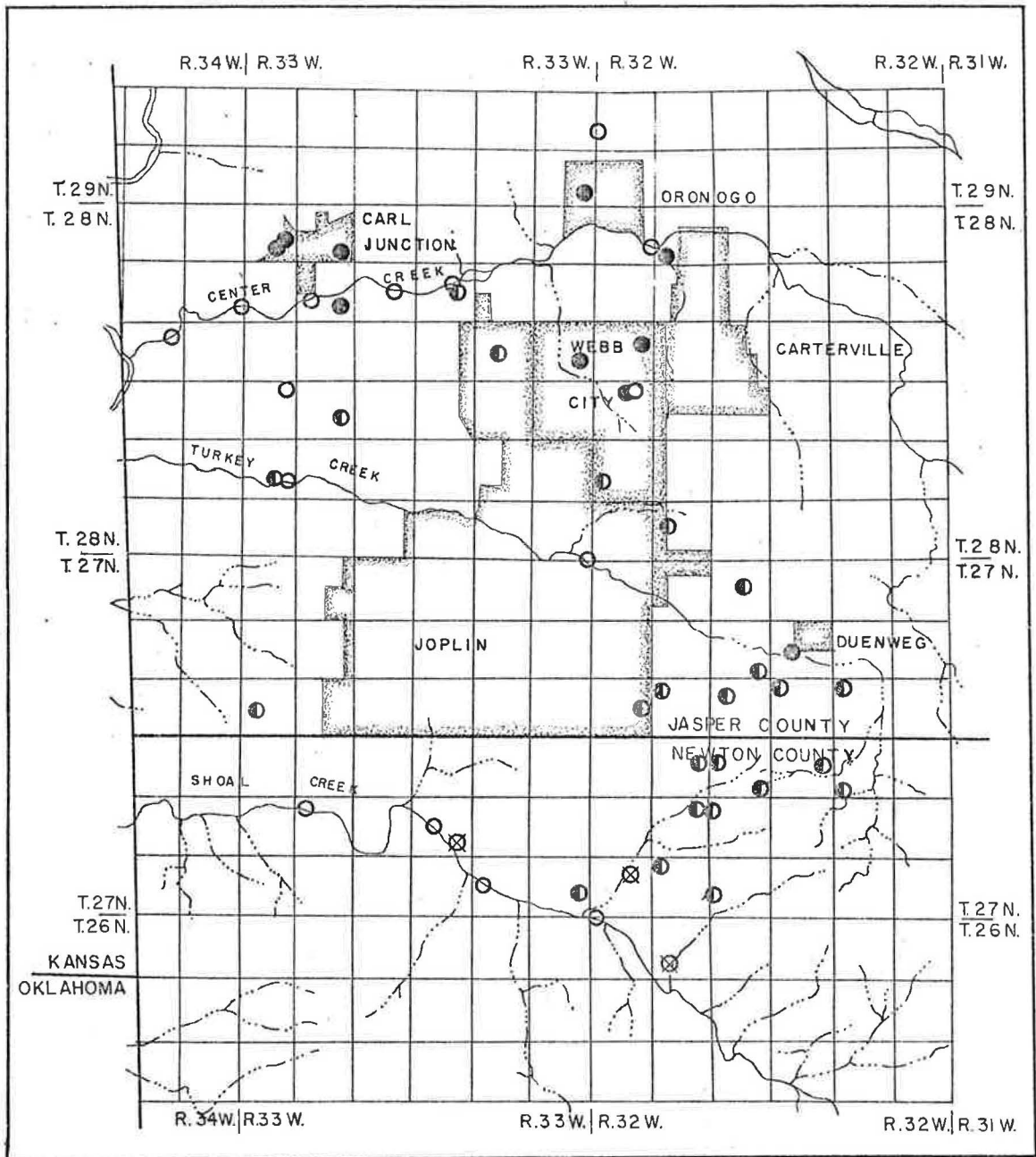


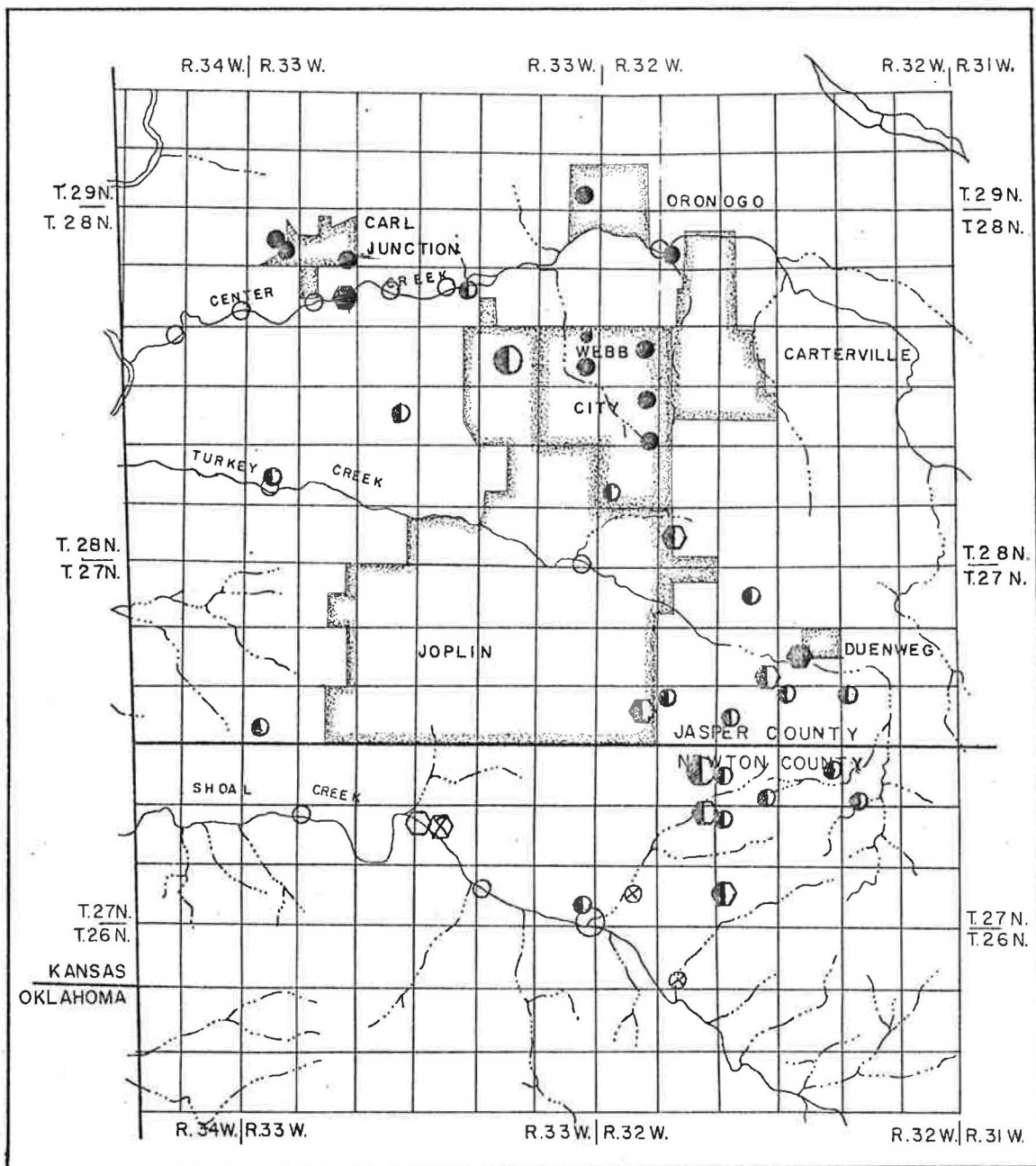
Figure 12. Location and types of water samples from the Joplin area, Missouri.

Lead: The overall range of lead values in the water samples in this area is from less than 1 ppb to 18 ppb. The maximum value of lead in the deep well samples was 5.5 ppb, in the shallow wells 18 ppb, in springs 6 ppb, in lakes 10 ppb, and in the streams 12 ppb (fig. 13). The fall lead values were generally higher than those of the spring water samples. Lead concentrations in the water samples are all below the PHS standards for drinking water. In general, the lead concentrations in the water samples were close to the detection limit of the instrument.

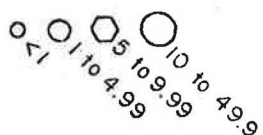
Zinc: Zinc content in the water samples ranges from 10-11,500 ppb. The maximum values of zinc in deep well waters were 240 ppb, in shallow wells 3,800 ppb, in springs 200 ppb, in small lakes to 11,5000 ppb and in surface streams 1,700 ppb (fig. 14). Zinc showed a tendency to be higher in the fall samples than in the spring samples.

Zinc content in the shallow aquifer and in some surface waters are strongly anomalous and exceed PHS standards for drinking water. They locally exceed optimal conditions for aquatic life such as fish. Deep well water samples show low values of zinc compared with those of the shallow wells and offer an alternate source of low zinc water.

Copper: Copper content in water samples range between less than 1 ppb to 330 ppb. The highest copper content in a deep well sample was 28 ppb. In shallow wells copper content reached 95 ppb, in springs 1.5 ppb and in lakes 330 ppb, and in surface streams 45 ppb (fig. 15).



Pb CONTENT (ppb)



SCALE, MILES



SAMPLE SITE

- Shallow well
- Deep well
- Surface stream, Lake
- ⊗ Spring

Figure 13. High lead content in water samples from the Joplin area, Missouri.

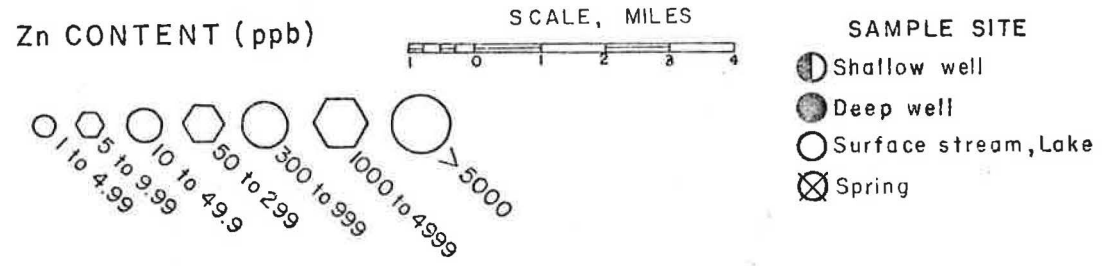
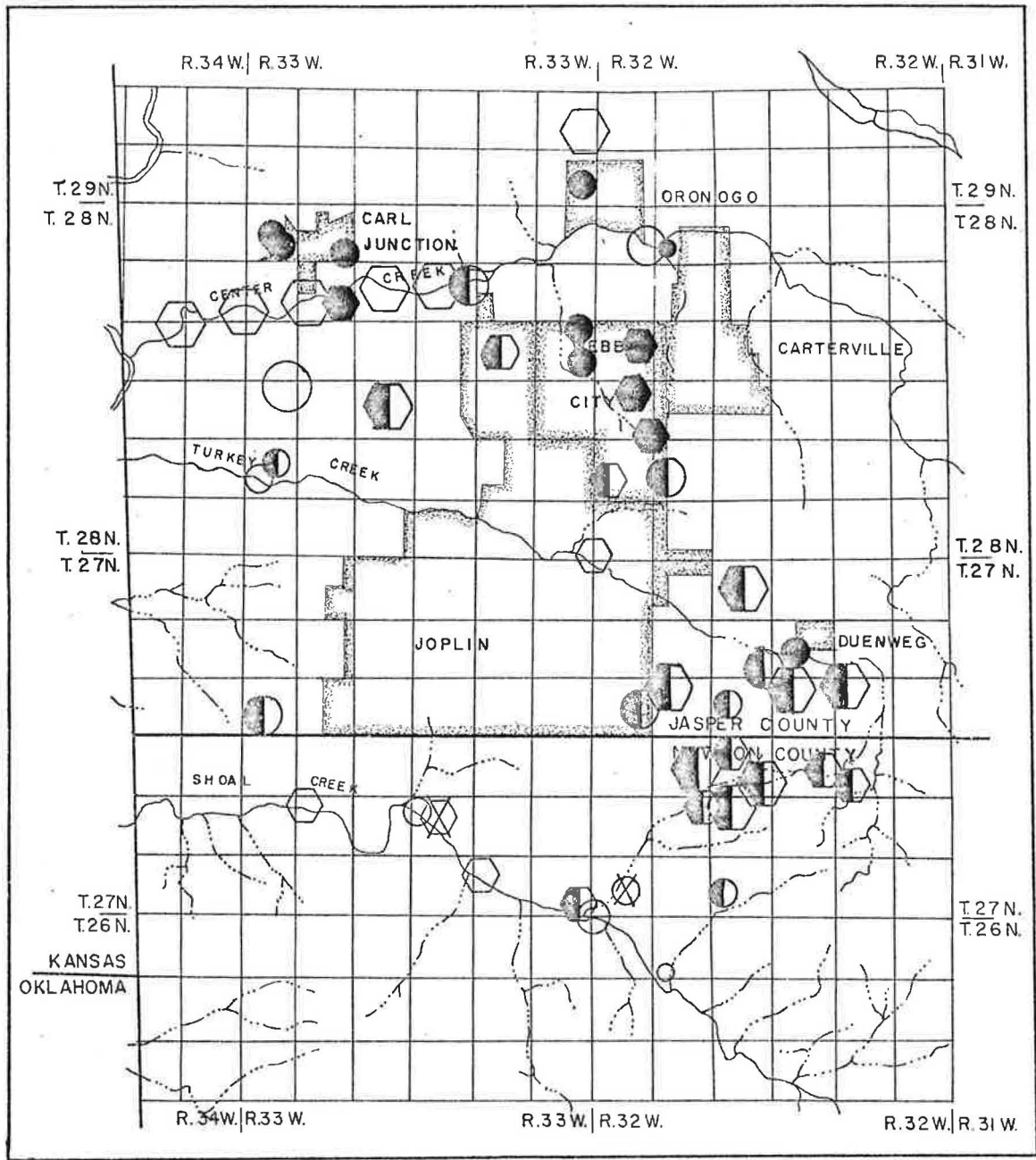


Figure 14. High zinc content in water samples from the Joplin area, Missouri.

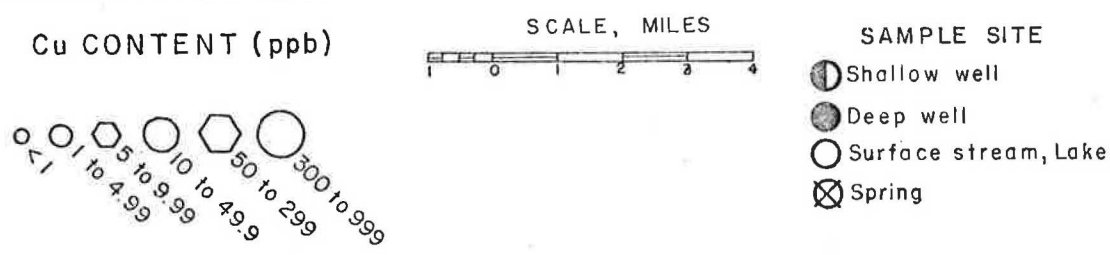
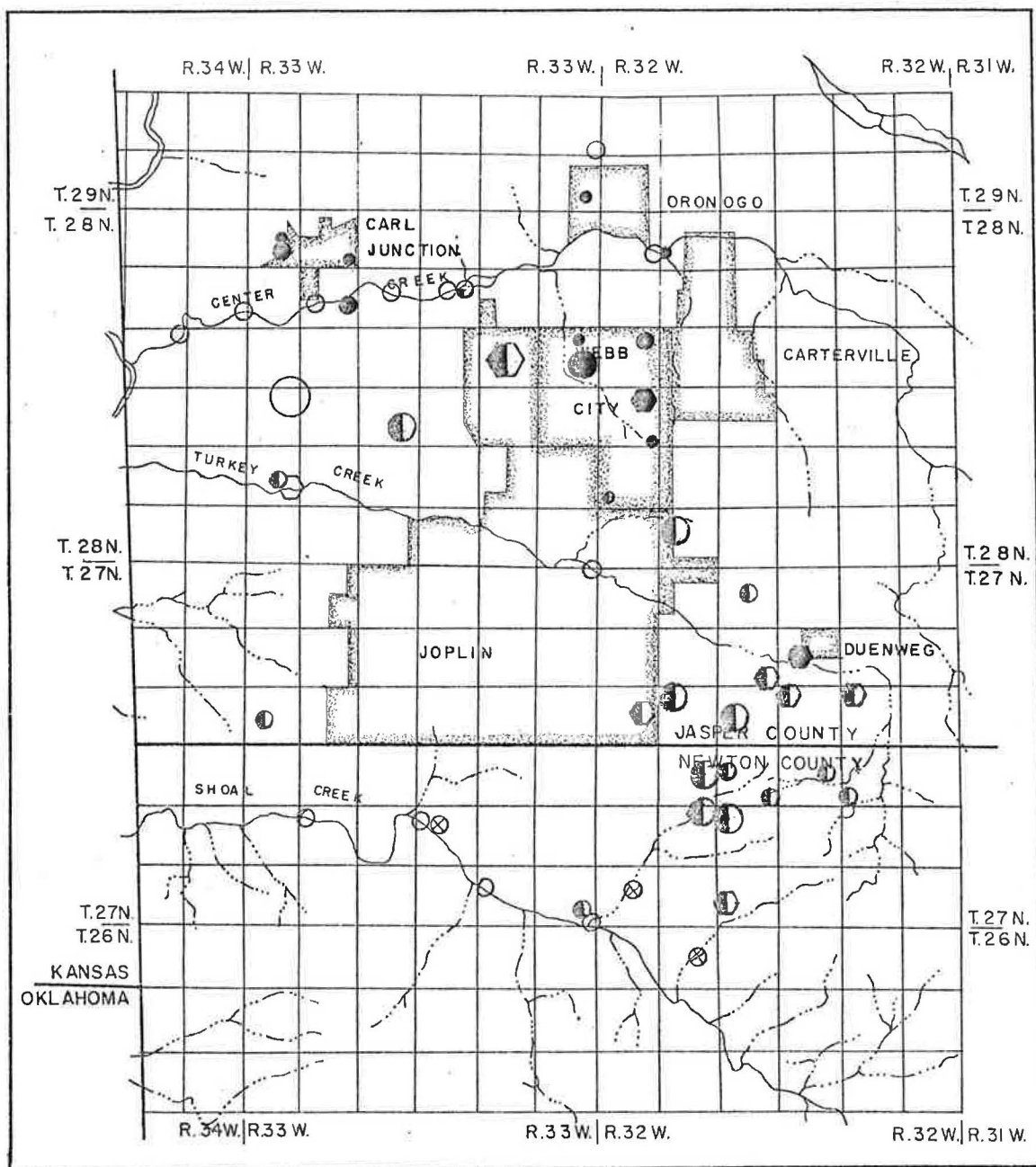


Figure 15. High copper content in water samples from the Joplin area, Missouri.

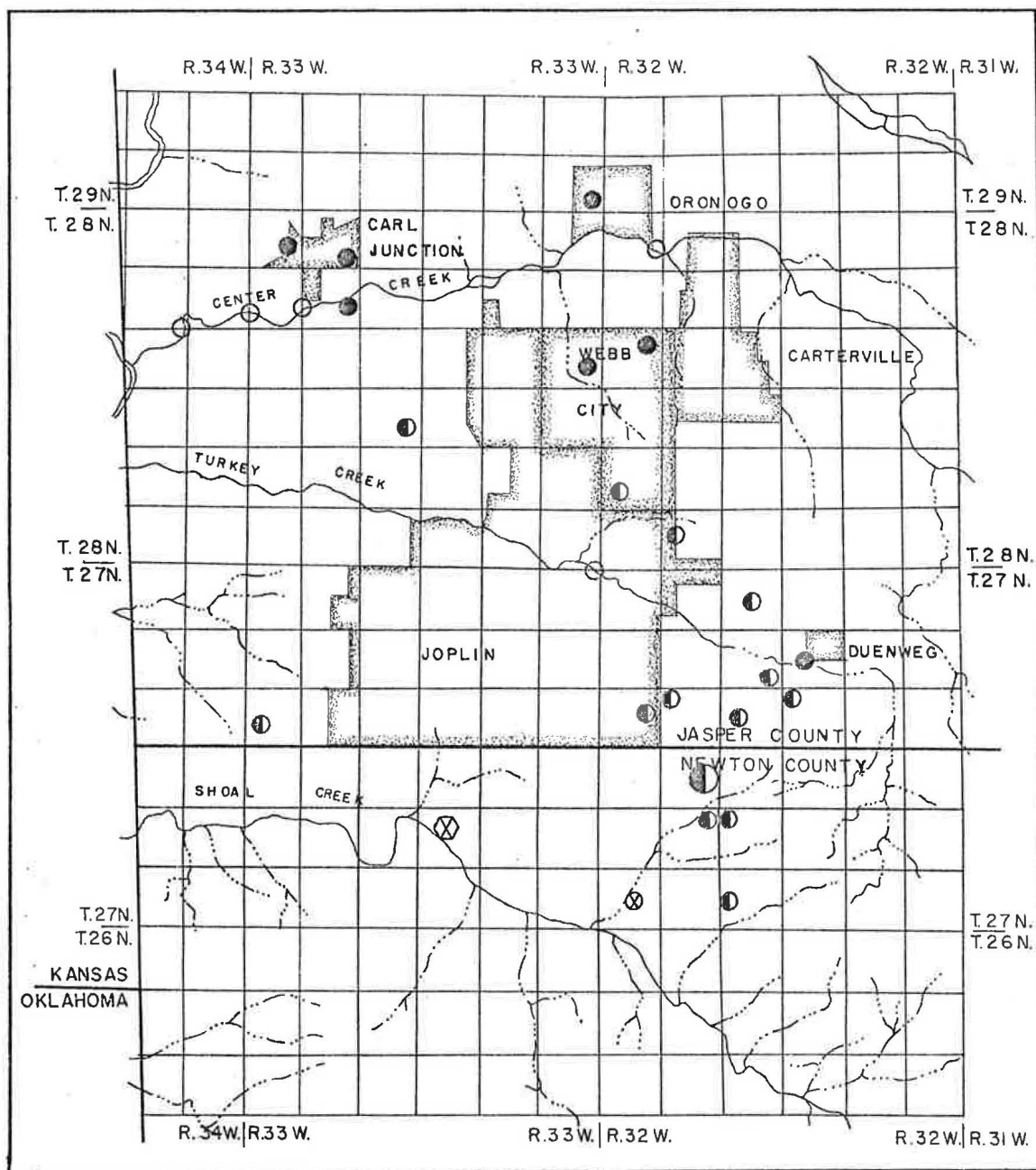
In most water samples, copper content is low and all values fall well below the PHS standards for domestic use from wells. Copper content in one open pit lake exceeded optimal conditions for fish life. The seasonal variation of copper values from one well was found to be nearly as great as the variation in values for the whole area.

Cadmium: Cadmium content in water samples ranged from less than 1 ppb to 16.5 ppb. The highest value of cadmium in deep well waters was only 2 ppb (fig. 16). In shallow wells the highest content of cadmium was 12.5 ppb, in springs 8 ppb, in lakes 7 ppb and in surface streams 2 ppb. Cadmium values in some shallow wells exceeded the PHS standards for drinking water.

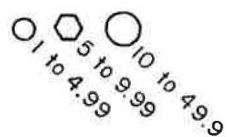
For most water samples, cadmium concentrations are close to or below the limit of detection of the instrument. Because of low correlation between fall and spring values, no statement can be made regarding seasonal variation in the waters sampled.

Mercury: No mercury values in excess of 0.1 $\mu\text{g}/\text{l}$ were detected in the Joplin area water samples. Because of this very low content of mercury in the waters of the district, no map was prepared.

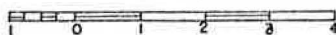
Iron: In the Joplin area the value of iron concentration in water samples ranged between 1 ppb and 119,000 ppb. The maximum iron detected in deep well water samples was 480 ppb. Shallow wells contained as much as 1,420 ppb, springs 11 ppb, and one lake 119,000 ppb (fig. 17). Several samples contained iron in excess of the PHS standard for culinary water. The



Cd CONTENT (ppb)



SCALE, MILES



SAMPLE SITE

- Shallow well
- Deep well
- Surface stream, Lake
- ⊗ Spring

Figure 16. Cadmium content >1 ppb in water samples from the Joplin area, Missouri.

variations and high values of iron may partly be related to the filter pore size used. While Brown et al. (1970) recommend the 0.45 μg size, Feder (1972) notes a considerable variance in iron analyses when a smaller pore size is used. The highest iron values were recorded from the large pore size filter. This, however, does not change the fact that iron content is locally very high in the Joplin waters.

PHS Water Quality Standards: Ten sample sites in the Joplin area had heavy metal content near to or in excess of the PHS standards for drinking water. Six were shallow well environments, one a deep well and three surface waters. Iron exceeded the standard in five cases, and closely approached it in two others. Cadmium exceeds the established value at two sites, and zinc at one site. Zinc showed relatively high values, but below the PHS standards for many of the shallow wells and for surface samples in the Center Creek area. For the relatively few water sample sites for the 100 square mile area around Joplin, 25 percent of the shallow well sites, 10 percent of the deep and 16 percent of the surface water samples exceeded the PHS drinking water standards.

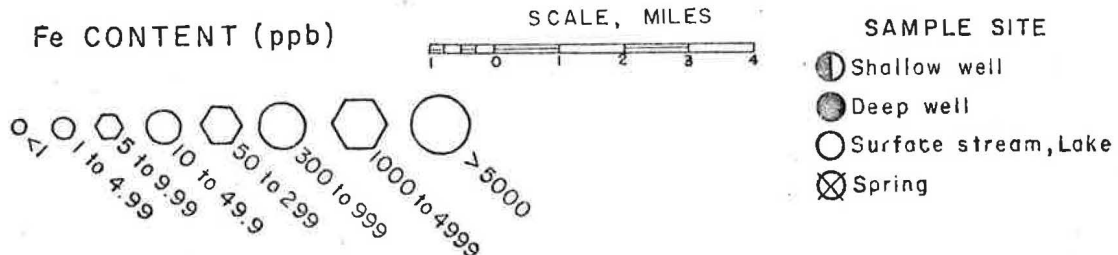
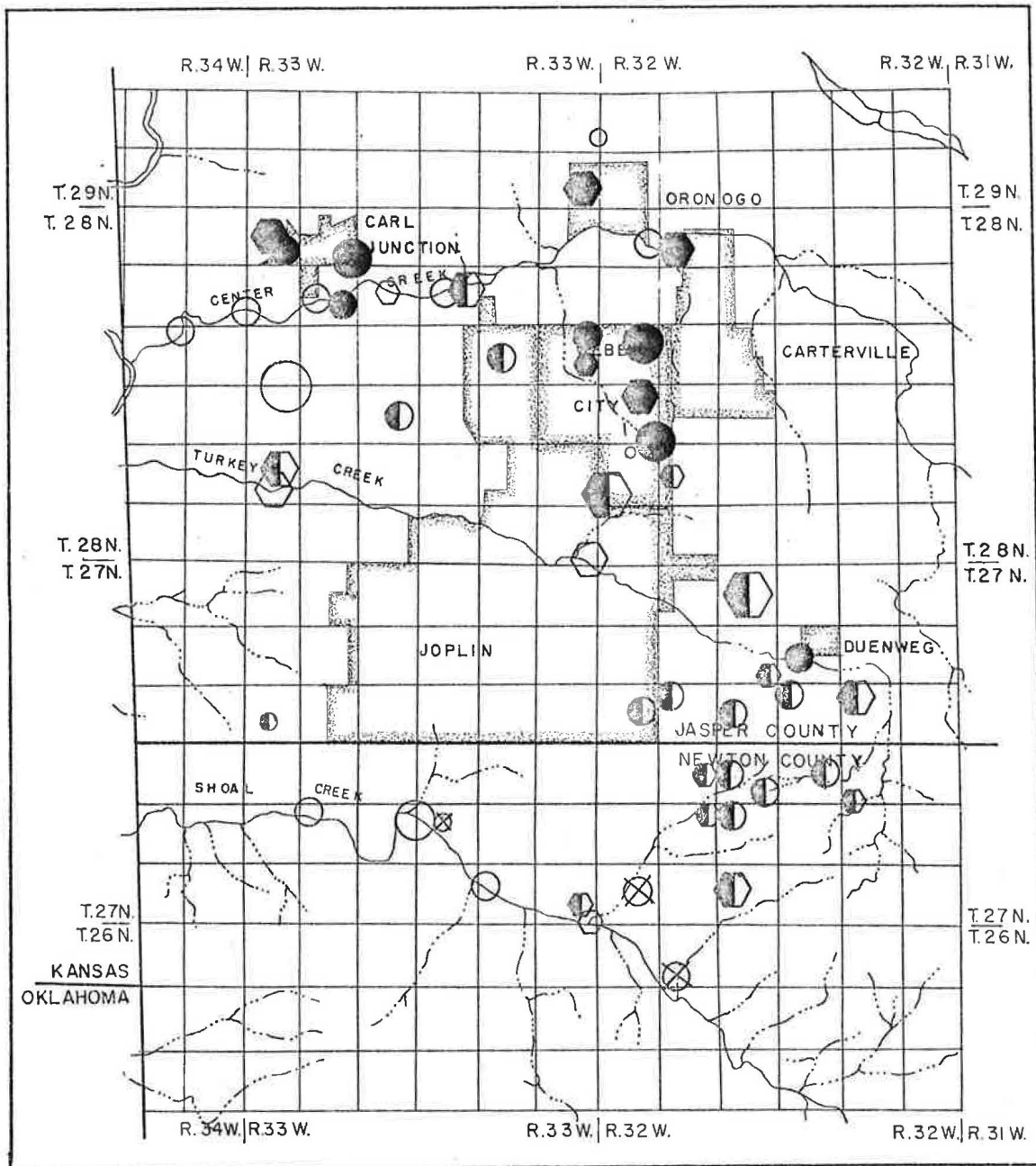
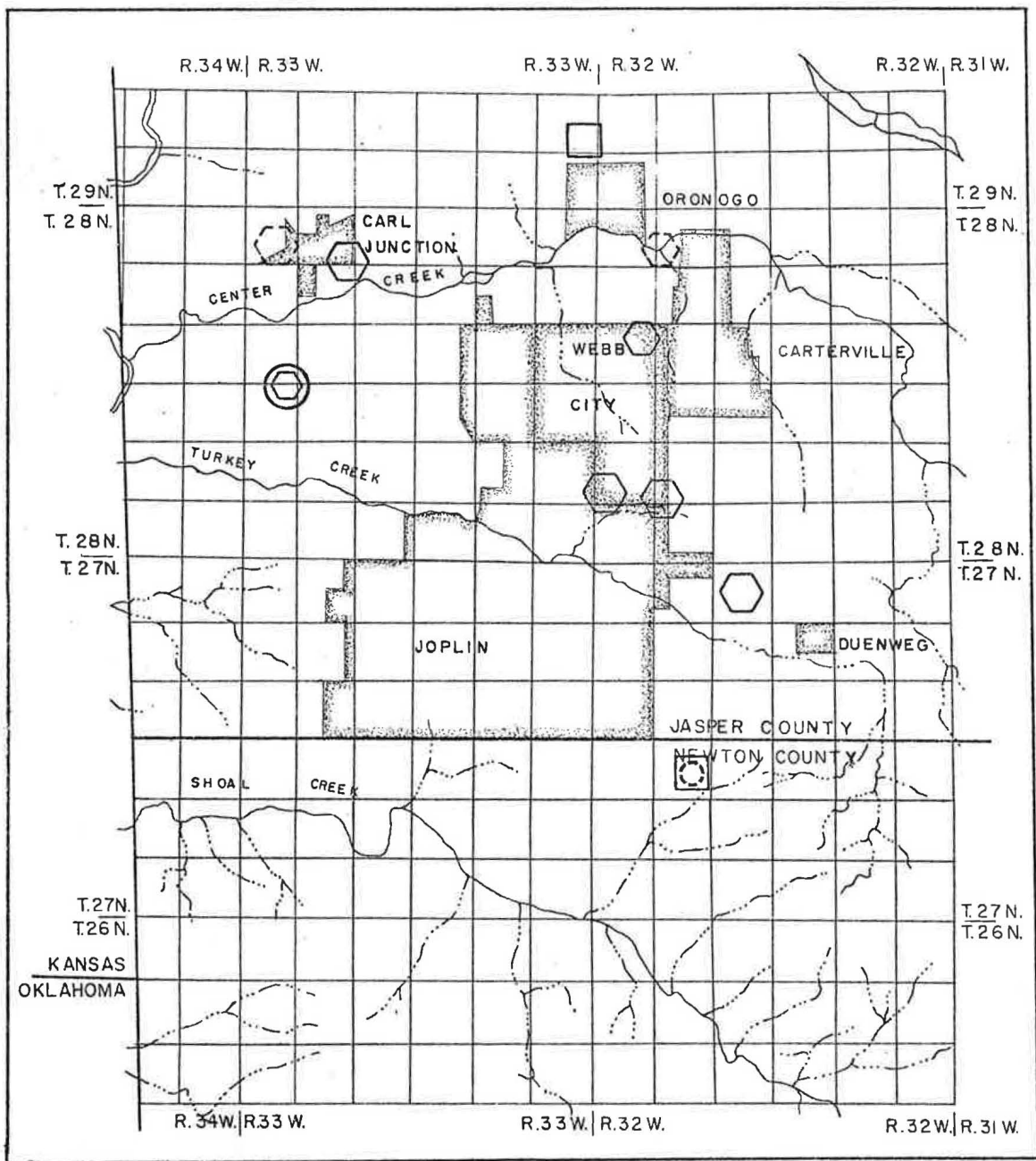


Figure 17. High iron content in water samples from the Joplin area, Missouri.



PHS RECOMMENDED STANDARDS

Pb < 50ppb	Zn < 5,000 ppb	<table border="1"> <thead> <tr> <th></th> <th>Cd</th> <th>Zn</th> <th>Fe</th> </tr> </thead> <tbody> <tr> <td>Content > PHS Standard</td> <td>□</td> <td>○</td> <td>⬡</td> </tr> <tr> <td>Content near PHS Standard</td> <td></td> <td>⊙</td> <td>⬢</td> </tr> </tbody> </table>		Cd	Zn	Fe	Content > PHS Standard	□	○	⬡	Content near PHS Standard		⊙	⬢
	Cd		Zn	Fe										
Content > PHS Standard	□		○	⬡										
Content near PHS Standard		⊙	⬢											
Cu < 1,000ppb	Hg < 5ppb													
Cd < 10ppb	Fe < 300 ppb													

SCALE, MILES

Figure 18. Water samples from the Joplin area, Missouri, with heavy metal content near to or in excess of PHS standards for drinking water.

CONCLUSIONS AND APPLICATIONS

In the Springfield area known mineralized areas of lead, zinc and iron sulfides are rather small and insignificant when compared with the Joplin area. Yet, patterns and contents of the heavy metals in the waters of Springfield are quite distinct and readily apparent.

Mercury, which is almost non-detectable in the Joplin area, is present in the Springfield waters in less than 1 ppb from all water sample environments. It does not exceed PHS standards.

Cadmium values in the waters are generally higher in the shallow well environment mainly outside the city limits, and in the surface waters. Deep wells in the city mainly have lower values. One deep and one shallow well both outside the city exceed PHS standards for drinking water.

Zinc content in the waters is variable. In at least one case east of Springfield in a shallow well the content exceeds the PHS standards. Generally, however, values range between 500 and 5,000 ppb. Pearson Creek shows anomalously high zinc values. These are probably related to known lead-zinc mineralization in this area. Surface waters throughout the Springfield area have generally less than 100 ppb of zinc.

Copper content of waters in the Springfield area is very low and ranges from 20-30 ppb. This range is far below the PHS upper limit standard of 1,000 ppb. Just beyond the western and northern boundaries of the city, the copper content from well samples appears to be slightly higher.

Lead content, while variable throughout the area, falls well within the upper limits of the PHS standards. Higher lead values tend to occur at the same sample sites where the zinc values are also higher. Pearson Creek and Wilson Creek show an overall higher lead content. A surface water sample in the city exceeds the PHS standards.

Iron content in the waters of the Springfield area is quite variable, but does show a pattern. Almost all of the higher values occur in the western half of the studied area. Here iron values range to as much as 400-500 ppb, though mainly they are in the 100-200 ppb range. By far the majority of deep wells within the city have very low iron content. One in the north-east quarter, however, is in the range of 100-200 ppb. A shallow well in the northwest part of the city has 300-400 ppb and a deep well five miles southwest of the city limits has 400-500 ppb. Only these latter two sample sites show iron values in excess of the PHS standards.

In the Joplin area, the relationship between the concentration and distribution patterns of heavy metal values, the rock type of aquifers, known stratigraphic position of sulfide mineralization, and seasonal variations in heavy metal content due to dilution or leaching were found to be significant.

Lead, copper and mercury content in the waters are all below the suggested PHS standards for drinking water. Zinc, cadmium and iron contents in some shallow and deep wells exceed the recommended PHS standards. Zinc and some copper values are also higher than optimal for aquatic life such as fish.

The high zinc values in the shallow aquifers and in some of the surface waters are strongly anomalous and relate to known mineralized areas and the relatively good solubility of zinc in nearly neutral waters. It is very probable that in this area shallow aquifers are interconnected with mine waters, or that the ground waters percolate through the brecciated and mineralized areas and dissolve heavy metals from the host rock resulting in the anomalous values.

The influence of sulfide mineralization in the shallow Mississippian rocks is greater on the metal content of the shallow wells than on those of the deep wells in the older, mainly non-mineralized rocks or in the surface waters. Some small lakes near or in mined-out areas also show high anomalous heavy metal values. Mean fall season values of lead, zinc, copper and cadmium in the waters are generally higher than those of the spring season.

Mercury values are negligible in the Joplin area.

The iron content generally appears to be independent of known mineralization. There is a tendency to be higher in water samples from springs, though the highest values are in water-filled old mine workings in the Joplin area.

Alternate Sources of Water: There is little question that the shallow well environments both in Joplin and Springfield have much higher heavy metal contents than the deeper wells in the Cambro-Ordovician section. This fact suggests the long range necessity of developing water supplies from the deeper sources due to the erratic quality of shallow water samples.

For the near future, in the event one or more of the sample sites containing heavy metal content in excess of PHS standard persists, then a deeper source of water is recommended. Obviously, in those rare cases where deep water sources have excess heavy metals, a shallower source might be tested to see if the standards can be met. Here geological conditions, such as mineralization, fault systems, and hydrologic conditions must be investigated as to the cause of deep well water pollution. Failure to improve in the quality of the shallow well waters might require abandonment of the well site. Normally, there is considerable heavy metal variation over relatively moderate distances (ca. 1 mile), hence, a new drill hole may tap acceptable water for a relatively small volume user. This will require additional sampling and analysis of the waters.

As a final point, only a relatively small number of water wells of the total present in the areas were selected for sampling. The fact that approximately ten percent of the wells sampled in Springfield and to 25 percent in Joplin approached or exceeded the PHS standards for one or more metals for drinking water suggests that in areas of anomalously high heavy metal values other water wells not sampled may carry heavy metal content in excess of those acceptable. Additional sampling and analyses should be carried out to identify such water sources and recommendations made for more acceptable water sources. Indeed, direct sampling of all new wells for heavy metal content prior to use would be a logical approach to establish quality water sources for human use.

PUBLICATIONS, REPORTS, TALKS PRESENTED

A summary report of this investigation has been accepted for publication in the 7th Annual Conference on Trace Substances in Environmental Health (Proctor, et al., 1973). This will be published just after mid-year. Preliminary findings of the study were presented at the annual meeting of the Water Resources Research Center in Columbia (Proctor, et al., 1972). An abstract of the final report will appear in the annual report of the Water Resources Research Center this spring (Proctor, et al., 1973). Possibly one other publication will result from the investigation this year in a national journal.

TRAINING ACCOMPLISHMENTS

Three graduate students directly participated in the research work. Two of the three will receive their M.S. degrees in June, 1973. Part of the research effort and the results from the Joplin and Springfield area, respectively, will be presented as theses as part of the graduate degree requirements. In addition, results of the study have and will be used in classes in ground water geology, and applied geochemistry as examples of water quality investigations. The publications in progress and planned will make available results of considerable value to other higher education courses in water resources and environmental health.

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APPENDIX I

Mercury Analytical Method

This method permits a more sensitive determination of the mercury content of suitable samples than the normal flame methods of Atomic Absorption Spectrophotometry, while using the same basic equipment. Elimination of the flame reduces the inherent noise level of the system. The method also permits a longer residence time for the mercury in the beam path. The procedure relies on the high volatility of elemental mercury in water solutions.

Place 100 ml of water to be analyzed in a suitable clean glass bottle of a type that can be stoppered. It should also permit the introduction of a stream of air through the solution and the passing of this stream into the beam path of the atomic absorption instrument. To the water solution add 5 ml of concentrated sulfuric acid, 2.5 ml of concentrated nitric acid and 1 ml of 5% (w/v) potassium permanganate solution. Allow the mix to stand for 15 minutes. After 15 minutes add 2 ml of 3% (w/v) potassium persulfate and again allow to stand. These steps are designed to destroy organo-mercury compounds. After 30 minutes add sufficient $\text{NaCl} - (\text{NH}_2\text{OH}) \cdot \text{H}_2\text{SO}_4$ solution until a clear solution is obtained.

A standard series should also be prepared containing a blank and at least 3 other known amounts to bracket the expected mercury contents of the unknowns. Treat the standards in the same manner as the unknowns. Just before inserting the aeration apparatus, add 5 ml of supersaturated stannous sulfate solution.

The aeration assembly requires only a glass tube through a rubber stopper sufficiently long to be immersed near the bottom of the solution when the stopper is inserted into the bottle. Adjust the rate of air flow to a slow bubbling action so that liquid is not bubbled into the exhaust tubing of the bottle. The exhaust of the bottle is carried in tubing to a glass or metal absorption cell with quartz glass windows on each end. This is positioned in the beam of the instrument and is placed where the flame normally is present. The ideal size of the absorption cell is about 6 inches long and one inch diameter. The mercury vapor exhaust of the absorption cell is vented to a safe disposal area. Tygon or equivalent tubing is recommended over rubber tubing to prevent carry over problems. A 100 watt lamp placed close to the absorption cell gently heats the cell and prevents water build-up in the absorption cell.