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Total Maximum Daily Load Development
Paducah Gaseous Diffusion Plant: Existing Data Review

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Introduction

The Kentucky Research Consortium for Energy and the Environment (KRCEE) was created to support Department of Energy (DOE) efforts to complete expeditious and economical environmental restoration of the Paducah Gaseous Diffusion Plant (PGDP) and surrounding areas such as the Western Kentucky Wildlife Management Area. General activities include the following:

- Application of technical expertise to assess, and accelerate implementation of cost effective technologies and methodologies that result in accelerated clean-up and risk reduction.
- Establishment of problem-specific project teams drawn from disciplines of expertise at participating universities that work with DOE and its contractors to accelerate implementation of project concepts and plans. Project team focus is on risk prioritization and accelerated implementation of cost-effective remedial activities to minimize impacts on public health and the environment.
- Technical review of proposed remediation plans and any non-consensus technical issues associated with their implementation.
- Use of project teams to interface directly with DOE national laboratories, the United States Environmental Protection Agency (EPA), and state regulatory agencies to help forge consensus solutions to technical problems related to clean-up and ongoing operations of the PGDP site.
- Accomplishment of targeted long-term and short-term projects tasks designed to support the accelerated clean-up at PDGP.

KRCEE is administered through the University of Kentucky Tracy Farmer Center for the Environment (TFCE). Annual work plans, deliverables, and associated project budgets address short-term and long-term tasks relevant to ongoing remediation efforts. Project teams made up of faculty and professional staff were drawn from the University of Kentucky (the main campus and the Paducah campus), the University of Louisville, and Murray State University.

Currently, broad projects and issues related to DOE's activities at PGDP include the following: 1) Scrap metal removal and remediation of underlying surface soils, 2) Surface water remediation and release control including sediment control and Total Maximum Daily Load (TMDL) issues, 3) Groundwater remediation including groundwater modeling and proposed remediation technologies, 4) Waste disposal including C-746-U landfill issues, 5) Burial grounds including assessment remedial action feasibility, 6) Site wide soils and drainage ditch clean up using real-time characterization and remediation, 7) Demolition and debris including disposition of volumetrically contaminated metals, 8) seismic issues, and 9) risk assessment issues.

Specific Scope of Work

In support of the general goals of the KRCEE, Murray State University agreed to conduct work related to surface water issues.

To assess the surface water, a hydrologic characterization of the PGDP facility was conducted. The tasks for the project included developing and calibrating continuous simulation hydrologic models for Bayou Creek and Little Bayou Creek watersheds using the HSPF watershed model. Another task included developing a water budget for the PGDP facility identifying and incorporating significant water inputs and outputs. Finally, available chemical data from PGDP outfalls and from sampling sites along both creeks were compiled, reviewed, and summarized.

The deliverables for the project included quarterly progress reports, quarterly presentations, and a summary report describing the development and calibration of the models, the plant water budget, and the chemical data.

Bayou Creek and Little Bayou Creek are on the Kentucky 2002 303(d) list of impaired waters. Under the provisions of the Clean Water Act, individual TMDLs must be developed for each creek. Constituents of concern for Bayou Creek include metals (iron, lead, copper, and mercury) and Technetium (^{99}Tc). Constituents of concern for Little Bayou Creek include metals (iron, lead, copper) and (^{99}Tc). The work included assessing which of these parameters might require TMDL development and may include actual TMDL development once agreement is reached between DOE and state regulatory agencies on how to proceed.

Acknowledgments
The authors would like to acknowledge with appreciation the assistance of Dr. Ramesh S V Teegavarappu and Dr. Chandramouli Viswanathan of Department of Civil Engineering at the University of Kentucky. Both provided unselfish assistance on the use and calibration of the HSPF model used in part of this research. Dr. Alan Fryer and Mr. Josh Sexton of the Department of Geology at the University of Kentucky kindly provided information on the losing and gaining sections of Bayou and Little Bayou Creeks that was very much appreciated. The authors also recognize the support of Dr. Daniel Claiborne of the Department of Industrial and Engineering Technology at Murray State University who arranged office space and staffing to accommodate project needs. Finally, the authors acknowledge the support provided by project director Dr. Lindell Ormsbee and assistant director Mr. Steve Hampson throughout the entire duration of this project.

Summary of Existing Data

Location and Site Description

The Paducah Gaseous Diffusion Plant (PGDP) is located on a 3,400-acre site in McCracken County approximately 15 miles west of Paducah, Ky., and approximately 3 miles south of the Ohio River. The PGDP was completed in 1953 with production starting as early as 1952. The facility enriches uranium through a diffusion cascade process that requires extensive support facilities. The diffusion process encompasses five buildings with approximately 740 acres fenced. Support facilities at the plant include cooling towers, a chemical cleaning and decontamination facility, water and wastewater treatment plants, a phosphate reduction facility, four electrical switchyards, a steam plant, and a laboratory. Including various contractors located on the site, the facility employed approximately 2,000 people at its peak. The PGDP is surrounded by a buffer of land owned by the Department of Energy (DOE) and leased to the Commonwealth of Kentucky.

The PGDP discharges treated wastewater and storm water runoff to both Bayou and Little Bayou Creeks, which drain northerly through privately owned land and the West Kentucky Wildlife Management Area (WKWMA) to the Ohio River. Effluent from the PGDP is a major source of flow in both Little Bayou Creek and Bayou Creek during low-flow periods.

Problem Definition

The PGDP is one of two operational facilities in the United States that commercially enrich uranium for use in nuclear reactors. PGDP began the production of enriched uranium in 1952. Discharge of metals in process wastewater and surface water runoff can be attributed to the facility processing and storage activities.

Technetium 99 (^{99}Tc) is from the nuclear fission of uranium. Most of the technetium produced in a nuclear reactor originates from the decay of zirconium 99. Zirconium 99 is a direct product of uranium fission. Technetium 99 has a half-life of 212,000 years. Processing of recycled uranium from nuclear reactors was conducted from 1953 to 1964. Only virgin mined uranium was processed from 1964 to 1969. The processing of recycled uranium began again in 1969 and was halted permanently in 1976. During the recycling periods, PGDP received 100,000 tons of recycled uranium containing an estimated 661,000 grams of ^{99}Tc. ^{99}Tc is believed to have been deposited on internal surfaces of process equipment and on waste products.

Data Collection

Site chemical and flow data were collected from three sources, the Oak Ridge Environmental Information System (OREIS), Department of Energy (DOE) Annual Reports, and an file transfer protocol (ftp) site maintained by the Kentucky Research Consortium for Energy and the Environment.

The OREIS database served as the primary data source (Bectel Jacobs, 1987-2003). The database was searched for outfall surface water discharge and stream sampling data. The **L** site designation refers to in-stream sampling sites. The outfalls are designated as **K**, followed by the corresponding outfall number.

The ftp site data (Appendix A) were compared to the collected data for discrepancies or omissions and the compiled data were updated accordingly. DOE annual site reports were reviewed and relevant information extracted. Electronic copies of the 2001, 2002 and 2003 reports were accessed and printed from the Bechtel Jacobs website, (Bectel Jacobs, 2005). Paper copies of the DOE reports for 1987 through 2000 were obtained from the DOE Environmental Information Center in Paducah, Kentucky. The DOE reports were also used to obtain background information, monitoring locations, and outfall descriptions.

All available K and L site data for the period from 1987 to 2004 were individually collected and sorted (Appendix B). The metals of concern, copper (Cu), iron (Fe), lead (Pb), mercury (Hg), and technetium (^{99}Tc), were extracted and sorted by date. Flow data were also compiled. The number of samples recorded within a year varied. A compilation of the extracted data is contained in Appendix C. Annual minimum, maximum, and average concentrations are included.

Flows were grouped in a similar manner (Appendix D). The coordinates for the L and K sites are contained in Appendix E. The data were grouped on the basis of discharge to Bayou Creek or Little Bayou Creek and sorted by chemical name and year. Annual maximum, minimum, and average concentrations were calculated (Appendix F).

Because of uncertainty over how critical low flows might be examined, the collected data were further examined for the 1993 to 2003 time period (for a 10 year minimum average flow), and the 1996 to 2003 time period corresponding to available gauging station data.

Historical Monitoring Results

Chemical and flow measurements were recorded from stream sampling sites and at the plant outfalls. Figures 1 and 2 show the location of the stream sites and outfalls, respectively. The L site locations are described in Table 1. Table 2 provides a description of inputs to each outfall. Figure 3 shows the plant site and the relative proximity of outfalls.

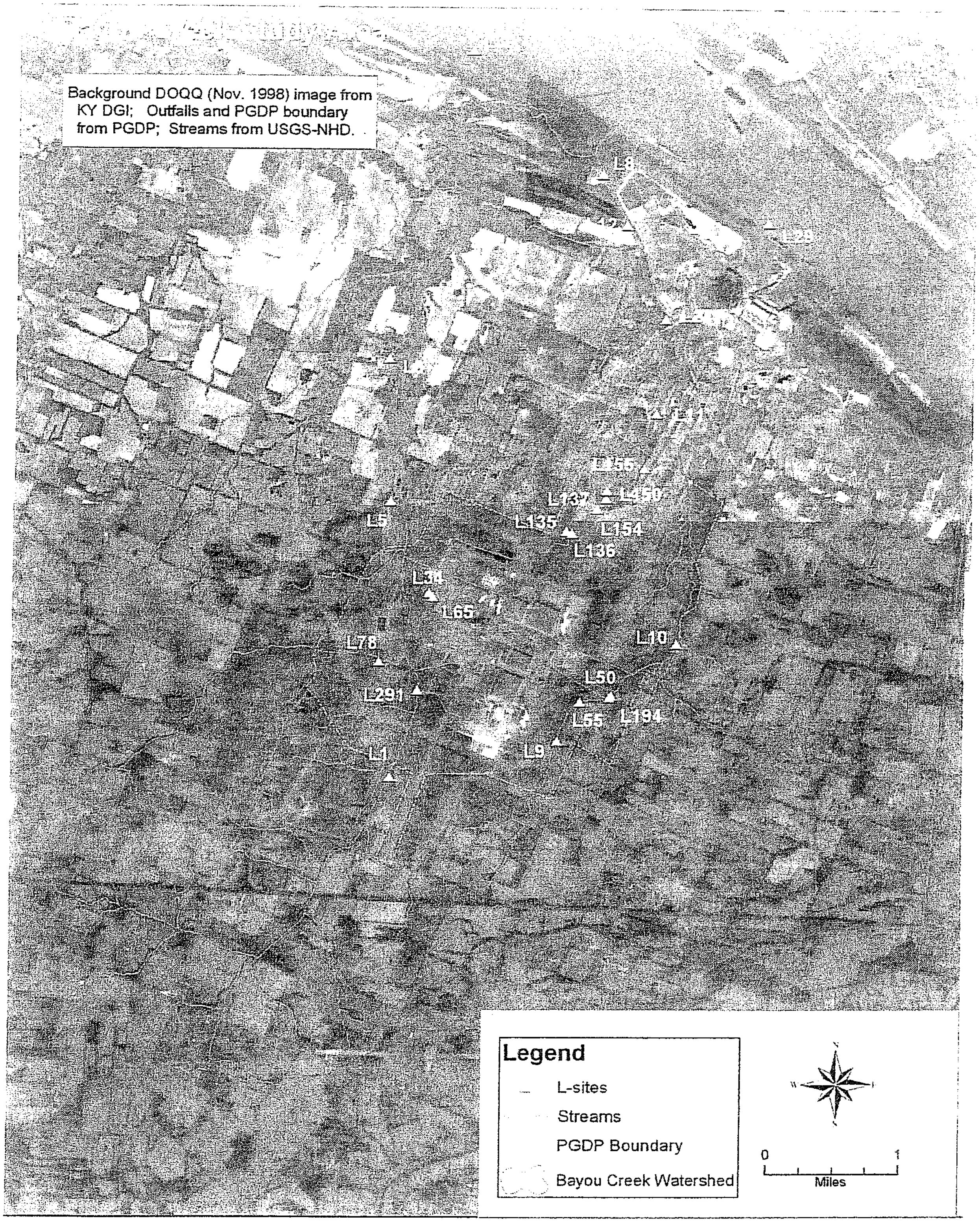

Figure 1 - L-sites study areas

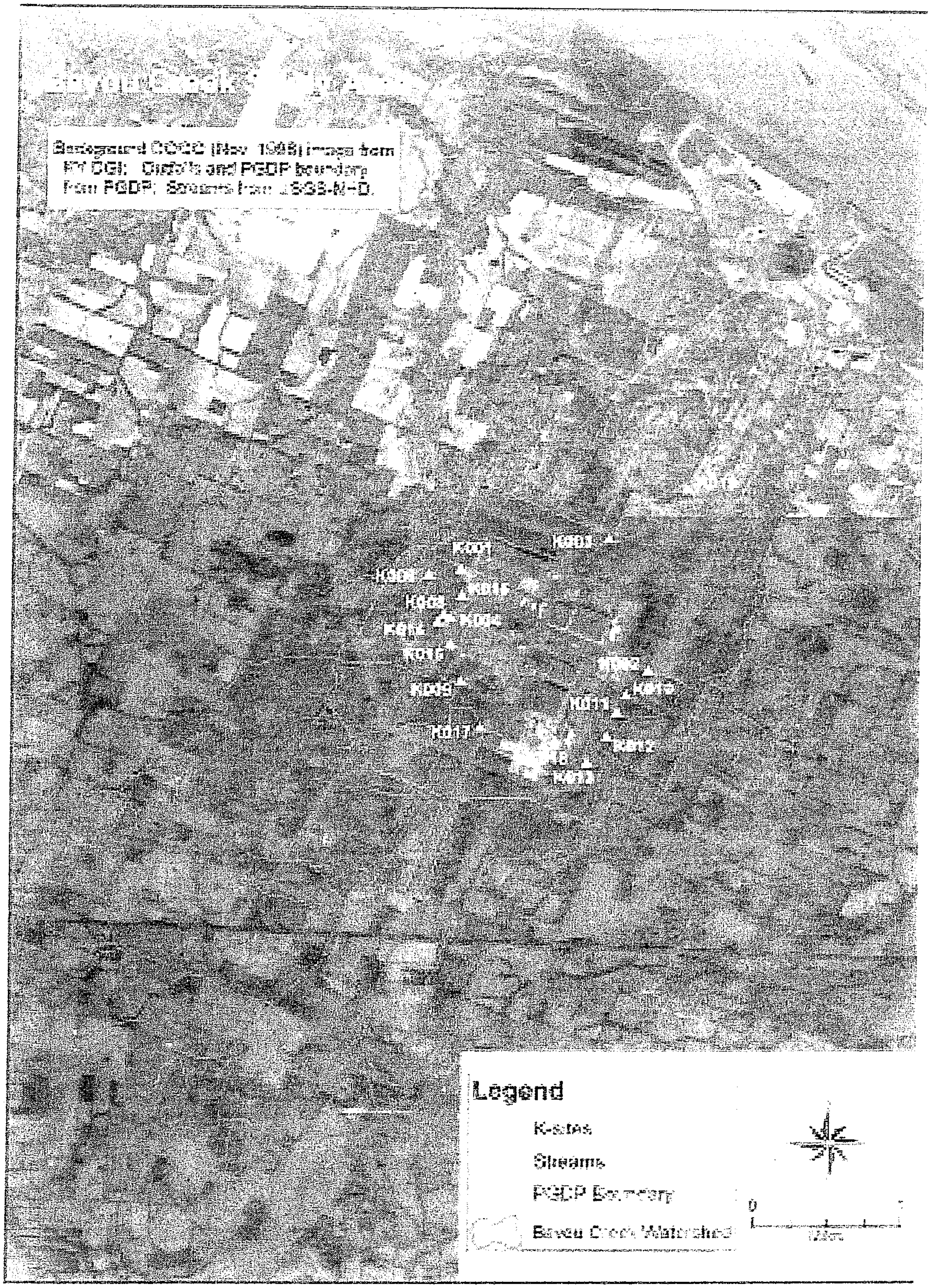

Figure 2- K-sites study areas

Table 1 - Stream sampling locations, Bayou and Little Bayou Creeks

Location	Description
L1	Upstream of plant effluents in Bayou creek
L5	Downstream of plant effluents in Bayou Creek
L6	Downstream of plant effluents in Bayou Creek
L8	Mouth of Bayou and Little Bayou Creeks
L10	Downstream of plant effluents in Little Bayou Creek
L11	Downstream of plant effluents in Little Bayou Creek
L12	Downstream of plant effluents in Little Bayou Creek
L29	Ohio River upstream of confluence with Bayou and Little Bayou Creeks
L30	Ohio River downstream of confluence with Bayou and Little Bayou Creeks
L55	Little Bayou Creek at confluence with Outfall 011
L56	Little Bayou Creek at confluence with Outfall 013
L64	Massac Creek background location
L135	Upstream of C-746-S&T Landfill, surface runoff
L136	At C-746-S&T Landfill, surface runoff
L137	Downstream of C-746-S&T Landfill, surface runoff
L150	At C-746-U Landfill, surface runoff
L154	Upstream C-746-U Landfill, surface runoff
L155	At C-746-S&T Landfill, surface runoff
L194	Little Bayou Creek downstream of Outfall 010
L241	Downstream of plant effluents in Little Bayou Creek
L291	Upstream of plant effluents in Bayou creek
L306	Ohio River at Cairo, Illinois

Table 2 - Description of outfalls

Table of Outfalls at PGDP		
Location	**Drainage Source**	**Contributing Processes**
1	C-616, C-335, C-535, C-537, C-337A	RCW in blowdown treatment, C-337A vaporizer condensate, C-335 air plant, switch yards, scrap yards, C-335 roof
2	C-337, C-360, C-637	C-337 roof, C-360 autoclave condensate, C-637 windage
3	North edge of plant	Storm water overflow of diversion ditch, transformer oil filtration
4	Sewage treatment plant	Sewage treatment liquid effluent
5	C-611 primary sludge lagoon	Process and sanitary water treatment (water supply)
6	C-611 secondary lagoon	Process and sanitary water treatment (water supply)
7	Outfall eliminated	
8	Main central plant sewer and sewage treatment plant	C-600 air plant, paint shop, sewage plant, motor cleaning, roof drains, degreasers
9	C-720, C-710, C-100 area, C-200, C-333	Maintenance shops, laboratory, roof drains, cascade
10	C-331, C-531, Kellogg pad (storage area)	Cascade, switchyard storage
11	C-620 air plant, C-315, C-340, C-333, C-533, C-540	Cascade, switchyard, metals plant (inactive) transformer oil filtration
12	C-333, C-333A, C-533, C-633	Cascade, switchyard, C-333A vaporizer condensate, cooling tower windage
13	Southeast corner of plant	Surface drainage, cylinder storage areas
14	C-611 U-shaped sludge lagoon	Sanitary water sand filter backwash
15	West central plant areas, C-749, C-404	Surface drainage from closed radioactive waste disposal areas
16	Small area south of C-615	Surface drainage only
17	Southwest corner of plant	Surface drainage, cylinder storage yards
18	NA	NA
19	NA	NA

NA – Not Available

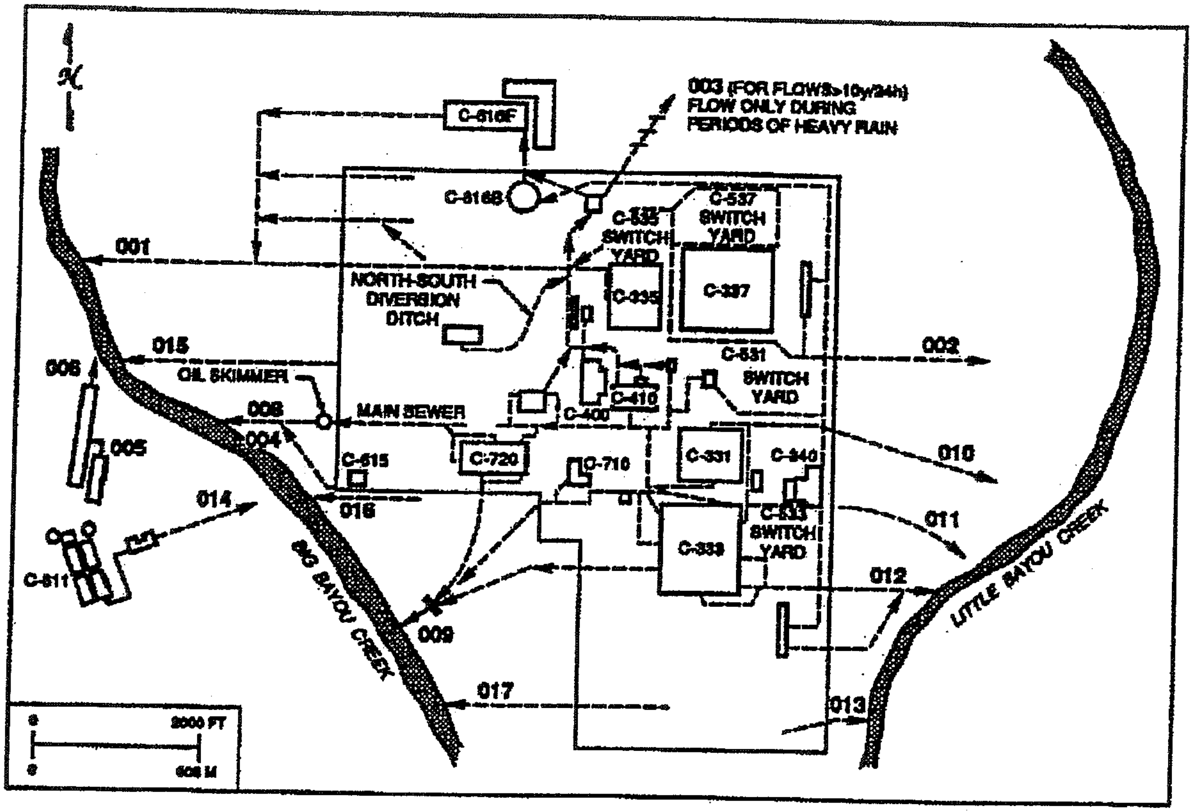

Figure 3 - Approximate outfall locations, PGDP

Copper, iron, lead, mercury, and technetium data from individual sampling events are presented in Appendix B. Hardness data are included since the copper and lead water quality limits depend on the hardness level. Table 3 presents a summary of the total number of samples for each of the parameters at each stream site and outfall. The average, minimum, and maximum values observed for the entire data period are included in Appendix C.

Table 3 - Total samples from each location, 1987-2003.

Count (L-sites)						
Station	Copper	Hardness	Iron	Lead	Mercury	Tech-99
L1	50	45	61	50	8	143
L10	44	44	50	43	4	118
L11	42	40	41	42	6	33
L12	7	6	8	8	7	28
L18						1
L135			45			
L136			45			
L137			42			
L150			34			
L154			39			
L194	16	16	16	16	4	12
L241	7	4	7	7	7	25
L291	16					21
L306	21	21	21	21	6	
L34	1		1	1	1	2
L5	45	43	44	45	4	135
L55	14	10	14	14	4	10
L56	15	15	15	15	4	10
L6	14	9	13	12	7	19
L8	7	4	7	7	6	21

Count (Outfalls)						
Sites	Copper	Hardness	Iron	Lead	Mercury	Tech-99
K001	281	325	281	150	40	534
K002	122	60	169	63		33
K003	4		4	1	1	1
K004	9	9	9	8	3	2
K006	106	218	106	108	8	5
K008	177	214	236	104	4	226
K009	163	214	224	108	6	52
K010	142	150	191	83	4	197
K011	138	119	195	77	5	337
K012	111	52	158	55	6	99
K013	108	52	108	58	7	14
K016	98	45	98	46	3	14
K017	140	154	140	85	22	31
K018	80	61	80	65	5	50
K018N	1		1	1	1	1
K019	19	43	19	19	19	14

The number of samples collected at each location for each parameter was highly variable. In some years, the data were collect biweekly. In other years, the data were collected quarterly or not at all. Outfalls tended to have a much higher sampling frequency than the stream sites. At the stream sites, the average sampling frequency for copper, iron, and lead was approximately quarterly, depending on the site. Samples were collected for mercury analysis only over a short period. Samples were analyzed for ^{99}Tc more frequently than the other metals upstream and downstream of the plant site, but no more than monthly on an average basis.

Appendix F includes a summary of the chemical data and flows on an annual basis for each of the Bayou Creek and Little Bayou Creek outfalls and the stream sampling sites. Although some data were available from 1987 until 2004, the data tended to be more complete in the period from 1993 through 2003. Furthermore, a ten year period was one of the alternatives examined for developing critical flow periods. Therefore, most of the historical data observations presented in this report are based on the ten year period. Annual averages, rather than discrete values, were used when compiling overall results because the dates each parameter was measured and the flow rates were obtained were not necessarily the same. Furthermore, the annual averages tend to dampen anomalies and provide a better overall indication of water quality.

Overall average flows in million gallons per day (mgd) for the stream sites and outfalls are presented in Table 4 and 5. PGDP outfalls account for most of the Bayou Creek and essentially all of the Little Bayou Creek dry weather flows. The flows presented in the tables were measured infrequently, and may or may not include precipitation runoff. Therefore, direct comparison of outfall totals and stream flows is not possible. These average flows were used only to compute probable average mass loadings.

Table 4 - Overall average flows, mgd, stream sites, 1993 -2003.

Average Flows 1993-2003				
Bayou Creek		Little Bayou Creek		
L-Site	MGD	L-Site	MGD	
1	13.81	9	NA	
291	5.56	56	0.27	
78	NA	55	0.349	
65	NA	194	1.81	
34	NA	50	NA	
5	14.51	10	1.365	
6	24.31	135	2.14	N-S Diversion
		136	0.805	N-S Diversion
		137	2.374	N-S Diversion
		150	0.551	N-S Diversion
		154	2.175	N-S Diversion
		155	18.807	N-S Diversion
		11	1.9	
		241	3.214	
		12	2.98	
		8	14.976	

Table 5 - Overall average flows, mgd, outfalls, 1993-2003.

Average Flows 1993-2003				
Bayou Creek			Little Bayou Creek	
Outfall	MGD		Outfall	MGD
1	2.24		2	0.68
4	0.662		3	NA
5	NA		10	0.566
6	0.941		11	0.352
8	0.97		12	0.677
9	0.72		13	0.751
14	NA		18	1.313
15	1.313		19	0.495
16	0.456		NA	NA
17	1.217		NA	NA
Total	**8.519**			**4.834**
Combined Total		**13.35**		

NA – Not Available

Table 6 shows the average metals concentrations measured at the L-Sites in Bayou Creek for the years 1993 – 2003. Table 7 shows the average metals concentrations measured in the Bayou Creek outfalls for the years 1993 – 2003.

Table 6 - Bayou Creek L-site average annual concentration, mg/L 1993-2003.

L-Site	Cu mg/l	Fe mg/l	Hg mg/l	Pb mg/l
1	0.03	1.13	2.3E-04	0.10
291	0	0.56	NA	0
5	0.03	0.47	NA	0.13
6	0.02	0.49	2.0E-04	0.12

NA – Not Available

Table 7 - Bayou Creek outfalls average metals concentration, mg/L, 1993-2003.

Outfall	Cu mg/l	Fe mg/l	Hg mg/l	Pb mg/l
1	0.02	0.49	1.6E-04	0.10
4	0.02	0.32	8.0E-05	0.15
6	0.01	0.67	1.5E-04	0.07
8	0.01	0.25	1.6E-04	0.09
9	0.01	0.57	1.0E-04	0.10
15	0.02	1.32	1.5E-04	0.15
16	0.01	0.69	1.3E-04	0.09
17	0.02	1.00	1.2E-04	0.12

Table 8 shows the average metals concentrations measured at the L-Sites in Little Bayou Creek for the years 1993 – 2003. Table 9 shows the average metals concentrations measured at the outfalls in Little Bayou Creek for the years 1993 – 2003.

Table 8 - Little Bayou Creek L-site average metals concentration 1993-2003.

L-Site	Cu mg/l	Fe mg/l	Pb mg/l
194	0.02	0.79	0.14
10	0.002	0.55	0.001
136	NA	0.68	NA
135	NA	1.68	NA
154	NA	2.57	NA
137	NA	2.38	NA
150	NA	5.42	NA
155	NA	3.36	NA
11	0.007	0.93	0.001
8	0.021	1.10	0.10

NA – Not Available

Table 9 - Little Bayou Creek outfalls average metals concentration 1993-2003.

Outfall	Cu mg/l	Fe mg/l	Pb mg/l
2	0.03	0.99	0.12
10	0.01	0.61	0.08
11	0.02	0.78	0.10
12	0.02	1.23	0.10
13	0.02	1.55	0.10
18	0.01	3.10	0.03
19	0.03	0.72	0.14

TMDL development ultimately requires estimation of chemical masses and mass flows. To determine mass flow of ^{99}Tc in the Bayou and Little Bayou Creeks, a conversion is required to calculate a mass from the annual surface water monitoring data which are documented in units of picocuries per liter (pCi/L). The curie (Ci) is a common unit used in measuring the amount of radioactivity of a material and describes the rate at which a radioactive substance is decaying through alpha, beta, and/or gamma radiation. Using the properties of a known radionuclide, a correlation between radioactivity and the mass of the substance can be determined. This relationship provides a method to calculate the desired units of mass from the recorded ^{99}Tc data.

First, a decay constant (λ) is found by using the equation

$$\lambda = \frac{\ln 2}{T_{\frac{1}{2}}} \qquad (7)$$

where $T_{1/2}$ equals the half-life of the substance in seconds, which is 6.72 X 10^{12} seconds for ^{99}Tc, and the resulting units are disintegrations per second (dps) or Becquerel (Bq). The amount of radioactivity present can then be calculated by multiplying this decay constant by the number of atoms present. The number of atoms per gram can be determined using Avogadro's number, 6.02 X 10^{23}, and the atomic mass (M) of the element. The specific activity, denoted (SA), provides the radioactivity per gram and is calculated using

$$SA = \frac{(6.02x10^{23})\lambda}{M} \qquad (8)$$

where M = atomic mass. Solving equation (8) using the properties of ^{99}Tc yields an SA of 6.24 X 10^{8} dps/g or Bq/g. Dividing by 3.7 X 10^{10} dps/Ci gives 0.017 Ci/g or 1.7 X 10^{5} Ci/mg, which is equal to 1.7 X 10^{7} pCi/mg. Using this number, which shows the amount of activity per *mg* of ^{99}Tc, the surface water monitoring data that were recorded in units of pCi/L can easily be converted to suitable units of mg/L from which a mass flow can be calculated.

Table 10 shows the ^{99}Tc concentration measured at the L-Sites for the years 1993 – 2003. Table 11 shows the average ^{99}Tc concentration measured in the Bayou Creeek outfalls for the years 1993 – 2003.

Table 10 - ^{99}Tc concentration summary for Bayou Creek L-sites, mg/L 1993 – 2003.

L-Site	Max(mg/l)	Min(mg/l)	Avg(mg/l)
1	4.9E-07	0	2.1E-07
291	3.1E-07	0	2.0E-07
5	1.1E-06	1.8E-07	5.4E-07
6	8.3E-07	4.6E-07	6.1E-07

Table 11 - ^{99}Tc Concentration summary for Bayou Creek outfalls, mg/L, 1993 – 2003.

Outfall	Max(mg/l)	Min(mg/l)	Avg(mg/l)
1	2.8E-06	2.8E-07	1.0E-06
4	7.9E-07	0	2.4E-07
6	9.5E-07	0	3.0E-07
8	1.3E-06	3.6E-07	7.1E-07
9	1.0E-06	0	4.8E-07
15	3.2E-06	9.6E-07	2.0E-06
16	4.7E-07	3.0E-07	4.0E-07
17	7.0E-07	5.6E-08	3.8E-07

Table 12 shows the ^{99}Tc concentration measured at the L-Sites in Little Bayou Creek for the years 1993 – 2003. Table 13 shows the ^{99}Tc concentration measured the Little Bayou Creek outfalls for the years 1993 – 2003.

Table 12 - ^{99}Tc concentration summary for Little Bayou Creek L-sites, mg/L 1993 – 2003.

L-Site	Max(mg/l)	Min(mg/l)	Avg(mg/l)
56	6.9E-07	0	4.3E-07
55	7.6E-07	1.3E-07	2.7E-07
194	1.2E-06	1.5E-07	6.4E-07
10	5.6E-07	0	3.2E-07
11	5.9E-07	0	3.1E-07
241	3.0E-07	1.5E-06	2.1E-07
12	2.1E-07	1.0E-06	1.5E-06
8	2.7E-07	2.4E-07	8.9E-07

Table 13 - ^{99}Tc concentration summary for Little Bayou Creek outfalls, mg/L 1993 – 2003.

Outfall	Max(mg/l)	Min(mg/l)	Avg(mg/l)
2	2.8E-06	2.5E-07	6.8E-07
10	2.2E-06	1.9E-07	7.6E-07
11	7.3E-07	0	1.7E-07
12	1.3E-06	2.2E-07	5.9E-07
13	9.5E-07	2.9E-07	5.8E-07
18	2.3E-06	6.5E-07	1.4E-07
19	7.5E-07	0	3.1E-07

Target Levels
Bayou and Little Bayou Creeks are not classified as drinking water sources, so the EPA safe drinking water standards do not apply. The Kentucky surface water standards for warm water aquatic habit (KAR Title 401, Chapter 5:031) are applicable, and the measured water quality data were compared with the chronic exposure standards in this evaluation. Estimated and actual limits are shown in Table 14. The estimated limits vary with the degree of hardness, whereas the actual limits are fixed.

Table 14 - Chronic surface water standards, mg/l

Cu	0.009 mg/L	Estimated
Fe	1.0 mg/L	Actual
Hg	9.1E-04 mg/L	Actual
Pb	0.003 mg/L	Estimated

Notes: Copper and lead are based on an average total hardness of 100 mg/L as $CaCO_3$

Radioactive effluents are controlled under DOE Order 5400.5, Radiation Protection of the Public and the Environment. This order limits the dose to 100 mrem/year from all pathways resulting from the operation of a DOE facility. To aid in meeting this order, the EPA drinking water standard, 900 pCi/L has been established as the PGDP release criteria. For ^{99}Tc, this corresponds to a concentration of 5×10^{-5} mg/L.

Specific Constituents
In the following sections, several figures present ranges of chemical concentrations graphically. The green dots indicate locations where the average annual concentrations were less than one half of the estimated water quality criteria. The yellow dots indicate concentrations that are between one half and one and one half times the estimated water quality criteria. The red dots represent concentrations that are more than one and one half times higher than the estimated water quality criteria. The water quality criteria apply only to the streams, but the outfalls are delineated similarly to indicate potential focus areas.

Hardness
Hardness is used to calculate the water quality criteria for copper and lead. Although hardness data were obtained for the outfalls, only the stream, or L site, data apply to the water quality criteria.. The calculated water quality criteria are directly proportional to hardness, i.e. low hardness values lead to lower criteria.

In Bayou Creek, the average annual hardness was 100 mg/L as $CaCO_3$ and ranged from 44 to 194 mg/L as $CaCO_3$. In Little Bayou Creek, the mean annual hardness was 85 mg/L as $CaCO_3$ and ranged from 66 to 122 mg/L as $CaCO_3$. Using an approximate hardness of 100 mg/L as $CaCO_3$ yields a copper limit of 0.009 mg/L. Using a minimum hardness of 44 mg/L as $CaCO_3$ yields a copper limit of 0.005 mg/L. Similarly, the lead limit based on the approximate average hardness would be 0.003 mg/L. At the minimum hardness, the lead limit would be 0.001 mg/L.

Although discrete samples showed a wider range of hardness than the annual averages, hardness values of less than 40 mg/l are uncommon. The extremely low levels reported are anomalies. Therefore, use of 100 mg/L as $CaCO_3$ as a typical value seems appropriate. The minimum average annual value of 44 mg/L as $CaCO_3$ could be considered in the margin of safety required for TMDL development.

Copper

Figure 4 shows the distribution of copper in Bayou and Little Bayou creeks based on overall annual averages from 1993 to 2003. The average annual copper concentration in Bayou Creek was 0.026 mg/L, and the average annual copper concentration in Little Bayou Creek was 0.009 mg/L. The average concentration in Bayou Creek exceeds the estimated water quality criterion at a hardness of 100 mg/L as $CaCO_3$, whereas the average concentration in Little Bayou Creek is equal to the criterion at a hardness of 100 mg/L as $CaCO_3$.

Note that the average copper concentration in Bayou Creek exceeds the estimated water quality criterion upstream of the plant site as well as downstream of the plant site. The former KOW site is upstream of PGDP, but anecdotal information indicates that activities at KOW were limited to production of explosives, not projectiles. Potential sources of copper upstream of PGDP have not been identified. In Little Bayou Creek, the average copper concentration is higher than the estimated water quality criterion at L194, which is downstream of several outfalls. Further downstream, the average copper concentrations are less that the estimated criterion. The existing data indicate that a TMDL is warranted for copper in Bayou Creek, but possibly not for Little Bayou Creek. The data for Little Bayou Creek are inconclusive, and additional stream chemical and flow monitoring are recommended.

Figure 5 shows the copper distribution in the outfalls for the same period.
Only K002 and K019, which discharge to Little Bayou Creek, have average copper concentrations clearly exceeding the estimated criterion. Although Bayou Creek appears to have copper concentrations that are more likely to exceed the estimated water quality criterion than Little Bayou Creek, PGDP outfalls seem to have more of an impact on Little Bayou Creek.

Iron

Figure 6 shows the distribution of iron in Bayou and Little Bayou creeks based on overall annual averages from 1993 to 2003. The annual average iron concentration in Bayou Creek is 0.73 mg/L, which is less than the water quality standard. The annual average iron concentration in Little Bayou Creek is 0.90 mg/l, which is also less than the standard. The maximum annual average iron concentrations in Bayou Creek and Little Bayou Creek were 4.3 mg/L and 1.9 mg/L respectively. Discrete data points have showed much higher concentrations, but those extremely high concentrations appear to be anomalies. L sites along the north/south diversion ditch show average iron concentrations higher than the water quality standard, but Little Bayou Creek does not appear to be impacted.

Average iron concentrations in the outfalls are shown in Figure 7. Although some of the outfalls have average concentrations exceeding the water quality limits, the overall impact in the creeks is low.

Mercury
Figure 8 shows the distribution of mercury in Bayou Creek based on overall annual averages from 1993 to 2003. Examination of mercury in Little Bayou Creek was not part of this project. Mercury was measured infrequently, but the available data indicate that the average stream concentrations may be below the water quality standard upstream and downstream of the plant site.

Information from the National Atmospheric Deposition Program, Mercury Deposition Network, (NADP, 2005) indicate that wet deposition mercury concentrations in this area would average 12 to 14 micrograms per square meter. Atmospheric deposition would be a likely source of mercury in Bayou Creek. Additional monitoring is needed to verify mercury levels in Bayou Creek.

Figure 9 shows the average mercury distribution in the outfalls for the same period. No outfall contains an average concentration exceeding the water quality standard, but mercury was measured infrequently.

Lead
Figure 10 shows the distribution of lead in Bayou and Little Bayou creeks based on overall annual averages from 1993 to 2003. The annual average lead concentration in Bayou Creek was 0.09 mg/L, which exceeds the water quality standard. In Little Bayou Creek, the annual average lead concentration was 0.04 mg/L, which also exceeds the standard.

In Bayou Creek, the average lead concentration is above the water quality standard upstream of the plant and downstream of the plant. In Little Bayou Creek, the average lead concentration exceed the water quality standard at L194, which is downstream of several outfalls. Although the average stream lead concentration data are somewhat inconclusive regarding the plant site contribution, data from the outfalls (Figure 11) clearly indicate that the average lead concentrations in all outfalls exceed the water quality standard. A TMDL for lead is warranted.

Technetium
Figure 12 shows the distribution of technetium in Bayou and Little Bayou creeks based on overall annual averages from 1993 to 2003. The mean annual levels of technetium in Bayou Creek and Little Bayou Creek were 6.6pCi/L and 14.2 pCi/L, respectively. All average technetium concentrations are well below the designated water quality objective. The highest annual average technetium level observed at any location was 50 pCi/L (0.000003 mg/L). TMDL development for technetium is not warranted.

Similarly, the outfalls show no average annual concentrations of technetium exceeding the designated water quality criterion (Figure 13).

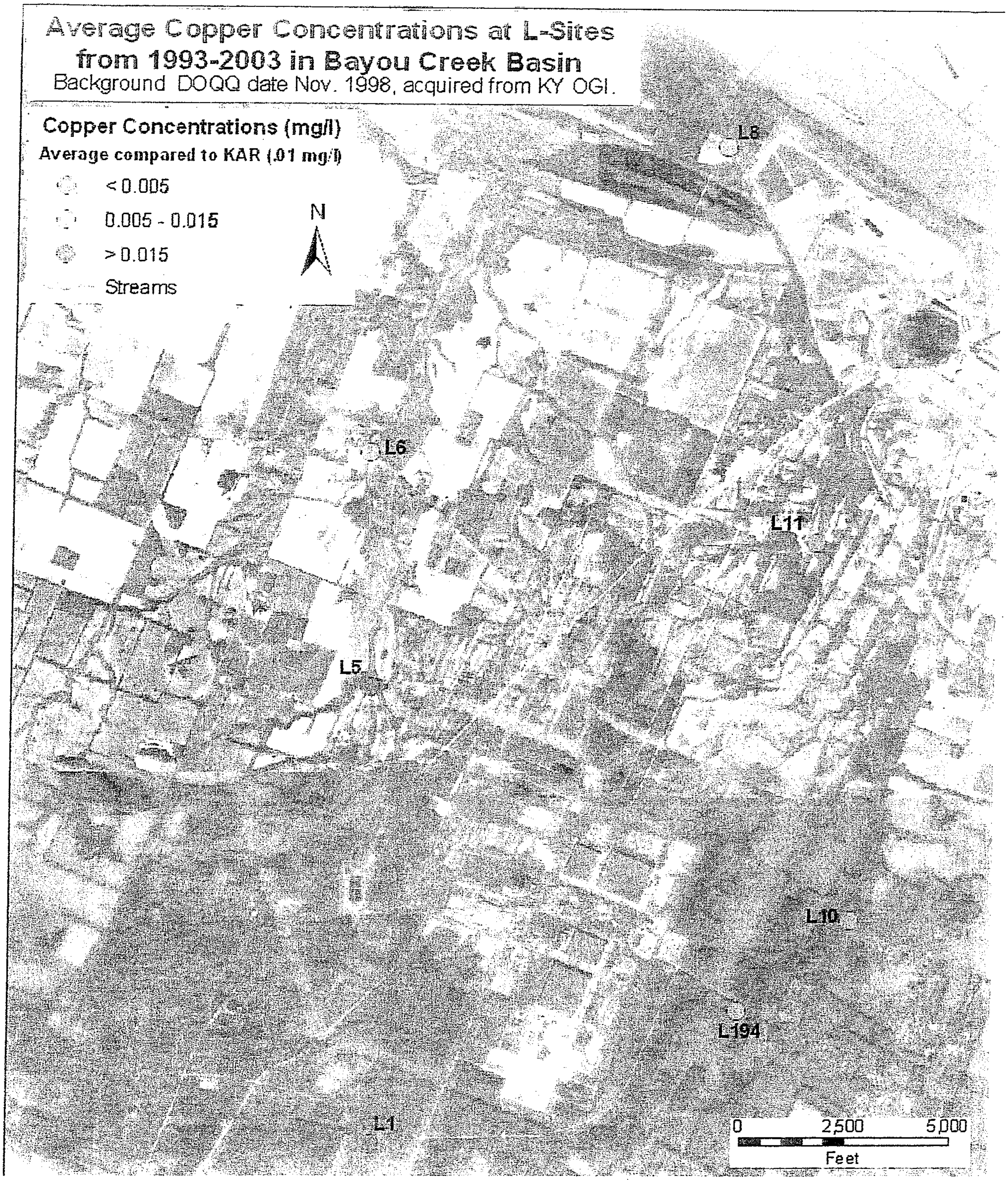

Figure 4 - Average copper concentration at L-sites, mg/l, 1993-2003.

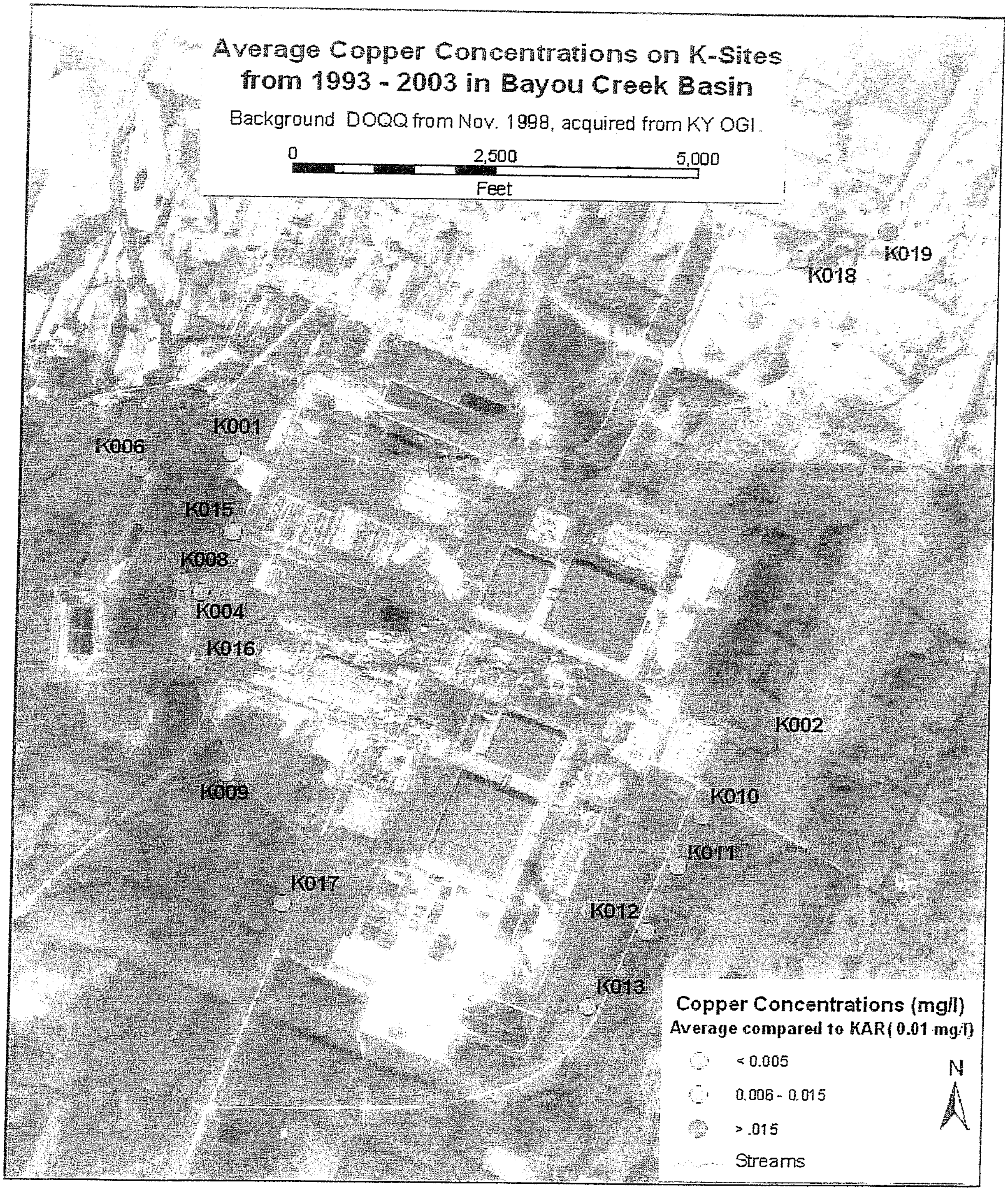

Figure 5 - Average copper concentrations at K-sites, mg/l, 1993-2003.

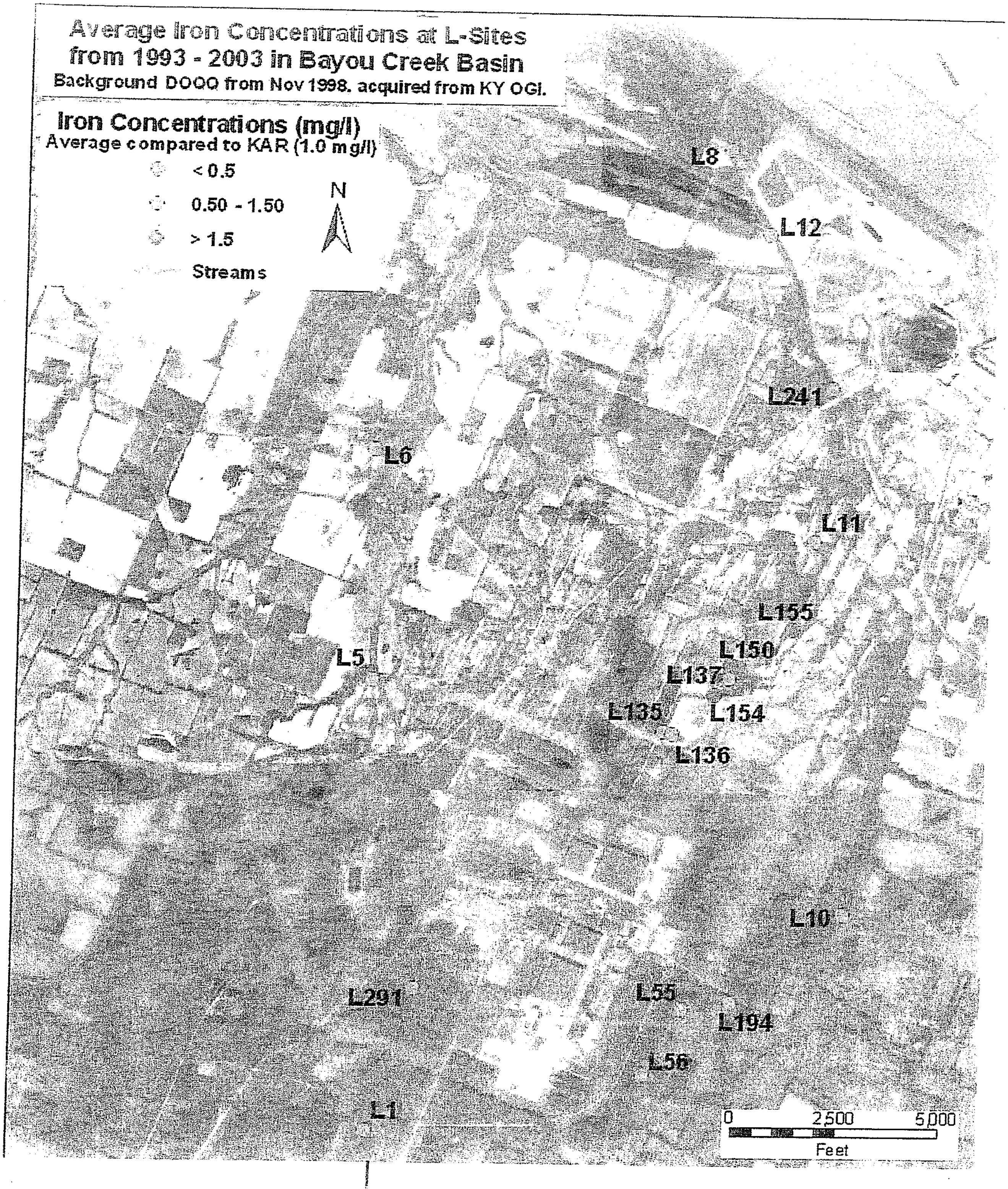

Figure 6 - Average iron concentrations at L-sites, mg/l, 1993-2003.

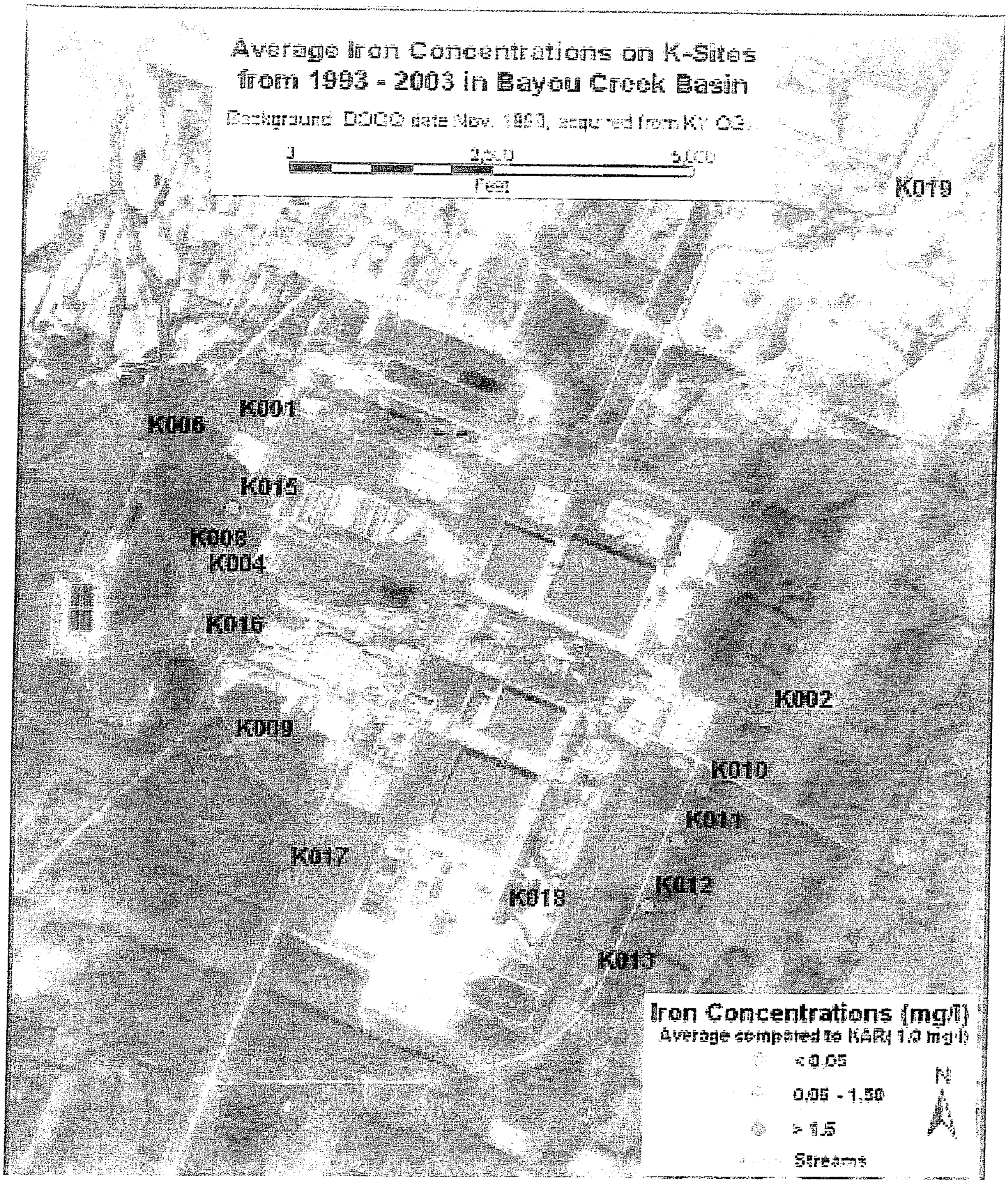

Figure 7 - Average iron concentrations at K-sites, mg/l, 1993-2003.

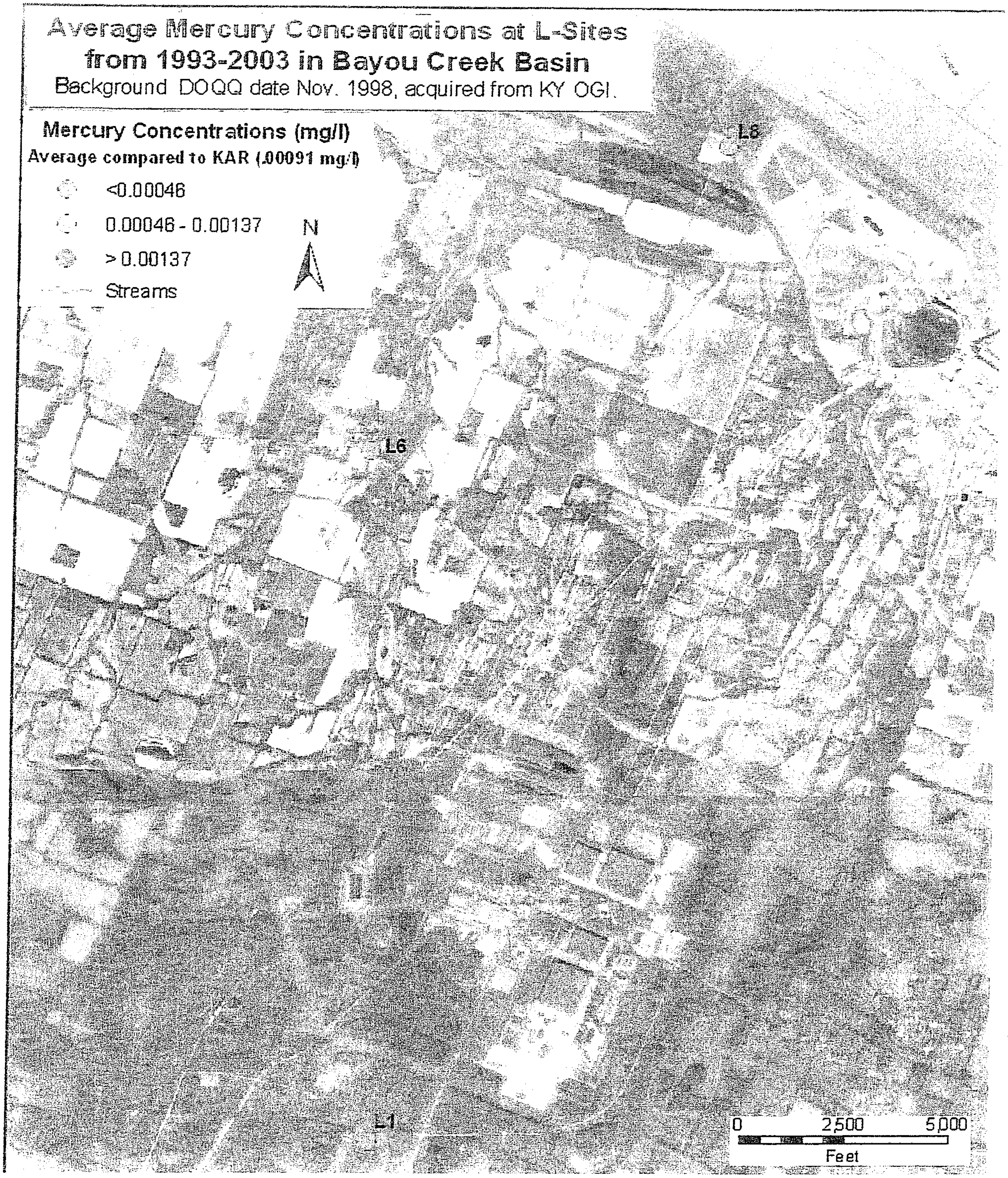

Figure 8 - Average mercury concentrations at L-sites, mg/l, 1993-2003.

Figure 9 - Average mercury concentrations at K-sites, mg/l, 1993-2003.

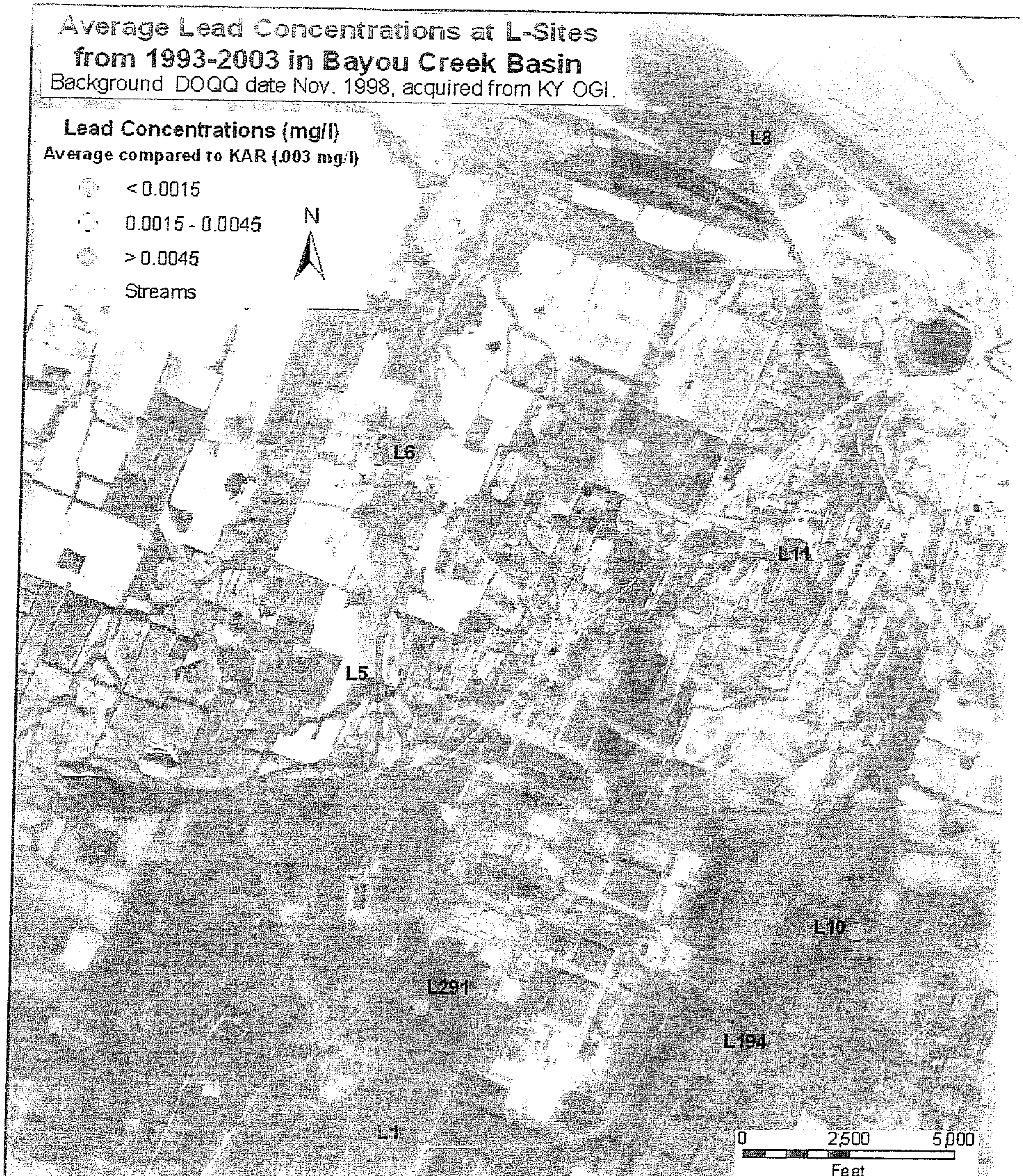

Figure 10 - Average lead concentrations at L-sites, mg/l, 1993-2003.

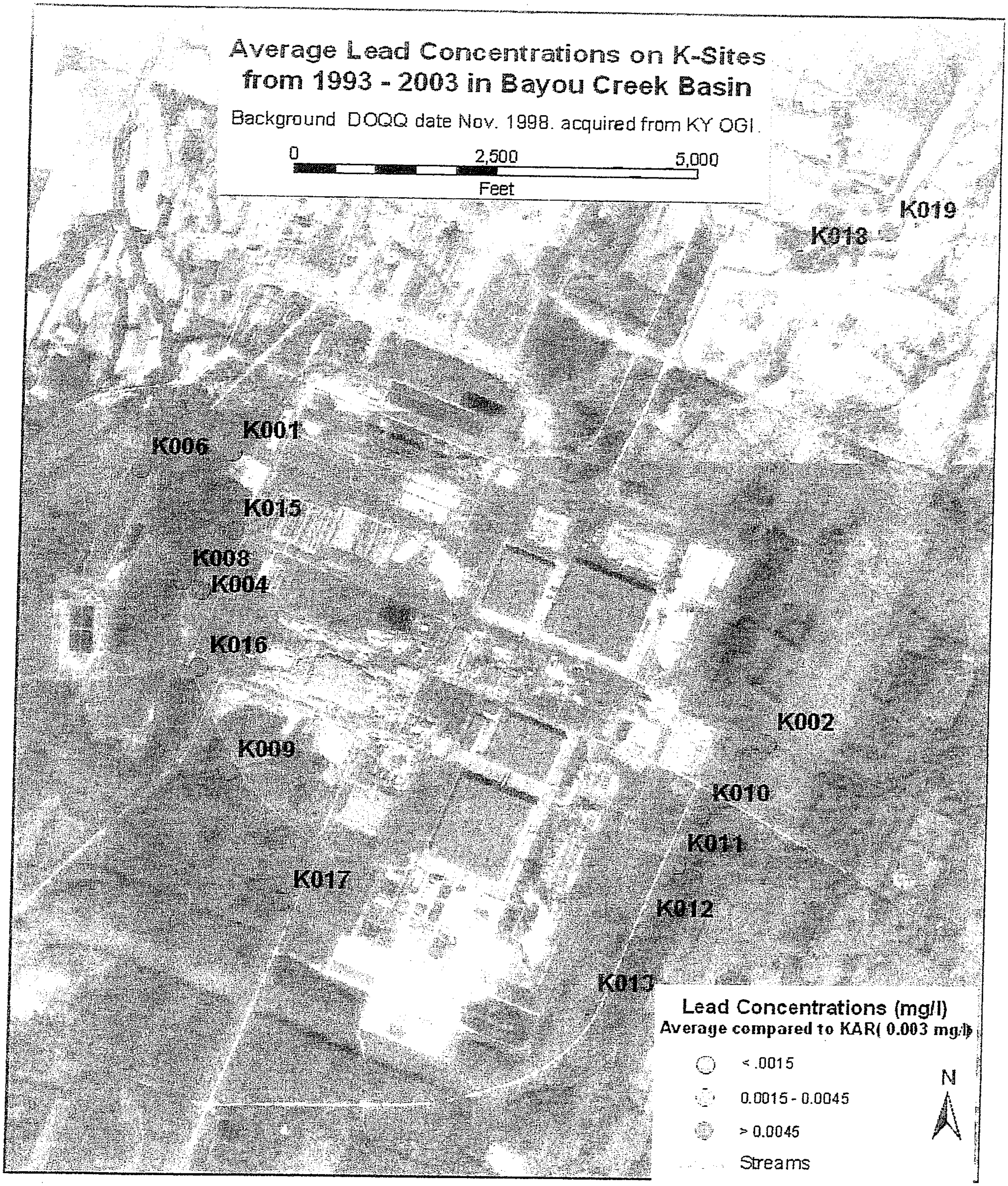

Figure 11 - Average lead concentrations at K-sites, mg/l, 1993-2003.

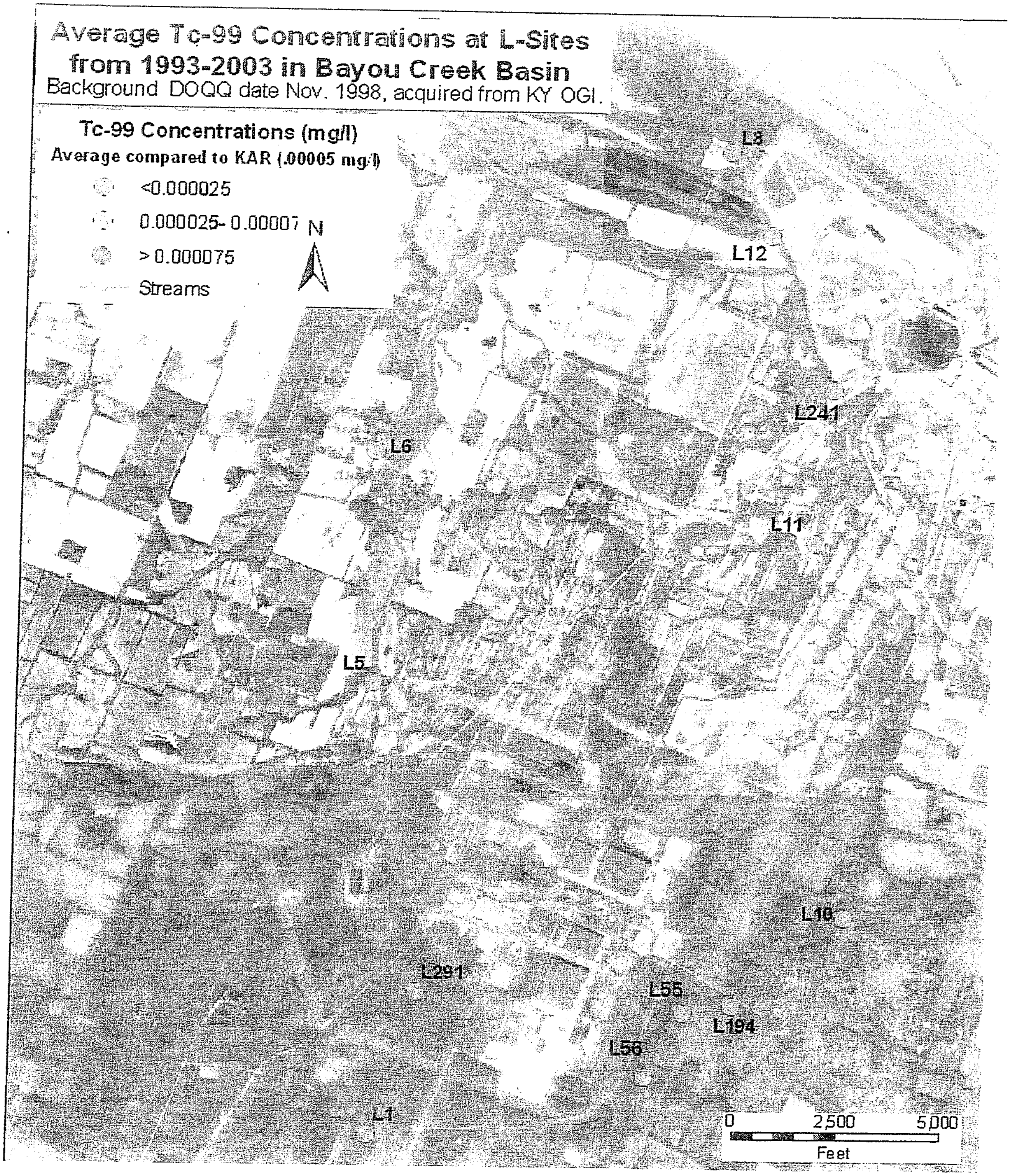

Figure 12 - Average ^{99}Tc concentrations at L-sites, mg/l, 1993-2003.

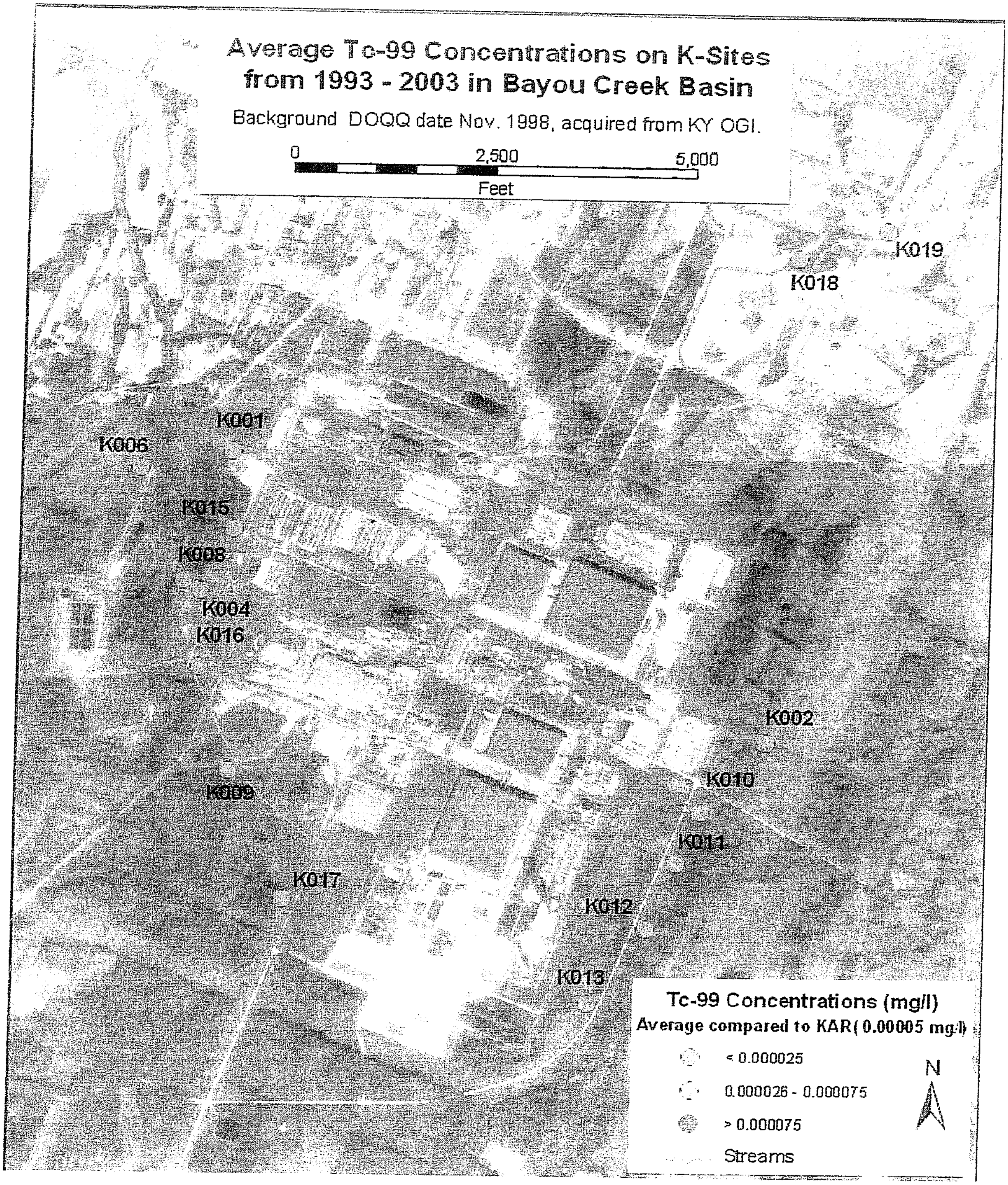

Figure 13 - Average ^{99}Tc concentrations at K-sites, mg/l, 1993-2003.

Historical Mass Loadings

Mass loadings based on average annual flows and average annual chemical concentrations for Bayou Creek are shown in Table 15. Stream sites L1 and L6 are upstream and downstream of the plant outfalls discharging to Bayou Creek. The column marked "Change" is the calculated difference between the masses at each location. The column marked "Outfall Input" is the mass obtained using the sum of the average flows and concentrations for each individual outfall.

Table 15 - Mass in lbs/day based on average flow and average concentration, Bayou Creek 1996-2003.

Bayou Creek Mass Balance				
Metal	Upstrm (L1)	Down (L6)	Change	Outfall/Input
Copper	2.15	3.69	1.54	1.78
Iron	134	132	None	38-774
Lead	12.9	20.5	7.6	10.2
Mercury	0.06	0.06	None	0.009

Mass loadings based on average annual flows and average annual chemical concentrations for Little Bayou Creek are shown in Table 16. Site L241 is downstream of the plant outfalls discharging to Little Bayou Creek. Several outfalls are upstream of site L194, but data were not as comprehensive at other upstream sampling sites. Hence, the change in mass between L194 and L241 represents only a portion of the outfalls.

Table 16 - Mass in lbs/day on average flow and average concentration, Little Bayou Creek, 1996-2003.

Little Bayou Creek Mass Balance				
Metal	Upstrm (L194)	Down (L241)	Change	Outfall/Input
Copper	0.45	0.57	0.12	0.6
Iron	9.45	44.1	34.6	43.8
Lead	2.28	2.20	None	1.8

Mass calculations indicate that about 40 percent of the copper in Bayou Creek can be attributed to the plant outfalls. Although the change in mass in Little Bayou Creek was small, given the location of L194 relative to the outfalls and the calculated outfall mass input, the outfalls are the apparent source of most of the copper in Little Bayou Creek. Figure 14 shows the relative mass of copper contributed by each outfall based on average concentrations and average flows. The color of the dots simply indicates relative mass contributions from each outfall and has no relationship to water quality criteria. For Bayou Creek, K017 and K001 contribute higher proportions of the copper than the other outfalls. In Little Bayou Creek, each outfall contributes approximately the same mass of copper.

The negligible change in iron mass for Bayou Creek indicates that much of the iron is from a source upstream of the plant site. Examination of the outfall contribution data does indicate some mass input, but the input might only be about 25 percent of the total mass of iron in the stream. The high mass input of 774 lbs per day shown in Table 15 was due to a single, abnormally high concentration. The lower value of 38 lbs per day is more representative of typical concentrations. In Little Bayou Creek, the outfalls contribute most of the iron.

Figure 15 shows the relative mass of iron contributed by each outfall. K017, K015, and K001 are the main contributors to Bayou Creek. K013 is the largest contributor to Little Bayou Creek.

The mass of mercury contributed by the outfalls to Bayou Creek is only 15 percent of the mass already in the stream. Although mercury may not be a surface water issue in Bayou Creek, the relative mass contributions of each outfall were still examined (Figure 16). K017, K008, and K001 are the largest mercury contributors to Bayou Creek.

About 40 percent of the lead in Bayou Creek is input via the plant outfalls. The mass of lead in Little Bayou Creek actually showed a slight decrease downstream, but examination of the outfall inputs indicates that most of the lead in Little Bayou Creek is due to the outfalls.

Relative lead inputs from the outfalls are shown in Figure 17. All outfalls have average lead concentrations exceeding the water quality standards, but in Bayou Creek, outfalls K017 and K001 contribute larger masses of lead than the other outfalls. In Little Bayou Creek the mass contribution of lead is evenly distributed among all the outfalls.

Although TMDL development is not warranted for technetium, the average mass contribution of each outfall was still examined (Figure 18). K015 and K001 contribute larger portions of the technetium mass to Bayou Creek. Otherwise, the technetium mass contributions are evenly distributed among the outfalls.

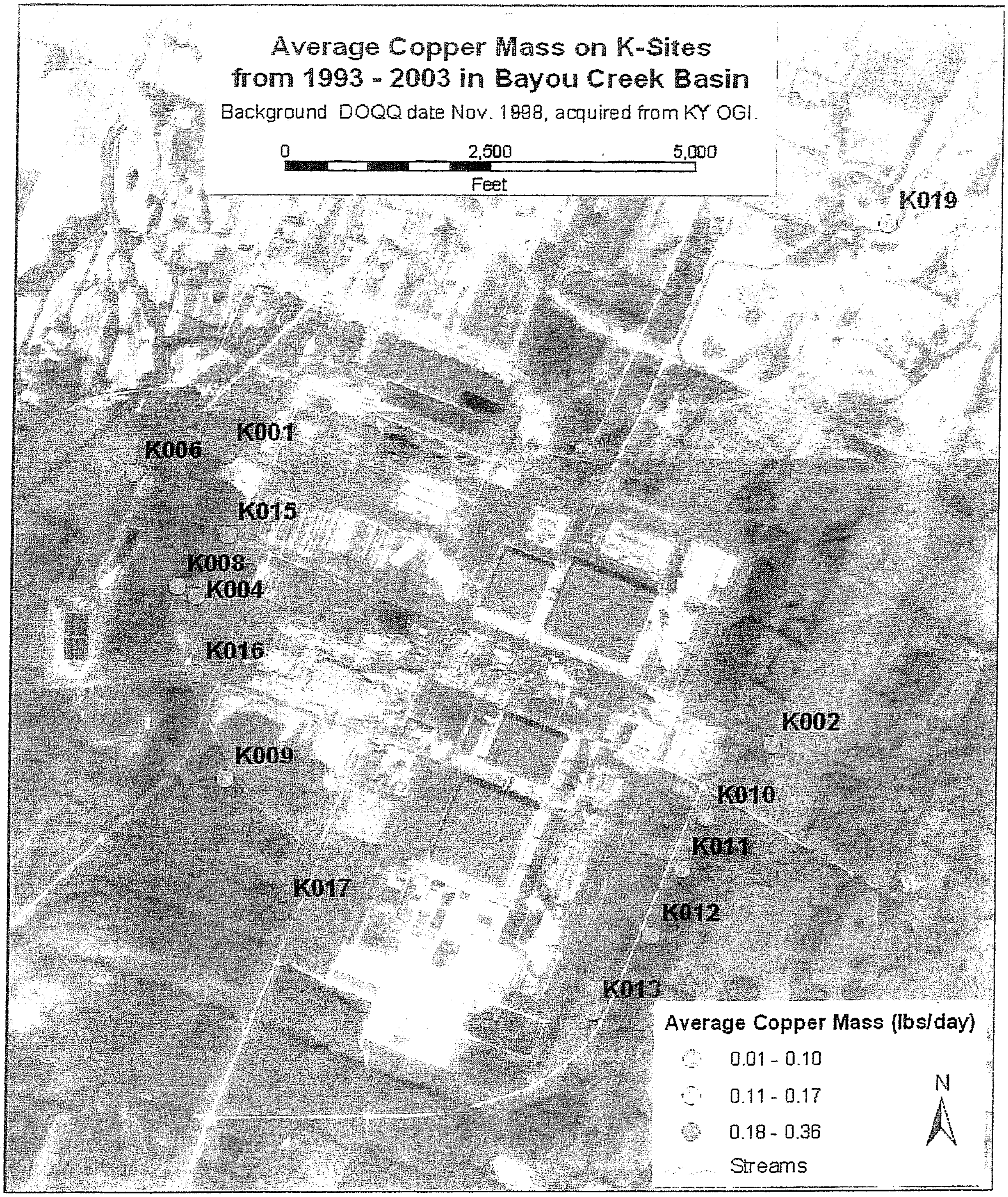

Figure 14 - Average copper mass at K-sites, lbs/day, 1993-2003.

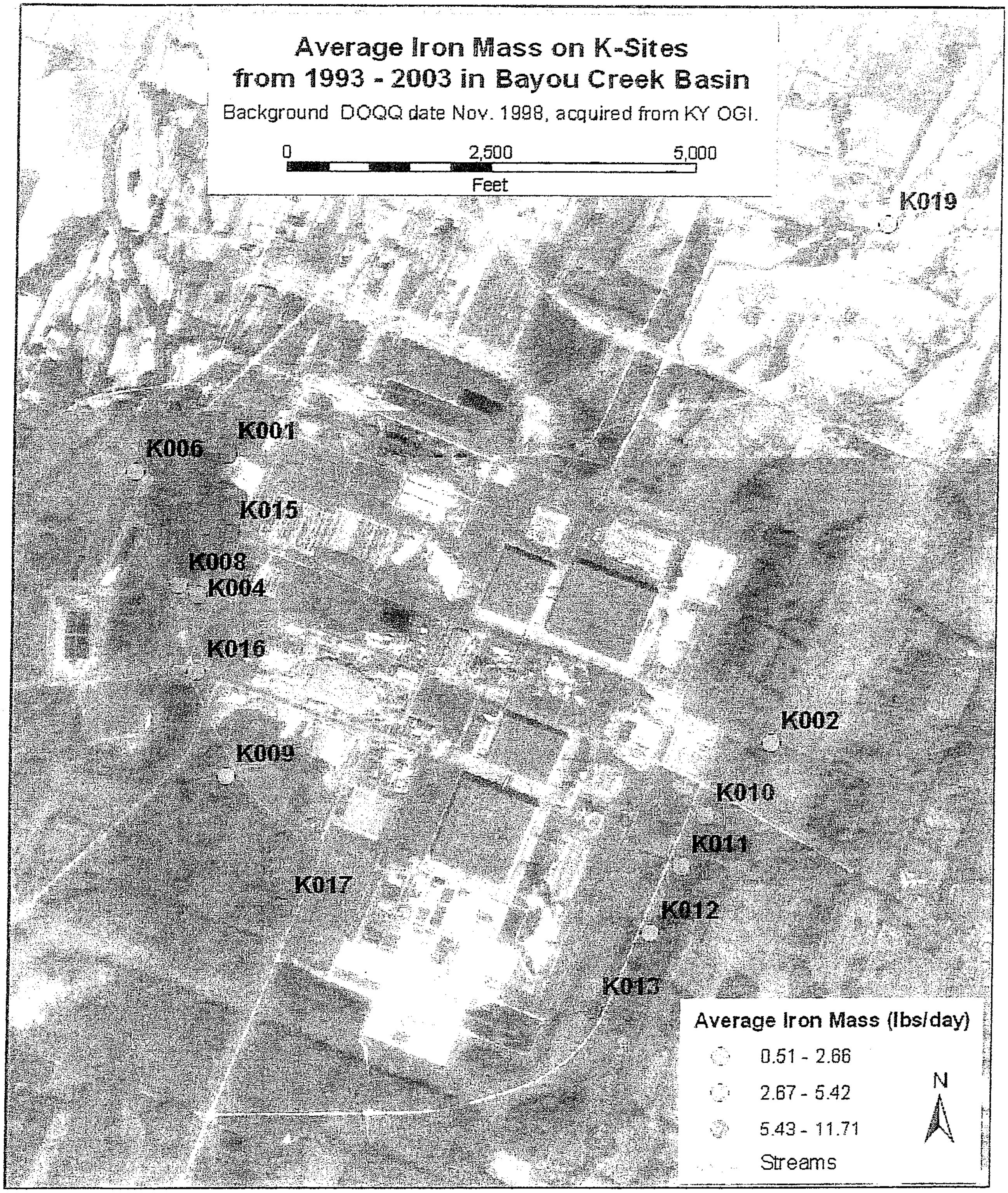

Figure 15 - Average iron mass at K-sites, lbs/day, 1993-2003.

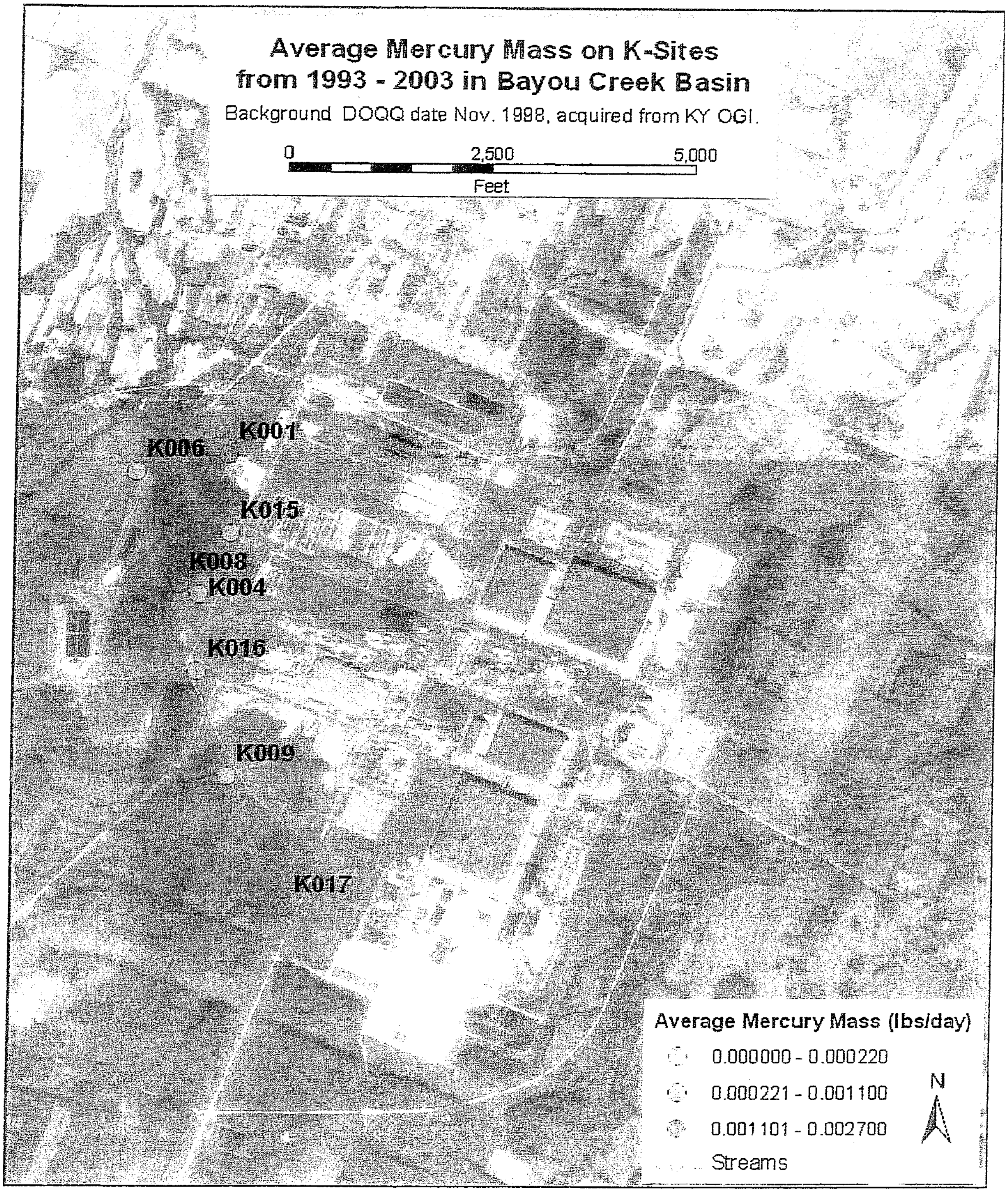

Figure 16 - Average mercury mass at K-sites, lbs/day, 1993-2003.

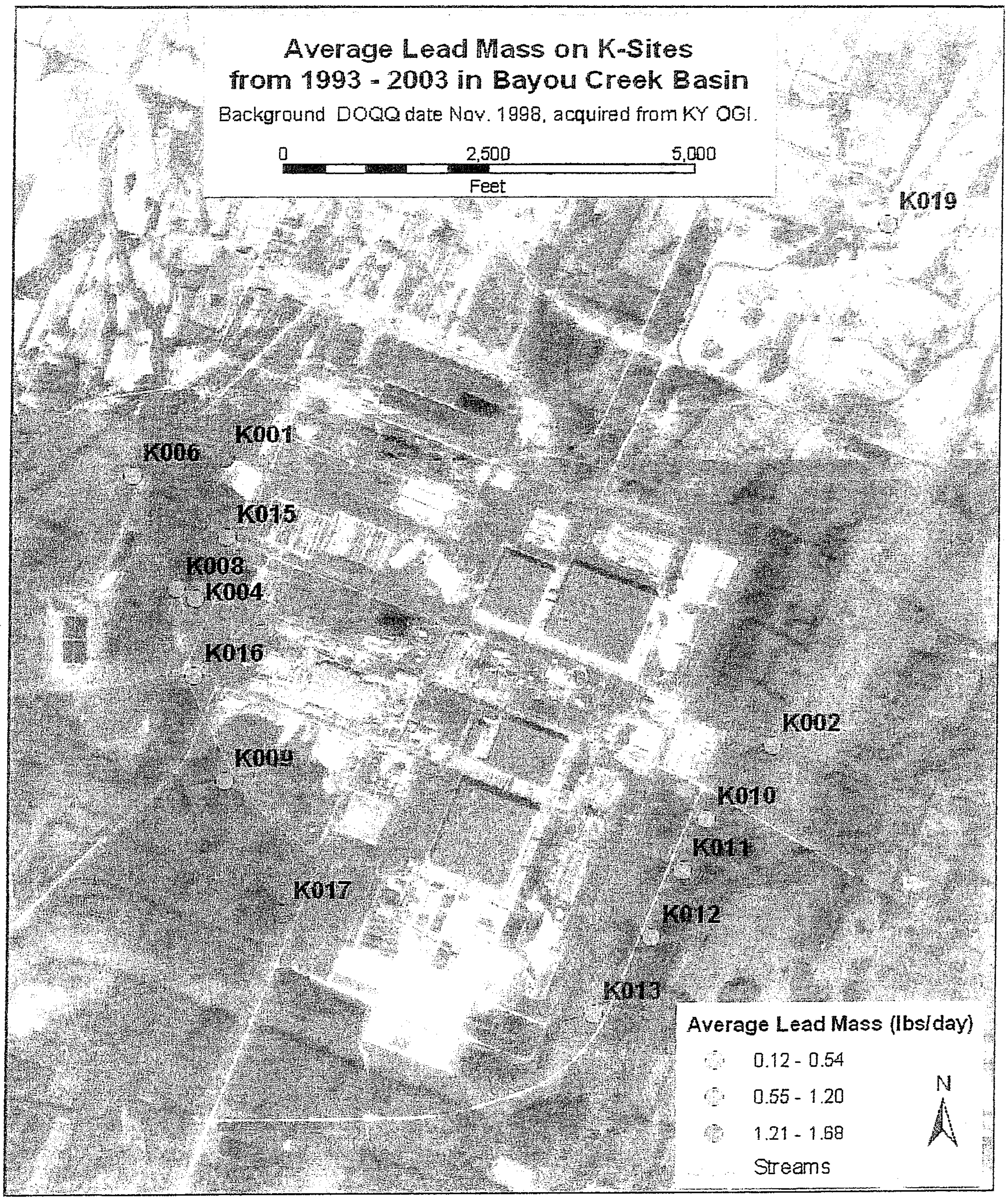

Figure 17 - Average lead mass at K-sites, lbs/day, 1993-2003.

Conclusions and Recommendations

Based on the historical data, TMDLs are warranted for lead in Bayou Creek and Little Bayou Creek. A TMDL for copper is warranted for Bayou Creek, but the data are inconclusive for Little Bayou Creek. Additional monitoring is advisable to confirm the copper level in Little Bayou Creek. Although some discrete data have shown iron concentrations above the water quality limits, annual and overall average iron concentrations in both creeks are below the limit of 1.0 mg/L. A TMDL for iron does not appear to be necessary, but additional monitoring is advisable to confirm the level of iron in both creeks.

Mercury data are sparse, but the measured concentrations are well below the water quality limits. Data from national atmospheric monitoring indicates that atmospheric deposition could easily be the primary source of mercury in Bayou Creek and Little Bayou Creek. The background level of mercury in both creeks appears to be substantially higher than the level of mercury contributed by the PGDP outfalls. Additional monitoring is needed to confirm mercury levels and to determine whether or not TMDL is required.

Surface water levels of ^{99}Tc are well below the DOE-specified limit of 900 pCi/L. The highest observed level from 1993 to 2003 was 50 pCi/L. ^{99}Tc monitoring was more frequent in the streams and the outfalls than the other parameters. A TMDL for ^{99}Tc does not appear to be necessary, and additional monitoring should not be required.

Stream sampling data for all the parameters are sparse, especially for mercury. Outfall data are more comprehensive than the stream data, but comparison of stream and outfall chemical and flow data is difficult due to the differences in sampling frequency. Prior to final TMDL development, a coordinated sampling and flow measurement program for the streams and outfalls is advisable. Stream sampling should include additional sites upstream of PGDP. A major goal of this program would be to increase the sampling frequency for a period of time, but more importantly, obtain simultaneous chemical and flow data from the streams and outfalls. Indications are that TMDLs for iron and mercury are not needed, but confirmatory sampling is advisable.

Additional monitoring of flow, copper and hardness in Little Bayou Creek is especially needed because of the inconclusiveness of the historical data. At a minimum, data should be collected upstream and downstream of the plant outfalls. An additional upstream monitoring station might be of use in examining other upstream sources of copper.

References

Bectel Jacobs (1987-2003) ORESIS database. http://www-oreis.bechteljacobs.org/oreis/help/oreishome.html

Bectel Jacobs. (2005) www.bechteljacobs.com/pad-reports.shtml.

NADP (2005). National Atmospheric Deposition Program, Mercury Deposition Network Data Base, http://nadp.sws.uiuc.edu