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Ground-Water Contamination by Volatile Organic Compounds: Sources of Error, Temporal and Spatial Variability

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GROUND-WATER CONTAMINATION BY VOLATILE ORGANIC COMPOUNDS: SOURCES OF ERROR, TEMPORAL AND SPATIAL VARIABILITY

by

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GROUND-WATER CONTAMINATION BY VOLATILE ORGANIC COMPOUNDS: SOURCES OF ERROR, TEMPORAL AND SPATIAL VARIABILITY

Gary Thomas Blinkiewicz, M.S.

Western Michigan University, 1993

Data on the distributions of VOC's (volatile organic compounds), principally trichloroethane and dichloroethylenes, in a shallow sand and gravel aquifer near Rockford, IL have been collected for a number of years. Synoptic sampling events from a dense monitoring well network within a greater than 4 mi^2 area, provide the basis for the evaluation of sources of variability in concentrations in space and time. Sampling, and analysis-related variability in these data contribute less than 10% of total variance. Spatial and temporal variability over periods of months to years are significant. Results suggest that contaminant distributions can be resolved best by using more spatially distributed sampling points and fewer (i.e., quarterly rather than more frequent) sampling events per year.

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CHAPTER I

INTRODUCTION

An enormous effort has been expended to collect "representative samples" of ground water to develop accurate monitoring data. The usefulness of these data depends on their actual quality, the integration of chemical and hydrogeologic information, and on the way they are interpreted. Whether or not monitoring data can be applied to some useful outcome, such as a ground-water cleanup effort, will often hinge on an assessment of natural variability in contaminant distributions. Statistics provide an interpretive tool to assess variability and identify sources of error. Using statistics, observations can be made between different groups of data in order to base decisions on the sampling point intensity with which an area should be sampled. In this way the overall extent of movement and contaminant plume size can be determined prior to selection of remedial action.

Berryman, Bobee, Cluis, and Haemmerli (1988) stated that tremendous amounts of public funds have supported water monitoring programs over the past few decades due to concern over the quality of natural water. One of the most important objectives of water quality programs is temporal trend analysis. Trend analysis aids in decision making associated with evaluating the success of treatment regulations and action can be taken if water quality deteriorates and human use is adversely affected. In order to detect or assess trends it is necessary that data should be collected at given locations, on a regular schedule, and an appropriate time period or period of years must be chosen for sample collection (Hirsch, Slack, & Smith, 1982).

Spatial trend analysis is also needed for proper evaluation of a water quality program. In water quality monitoring, the concentrations of the contaminant over a sampling site are often correlated spatially (Flatman, 1986). Intuitively, samples that are spatially related usually yield similar concentration values (i.e., redundant information) while samples that are farther away from each other may be expected to show differences in concentration (Flatman, 1986). If spatial analysis is used, representative estimates of a region can be computed and the estimation of the effective number of monitoring points can be obtained.

Statement of Purpose

The purpose of this study is threefold. First, to incorporate ground-water sampling procedures which provide ground-water samples representative of actual hydrogeochemical conditions (Barcelona, Wehrmann, & Varljen, 1993). This can be achieved by using dedicated bladder pumps coupled to consistent field procedures which include using laboratory analytical standards and field spikes to reduce the amount of determinant (systematic error) so the sample result is an accurate estimate of the "true" value at a location. In environmental science we acknowledge there is no "true" value, rather a continuum of values exists of which the mean or some other statistic is representative. Second, improved site characterization methods for volatile organic compounds (VOC's) include both spatial and temporal analysis (Wehrmann, 1991). The temporal characterization method of analysis used in this project is the Wilcoxon matched-pairs signed-ranks test. It can be used to determine whether a statistical difference exists between sampling points in an area over the short term (i.e., weekly) and to sampling an area over the long term (i.e., quarterly to annually). Third, spatial tests include the application of variograms and kriging, both of which provide

estimates of concentration in an area in the form of contour maps. These concentration contour maps can then be used to influence the desirability of adding or deleting sample points on the limits of a contaminant distribution.

Review of Related Literature

Barcelona, Lettenmaier, and Schock (1989) studied water-quality variability in an area in Illinois which was monitored biweekly for major ions in a shallow sand and gravel aquifer. Ground-water data were collected at a relatively high sampling frequency. Ground-water quality time series effects were calculated using sampling-related sources of variance, and laboratory analytical and field spiked standards. The general statistical approach to reducing the sources of variation was to collect replicates, randomize the sampling, and apportion fractions of the total variance in a population to laboratory, sampling, and natural sources. The goal was to identify major sources of error and reduce the effects of error sources which are controllable (e.g., sampling and analytical). The sources of variation equation was introduced, which establishes where error is attributable in the overall movement process. Natural error, laboratory analytical error, and field sampling error were all accounted for through the percentage of their occurrence. In their study, Barcelona et al. (1989) were able to demonstrate control over sampling and analytical errors for inorganic water quality parameters and anlyze the time series data for optimal sampling frequency.

Many papers have been written which deal with statistical methods for characterizing ground-water quality. Harris, Loftis, and Montgomery (1987) and Loftis, Montgomery, Harris, and Sanders (1986) discussed the following characteristics of background data: normality, seasonality, and serial dependence. Skewness, or large departures from normality, can be either in the positive or negative

direction, which correspond to right or left censoring of the data, respectively. One solution to evaluating these departures from normality is to apply the Shapiro and Wilk test (Harris et al., 1987). Most statistical tests incorporate parameters which are time independent. An inherent assumptions in such testing is the stationarity of the time series. When transient seasonality or hydrogeologic affects are involved, this stationarity assumption may be violated and statistical tests rendered invalid. Comparisons between the time series can be made after first recognizing and removing seasonality. Subsequent statistical tests for temporal comparisons include the student's t-test if the data are normally distributed and the Mann-Whitney U test for non-normally distributed data.

Serial correlation can result in reduced effective sample sizes and redundant information collection. Independent (i.e., non-autocorrelated) of data is needed for many statistical procedures and correction can only be achieved through increasing the time period between set numbers of observations or by averaging the data. Many of the following characteristics were tested in Montgomery, Loftis, and Harris (1987) using state regulatory agencies' ground-water quality data records. Lettenmaier (1976) and van Belle and Hughes (1984) discussed nonparametric tests which could be used for analysis when water-quality data sets are not normally distributed. Hirsch and Slack (1984) and Hirsch et al. (1982) discussed the use of the Mann-Kendall test to correct for problems associated with serial correlation. In a paper by Kehew and Brewer (1992) nonparametric statistics were used to compare water quality data sets from glacial drift aquifers and bedrock aquifers in Barry County, Michigan. Non-parametric methods were used because most of the parameters measured were skewed and the assumptions of normality or independence were not required. Two-sample tests using these non-parametric tests suggest that ground water in the underlying sandstone

aquifer is derived from recharge through the glacial drift.

Spatial estimation methods have been introduced relatively recently for the characterization of ground-water quality. Spatial estimation of chemical distributions is often accomplished by a procedure called kriging. Simpson (1985) and Flatman (1986) both used kriging techniques on sets of lead (Pb) measurements from soil cores near lead smelters. The results of kriging are primarily visual in that concentration contour plots and standard deviation plots of concentration are produced. From these, the spatial extent of contamination in any given area can be estimated. Variograms, or variances of paired sample measurements as a function of the distance between samples, and kriging are used to provide estimates of contamination which show the natural variability of the contaminant distribution in an area.

Spatial geostatistics were applied to a contaminated ground-water situation in papers by Cooper and Istok (1988a) and Cooper and Istok (1988b). Semi-variograms of total volatile organic compounds (TVOC's) were developed and kriging was performed on these models. Contaminant extent was then mapped with a series of contour maps. The authors urged caution when using kriging on small data sets and to limit kriging "to areas between sample values" (Cooper & Istok, 1988b, p. 298). Istok, Smyth, and Flint (1993) use multivariate geostatistical methods to determine the extent of contamination by the herbicide Dacthal, dimethyl tetrachloroterephthalate (DCPA), in the state of Oregon. Both nitrate and DCPA were sampled to determine whether a correlation existed between the two parameters, because future sampling would include a larger number of less expensive nitrate analyses. Results indicated that nitrate sampling can be used as a cost effective method to screen samples for the more detailed pesticide analysis.

CHAPTER II

SITE INVESTIGATION

Background History

The study site, located in Winnebago County in north-central Illinois (Figure 1), covers a four square mile area in the city of Rockford. The geology in the area is primarily alluvial sand and gravel (Barcelona et al., 1993). The alluvial sand and gravel lie within the Rock Bedrock Valley which trends from north to south (Wehrmann & Barcelona, 1990). One hundred percent of the ground water in the area is either from Pleistocene glacial drift, Ordovician dolomite, or Cambrian sandstone (Wehrmann, Holm, LeSeur, Curtiss, Stecyk, & Berg, 1989). The water-table aquifer included in the study area contains up to 250 feet of glacial drift, which lies above the Ordovician St. Peter Sandstone (Barcelona et al., 1993). Most domestic wells in the area are shallow wells drilled in the glacial drift. Mixed zoning in the area permitted both residential development and industrial and commercial development to be in close proximity (Wehrmann & Barcelona, 1990). Since 1970, over 300 domestic and 16 public water supply wells have been polluted with volatile organic compounds (VOC's) in this area (Wehrmann et al., 1989). The Rockford Water Department (RWD) began monitoring for 33 VOC's in December 1981 when volatiles were discovered in a municipal well (Wehrmann et al.,1989). Since 1983, all municipal wells with TVOC concentrations over 10 $\mu g\ l^{-1}$ had been sampled monthly and if they were under 10 $\mu g\ l^{-1}$ they were sampled every two months (Wehrmann et al., 1989). The area was listed as a National Priority List (NPL) site under the Comprehensive

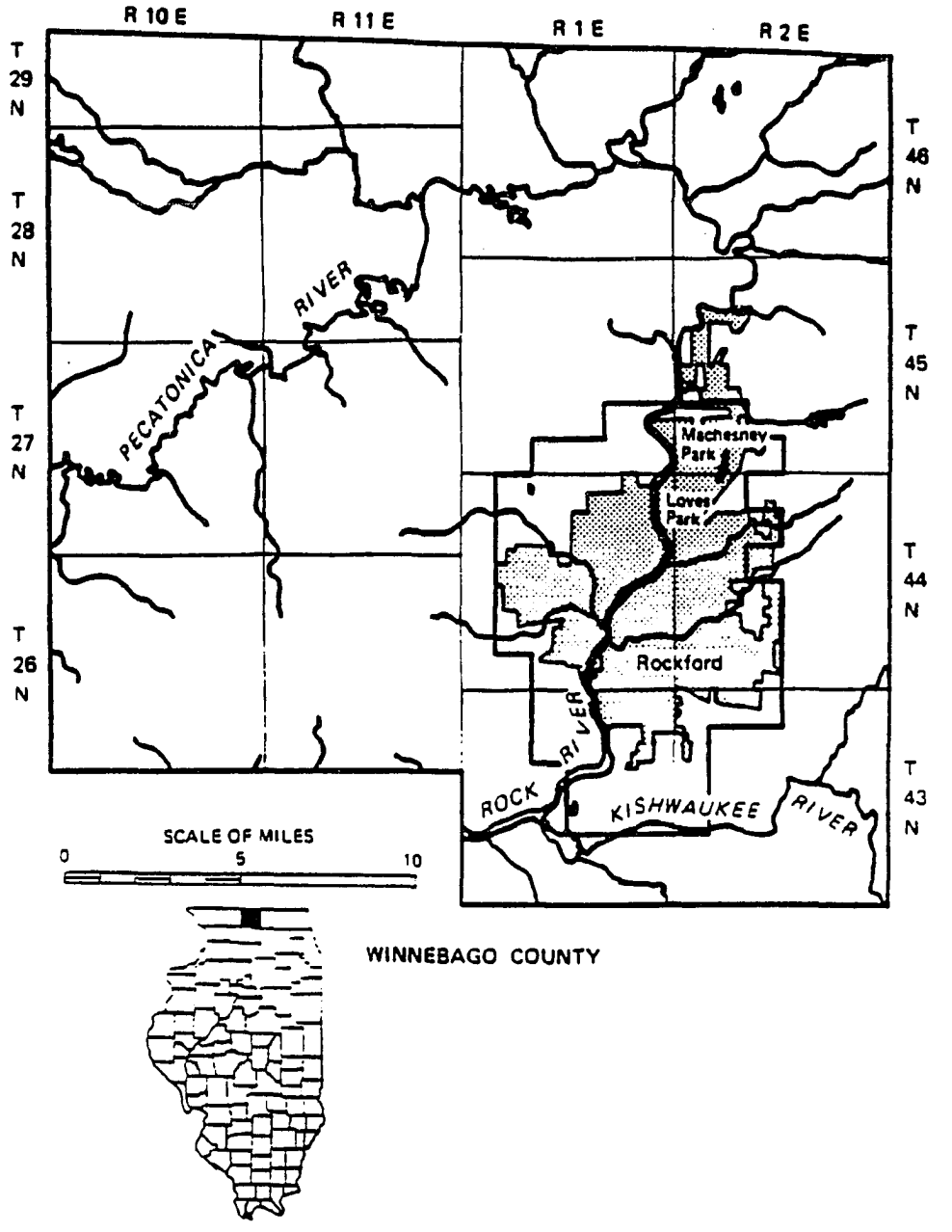

Figure 1. Location of Study Area.

Source: Wehrmann et al. (1989).

Environmental Response, Compensation and Liability Act (1980). This act is referred to as "Superfund" which targets the cleanup of releases of hazardous substances in the air, on land, and in this case in the water.

The primary direction of ground-water flow in the area was determined from at least quarterly water level measurements from a large network of wells (Wehrmann et al., 1989). Figure 2 shows the trend of equipotential lines for all wells for August 1991 data gradually decreasing from west to the east. If a perpendicular flow line is drawn across the equipotential lines, the approximate flow direction can be determined. In this case it was to the west-northwest. The average gradient in the area was 0.005 ft/ft (0.005m/m) and the average hydraulic conductivity (K) was 1.45×10^{-3} ft/sec (4.43×10^{-4} m/sec) (Table 1). Figure 3 shows a total volatile organic compound map of the area in August 1991 in which measured concentrations were over 100 $\mu g\ l^{-1}$. Two concentrated areas of volatiles have been characteristic features of this plume. A third concentrated area seemed to be developing in the northwest as well as a tongue of low VOC concentrations separates the two areas of high concentration.

Field Methods and Monitoring Design

Eighteen volatiles, along with selected trace metals from water samples, were analyzed initially at the WMU Institute for Water Sciences Water Quality Laboratory. Five principal contaminants were chosen from these eighteen to be used for statistical purposes in this paper. They are 1,1,1 Trichloroethane (1,1,1 TCA), 1,1 Dichloroethane (1,1 DCA), cis 1,2 Dichloroethylene (cis 1,2 DCE), 1,1 Dichloroethylene (1,1 DCE), and Trichloroethylene (TCE).

The monitoring network (Figure 4) in this four square mile area consisted of nearly 40 two-inch diameter stainless steel (SS) and poly-vinyl chloride (PVC) wells

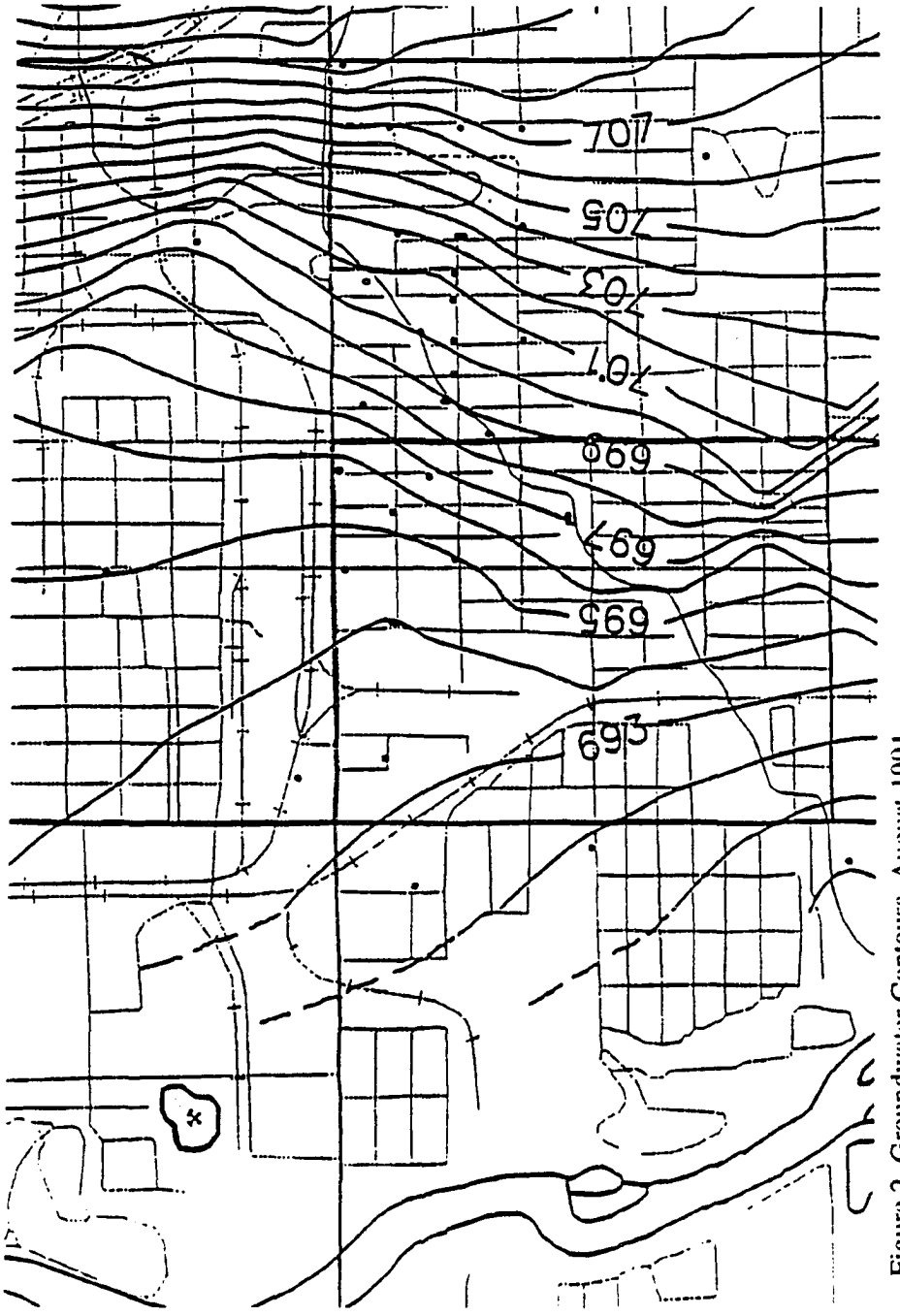

Figure 2. Groundwater Contours, August 1991.

Source: Wehrmann, H. A. (1989).

Figure 3. Total VOC Concentrations, August, 1991.

Source: Wehrmann, H. A. (1991).

Table 1

SE Rockford Hydraulic Conductivity Data

Well Number *	Date Drilled	Depth feet	Aquifer Type	Date Slug Tested	DTW @ Test	Water Height Over Screen	Aquifer Thickness	Average K gpd/sqft
1	11/87	87.50	Sand	9/90	39.1	43.40	146	1400
2	11/87	52.50	Sand	9/90	40.3	7.20	145	870
3	11/87	92.50	Sand	8/89	45.2	42.30	195	1110
4	11/87	52.50	Sand	9/90	44.0	3.50	196	690
5	11/87	125.00	Sand	9/90	40.6	79.40	144	—
6	11/87	125.00	Sand	8/89	45.1	74.90	195	1100
7	10/89	62.60	Sand	12/89	40.0	17.60	260	980
8	10/89	32.57	Sand	12/89	20.2	7.37	210	290
9	10/89	49.88	Silty Sand	9/90	22.0	22.88	198	2
10	10/89	22.30	Till	—	—	—	—	—
11	10/89	25.39	Till	7/91	20.0	0.39	?	22
12	10/89	57.55	Sand	9/90	38.8	13.75	256	930
13	7/90	96.08	Clay	9/90	41.2	49.88	84	15
14	7/90	25.03	Till	—	—	—	95	—
15	7/90	51.48	Silty Sand	9/90	42.9	3.58	27	230
16	7/90	47.78	Sand	9/90	30.4	12.38	150	860
17	7/90	45.28	Sand	9/90	28.3	11.98	97	920
18	7/90	73.90	Sand	9/90	66.2	2.70	29	480
19	7/90	49.53	Silty Sand	9/90	36.9	7.63	198	570
20	7/90	53.60	Sand	9/90	30.3	18.30	220	1400?
21	10/90	46.68	Sand	7/91	27.2	14.48	148	1040
22	10/90	45.50	Sand	7/91	29.5	11.00	81	1000
23	10/90	60.44	Sand	7/91	35.1	20.34	40	520
24	10/90	42.88	Sand	7/91	31.0	6.88	104	370
25	10/90	40.24	Sand	7/91	19.7	15.54	240	780
26	10/90	72.27	Sand	7/91	53.5	13.77	62	560
27	10/90	61.88	Sand	7/91	48.9	7.98	41	470
28	10/90	99.34	Sand	7/91	72.4	24.44	48	64
29	10/90	36.86	Sand	7/91	21.2	10.66	199	1200?

*All wells have 5 foot long screens except MW10 & MW28 (2.5 foot) and MW41 & MW45 (10 foot).

Table 1--Continued

Well Number *	Date Drilled	Depth feet	Aquifer Type	Date Slug Tested	DTW @ Test	Water Height Over Screen	Aquifer Thickness	Average K gpd/sqft
30	10/90	50.32	Sand	7/91	33.4	11.92	227	880
31	5/91	62.48	Sand	7/91	28.8	28.68	151	660
32	5/91	49.98	Sand	7/91	32.4	12.58	43	1600?
33	5/91	46.00	Sand	7/91	34.8	6.20	50	1300
34	5/91	44.61	Sand	7/91	33.1	6.51	67	1000
35	5/91	44.79	Sand	7/91	28.0	11.79	102	1600?
36	5/91	49.84	Sand	7/91	31.8	13.04	78	1200?
37	5/91	44.24	Sand	7/91	25.7	13.54	139	1700?
38	5/91	48.90	Sand	7/91	31.6	12.30	173	760
39	5/91	50.97	Sand	7/91	34.2	11.77	206	1350
40	5/91	65.50	Sand	7/91	28.3	32.20	242	1900?
41	5/91	85.44	Sand	7/91	28.4	47.04	242	1200?
42	5/91	53.80	Sand	7/91	33.7	15.10	220	1800?
43	5/91	81.42	Sand	7/91	40.1	36.32	265	2200?
44	5/91	52.38	Sand	7/91	39.7	7.68	40	500
45	5/91	72.40	Sand	7/91	40.3	22.10	40	750
46	5/91	75.12	Sand	7/91	31.1	39.02	264	2300?
47	5/91	54.94	Sand	7/91	43.6	6.34	261	1150
48	5/91	50.35	Sand	7/91	33.4	11.95	217	1700?
16A	8/91	48.00	Sand	8/91	28.8	14.20	151	960
17A	8/91	45.00	Sand	8/91	26.6	13.40	98	1100
21A	8/91	47.00	Sand	8/91	26.8	15.20	148	1900?
35A	8/91	45.00	Sand	8/91	27.6	12.40	102	1400?

*All wells have 5 foot long screens except MW10 & MW28 (2.5 foot) and MW41 & MW45 (10 foot).

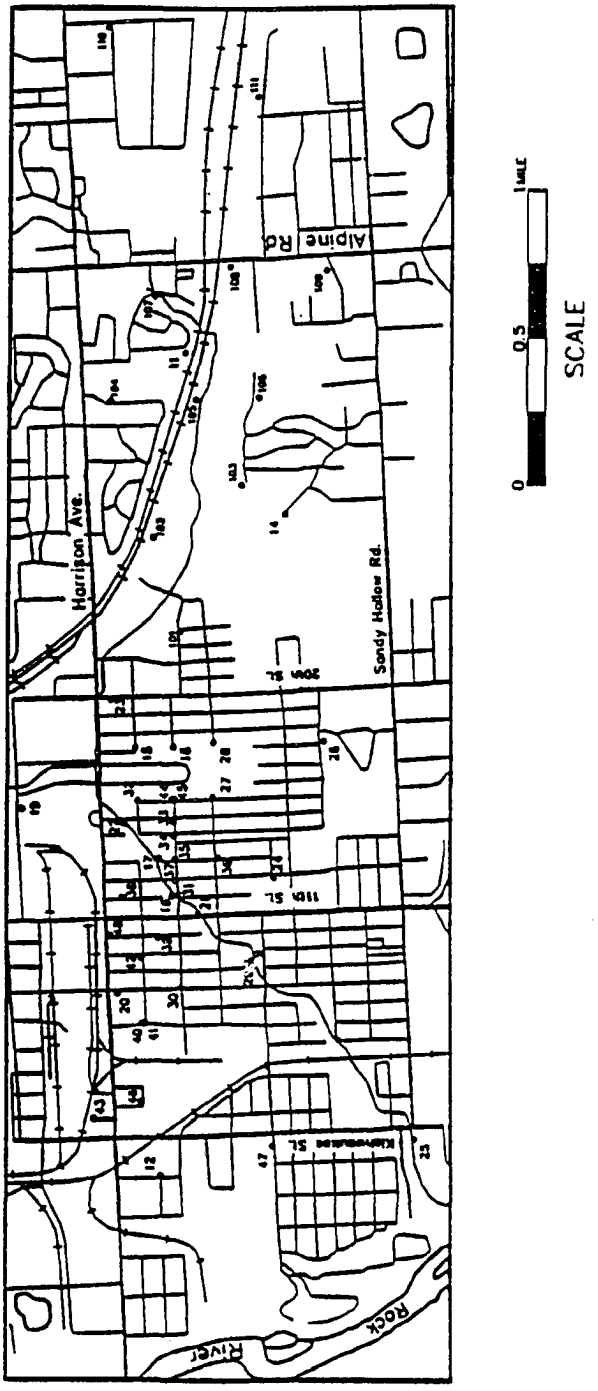

Figure 4. Southeast Rockford Monitoring Well Locations.

Source: Wehrmann, H. A. (1991).

installed by hollow-stem auger drilling by the joint effort of WMU and ISWS (Barcelona et al., 1993). Typically, the SS screen length was five feet, with the screen interval being at least ten feet below the static water level of the aquifer. One length of SS riser followed by PVC riser was used to complete the well to the surface.

Specific depths of the monitoring wells and water heights over the screen are listed in Table 1. During installation, the augers were pulled up with the well inside the augers to allow for collapse around the screen. Three feet of granular bentonite was used as a seal at the water table and cemented flush mount well protectors were installed at the surface. Development of these 40 wells was accomplished by either a submersible pump or compressed air pumped at a rate of 5 to 10 gallons per minute (20-41 L/min) to free the water of particulate matter.

Sampling of the monitoring network was conducted on a quarterly basis. The sampling was initiated in November 1990 and was continued on a quarterly basis to September 1992. Quality assurance and quality control (QA/QC) procedures were strictly adhered to when sampling the area and analyzing samples in the laboratory. First, wells were opened and were manually measured for water level using a water level probe (Slope Indicator Co.), and temperature using a thermistor probe (Omega Instruments). Polytetrafluoroethylene/fluoroethylene polymer (PTFE/FEP) or stainless steel/fluoroethylene polymer (SS/FEP) bladder pumps (QED, Inc.) were dedicated to use in all of the wells. [A bladder pump is a positive displacement device which uses a pulse of gas to compress the bladder and push the water sample to the surface (Fetter, 1988).] The pumps were outfitted with FEP tubing to a flow cell aboard the WMU water quality sampling vehicle. The pumps were operated at a rate of 1.0 +/- 0.1 L/min and monitored for dissolved oxygen, pH, temperature, and conductance through the flow cell. Pumping continued until the indicator parameters stabilized to +/- 0.1 mg

O_2/L, +/- 0.05 pH units, +/- 0.1 C°, and +/- 5.0 µS/cm at which time these readings were recorded. Stabilization of the indicator parameters occurred after less than one bore volume was pumped from the wells. Three samples were then taken in 40 mL vials and at least one sample was spiked to evaluate error involved in storage and analysis (Barcelona et al., 1993). Samples were then placed in a cooler with ice and transported to the WMU-ISWS laboratory for analysis using gas-chromatography within 24 hours. Sample spikes, laboratory standards, and field blanks were used to account for errors in the steps of storage, handling, and laboratory analytical procedures.

CHAPTER III

SOURCES OF ERROR IN THE SAMPLING PROCEDURE

Types of Error

Two main types of error need to be considered during the sampling process. The first is indeterminate or random error. These errors occur due to the imprecision or variability in analytical measurements when reported for the same sample (Skoog & Leary, 1992). Precision is then a measure of the reproducibility of results or agreement between any two replicate measurements (Skoog & Leary, 1992). Random error sources include analytical, sampling, or operator inconsistencies and natural variability. The standard deviation and variance are statistical parameters that can be calculated to measure precision. Random error can be evaluated and sometimes controlled by replication of sampling and analysis procedures.

The second type of error is determinate or systematic error. This type of error affects the accuracy [or correctness] of a measurement relative to a known result (Skoog & Leary, 1992). Systematic errors have a definite value and when measurements are made in the same way, bias becomes a problem in the technique (Skoog & Leary, 1992). Sources of this bias include calibration errors, temperature fluctuations, improper extractions of the sample, blanks, contamination of equipment, mechanical losses, time-dependent instrument errors (i.e., drift), and operator bias in measurement procedures. Determinate errors can be detected and minimized using proper equipment and simple sampling and analytical QA/QC procedures.

Source of Variance Equation

The total variance (square of the standard deviation) may be considered to be the sum of the individual error contributions from several different sources (Taylor, 1987). For environmental data these sources include natural, sampling, and laboratory analytical variances (Barcelona et al., 1989).

A general approach to reducing the effect of any of these sources of variation is to collect replicate samples and to randomize their occurrence (Barcelona et al., 1989). Taking replicate samples can reduce the amount of percentage error attributable to field sampling variance and laboratory analytical variance of the total variance. An equation which uses these sources of variance as an estimate of total variance is as follows:

$$\sigma^2_t = \sigma^2_n + \sigma^2_l + \sigma^2_f$$

where

σ^2_t = total variance

σ^2_n = natural variance

σ^2_l = laboratory analytical variance

σ^2_f = field sampling variance

When total variance is known, percentage error attributable to individual components of the equation can be evaluated.

The following procedure was followed to arrive at individual sources of variation for this project. The total variance was computed by first using the standard deviation of the number of replicate VOC sample results taken at a particular well site, and then squaring this number to obtain the total variance attributable to a specific well

site. The laboratory analytical variance was calculated by finding the standard deviation of a series of laboratory instrument calibration standards which were used in the analytical procedures in the laboratory. This result was then normalized by dividing by the true value of the corresponding standard. This number was then squared and assigned to represent the laboratory analytical variance. The field sampling variance was determined by calculating the standard deviation of field sample spikes. The standard deviations were then normalized by dividing by the true concentration value of the field spike. Field spikes also contained the effects of the laboratory analytical variance. Therefore, before these variances were introduced in to the equation, they were subtracted from the field sampling variance. The natural variance was computed by subtracting the field sampling variance and laboratory analytical variance from the total variance. Percentages of the total were calculated to determine the percentage of variance attributable to laboratory analytical, field sampling, and natural variability.

CHAPTER IV

DESIGN AND METHODOLOGY, TEMPORAL AND SPATIAL ANALYSIS

Normally Distributed Data

The normal distribution curve or Gaussian curve (Figure 5) is a symmetrical, bell shaped distribution in which the bulk of the measurements are located near the center of the distribution and a few of the measurements are located at the extremes (Popham & Sirotnik, 1992). In a population with a normal distribution, the mean (average), median (midpoint), and mode (most frequent sample) are the same (Popham & Sirotnik, 1992). When data sets are not symmetrically distributed, the distribution of values in a data set are said to be skewed. In these cases there are disproportionately larger numbers of values at either or both extremes of the distribution. Thus skewness may be either positive or negative. Data sets that have median values larger than mean values show negative skewness (Figure 6) and are considered to be right censored. Data sets that have median values smaller than mean values show positive skewness (Figure 7) and are considered to be left censored. Skewed curves show extremes or tails in the direction of skewness, to the right if the distribution is positively skewed and to the left if the distribution is negatively skewed (Popham & Sirotnik, 1992).

Well Pairs

Well pairs were constructed to provide data for spatial and temporal statistical comparisons over short distances or time periods (i.e., weekly to quarterly). For this

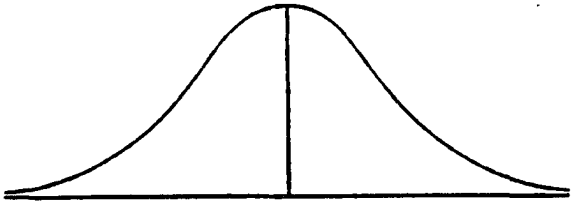

Figure 5. Normal Distribution Curve.

Source: Popham, W.J, & Sirotnik, K. A. (1992).

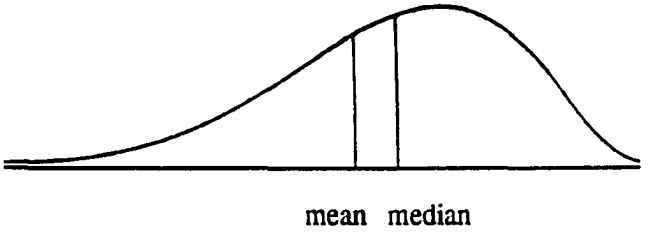

Figure 6. Negatively Skewed Distribution.

Source: Popham, W.J, & Sirotnik, K. A. (1992).

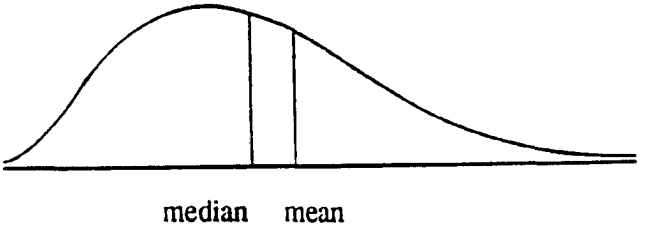

Figure 7. Positively Skewed Distribution.

Source: Popham, W.J, & Sirotnik, K. A. (1992).

project, short term variability consisted of sampling wells spaced within three to five feet (1-2m) in distance of each other over a one to two week time period. These additional monitoring wells were placed next to wells 16, 17, 21, and 35 (Refer to Figure 4) in this study and are labeled 16A, 17A, 21A, and 35A. These well pairs were used for statistical comparisons between extended interval monitoring periods (i.e., 9 months), for this project which included August 1991 through May of 1992.

Wilcoxon Matched-Pairs Signed-Ranks Test

The Wilcoxon matched-pairs signed-ranks test was used to compare the water quality data. The Wilcoxon matched-pairs signed-ranks test can be applied to test not only whether the members of a pair of observations differ, but also the magnitude of the difference (Daniel, 1990). Once the magnitudes of the differences are determined, they can be ranked. When this procedure is applied to water sampling results, it can be used to distinguish statistical differences in sampling over short temporal intervals. In this study, the Wilcoxon matched-pairs signed-ranks test was utilized to determine whether a short interval (i.e., one to two week) time periods provided redundant data. Unlike the Student's t-test, which is limited in applicability to data sets with normal distributions and equal variances, the Wilcoxon signed rank test is a nonparametric test which can be applied to non-normally distributed data (Siegel, 1956). Using the Wilcoxon matched-pairs signed-ranks test, if we sum the ranks having a plus sign and the ranks having a minus sign, we would expect the two sums to be about equal, which would confirm the null hypothesis, H_o (Siegel, 1956). In other words, we would expect the sum for the wells with increasing concentrations to be equal to the sum of the wells with decreasing concentrations. After testing, if the water sampling data indicate that significant differences do not exist between the two sampling events, the null

hypothesis cannot be rejected. Conversely, if the water sampling data show a difference between the sampling events, the null hypothesis can be rejected.

After stating the null hypothesis, it is necessary to choose a level of significance. The level of significance is the small probability that when a statistical test is run, the result will produce a value under which the null hypothesis will be rejected when it actually is true (Siegel, 1956). The level of significance is symbolized as α, and typically is set at a level between 0.10 (i.e., 10%) and 0.01 (i.e., 1%). Alpha is the probability of being wrong in rejecting H_o. There are two types of errors which can be made in deciding on H_o: a Type I error, or rejecting H_o when in fact it is true; and a Type II error, or accepting H_o when in fact it is false (Siegel, 1956). A Type I error has been described as placing faith in something that does not work or is incorrect. It is an error of commission and can result in wasted money or effort. A Type II error may result in not investing enough effort or not spending money profitably when an opportunity exists to do so. It represents a missed opportunity. Given this definition, alpha was set at 0.05 (i.e., 5%). This level was chosen because it is an accepted conventional level and also to dismiss potential bias in support of favored outcome.

Discussion of Kriging

Kriging is a popular geostatistical technique used for spatial analysis. Kriging has been called the best linear unbiased estimate (BLUE) of [known] concentrations of contaminants at a certain point near points with known concentrations (Istok & Cooper, 1988). Ordinary kriging is "linear" because estimates are weighted linear combinations of the sampling data, "unbiased" because kriging tries to keep the mean error equal to zero, and "best" because it aims to minimize the variance of the errors (Isaaks & Srivastava, 1989). If contaminant measurements are known for certain points, these

measurements can then be used to calculate kriged estimates of contaminant concentrations at unmeasured points within the plume (Istok & Cooper, 1988). Estimates over a large area where many samples have been collected constitutes global estimation (Isaaks & Srivastava, 1989). Local estimation techniques focus on a small area, with relatively few samples. Estimations may then be made using samples located outside the area to calculate estimates within the bounded area (Isaaks & Srivastava, 1989).

The history of kriging dates back to the 1960's when it was developed primarily as a tool to evaluate ore bodies for mining exploration and production (Simpson, 1985). The theoretical work in developing kriging was accomplished by G. Matheron while he was at the Paris School of Mines (Simpson, 1985). The word "krige" was named after D.G. Krige who specialized in mining estimation for ore in South African gold mines (Delhomme,1978). In the past, kriging has been used to estimate both oil reserve and ore body extent (Simpson, 1985). Recently, it has been applied to estimate the extent of ground-water and soil contamination.

The software package used for kriging chemical concentration and water level data was GEO-EAS 1.2.1. (Englund, 1991). It was developed for the U. S. Environmental Protection Agency (U.S. EPA) by Evan Englund at the Environmental Monitoring Systems Laboratory in Las Vegas, Nevada (Englund, 1991). The construction of a data file requires only the input of the X and Y coordinates of its geographic location and an associated concentration value at that specific location. From this input, numerous types of statistics including histograms, box plots, and probability plots can be generated. A separate subprogram for computation, interpretation, and modeling of variograms is included to describe the spatial correlation structure of any water sampling data set. Input from the parameters that generated the

variogram calculations are then input to the subprogram krige. Two types of kriging are used for computation. Point kriging estimates the contaminant at a point from a set of nearby water samples using punctual kriging (Englund, 1991). Block kriging takes these estimates at all of the points and averages them together for one single value for the whole block (David, 1977). In GEO-EAS, the block area is a two by two, three by three, or four by four array of points centered at a particular grid node (Englund, 1991). The output for all kriged results is primarily visual, or in the form of a contour map. The output can include contaminant plume extent and estimated values of contaminant concentrations within this plume. Alternatively, a standard deviation plot may be made to show where the deviations of the kriged estimates are high due to the large distances between sampling points used to make concentration estimates.

Semivariogram

A semivariogram must be calculated before kriging can be performed. The semivariogram uses time or space relationships between sample observations to calculate a statistic (Flatman, 1986). A semivariogram shows relationships of both observation separation or distance between sample points (lag) and variance of contaminant estimates between sample pairs at each lag (Flatman, 1986). Various components of the variogram provide insight into the spatial correlation structure of the data. The range is the distance or time at which the variogram model plateaus to a maximum value (Englund, 1991). The sill is this initial plateau value. The nugget effect (C_o) is the vertical jump from the zero value at the origin to the value of the variogram plateau with relatively small separation distances (Englund, 1991). These three components are displayed in Figure 8. In this analysis, either an omnidirectional variogram or various directional variograms were used for the analysis of spatial

continuity. A small directional tolerance wasn't used because this provided too few pairs of concentration values for reasonable curve matching. In these cases, the directional variograms become too scattered and erratic to be useful in the kriging algorithm (Isaaks & Srivastava, 1989).

The variogram model is the basis for interpretation of the spatial correlation of the data set. Therefore, kriging weights assigned to the samples during variogram computation control the quality of the results (Englund, 1991). Contouring methods make the assumption that spatial correlation exists, or that a measurement at any point nearby is better than locations far away. Variograms can be used to quantify this relationship by how well a measurement can represent another point a certain distance away (Englund, 1991). Variograms plot the average difference (variance) of pairs of measurements against the distances separating the pairs (Englund, 1991). A "true variogram" is a plot of all possible pairs of measurements which satisfy all distance and direction relationships if all samples could be collected (Englund, 1991). Since the data set for this site was limited, variances for groups of pairs of measurements for distance and direction are graph plotted using variance versus distance and curve matched to approximate the "true variogram".

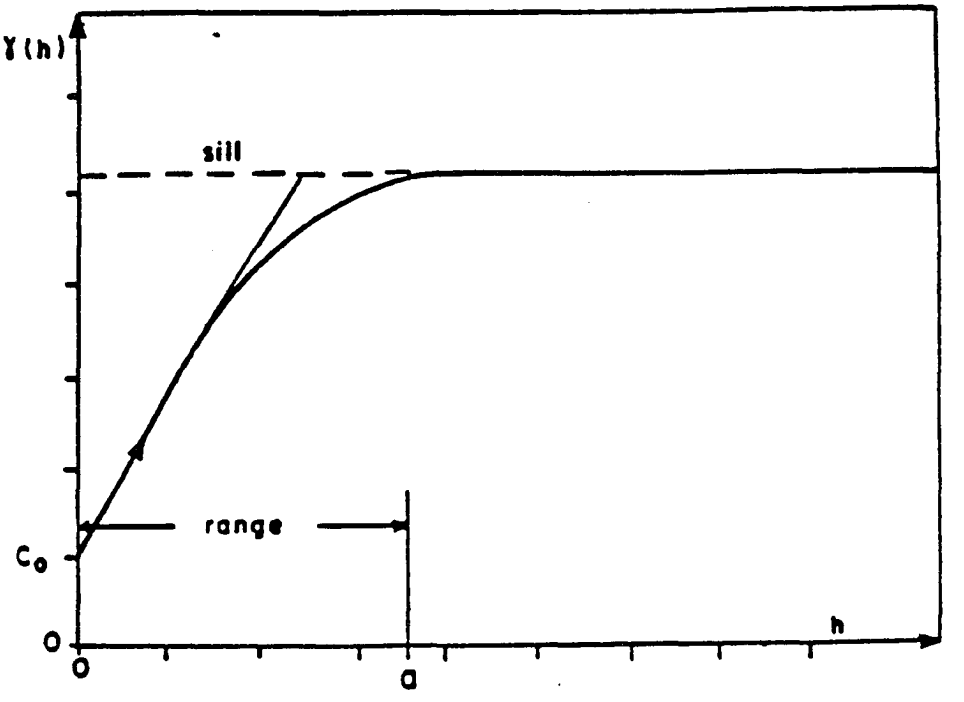

Figure 8. Spherical Model Variogram.

Source: David, M. (1977).

CHAPTER V

RESULTS AND DISCUSSION

Database Structure

The databases created for this study consisted of ground-water sample results from the water quality laboratory which included duplicate determinations for laboratory analytical standards, field sample spikes, blanks, and concentrations for each of the samples. First, each of the more than 500 samples were recorded and transferred to computer Lotus® spreadsheet data files (I otus Development Corp, 1991). One file was created for chemical parameter and within a file, samples were sorted by well location. Second, the known concentrations were used to derive variances related to the sources of error equations. Medians were used for concentration values for each of the parameters. Third, files were created within the Macintosh® software package Statview® 4.0 which was utilized to calculate the Wilcoxon matched-pairs signed-ranks test results as well as descriptive statistics and box plots. Fourth, files containing information related to well locations and known concentration levels were created to operate the IBM® software package GEO-EAS 1.2.1 used to produce kriged contour plots which serve as the foundation of this study's spatial analysis (Englund, 1991).

Sources of Error in the Measurement Process

The percentages of total variance attributable to laboratory analytical, fieldsampling, and natural variability were calculated individually for each of the five

principal contaminants over seven quarterly sampling periods since the study began in November 1990 (Appendix A). Water sample data including field spikes, laboratory analytical standards and natural variability from each of the seven quarterly sampling periods were included in these results. Each was applied to the method previously described and variances for each were inserted into the variance error equation for calculation.

The results of this procedure are listed in Table 2. Percentage contributions to the total variances of each of the five contaminants have been listed in the table from the sampling period between November 1990 to September 1992. The results have been normalized to 100%. When routine quality assurance quality control (QA/QC) procedures were used in conjunction with simple water sampling and analysis procedures, the percentage error contributions for laboratory analytical and field were relatively small. The results indicate that for all five volatile organic compounds, percentages attributable to laboratory analytical errors were less than 4% of the variance. The field sampling error contributions combined with the results of laboratory error, demonstrated that in all cases, the average variability attributable to procedural (i.e., avoidable or controllable) sources was 13%. The higher field sampling variance for TCE, which was primarily due to the low concentrations (e.g., <20 ppb) in the study area for this contaminant, is the notable exception.

These results clearly show that determinate and random errors were controlled by the study procedures. Utilization of simple dedicated sampling equipment, field and laboratory procedures allows one to control human-induced errors and make judgments about true concentration levels. The results further suggest that routine monitoring and assessment programs should focus on extending QA/QC procedures to the field from the laboratory, which has been the traditional focus of ground-water and

hazardous waste investigations.

Table 2

Mean Percentages of Total Variance Attributable to Laboratory Error, Field Error, and Natural Variability, November 1990-September 1992

VOC	Laboratory %	Field %	Natural %
111 TCA	1.29	3.26	95.45
TCE	1.95	12.75	85.30
c12 DCE	1.69	4.72	93.59
11 DCA	1.02	5.22	93.76
11 DCE	3.61	4.15	92.24

Normal Distribution

As discussed in the literature review section, ground-water data sets are not often normally distributed. An evaluation of the assumption of normally distributed data can be made directly from the sample mean and median. In a normal distribution, the mean and median are equal. Data sets are described as skewed when values for both the mean and median are different. The mean, median, and other descriptive statistics for each of the 5 contaminants for all wells are contained in Appendix B. The results indicated that for each of the five contaminants, the median was less than the mean—a characteristic of a positively skewed or left censored data set. Skewed distributions have also been described as lacking symmetry in the frequency distribution. A symmetric distribution has a skewness value of zero. Values obtained for skewness for all five volatile organic compounds are positive and greater than zero.

This indicates a spreading of the right tail or positive skewness.

Box plots may also be used to visually illustrate skewness of the distribution of each of the contaminant concentrations. The box plots for each of the contaminants are displayed in Appendix C. A box plot is a graph which shows the 10th, 25th, 50th (median), 75th, and 90th percentiles of a variable. Outliers were shown outside these percentile values, and their positions have been designated by circles. These box plots indicate there was a wide spread of the percentile ranges over the data sets because of differences in the concentration ranges. The line in the middle of each box was the 50th percentile or the median value and for a normal distribution this should be centered in the middle of the box. In almost all of the box plots this was not the case and skewness of the data exists. The median line was most often plotted in the lower part of the box, (i.e., more of the distribution existed above it) providing evidence of positive skewness.

Temporal Analysis

The purpose of the temporal data analysis was to draw conclusions about two separate, time-related trends: (1) the general trend of contaminant concentrations at certain wells over the course of the project, and (2) short term versus longer term variability of contaminant concentrations over the entire study area. The first trend was analyzed utilizing the data from three well pairs (i.e., wells: 16/16A, 17/17A,and 21/21A) while the second trend was examined utilizing the Wilcoxon matched-pairs signed-ranks test on the entire data set.

The general temporal trend observed in this study was an increase in contaminant concentrations over time (Appendix D). This increasing trend was observed consistently in wells 17/17A, where increases continued throughout the

study. Noticeable concentration spikes or concentration increases occurred in August 1991 and March 1992, in a majority of the well pairs. Given that these concentrations variabilities were generally greater than those attributable to laboratory or field sources of error they must be considered part of the natural variability in contaminant concentrations.

The squares in the well pair graphs show the corresponding concentrations of the contaminant for the corresponding paired wells. The well pair graphs are somewhat deceptive because of the varying concentration scales of the graphs. Actually, for the volatile compounds, TCE, c1,2 DCE, 1,1 DCE, and 1,1 DCA, all of the differences in concentration except for one case, 16/16A for 1,1 DCE, showed changes of less than 10 ppb over the short term (i.e., one to two weeks). For 1,1,1 TCA, differences in concentration were less than 40 ppb sampling over the short term.

The Wilcoxon matched-pairs signed-ranks test was applied to well pair data in order to draw conclusions about differences between samples taken on a short term basis (one to two weeks). Well pair water sampling data were examined from August 1991 and May 1992, for 1,1,1 TCA, TCE, c1,2 DCE, 1,1 DCA, and 1,1 DCE. All Wilcoxon matched-pairs signed-ranks tests for these ten tests yielded a probability greater than the predetermined alpha level, as illustrated in Table 3. Thus, the null hypothesis could not be rejected and conclusions cannot be drawn about whether differences exist between samples taken over the short term (i.e., one to two weeks) of each other. An implication here for monitoring operation is that if a particular water sample is lost it can effectively be recollected within a week or so without biasing the concentration trend.

In order to determine if significant concentration differences occurred between samples taken over the longer term, the Wilcoxon matched-pairs signed-ranks test was

Table 3

Wilcoxon Matched-Pairs Signed-Rank Tests Probabilities for Well Pairs

Sampling Period	111 TCA	TCE	c12 DCE	11 DCA	11 DCE
August 1991	.1088	.1088	.5930	.1088	.1088
March 1992	.4652	.4652	.1441	.9999	.9999

* $p < .05$

applied to data gathered using all well locations. The quarterly sampling events of November 1990 and February 1991, February 1991 and May 1991, May 1991 and August 1991, August 1991 and December 1991, December 1991 and March 1992, and March 1992 and September 1992 were included in the analysis. Five of the six statistical tests result in a rejection of the null hypothesis for 1,1,1 TCA (Table 4). This means that significant temporal concentration differences exist between five of the six tests performed for successive quarterly sampling events.

The contaminant TCE yielded three statistical rejections in comparisons of quarterly data over the sampling period. The contaminant c1,2 DCE yielded only one rejection in six tests which means that a difference in contamination level existed only between the sampling period from May 1991 to August 1991. Four of the six quarterly sampling comparisons for 1,1 DCA yielded probabilities less than the stated alpha level and thus, were actually different from each other. The contaminant 1,1 DCE showed one statistical rejection for the period May 1991 and August 1991. Overall, the results of the tests showed that sampling on a quarterly basis maybe expected to yield statistically significant differences while shorter sampling intervals may not be statistically different. These results provide support for using quarterly sampling

Table 4

Wilcoxon Matched-Pairs Signed-Ranks Test Probabilities for Quarterly 111 TCA, TCE, c12 DCE, 11 DCA, and 11 DCE

Sampling Period	111 TCA	TCE	c12 DCE	11 DCA	11 DCE
Nov 90-Feb 91	.6832	.0164*	.5337	.5937	.6379
Feb 91-May 91	.0125*	.4420	.7221	.2132	.4328
May 91-Aug 91	.0003*	.0001*	.0003*	.0002*	.0190*
Aug 91-Dec 91	.0086*	.0001*	.1300	.0025*	.1579
Dec 91-Mar 92	.0001*	.7375	.3313	.0001*	.1311
Mar 92-Sept 92	.0006*	.5506	.5732	.0002*	.0918

* $p < .05$

frequency to provide non-redundant data in preliminary network designs. This was also found to be the case for temporal variability of inorganic constituents by Barcelona et al. (1989).

A noticeable rejection of the null hypothesis was observed in the testing of period May 1991 and August 1991 which showed a rejection for all five volatile organic compounds. For well pairs 16/16A, 17/17A, and 21/21A (Appendix D) this significant statistical difference may have been due to the large increase in concentrations which occurred for the August 1991 period. In most cases, dramatic increases in concentration were evident from May 1991 and August 1991. Three out five tests showed statistical differences from August 1991 and December 1991. Again referring to Appendix D, there was a sharp decrease in concentration from August 1991 to December 1991. This downward trend in concentration was again represented

by the sharp decline shown in the well pair graphs.

Annual Wilcoxon matched-paired signed-ranks tests were performed on all of the wells over the quarterly sampling periods between November 1990 and December 1991, and August 1991 and September 1992 (Table 5). These periods were chosen because they represent approximately one year between sampling periods. The results indicated statistical differences for four of the five volatile organic compounds. TCE showed statistical differences for both successive quarters and "annual" comparisons by the Wilcoxon matched-pairs signed-ranks test. 1,1,1 TCA showed no statistical differences. The other three contaminants showed at least one statistical difference between the "annual" data sets.

Table 5

Wilcoxon Matched-Pairs Signed-Ranks Test Probabilities for Annually 111 TCA, TCE, c12 DCE, 11 DCA, and 11 DCE

Sampling Period	111 TCA	TCE	c12 DCE	11 DCA	11 DCE
Nov 90-Dec 91	.0747	.0010*	.0329*	.1361	.0281*
Aug 91-Sept 92	.6204	.0001*	.7782	.0030*	.0674

* $p < .05$

Spatial Analysis

Kriging techniques were applied in data analysis to meet the following objectives: (a) to provide a two-dimensional picture of the changing extent and magnitude of contamination in ground-water within a specified depth range over quarterly sampling events; (b) to determine the effects of deletion of points on spatial

distribution of contaminants; and (c) to determine the minimum number of sampling points needed to get an accurate picture of the extent of the contaminant plume.

Spatial comparisons were made using U.S. EPA software GEO-EAS 1.2.1 (Englund, 1991). Variograms were important in the spatial analysis because they serve as the basis for interpretation of the spatial data set and control the "quality" of kriging estimations assigned to samples during the computation process (Englund, 1991). Variograms are a measure of how well a concentration value would be expected to represent another value located at a specific distance and direction away.

Variograms were computed using both contaminant concentrations (ppb) and X and Y geographic coordinates. Spherical variograms were generated using a maximum lag spacing of 2650 feet (807.7 m) and an increment of 250 feet (76.2 m). These were selected with the known scale of the X and Y monitoring well locations in mind. Considering the spacing of the monitoring well locations, a grid size of 4130 feet (1258 m) by 90 feet (27 m) was chosen. The X and Y sizes of cells were 60 feet (18 m) and 50 feet (15 m), and the number of X and Y cells were both 100 feet (30.5 m). Then, by inserting various values depending on the particular data set, a y-intercept (nugget), a maximum value (sill), and distance at which the model reached a maximum value (range) were determined (Englund, 1991). Through trial and error, a best fit model was chosen which most closely matched the true variogram for the monitoring site. On average, sill values ranged from 0.75 to 5, range values from 1500 feet (457.2 m) to 2700 feet (822.9 m), and the nugget values in all cases were zero.

Once an appropriate model of the variogram was chosen, the corresponding values for this variogram were then used as the inputs for the kriging subprogram. The kriging program then set up a block spaced grid and generated estimates from known sample values at specific locations. After computation, the kriged results were

displayed as contour maps. This yielded the visual representation of the spatial distributions of contaminants.

The first consideration of whether a monitoring well would be used to characterize the ground water at a particular site was the depth of the well. The wells chosen for kriging were between the depths of approximately 45 feet (14 m) to 60 feet (18 m) (Refer to Table 1). Wells finished at greater depth were excluded from the data input file in order to analyze spatial variability of volatile contaminants in a consistent depth range. The vertical variability of contaminants at distinct depths was not considered in this work.

Application of kriging to assess spatial trends focused on the major volatile organic contaminant 1,1,1 TCA. It was chosen for two reasons: (1) it had the highest concentration (ppb) levels of the five contaminants, and (2) it showed significant temporal variability over quarterly sampling periods as illustrated by the Wilcoxon signed rank test results.

Figure 9 presents the kriged contour plot for the November 1990 sampling event. Estimations for this contour map were limited due to the fact that not all of the monitoring wells had been installed at this time and the spatial predictions were based on 11 well sites. Contours were constructed where enough information was known to block krige an estimate. In most of the variograms, the nugget term was zero, a situation which requires at least eight samples to be in an area to calculate an estimation. The monitoring well locations are displayed as x's in the contour plots. The x's which were outside of the contour intervals are locations where there was not enough information to make a estimation and they were not contoured. The areal extent of the plume showed a characteristic tongue shaped lobe of lower concentration, below 47.52 ppb. The remainder of the site could be represented by an oval, consisting of

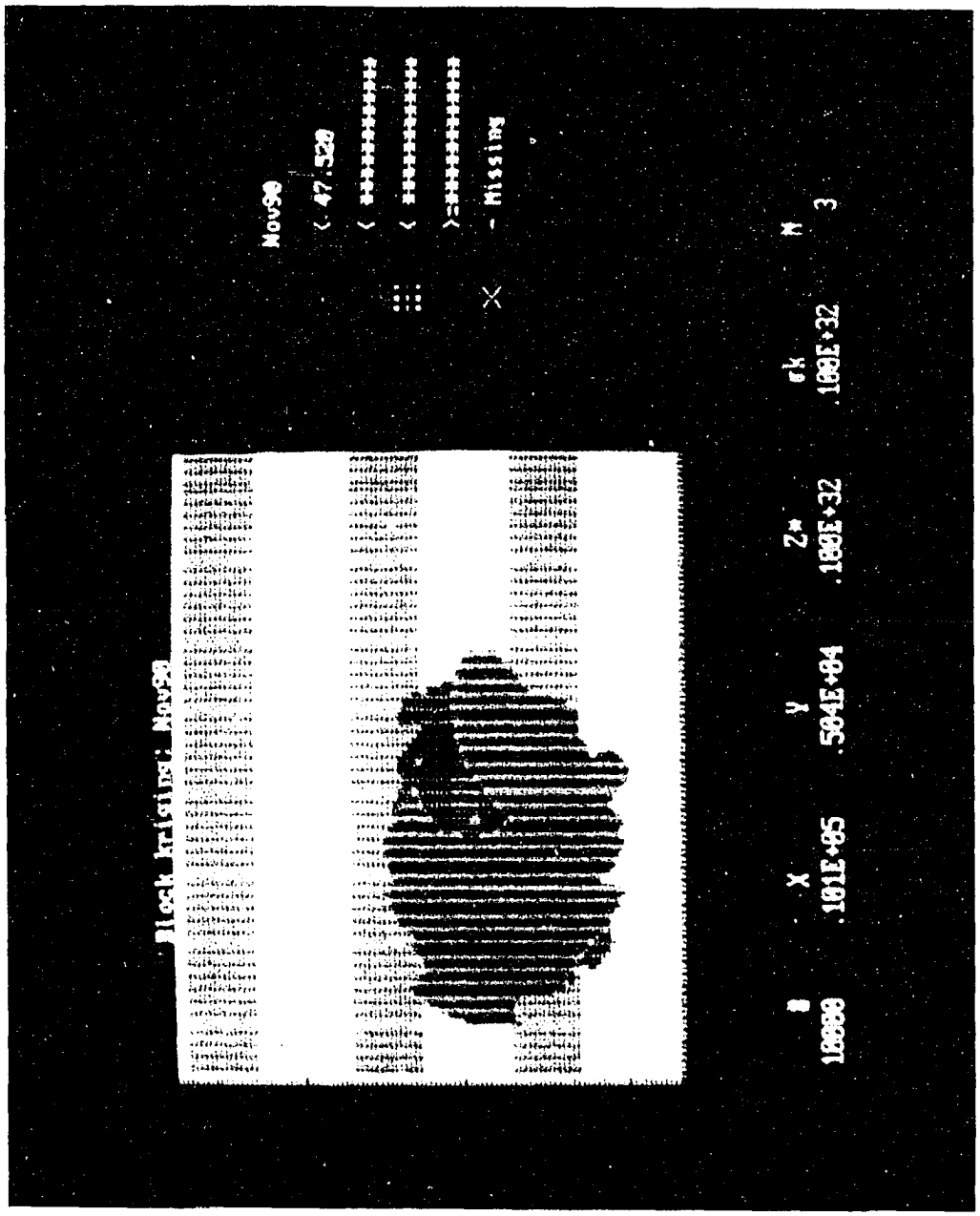

Figure 9. November 1990 111 TCA Kriged Contour Plot.

concentrations higher than 47.52 ppb. The February 1991 data for twelve well locations (Figure 10) showed very little change from November 1990 except that the low concentration tongue did not seem to be as extensive. A dramatic change in the spatial distribution of the plume was observed in May 1991 (Figure 11). First, 25 monitoring wells were used for estimation in this kriged contour plot. Second, plume delineations seemed to match the direction of ground-water flow which was to the northwest. The characteristic tongue of low concentration, now much better defined, existed at levels of less than 42.22 ppb. In addition, a new spatial feature was observed in the data from this period. Figure 11, which includes 25 monitoring wells, clearly shows development of two distinct high concentration zones in the overall plume with indications of a third developing in the far northwest. All three were approximately along the axis of the direction of groundwater flow. The higher concentration areas were in excess of 182.89 ppb in concentration. The two major higher concentration areas seemed to be divided by the tongue of lower concentration, which could be due to local changes in hydraulic conductivity, recharge, or preferential pathways of flow.

In August 1991 (Figure 12), the overall spatial extent of the contaminant plume (again with 25 wells) was essentially the same but does show an overall increase in higher concentration areas. The area of lower concentration in the tongue had increased with just the circular area of low concentration remaining at less than 21.93 ppb. An additional feature which developed was that the previously developing third higher concentration zone had merged with one of the already existing high concentration zones. The higher concentration zones for this quarterly sampling period increased in concentration to over 211.39 ppb.

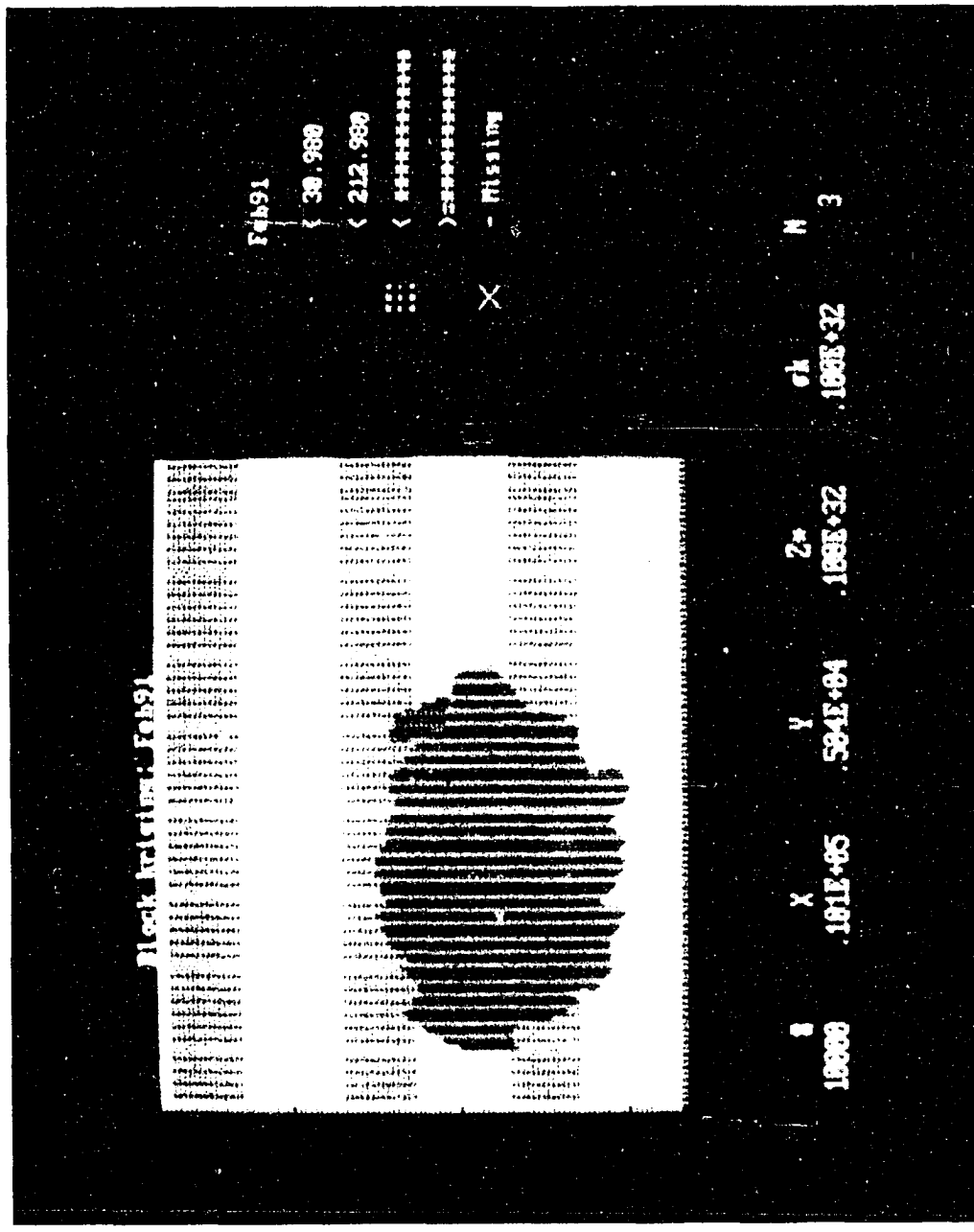

Figure 10. February 1991 111 TCA Kriged Contour Plot.

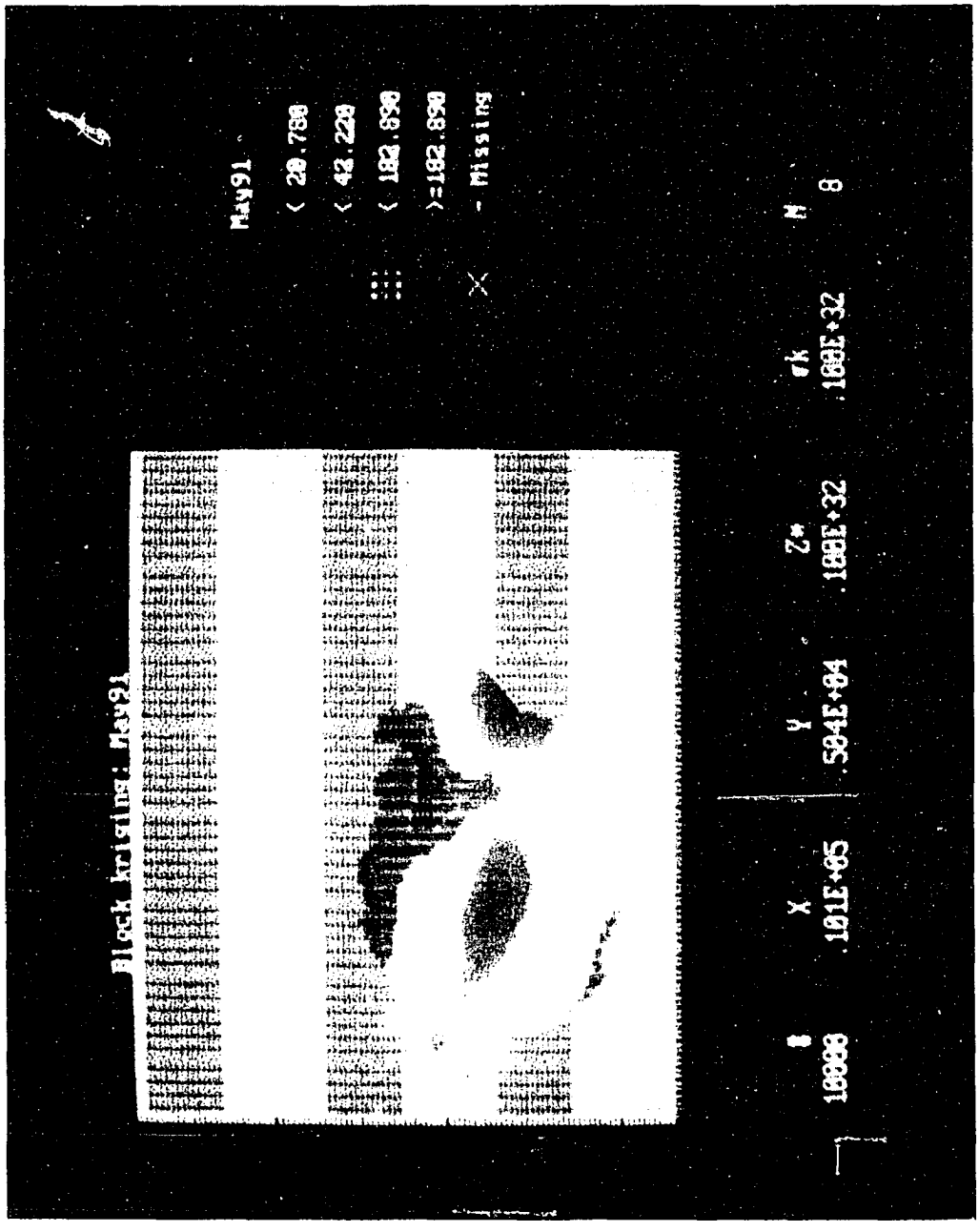

Figure 11. May 1991 111 TCA Kriged Contour Plot.

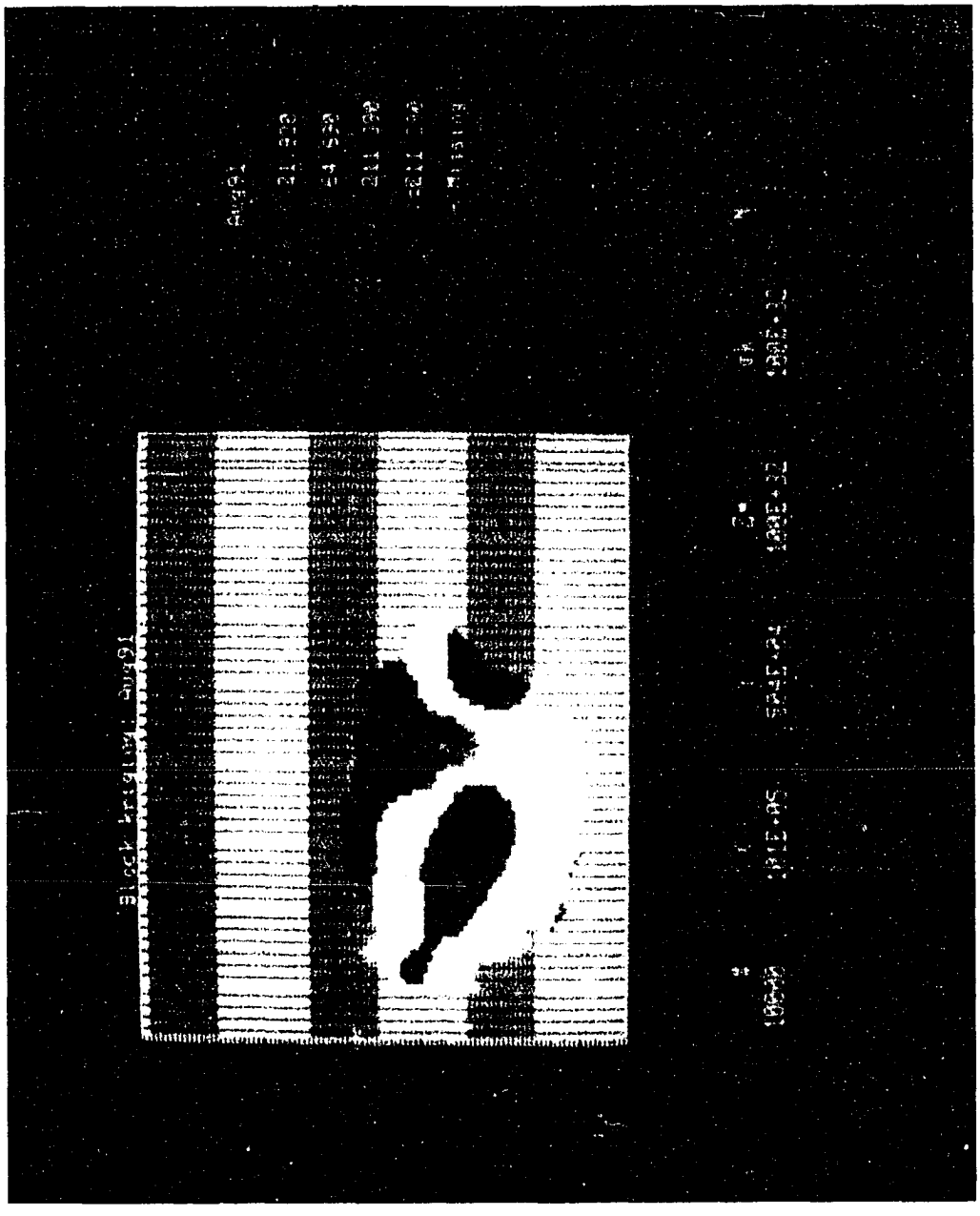

Figure 12. August 1991 111 TCA Kriged Contour Plot.

The kriged contour plot for December 1991 was rather deceptive (Figure 13). It appeared that concentration values have decreased significantly. Actually, a majority of the area of contaminant was in a range to 232.30 ppb. This explained why the areas of higher concentration have decreased and the third region of high concentration contaminant plume in the northwest separated. The higher concentration areas were in excess of 232.30 ppb. One characteristic, the contaminant levels in the tongue of low concentration, was roughly the same as that estimated from the August 1991 data set.

The March 1992 spatial estimation (Figure 14) represented the highest concentrations of the contaminant observed in the study. The low concentration tongue increased by 84.24 ppb. One of the highest concentration zones had again increased and merged with the third developing contaminant zone to form just two high concentration zones. The high concentration zones increased in both area and concentration, with maximum average concentrations in excess of 261.67 ppb.

The overall shape of the plume in September 1992 (Figure 15) was essentially the same except for a marked, uniform decrease in concentration from the March, 1992 levels. Areas of highest concentration increased slightly to 278.19 ppb while the area of highest concentration contours covered decreased. The extensive high concentration zones in the western and eastern portions of the study area were almost non-existent. Concentrations had risen, however, in the low concentration tongue, with average estimations of 1,1,1 TCA concentration up to 90.02 ppb.

In an experiment designed to evaluate the sensitivity of spatial contamination estimates to the number of well inputs, selected wells were removed and the kriging was repeated. It was expected that when selected wells were removed, corresponding changes would be observed in both the highly contaminated spatial zones within the plume. Wells 16, 21, 31, 35, and 37 were removed for three reasons: (1) they were

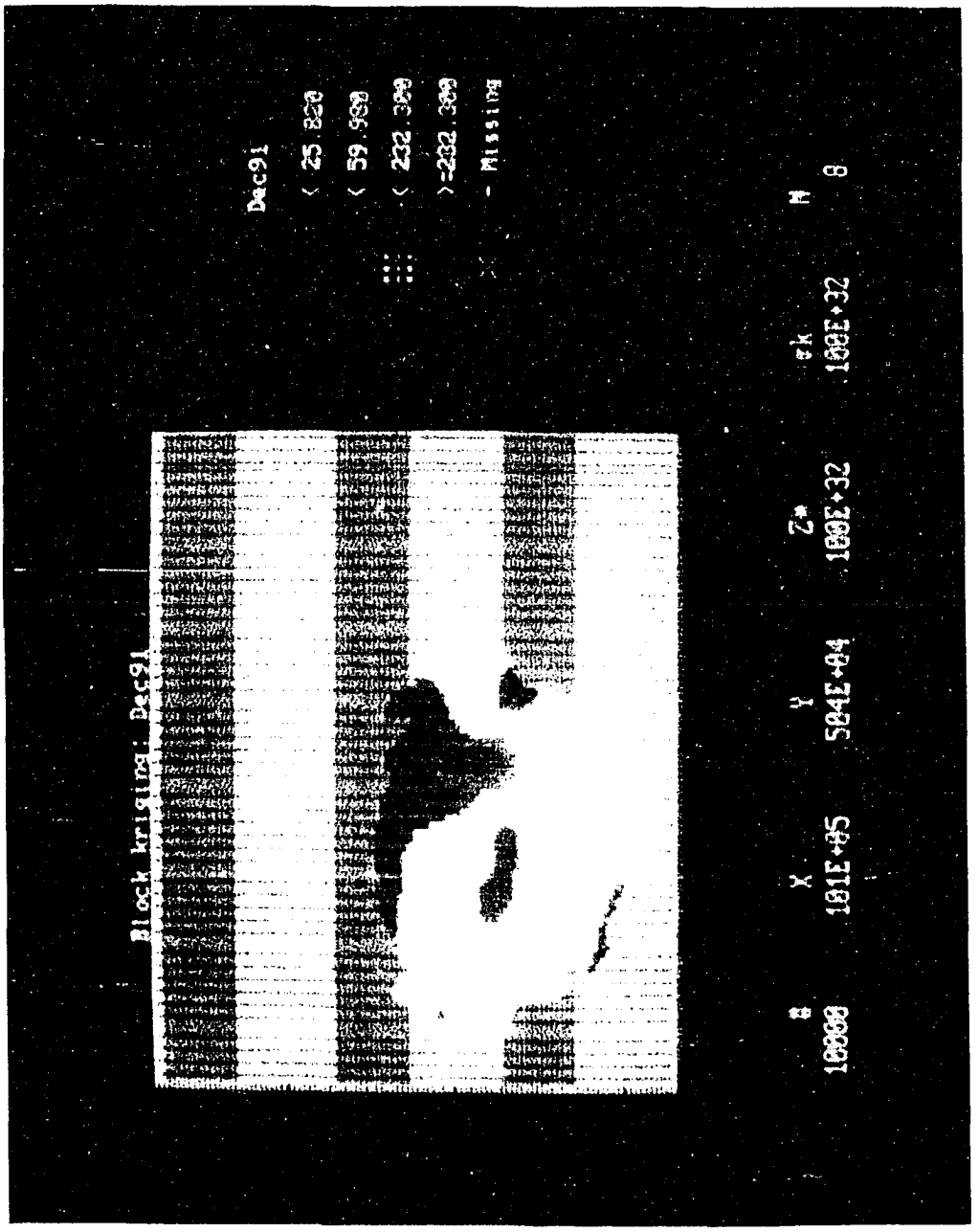

Figure 13. December 1991 111 TCA Kriged Contour Plot.

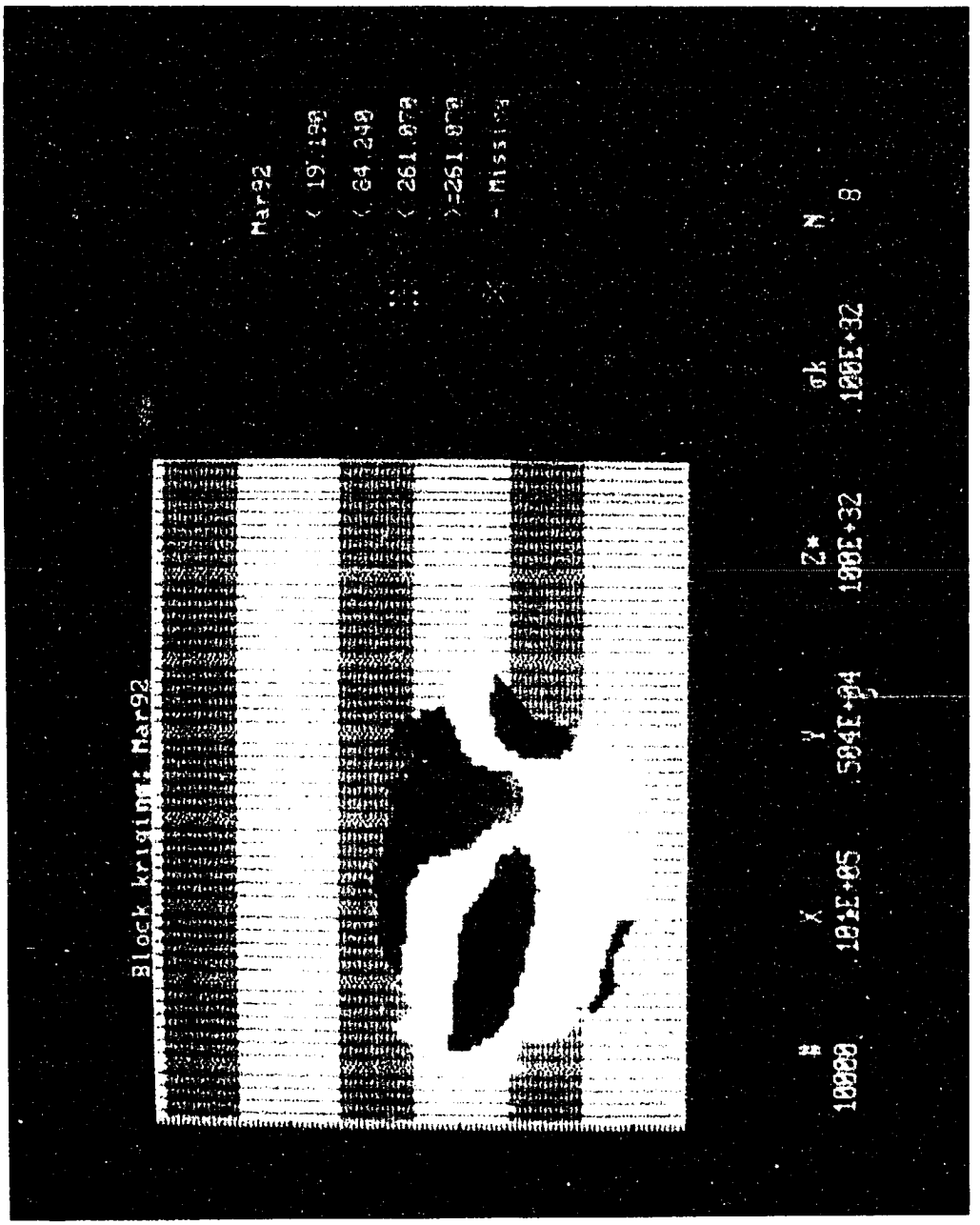

Figure 14. March 1992 111 TCA Kriged Contour Plot.

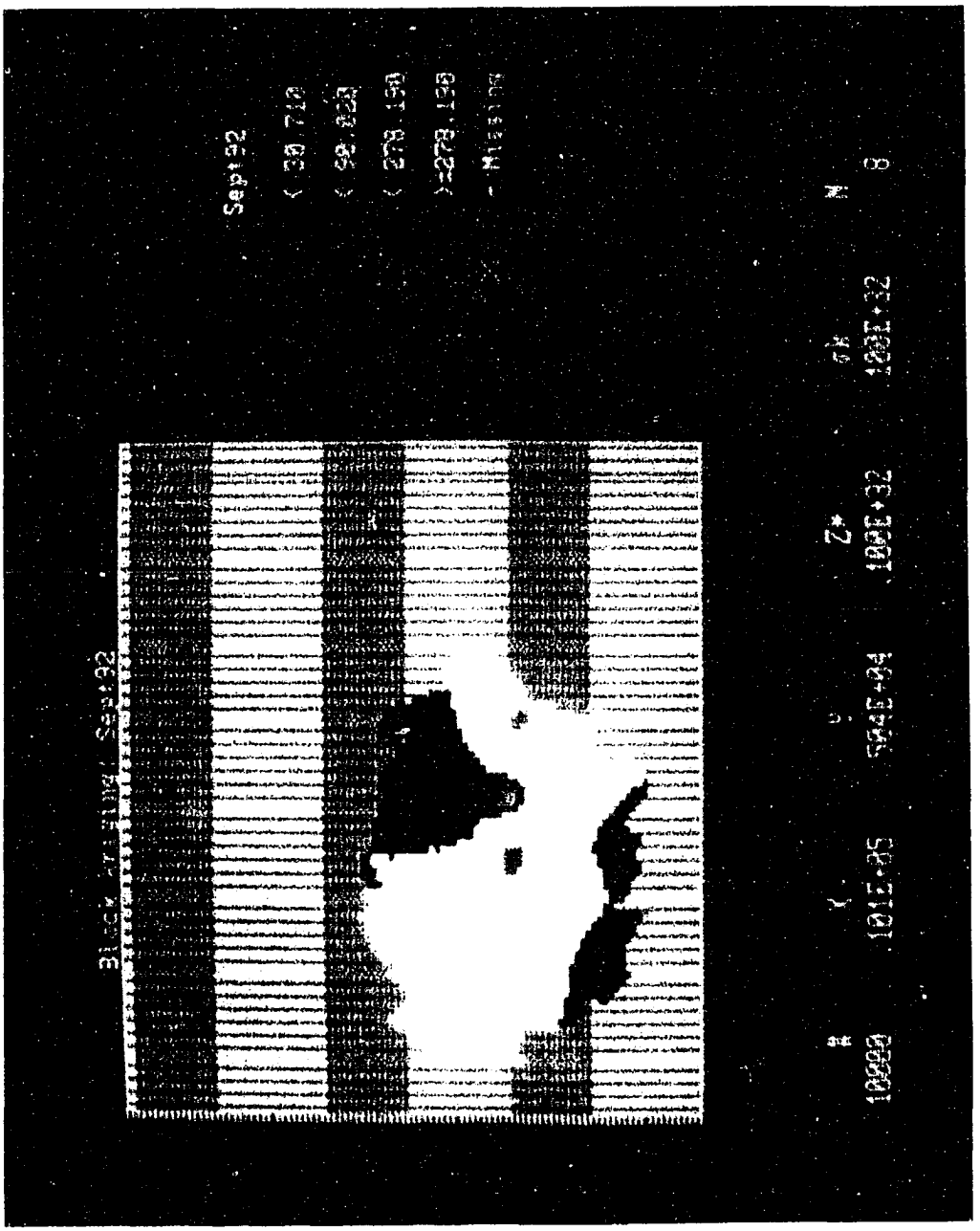

Figure 15. September 1992 111 TCA Kriged Contour Plot.

located in middle of the western high concentration plume, (2) they were in a line which was perpendicular to the direction of ground-water flow, and (3) they cut across the plume at different concentration levels. Three sampling periods were chosen for this experiment , December 1991, March 1992, and September 1992 (Figures 16,17, and 18). After reformulation of the variograms and the application of block kriging, the results indicate the substantial impact of deleting wells. In all three cases, estimations of concentration levels were deleted from the westernmost high concentration plume. The high concentration plume in the east was unaffected. The results show that if an area were undersampled (e.g., less than eight), an underestimation of the spatial extent of the contamination plume could result because that more than eight sampling points need to be in an area to make a block kriged estimation.

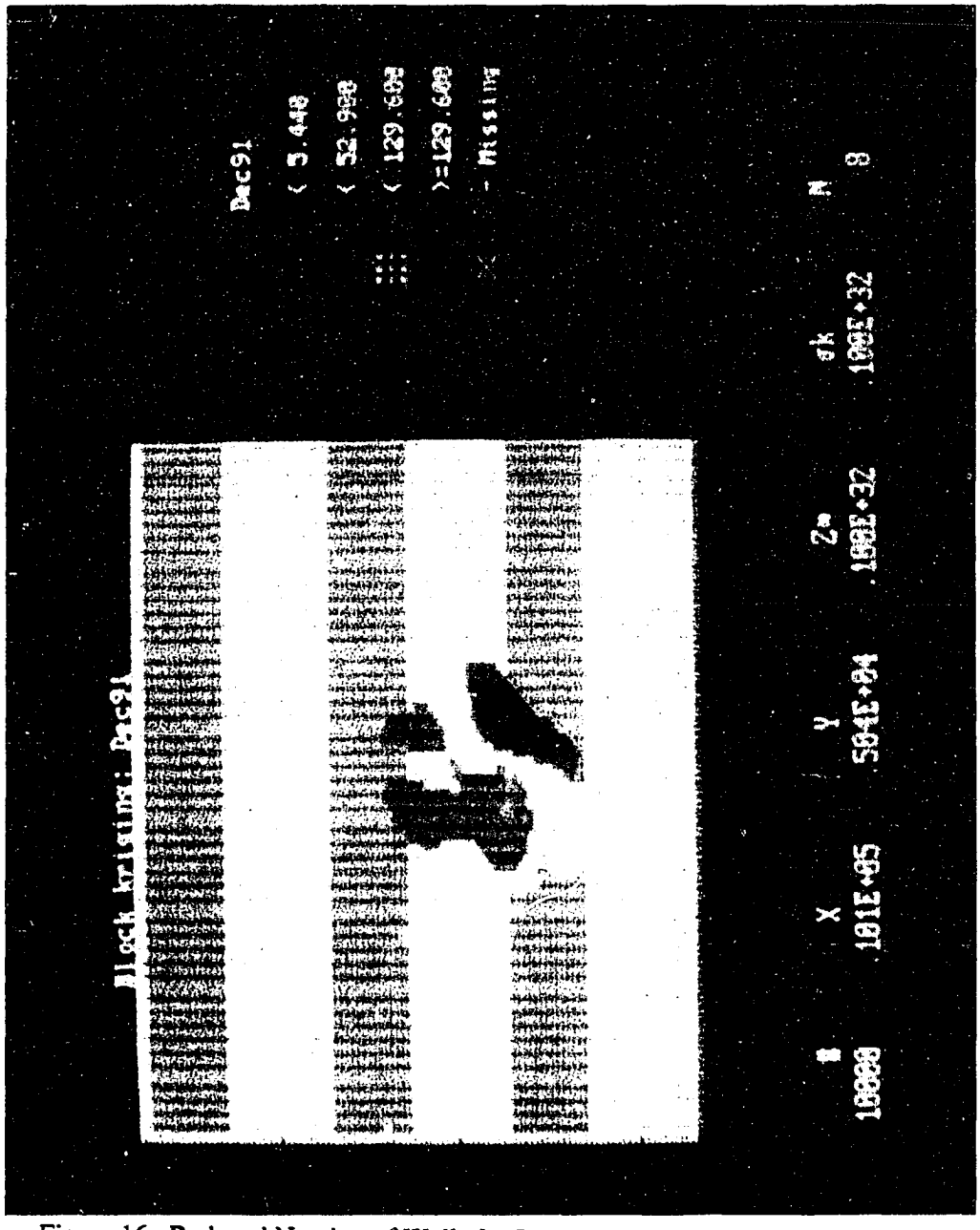

Figure 16. Reduced Number of Wells for December 1991 111 TCA Kriged Contour. Plot.

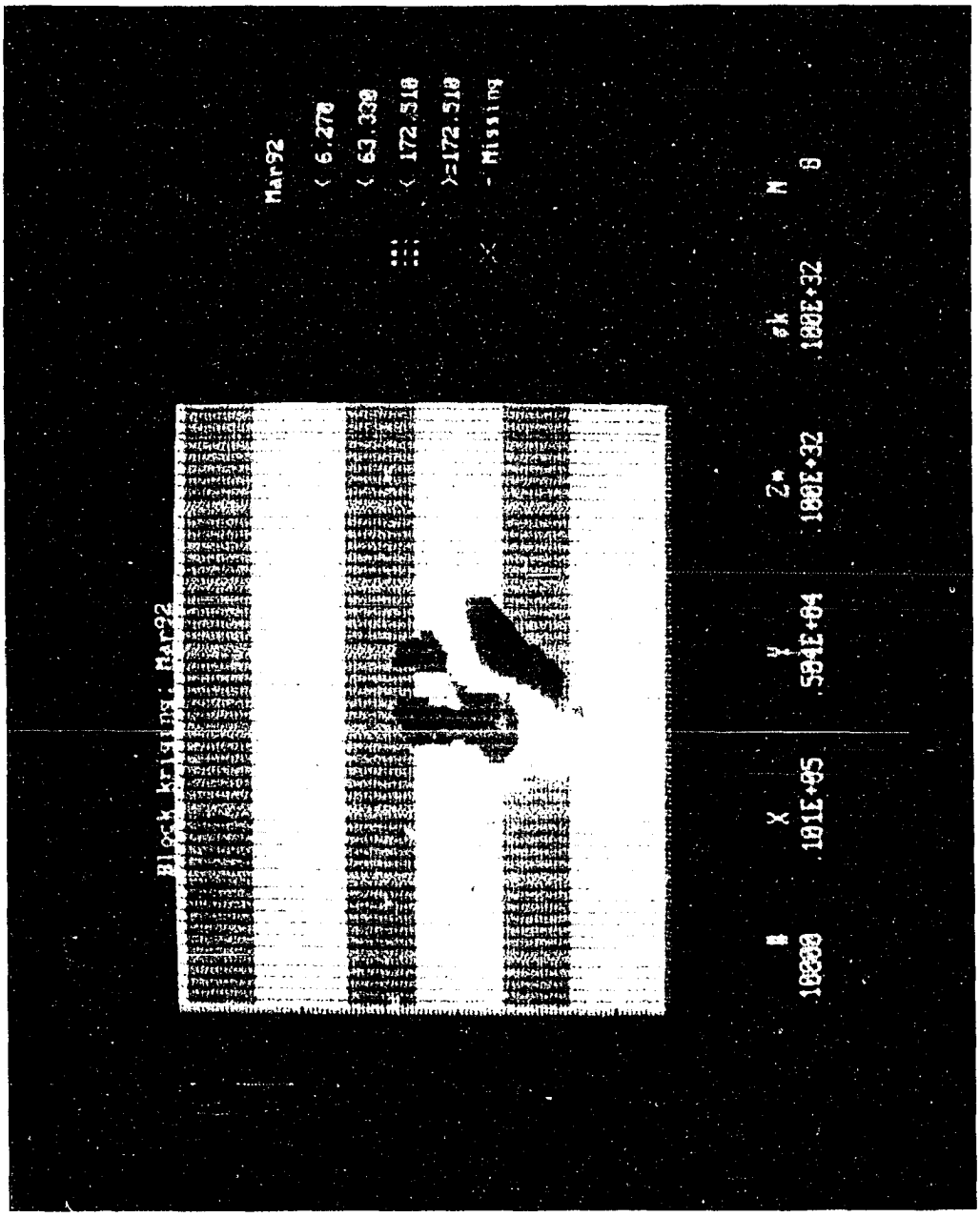

Figure 17. Reduced Number of Wells for March 1992 111 TCA Kriged Contour Plot.

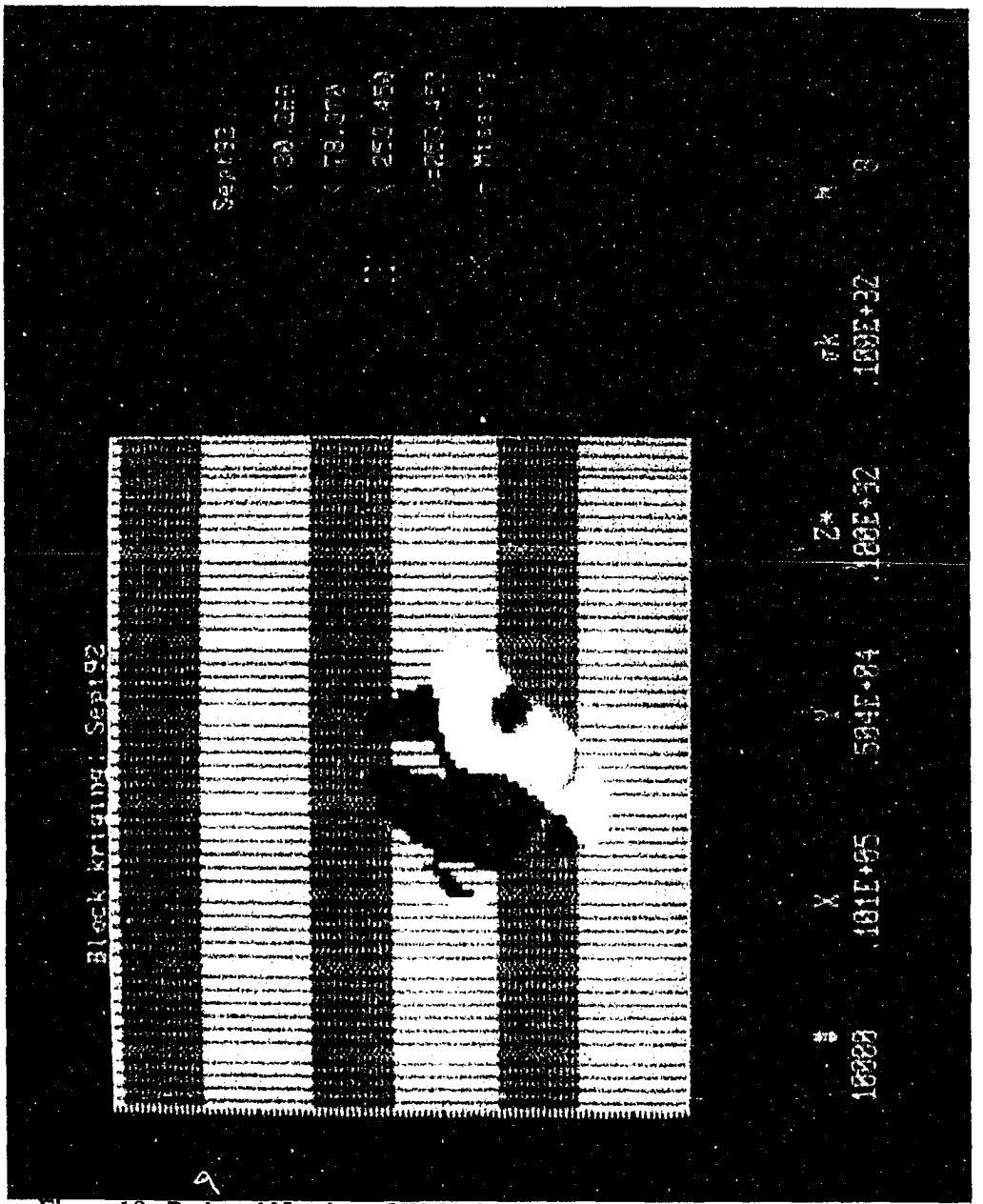

Figure 18. Reduced Number of Wells for September 1992 111 TCA Kriged Contour. Plot.

CHAPTER VI

CONCLUSIONS

Error control represents a major concern in environmental investigations. The control of determinate error or systematic error to obtain "representative" ground-water samples at minimum cost has most often been approached by laboratory based QA/QC programs. Simple, routine monitoring procedures which include the use of field sample spikes and dedicated sampling systems (e.g., pneumatic bladder pumps) have been found to control field and laboratory sources of error to less than 10% of total variability for dissolved organic contaminants at concentrations above 20 ppb. Below 20 ppb field and laboratory procedural errors may rise to approximately 20%. An increased emphasis on simple consistent sampling procedures and normal laboratory QA/QC permits the observation of natural concentration variability with minimum effort. These measures have been verified to be effective at a large ground-water contamination site in Rockford, Illinois.

Once the approximate levels of natural variability have been established, statistics can provide useful information for analyzing actual temporal and spatial concentration trends. Statistical testing on existing data sets can also provide guidance for cost-effective (i.e., non-redundant) sampling location and frequency selection without loss of information content. Short term sampling is not always the most cost effective way to sample an area. Considering the tests performed on the well pair data, short term sampling indicates redundancy in results can occur at time frames of days to weeks and distances between wells of the order of tens of meters. Quarterly sampling

over periods of months to years is a good starting point for network design since temporal differences between data sets can be resolved at this sampling frequency.

Spatial coverage of an area is also important, to determine the magnitude and extent of contamination as wells identify potential "hot spots". When kriging is applied, in order to achieve optimum concentration estimation, the most spatially diverse monitoring network of sampling points should be established within means. Spatial estimates of contaminant distributions over time have been found to be quite sensitive to the location and number of sampling points. Well locations at a density of (8 / 1000 m^2) have been found to be a minimum for adequate plume delineation in this glacial aquifer setting.

Appendix A

Percentage of Variance Attributable to Laboratory Error, Field Error, and Natural Variability

November 1990, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.06	99.94
20	0.00	0.00	0.00
12	0.00	0.00	0.00
21	0.02	0.25	99.73
16	0.00	0.01	99.99
17	0.00	0.00	0.00
15	NA	NA	NA
18	0.00	0.00	100.00
22	0.04	0.65	99.31
28	0.00	0.08	99.92
23	0.05	0.69	99.26
30	0.04	0.51	99.45
29	0.00	0.00	0.00
9	0.00	0.00	0.00
29	0.00	0.00	0.00
44	0.00	0.00	0.00
27	0.00	0.01	99.99
11	0.00	0.00	0.00
16	0.00	0.01	99.99
30	0.08	1.12	98.80

*NA indicated the estimated variance was negative.

February 1991, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	9.70	1.34	88.96
21	0.13	0.02	99.85
16	0.04	0.00	99.95
15	0.74	0.10	99.16
22	2.21	0.31	97.48
23	2.12	0.29	97.58
17	2.30	0.32	97.38
27	0.04	0.00	99.96
28	0.02	0.00	99.97
19	0.77	0.11	99.13
20	0.37	0.05	99.58
30	0.43	0.06	99.51
29	81.25	11.25	7.50
24	3.07	0.42	96.51
18	0.00	0.00	100.00

*NA indicated the estimated variance was negative.

May 1991, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.69	2.78	96.53
12	0.00	0.00	0.00
20	0.00	0.02	99.98
15	0.00	0.01	99.98
18	0.00	0.01	99.99
28	0.01	0.04	99.94
21	0.02	0.07	99.90
17	0.15	0.59	99.13
22	0.07	0.28	99.59
23	0.03	0.12	99.82
27	0.01	0.04	99.93
24	3.78	15.11	81.11
29	3.78	15.11	81.11
30	3.09	12.36	84.54
31	0.00	0.00	100.00
16	0.01	0.05	99.93
32	0.02	0.09	99.87
44	0.00	0.00	100.00
45	0.00	0.01	99.99
33	0.18	0.74	98.92
34	NA	NA	NA
35	0.01	0.06	99.91
36	0.89	3.58	94.74
37	0.02	0.10	99.85
38	0.03	0.11	99.84
39	0.02	0.10	99.85
48	0.89	3.58	94.74
11	0.00	0.00	0.00
42	0.00	0.01	99.99
41	0.00	0.00	0.00
46	0.01	0.05	99.93
43	0.71	2.83	95.83
40	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

August 1991, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
46	0.03	0.53	99.44
43	0.27	5.38	94.35
12	0.00	0.00	0.00
40	0.00	0.00	0.00
41	0.00	0.00	0.00
20	0.00	0.12	99.88
30	0.12	2.52	97.36
29	0.38	7.64	91.97
48	NA	NA	NA
42	0.33	6.53	93.14
39	0.00	0.08	99.92
19	2.07	41.54	56.38
23	0.14	2.90	96.96
15	1.80	36.07	62.12
18	0.00	0.06	99.94
28	0.01	0.14	99.85
24	NA	NA	NA
36	0.03	0.56	99.41
27	0.00	0.05	99.94
44	0.00	0.01	99.99
45	0.06	1.31	98.63
32	NA	NA	NA
22	0.64	12.90	86.46
33	0.82	16.36	82.83
34	0.69	13.84	85.47
35	0.04	0.91	99.04
37	0.00	0.08	99.92
38	0.03	5.48	94.25
16	0.01	0.14	99.85
31	0.04	0.74	99.22
16A	0.19	3.90	95.91
21	0.04	0.70	99.26
21A	0.00	0.08	99.91
17	0.03	0.67	94.30
17A	0.04	0.89	99.06

*NA indicated the estimated variance was negative.

December 1991, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
35	0.29	0.67	99.04
33	NA	NA	NA
43	0.64	1.48	97.88
46	0.04	0.10	99.86
41	0.00	0.00	0.00
40	0.00	0.00	0.00
30	0.14	0.32	99.53
20	0.56	1.28	98.16
29	13.33	30.56	56.11
42	0.04	0.09	99.87
48	16.11	36.91	46.98
39	0.01	0.03	99.96
19	1.31	3.00	95.69
23	1.89	4.34	93.76
38	0.11	0.25	99.64
16	0.03	0.07	99.90
31	0.02	0.06	99.92
21	0.09	0.21	99.70
36	0.12	0.28	99.60
24	7.41	16.98	75.62
27	0.02	0.04	99.95
44	0.01	0.02	99.97
45	0.01	0.02	99.97
32	0.75	1.72	97.53
22	0.49	1.12	98.39
34	5.24	12.01	82.75
37	0.10	0.23	99.66
17	0.22	0.51	99.26
15	6.06	13.89	80.05
18	0.00	0.01	99.99
28	0.00	0.01	99.99

*NA indicated the estimated variance was negative.

March 1992, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	NA	NA	NA
16	0.00	0.06	99.94
16A	0.00	1.18	90.81
17	0.07	2.16	97.83
17A	0.05	15.68	84.27
18	0.00	0.00	100.00
19	0.03	10.84	89.12
20	0.00	0.41	99.59
21	0.06	18.50	81.44
21A	NA	NA	NA
22	0.11	34.74	65.15
23	NA	NA	NA
24	NA	NA	NA
27	NA	NA	NA
28	0.00	0.63	99.36
29	NA	NA	NA
30	0.01	3.84	96.14
31	0.00	0.30	99.70
32	0.02	7.07	92.90
33	NA	NA	NA
34	NA	NA	NA
35	0.09	27.78	72.13
35A	0.00	0.03	99.97
36	0.00	1.72	98.28
37	0.00	0.11	99.88
38	0.01	2.71	97.28
39	0.00	1.61	98.38
40	0.00	0.00	0.00
41	0.00	0.00	0.00
42	0.04	12.34	87.62
43	0.01	3.36	96.63
44	0.00	0.69	99.30
45	0.00	0.03	99.97
46	0.00	0.26	99.74
48	NA	NA	NA

*NA indicated the estimated variance was negative.

September 1992, 111 TCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	0.23	0.14	99.63
16	0.01	0.01	99.98
17	0.08	0.04	99.88
18	0.02	0.01	99.97
19	0.02	0.02	99.96
20	0.10	0.06	99.83
21	0.01	0.00	99.99
22	1.75	1.05	97.19
23	0.09	0.05	99.86
24	3.12	1.88	95.00
27	0.18	0.11	99.70
28	0.00	0.00	100.00
29	1.23	0.74	98.02
30	0.46	0.28	99.26
31	0.11	0.07	99.82
32	0.08	0.05	99.87
33	0.00	0.00	100.00
34	14.28	8.57	77.14
35	0.00	0.00	100.00
36	0.30	0.18	99.52
37	0.12	0.07	99.81
40	0.00	0.00	0.00
42	0.01	0.01	99.98
43	5.88	3.53	90.59
44	0.26	0.16	99.58
45	0.00	0.00	100.00
46	0.01	0.00	99.99
47	0.06	0.04	99.90

*NA indicated the estimated variance was negative.

November 1990, TCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
20	0.00	0.00	0.00
12	0.00	0.00	0.00
21	0.69	12.28	87.04
16	0.03	0.51	99.46
17	0.00	0.00	0.00
15	0.00	0.00	0.00
18	NA	NA	NA
22	0.00	0.00	0.00
28	0.09	1.64	98.27
23	0.00	0.00	0.00
30	0.00	0.00	0.00
29	0.00	0.00	0.00
9	0.00	0.00	0.00
29	0.00	0.00	0.00
44	0.00	0.00	0.00
27	0.02	0.33	99.65
11	0.00	0.00	0.00
16	0.03	0.56	99.40
30	1.69	30.13	68.18

*NA indicated the estimated variance was negative.

May 1991, TCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
12	0.00	0.00	0.00
20	NA	NA	NA
15	0.00	0.00	0.00
18	NA	NA	NA
28	0.00	0.00	0.00
21	NA	NA	NA
17	0.13	90.24	9.62
22	0.00	0.00	0.00
23	0.00	0.00	0.00
27	0.12	78.56	21.32
24	0.00	0.00	0.00
29	0.00	0.00	0.00
30	NA	NA	NA
31	NA	NA	NA
16	NA	NA	NA
32	0.00	0.00	0.00
44	0.01	6.14	93.85
45	0.00	3.92	96.07
33	0.12	82.54	17.33
34	0.00	0.00	0.00
35	NA	NA	NA
36	NA	NA	NA
37	0.09	59.76	40.15
38	0.00	0.00	0.00
39	NA	NA	NA
48	0.00	0.00	0.00
11	0.00	0.00	0.00
42	NA	NA	NA
41	0.00	0.00	0.00
46	0.02	15.80	84.18
43	0.12	77.38	22.50
40	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

August 1991, TCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
46	0.61	1.21	98.17
43	0.39	0.77	98.84
12	NA	NA	NA
40	3.26	6.43	90.31
41	26.25	51.88	21.88
20	0.35	0.70	98.95
30	NA	NA	NA
29	1.35	2.68	95.97
48	5.60	11.07	83.33
42	0.33	0.65	99.01
39	0.27	0.53	99.20
19	4.80	9.48	85.71
23	NA	NA	NA
15	19.09	37.73	43.18
18	NA	NA	NA
28	0.15	0.30	99.54
24	NA	NA	NA
36	0.45	0.88	98.67
27	0.09	0.18	99.73
44	0.01	0.02	99.97
45	0.42	0.83	98.75
32	2.43	4.80	92.77
22	NA	NA	NA
33	NA	NA	NA
34	3.67	7.25	89.08
35	0.18	0.36	99.46
37	0.04	0.08	99.89
38	6.04	11.94	82.01
16	0.13	0.26	99.60
31	0.74	1.46	97.80
16A	NA	NA	NA
21	0.42	0.82	98.76
21A	0.07	0.14	99.79
17	2.54	5.03	92.42
17A	NA	NA	NA

*NA indicated the estimated variance was negative.

December 1991, TCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
35	0.72	2.20	97.07
33	NA	NA	NA
43	2.42	7.39	90.19
46	0.28	0.84	98.88
41	0.00	0.00	0.00
40	0.00	0.00	0.00
30	NA	NA	NA
20	NA	NA	NA
29	NA	NA	NA
42	0.92	2.81	96.26
48	0.00	0.00	0.00
39	0.87	2.66	96.47
19	NA	NA	NA
23	21.15	64.42	14.42
38	NA	NA	NA
16	2.39	7.28	90.33
31	0.09	0.28	99.63
21	0.75	2.29	96.95
36	0.74	2.24	97.02
24	NA	NA	NA
27	0.09	0.29	99.62
44	0.10	0.29	99.61
45	0.11	0.33	99.56
32	NA	NA	NA
22	NA	NA	NA
34	NA	NA	NA
37	NA	NA	NA
17	24.18	73.63	2.20
15	NA	NA	NA
18	0.27	0.82	98.86
28	0.04	0.11	99.86

*NA indicated the estimated variance was negative.

March 1992, TCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	NA	NA	NA
16	0.07	22.49	77.44
16A	0.02	6.96	93.01
17	NA	NA	NA
17A	NA	NA	NA
18	0.00	0.40	99.60
19	NA	NA	NA
20	NA	NA	NA
21	0.16	51.39	48.44
21A	0.19	62.38	37.42
22	NA	NA	NA
23	NA	NA	NA
24	NA	NA	NA
27	0.07	23.04	76.89
28	0.00	1.71	98.29
29	NA	NA	NA
30	NA	NA	NA
31	0.01	2.99	97.00
32	0.12	37.36	62.52
33	NA	NA	NA
34	NA	NA	NA
35	0.08	26.48	73.43
35A	0.02	6.57	93.41
36	0.10	31.14	68.76
37	0.01	2.62	97.37
38	NA	NA	NA
39	0.23	73.20	26.57
40	0.00	0.00	0.00
41	NA	NA	NA
42	NA	NA	NA
43	0.03	8.92	91.05
44	0.11	34.14	65.75
45	0.10	31.49	68.41
46	0.00	1.86	98.13
48	NA	NA	NA

*NA indicated the estimated variance was negative.

September 1992, TCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	0.35	0.00	99.65
16	0.12	0.00	99.87
17	1.09	0.01	98.90
18	1.35	0.01	98.64
19	0.00	0.00	0.00
20	8.33	0.08	91.58
21	1.54	0.02	98.45
22	0.00	0.00	0.00
23	0.00	0.00	0.00
24	0.00	0.00	0.00
27	0.64	0.01	99.35
28	0.02	0.00	99.98
29	0.00	0.00	0.00
30	0.12	0.00	99.88
31	0.02	0.00	99.98
32	1.10	0.01	98.89
33	0.12	0.00	99.88
34	0.00	0.00	0.00
35	0.04	0.00	99.95
36	0.16	0.00	99.84
37	0.25	0.00	99.74
40	0.00	0.00	0.00
42	0.07	0.00	99.93
43	25.00	0.25	74.75
44	0.22	0.00	99.77
45	0.03	0.00	99.97
46	0.04	0.00	99.96
47	5.56	0.06	94.39

*NA indicated the estimated variance was negative.

November 1990, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
20	0.12	3.26	96.62
12	0.00	0.00	0.00
21	0.13	3.32	96.56
16	0.00	0.07	99.93
17	0.00	0.00	0.00
15	0.00	0.00	0.00
18	0.10	2.53	97.38
22	0.00	0.00	0.00
28	0.01	0.37	99.62
23	0.00	0.00	0.00
30	0.00	0.00	0.00
29	0.00	0.00	0.00
9	0.00	0.00	0.00
29	0.00	0.00	0.00
44	0.00	0.00	0.00
27	0.00	0.08	99.92
11	0.00	0.00	0.00
16	0.00	0.08	99.91
30	0.03	0.81	99.16

*NA indicated the estimated variance was negative.

February 1991, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
21	1.50	2.47	96.02
16	0.26	0.42	99.32
15	0.86	1.41	97.73
22	10.60	17.40	72.00
23	19.63	32.22	48.15
17	1.46	2.40	96.14
27	0.21	0.34	99.45
28	0.15	0.25	99.60
19	0.00	0.00	0.00
20	0.27	0.44	99.28
30	6.31	10.36	83.33
29	0.00	0.00	0.00
24	0.00	0.00	0.00
18	0.02	0.03	99.95

*NA indicated the estimated variance was negative.

May 1991, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
12	0.00	0.00	0.00
20	0.02	0.07	99.91
15	0.15	0.59	99.25
18	0.01	0.04	99.95
28	0.20	0.78	99.01
21	0.10	0.37	99.53
17	1.56	5.94	92.50
22	0.00	0.00	0.00
23	0.00	0.00	0.00
27	0.12	0.47	99.40
24	0.00	0.00	0.00
29	0.00	0.00	0.00
30	1.00	3.80	95.20
31	0.06	0.21	99.74
16	0.36	1.36	98.28
32	0.02	0.09	99.89
44	0.00	0.02	99.98
45	0.01	0.04	99.95
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.26	1.01	98.72
36	0.57	2.16	97.27
37	0.06	0.24	99.69
38	0.26	1.01	98.72
39	0.31	1.17	98.52
48	0.00	0.00	0.00
11	0.00	0.00	0.00
42	0.12	0.46	99.42
41	0.00	0.00	0.00
46	0.06	0.22	99.71
43	0.00	0.00	0.00
40	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

August 1991, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
46	0.00	0.00	0.00
43	NA	NA	NA
12	0.00	0.00	0.00
40	0.13	1.63	98.24
41	5.00	61.67	33.33
20	0.00	0.04	99.96
30	0.87	10.72	88.40
29	0.00	0.00	0.00
48	0.00	0.00	0.00
42	0.14	1.74	98.12
39	0.56	6.85	92.59
19	0.00	0.00	0.00
23	0.00	0.00	0.00
15	NA	NA	NA
18	0.00	0.05	99.95
28	0.00	0.02	99.98
24	0.00	0.00	0.00
36	0.24	2.98	96.77
27	0.16	1.99	97.85
44	0.00	0.02	99.98
45	0.13	1.63	98.24
32	0.19	2.31	97.50
22	NA	NA	NA
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.13	1.59	98.28
37	0.10	1.26	98.64
38	NA	NA	NA
16	0.14	1.67	98.19
31	0.01	0.17	99.81
16A	0.01	0.08	99.91
21	0.19	2.33	97.48
21A	1.08	13.33	85.58
17	0.07	0.89	99.04
17A	0.59	7.33	92.08

*NA indicated the estimated variance was negative.

December 1991, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
35	0.02	0.39	99.59
33	0.00	0.00	0.00
43	NA	NA	NA
46	0.00	0.09	99.91
41	0.72	11.92	87.36
40	NA	NA	NA
30	NA	NA	NA
20	0.06	1.09	98.84
29	0.00	0.00	0.00
42	0.03	0.54	99.43
48	0.00	0.00	0.00
39	0.06	0.98	98.96
19	0.00	0.00	0.00
23	0.00	0.00	0.00
38	0.13	2.13	97.74
16	0.04	0.66	99.30
31	0.21	3.43	96.36
21	0.28	4.74	94.97
36	0.31	5.10	94.59
24	0.00	0.00	0.00
27	0.04	0.61	99.35
44	0.01	0.23	99.76
45	0.01	0.21	99.78
32	0.29	4.81	94.90
22	NA	NA	NA
34	0.00	0.00	0.00
37	0.81	13.39	85.81
17	0.35	5.83	93.82
15	NA	NA	NA
18	0.00	0.05	99.94
28	0.00	0.04	99.96

*NA indicated the estimated variance was negative.

March 1992, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	NA	NA	NA
16	0.00	0.08	99.92
16A	0.00	0.38	99.62
17	0.18	34.49	65.33
17A	NA	NA	NA
21	0.15	28.58	71.27
21A	0.26	50.22	49.51
22	NA	NA	NA
23	0.00	0.00	0.00
24	0.00	0.00	0.00
27	0.12	23.62	76.26
28	0.00	0.74	99.26
29	0.00	0.00	0.00
30	NA	NA	NA
31	0.01	1.58	98.41
32	NA	NA	NA
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.02	3.10	96.88
35A	0.02	4.79	95.18
36	0.05	10.49	89.45
37	0.01	2.38	97.61
38	0.10	18.88	81.02
39	0.22	43.11	56.67
40	NA	NA	NA
41	NA	NA	NA
42	0.00	0.27	99.73
43	NA	NA	NA
44	0.00	1.01	98.98
45	0.27	51.73	48.00
46	0.00	0.31	99.68
48	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

September 1992, c12 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	1.21	0.05	98.74
16	0.07	0.00	99.93
17	35.00	1.50	63.50
18	0.12	0.00	99.88
19	0.00	0.00	0.00
20	2.80	0.12	97.08
21	0.43	0.02	99.55
22	0.00	0.00	0.00
23	0.00	0.00	0.00
24	0.00	0.00	0.00
27	0.90	0.04	99.06
28	0.00	0.00	100.00
29	0.00	0.00	0.00
30	87.50	3.75	8.75
31	0.04	0.00	99.95
32	0.51	0.02	99.47
33	0.09	0.00	99.91
34	0.00	0.00	0.00
35	0.00	0.00	100.00
36	0.80	0.03	99.16
37	0.12	0.00	99.87
40	NA	NA	NA
42	0.09	0.00	99.91
43	NA	NA	NA
44	0.01	0.00	99.98
45	0.03	0.00	99.97
46	0.04	0.00	99.96
47	7.78	0.33	91.89

*NA indicated the estimated variance was negative.

November 1990, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
20	0.00	0.12	99.88
12	0.00	0.00	0.00
21	0.59	14.34	85.07
16	0.00	0.12	99.87
17	0.03	0.85	99.12
15	0.06	1.40	98.54
18	0.18	4.27	95.56
22	0.00	0.00	0.00
28	0.01	0.17	99.83
23	0.00	0.00	0.00
30	0.00	0.00	0.00
29	0.00	0.00	0.00
9	0.00	0.00	0.00
29	0.00	0.00	0.00
44	0.00	0.00	0.00
27	0.00	0.12	99.88
11	0.00	0.00	0.00
16	0.00	0.14	99.86
30	0.06	1.45	98.49

*NA indicated the estimated variance was negative.

February 1991, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
21	3.36	1.56	95.08
16	0.37	0.17	99.45
15	7.32	3.39	89.28
22	3.98	1.84	94.17
23	NA	NA	NA
17	1.45	0.67	97.87
27	0.33	0.15	99.52
28	0.13	0.06	99.80
19	0.00	0.00	0.00
20	0.02	0.01	99.97
30	13.22	6.13	80.64
29	0.00	0.00	0.00
24	0.00	0.00	0.00
18	0.08	0.04	99.89

*NA indicated the estimated variance was negative.

May 1991, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
12	0.00	0.00	0.00
20	0.00	0.05	99.94
15	0.05	1.13	98.81
18	0.02	0.46	99.52
28	0.11	2.70	97.18
21	0.05	1.27	98.67
17	0.12	2.93	96.94
22	0.00	0.00	0.00
23	0.00	0.00	0.00
27	0.64	15.07	84.28
24	0.00	0.00	0.00
29	0.00	0.00	0.00
30	0.82	19.18	80.00
31	0.01	0.16	99.83
16	0.15	3.58	96.27
32	2.25	52.75	45.00
44	0.00	0.08	99.92
45	0.00	0.11	99.88
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.12	2.78	97.10
36	0.00	0.00	0.00
37	0.02	0.46	99.52
38	0.43	10.05	89.52
39	1.28	30.14	68.57
48	0.00	0.00	0.00
11	0.00	0.00	0.00
42	0.02	0.52	99.46
41	0.01	0.33	99.65
46	0.18	4.22	95.60
43	0.38	8.79	90.83
40	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

August 1991, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
46	0.00	0.00	0.00
43	0.68	3.73	95.59
12	0.00	0.00	0.00
40	2.02	11.11	86.87
41	0.37	2.03	97.60
20	0.00	0.00	100.00
30	0.18	0.96	98.86
29	0.00	0.00	0.00
48	0.00	0.00	0.00
42	6.67	36.67	56.67
39	0.34	1.85	97.82
19	0.00	0.00	0.00
23	1.08	5.91	93.01
15	0.64	3.55	95.81
18	0.01	0.07	99.91
28	0.00	0.01	99.98
24	0.00	0.00	0.00
36	0.10	0.56	99.34
27	0.02	0.09	99.90
44	0.00	0.02	99.98
45	0.40	2.22	97.38
32	0.04	0.23	99.73
22	0.03	12.50	68.75
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.16	0.87	98.98
37	0.02	0.14	99.84
38	0.09	0.50	99.41
16	0.07	0.41	99.51
31	0.07	0.39	99.54
16A	10.00	55.00	35.00
21	0.19	1.03	98.78
21A	0.20	1.12	98.67
17	0.03	0.15	99.82
17A	0.33	1.84	97.83

*NA indicated the estimated variance was negative.

December 1991, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
35	0.60	6.00	93.40
33	0.00	0.00	0.00
43	NA	NA	NA
46	0.67	6.68	92.65
41	0.66	6.57	92.78
40	6.25	62.50	31.25
30	NA	NA	NA
20	0.00	0.01	99.99
29	0.00	0.00	0.00
42	0.82	8.23	90.95
48	0.00	0.00	0.00
39	0.10	1.03	98.86
19	0.00	0.00	0.00
23	NA	NA	NA
38	0.13	1.27	98.60
16	0.14	1.42	98.43
31	0.17	1.68	98.15
21	0.40	4.01	95.59
36	0.55	5.52	93.92
24	0.00	0.00	0.00
27	0.16	1.58	98.26
44	0.23	2.28	97.50
45	0.13	1.34	98.53
32	0.37	3.69	95.94
22	NA	NA	NA
34	0.00	0.00	0.00
37	8.33	83.33	8.33
17	1.00	9.95	89.05
15	NA	NA	NA
18	0.05	0.54	99.41
28	0.01	0.07	99.92

*NA indicated the estimated variance was negative.

March 1992, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	0.26	8.77	90.97
16	0.00	0.07	99.93
16A	0.04	1.42	98.53
17	0.05	1.59	98.36
17A	0.22	7.34	92.45
18	0.00	0.02	99.97
19	0.00	0.00	0.00
20	0.00	0.02	99.98
21	NA	NA	NA
21A	0.62	21.25	78.12
22	NA	NA	NA
23	0.00	0.00	0.00
24	0.00	0.00	0.00
27	NA	NA	NA
28	0.00	0.06	99.94
29	0.00	0.00	0.00
30	0.42	14.42	85.16
31	0.29	9.76	89.95
32	0.09	3.18	96.73
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.09	3.10	96.81
35A	0.04	1.31	98.65
36	0.15	4.98	94.88
37	0.00	0.08	99.92
38	0.04	1.24	98.72
39	NA	NA	NA
40	NA	NA	NA
41	0.07	2.34	97.59
42	0.03	0.94	99.03
43	1.02	34.87	64.10
44	0.01	0.30	99.69
45	0.07	2.29	97.64
46	0.02	0.62	99.36
48	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

September 1992, 11 DCA

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	0.56	0.22	99.22
16	NA	NA	NA
17	0.07	0.03	99.91
18	0.32	0.13	99.55
19	0.00	0.00	0.00
20	0.02	0.01	99.97
21	0.07	0.03	99.90
22	1.32	0.53	98.16
23	0.00	0.00	0.00
24	0.00	0.00	0.00
27	4.17	1.67	94.17
28	0.00	0.00	100.00
29	0.00	0.00	0.00
30	NA	NA	NA
31	0.13	0.05	99.82
32	0.38	0.15	99.46
33	0.03	0.01	99.96
34	0.00	0.00	0.00
35	0.02	0.01	99.97
36	2.50	1.00	96.50
37	1.47	0.59	97.94
40	0.91	0.36	98.73
42	0.16	0.06	99.78
43	25.00	10.00	65.00
44	0.02	0.01	99.97
45	0.04	0.01	99.95
46	10.00	4.00	86.00
47	NA	NA	NA

*NA indicated the estimated variance was negative.

November 1990, 11 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
20	NA	NA	NA
12	0.00	0.00	0.00
21	0.33	7.50	92.17
16	0.04	0.82	99.15
17	0.15	3.43	96.42
15	0.00	0.00	0.00
18	0.08	1.78	98.14
22	0.00	0.00	0.00
28	0.04	0.90	99.06
23	0.00	0.00	0.00
30	0.00	0.00	0.00
29	0.00	0.00	0.00
9	0.00	0.00	0.00
29	0.00	0.00	0.00
44	0.00	0.00	0.00
27	0.02	0.51	99.46
11	0.00	0.00	0.00
16	0.02	0.54	99.44
30	0.18	4.20	95.62

*NA indicated the estimated variance was negative.

February 1991, 11 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
21	12.78	5.28	81.94
16	3.91	1.62	94.47
15	17.04	7.04	75.92
22	57.50	23.75	18.75
23	NA	NA	NA
17	0.44	0.18	99.38
27	0.51	0.21	99.28
28	0.34	0.14	99.52
19	NA	NA	NA
20	1.27	0.53	98.20
30	17.04	7.04	75.92
29	0.00	0.00	0.00
24	NA	NA	NA
18	0.22	0.09	99.70

*NA indicated the estimated variance was negative.

May 1991, 11 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
19	0.00	0.00	0.00
12	0.00	0.00	0.00
20	0.11	0.31	99.58
15	0.00	0.00	0.00
18	0.24	0.70	99.05
28	0.40	1.16	98.44
21	2.40	6.93	90.67
17	0.00	0.00	0.00
22	0.00	0.00	0.00
23	0.00	0.00	0.00
27	0.32	0.93	98.75
24	0.00	0.00	0.00
29	0.00	0.00	0.00
30	9.00	26.00	65.00
31	0.04	0.13	99.82
16	0.70	2.04	97.25
32	0.00	0.00	0.00
44	0.04	0.10	99.86
45	0.02	0.06	99.92
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.82	2.36	96.82
36	0.00	0.00	0.00
37	7.20	20.80	72.00
38	1.71	4.95	93.33
39	5.14	14.86	80.00
48	0.00	0.00	0.00
11	0.00	0.00	0.00
42	0.09	0.26	99.66
41	0.00	0.00	0.00
46	0.02	0.05	99.93
43	1.33	3.85	94.81
40	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

August 1991, 11 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
46	0.00	0.00	0.00
43	0.73	0.86	98.41
12	0.00	0.00	0.00
40	0.00	0.00	0.00
41	0.00	0.00	0.00
20	0.02	0.03	99.94
30	2.96	3.49	93.55
29	0.00	0.00	0.00
48	0.00	0.00	0.00
42	0.60	0.70	98.70
39	0.16	0.19	99.64
19	0.00	0.00	0.00
23	16.77	19.76	63.47
15	0.00	0.00	0.00
18	0.12	0.14	99.74
28	0.72	0.84	98.44
24	0.00	0.00	0.00
36	3.55	4.19	92.26
27	0.06	0.07	99.87
44	0.09	0.10	99.81
45	0.38	0.45	99.16
32	0.00	0.00	0.00
22	NA	NA	NA
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	0.61	0.72	98.66
37	0.03	0.03	99.94
38	1.34	1.58	97.08
16	0.07	0.09	99.84
31	NA	NA	NA
16A	0.08	0.09	99.83
21	1.80	2.12	96.08
21A	0.18	0.21	99.62
17	1.50	1.76	96.74
17A	1.45	1.71	96.84

*NA indicated the estimated variance was negative.

December 1991, 11 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
35	3.60	3.17	93.23
33	0.00	0.00	0.00
43	17.79	15.65	66.55
46	0.05	0.05	99.90
41	0.00	0.00	0.00
40	0.00	0.00	0.00
30	NA	NA	NA
20	2.19	1.92	95.89
29	0.00	0.00	0.00
42	0.39	0.34	99.27
48	0.00	0.00	0.00
39	0.48	0.42	99.10
19	0.00	0.00	0.00
23	NA	NA	NA
38	7.95	7.00	85.05
16	8.77	7.72	83.51
31	0.12	0.11	99.77
21	NA	NA	NA
36	1.23	1.09	97.68
24	0.00	0.00	0.00
27	0.30	0.27	99.43
44	0.61	0.54	98.85
45	0.10	0.09	99.81
32	0.00	0.00	0.00
22	NA	NA	NA
34	0.00	0.00	0.00
37	35.97	31.65	32.37
17	3.88	3.41	92.71
15	NA	NA	NA
18	0.08	0.07	99.84
28	0.05	0.04	99.91

*NA indicated the estimated variance was negative.

March 1992, 11 DCE

Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	NA	NA	NA
16	0.01	0.50	99.49
16A	0.01	0.54	99.45
17	NA	NA	NA
17A	NA	NA	NA
18	0.03	1.31	98.66
19	0.00	0.00	0.00
20	0.06	2.83	97.11
21	NA	NA	NA
21A	NA	NA	NA
22	NA	NA	NA
23	NA	NA	NA
24	0.00	0.00	0.00
27	1.98	96.53	1.48
28	0.09	4.53	95.37
29	0.00	0.00	0.00
30	NA	NA	NA
31	0.01	0.45	99.54
32	0.00	0.00	0.00
33	0.00	0.00	0.00
34	0.00	0.00	0.00
35	NA	NA	NA
35A	0.27	13.37	86.35
36	0.07	3.34	96.59
37	0.06	3.14	96.80
38	NA	NA	NA
39	NA	NA	NA
40	0.00	0.00	0.00
41	0.00	0.00	0.00
42	0.04	2.05	97.91
43	0.10	4.86	95.04
44	NA	NA	NA
45	0.30	14.48	85.23
46	0.01	0.59	99.40
48	0.00	0.00	0.00

*NA indicated the estimated variance was negative.

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Percentage of variance attributable to laboratory error, field error, and natural variability

Well #	Laboratory %	Field %	Natural %
12	0.00	0.00	0.00
15	0.00	0.00	0.00
16	0.87	0.09	99.04
17	0.36	0.04	99.60
18	13.19	1.32	85.49
19	0.00	0.00	0.00
20	48.00	4.80	47.20
21	0.39	0.04	99.57
22	0.00	0.00	0.00
23	NA	NA	NA
24	0.00	0.00	0.00
27	25.00	2.50	72.50
28	0.53	0.05	99.41
29	0.00	0.00	0.00
30	1.81	0.18	98.00
31	NA	NA	NA
32	0.00	0.00	0.00
33	7.41	0.74	91.85
34	0.00	0.00	0.00
35	0.65	0.06	99.28
36	NA	NA	NA
37	5.77	0.58	93.65
40	0.00	0.00	0.00
42	85.71	8.57	5.71
43	2.65	0.26	97.09
44	0.44	0.04	99.51
45	0.15	0.01	99.84
46	0.57	0.06	99.37
47	NA	NA	NA

*NA indicated the estimated variance was negative.

Appendix B

Descriptive Statistics

Descriptive Statistics for 111 TCA

	Nov 90	Feb 91	May 91	Aug 91	Dec 91	Mar 92	Sept 92
Mean	73.737	78.573	113.319	143.835	119.612	177.645	129.761
Std. Dev.	98.662	97.193	125.333	143.962	111.996	171.689	116.247
Std. Error	24.666	25.095	21.818	24.334	19.798	28.615	21.969
Count	16	15	33	35	32	36	28
Minimum	0.000	1.600	0.000	0.000	0.000	0.000	0.000
Maximum	320.830	348.620	471.310	459.550	288.120	622.730	310.090
# Missing	22	23	5	3	6	2	10
Variance	9.734E3	9.447E3	1.571E4	2.073E4	1.254E4	2.948E4	1.351E4
Coef. Var.	1.338	1.237	1.106	1.001	.936	.966	.896
Range	320.830	347.020	471.310	459.550	288.120	622.730	310.090
Sum	1179.79	1178.6	3739.52	5034.220	3827.57	6395.220	3633.31
Sum Squares	2.33E5	2.249E5	9.264E5	1.429E6	8.467E5	2.168E6	8.363E5
Geom. Mean	•	35.291	•	•	•	•	•
Harm. Mean	•	11.968	•	•	•	•	•
Skewness	1.294	1.662	1.045	.721	.384	.673	.358
Kurtosis	.479	1.993	.197	-.965	-1.556	-.645	-1.537
Median	36.495	32.580	42.220	77.390	63.375	93.665	85.745
IQR	126.860	102.860	190.323	256.855	221.980	312.300	230.845
Mode	0.000	•	0.000	0.000	0.000	0.000	0.000
10% Tr. Mean	61.354	63.722	96.880	131.735	114.000	163.386	125.772
MAD	36.495	27.190	42.220	75.380	62.995	92.850	82.945

Descriptive Statistics for TCE

	Nov 90	Feb 91	May 91	Aug 91	Dec 91	Mar 92	Sept 92
Mean	8.652	16.270	28.458	42.921	36.104	37.398	39.005
Std. Dev.	15.513	23.808	35.119	44.427	42.262	41.677	42.354
Std. Error	3.762	6.147	6.113	7.510	7.471	6.946	8.004
Count	17	15	33	35	32	36	28
Minimum	0.000	0.000	0.000	1.140	0.000	0.000	0.000
Maximum	44.970	75.440	108.200	139.160	132.060	153.330	128.220
# Missing	21	23	5	3	6	2	10
Variance	2.41E2	566.805	1233.37	1973.747	1.786E3	1737.005	1.794E3
Coef. Var.	1.793	1.463	1.234	1.035	1.171	1.114	1.086
Range	44.970	75.440	108.200	138.020	132.060	153.330	128.220
Sum	147.09	244.050	939.120	1502.220	1155.34	1346.330	1092.13
Sum Squares	5.12E3	1.191E4	6.619E4	1.316E5	9.708E4	1.111E5	9.103E4
Geom. Mean	•	•	•	18.525	•	•	•
Harm. Mean	•	•	•	6.940	•	•	•
Skewness	1.430	1.351	.921	.725	.829	.888	.561
Kurtosis	.392	.584	-.437	-.893	-.578	-.196	-1.207
Median	0.000	1.990	12.490	22.980	13.000	23.990	20.160
IQR	12.540	29.645	53.642	79.083	70.455	77.345	84.910
Mode	0.000	0.000	0.000	•	0.000	0.000	0.000
10% Tr. Mean	6.808	12.970	23.640	38.328	30.628	32.908	35.906
MAD	0.000	1.990	12.490	20.940	13.000	23.680	20.160

Descriptive Statistics for c12 DCE

	Nov 90	Feb 91	May 91	Aug 91	Dec 91	Mar 92	Sept 92
Mean	30.279	27.183	33.775	52.154	54.557	56.301	62.100
Std. Dev.	50.712	37.258	42.689	64.387	69.487	63.818	67.288
Std. Error	12.299	9.620	7.431	10.883	12.284	10.636	13.196
Count	17	15	33	35	32	36	26
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	135.790	118.180	148.380	228.370	245.180	226.330	186.440
# Missing	21	23	5	3	6	2	12
Variance	2.572E3	1.388E3	1.822E3	4.146E3	4.828E3	4.073E3	4.528E3
Coef. Var.	1.675	1.371	1.264	1.235	1.274	1.134	1.084
Range	135.790	118.180	148.380	228.370	245.180	226.330	186.440
Sum	514.740	407.750	1114.58	1825.4	1745.83	2026.84	1614.6
Sum Squares	5.673E4	3.052E4	9.596E4	2.362E5	2.449E5	2.567E5	2.135E5
Geom. Mean	•	•	•	•	•	•	•
Harm. Mean	•	•	•	•	•	•	•
Skewness	1.326	1.285	1.043	1.134	1.248	.924	.601
Kurtosis	.060	.467	-.079	.153	.506	-.261	-1.171
Median	0.000	10.190	11.150	26.470	22.690	28.430	32.330
IQR	43.550	49.215	61.345	92.573	95.380	111.020	118.760
Mode	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10% Tr. Mean	25.263	22.275	27.816	42.927	43.032	48.556	56.732
MAD	0.000	10.190	11.150	26.470	22.690	28.430	32.330

Descriptive Statistics for 11 DCA

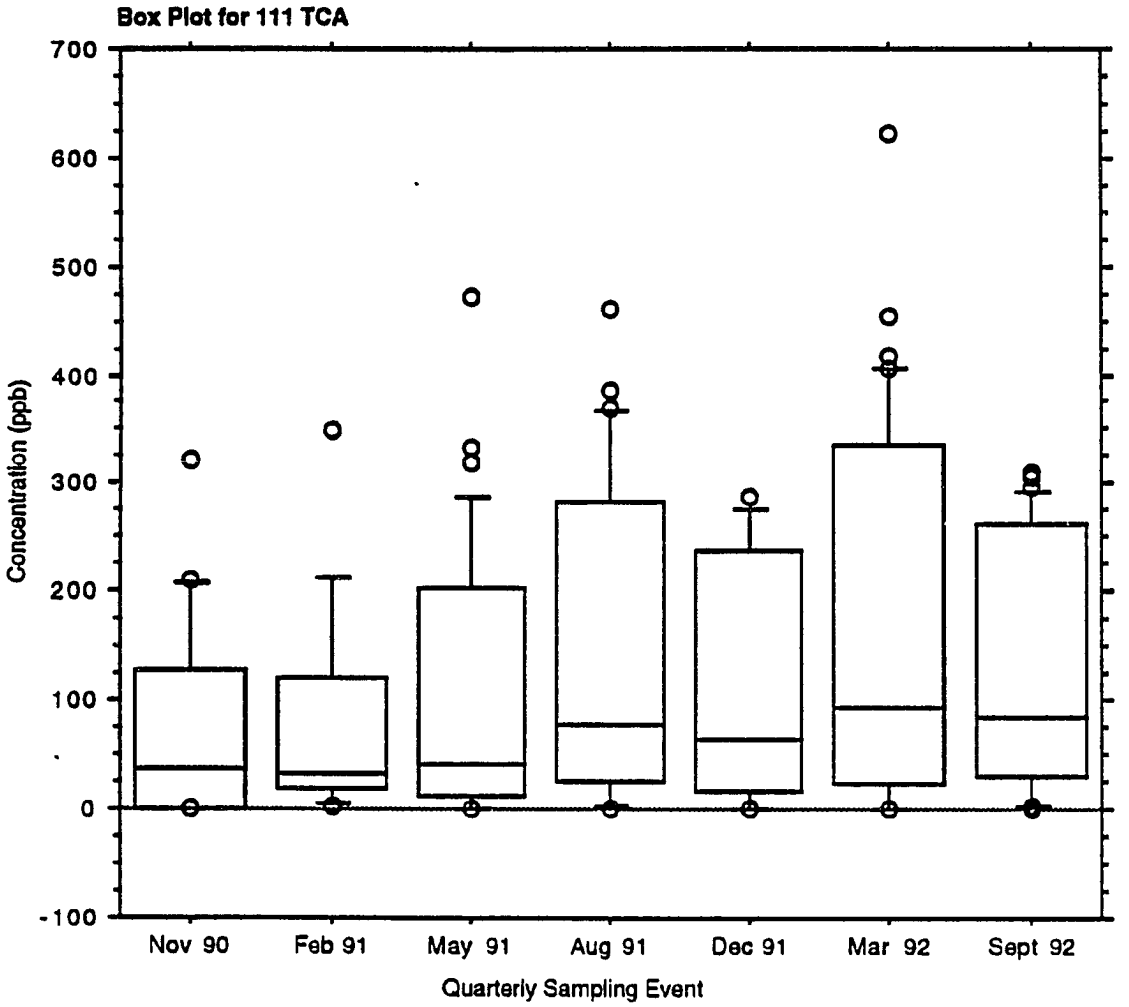
	Nov 90	Feb 91	May 91	Aug 91	Dec 91	Mar 92	Sept 92
Mean	33.894	39.071	30.691	51.724	43.712	68.192	42.564
Std. Dev.	51.417	62.085	39.917	73.266	61.789	82.334	63.117
Std. Error	12.471	16.030	6.949	12.384	10.923	13.722	12.147
Count	17	15	33	35	32	36	27
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	144.130	234.190	185.340	377.530	320.570	425.740	314.040
# Missing	21	23	5	3	6	2	11
Variance	2.644E3	3.855E3	1.593E3	5367.957	3817.920	6778.932	3983.725
Coef. Var.	1.517	1.589	1.301	1.416	1.414	1.207	1.483
Range	144.130	234.190	185.340	377.530	320.570	425.740	314.040
Sum	576.190	586.060	1012.79	1810.340	1398.790	2454.910	1149.240
Sum Squares	6.183E4	7.686E4	8.21E4	2.761E5	1.795E5	4.047E5	1.525E5
Geom. Mean	•	•	•	•	•	•	•
Harm. Mean	•	•	•	•	•	•	•
Skewness	1.201	2.260	2.078	2.771	2.970	2.414	3.069
Kurtosis	-.148	4.611	5.079	9.359	10.691	7.919	10.815
Median	0.000	12.820	13.750	26.580	26.505	63.860	17.870
IQR	62.025	48.900	47.847	81.077	56.725	98.255	58.573
Mode	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10% Tr. Mean	28.804	27.067	23.186	37.983	32.312	55.312	31.553
MAD	0.000	12.820	13.750	26.580	26.485	52.200	17.870

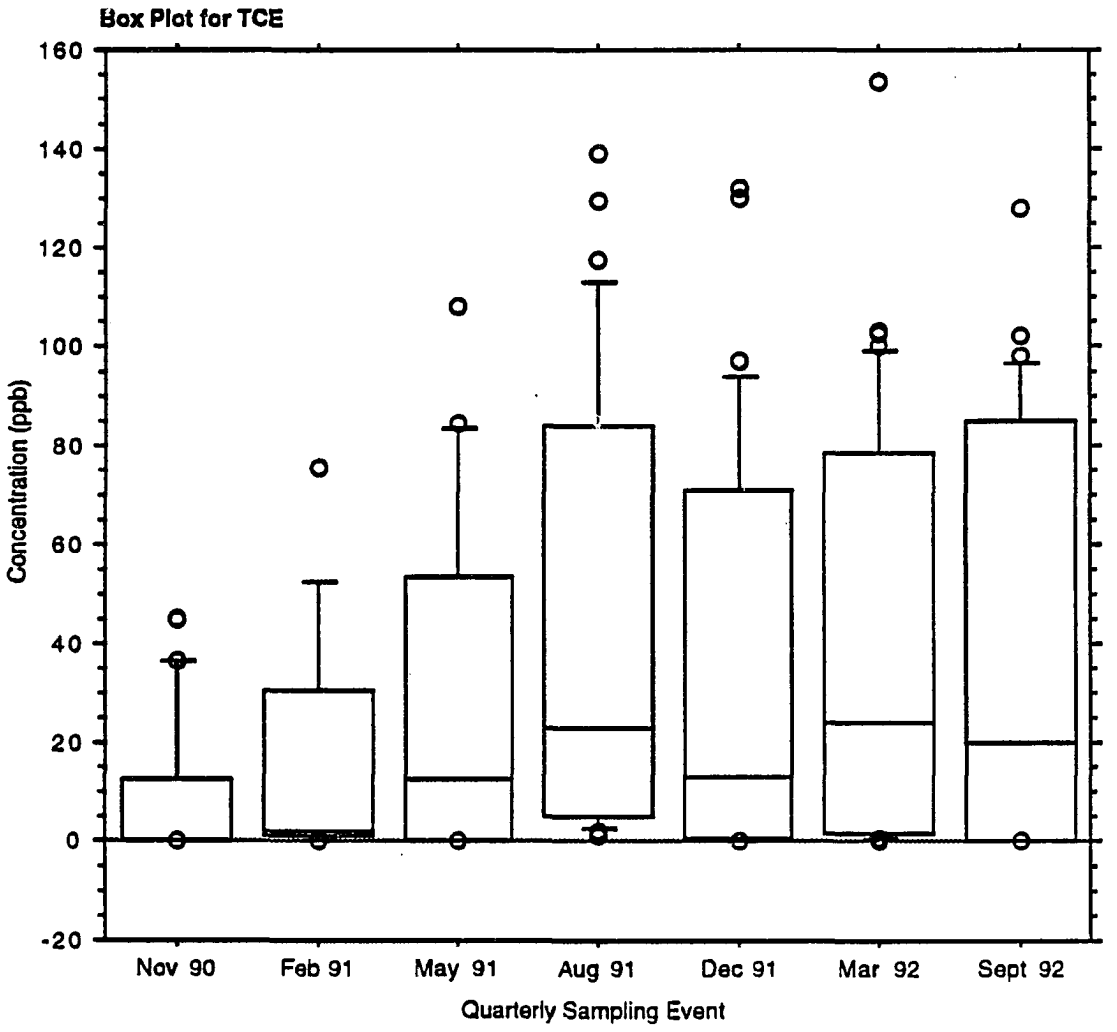
Descriptive Statistics for 11 DCE

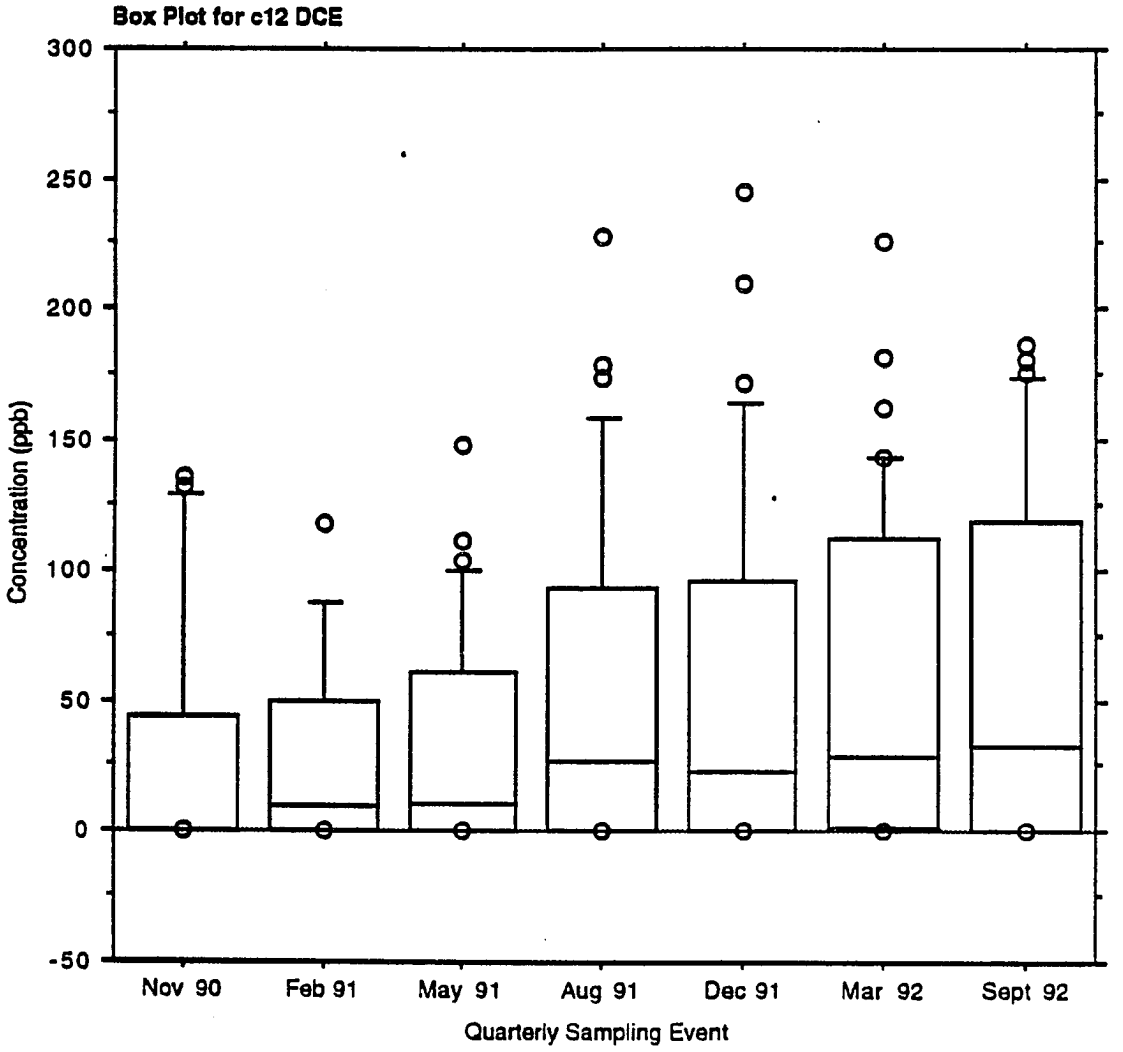
	Nov 90	Feb 91	May 91	Aug 91	Dec 91	Mar 92	Sept 92
Mean	10.676	8.873	14.590	18.890	19.367	21.268	20.619
Std. Dev.	17.682	10.446	19.240	24.280	25.209	25.435	24.155
Std. Error	4.289	2.697	3.349	4.104	4.456	4.239	4.649
Count	17	15	33	35	32	36	27
Minimum	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Maximum	51.100	28.470	88.060	97.630	101.310	107.660	96.070
# Missing	21	23	5	3	6	2	11
Variance	312.652	109.109	370.164	589.522	635.485	646.918	583.465
Coef. Var.	1.656	1.177	1.319	1.285	1.302	1.196	1.171
Range	51.100	28.470	88.060	97.630	101.310	107.660	96.070
Sum	181.480	133.090	481.460	661.140	619.740	765.660	556.710
Sum Squares	6.94E3	2.708E3	1.887E4	3.25E4	3.17E4	3.893E4	2.665E4
Geom. Mean	•	•	•	•	•	•	•
Harm. Mean	•	•	•	•	•	•	•
Skewness	1.395	.841	1.863	1.374	1.473	1.416	1.239
Kurtosis	.342	-.802	4.405	1.428	1.760	1.931	1.381
Median	0.000	4.170	6.440	6.310	8.080	11.315	6.960
IQR	13.743	17.673	25.777	32.557	35.970	39.490	38.417
Mode	0.000	0.000	0.000	0.000	0.000	0.000	0.000
10% Tr. Mean	8.693	8.048	11.367	15.286	14.955	17.639	17.788
MAD	0.000	4.170	6.440	6.310	8.080	11.315	6.960

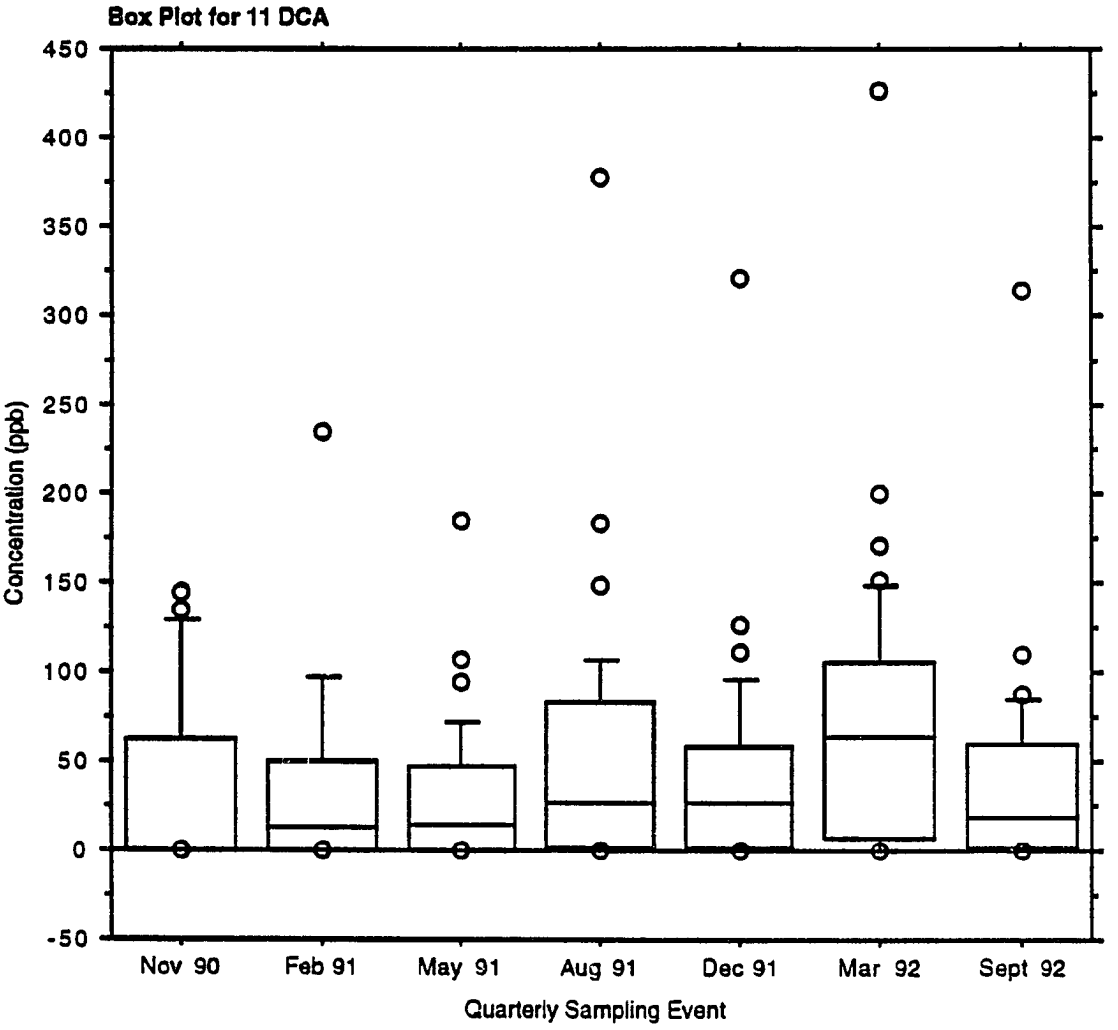
Appendix C

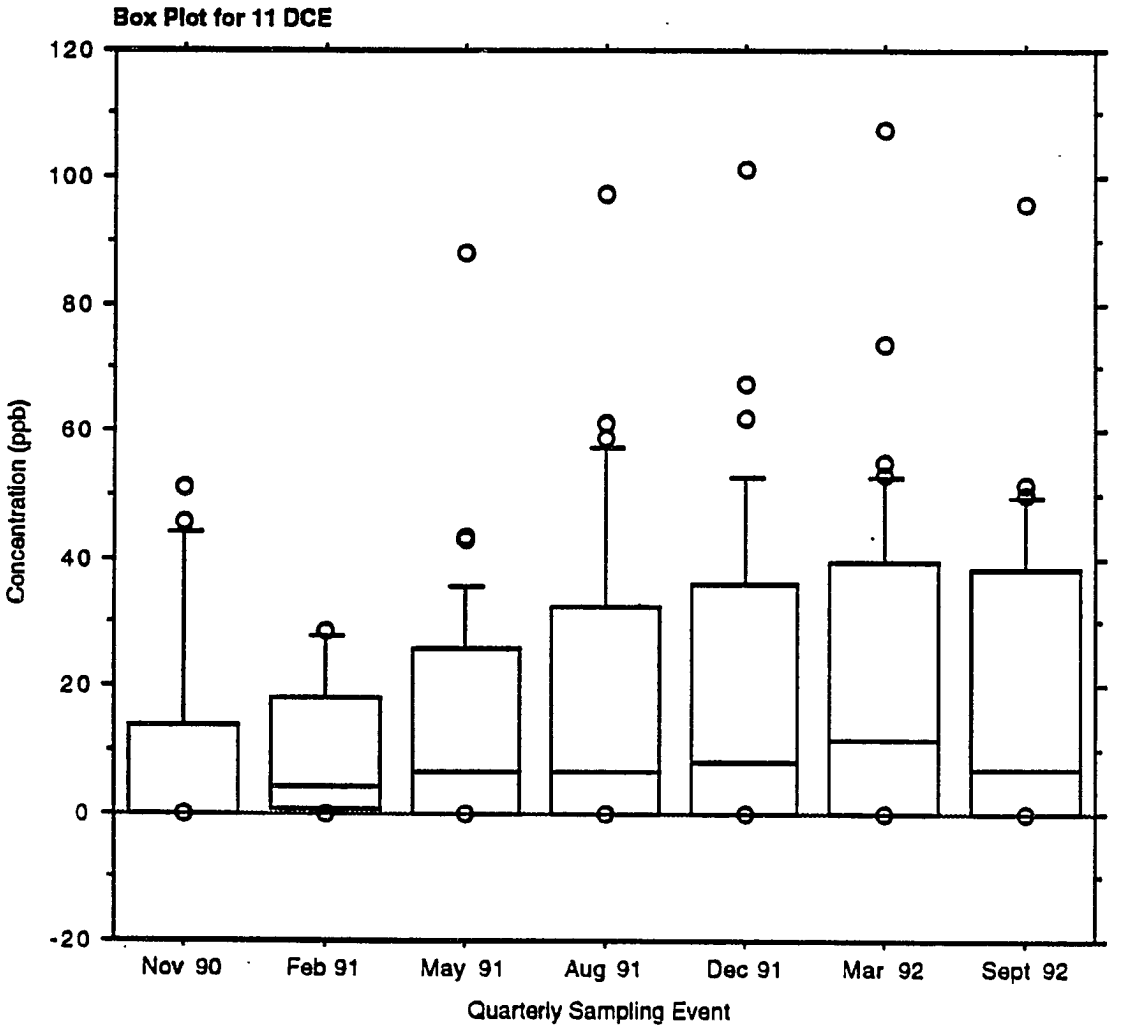
Box Plots





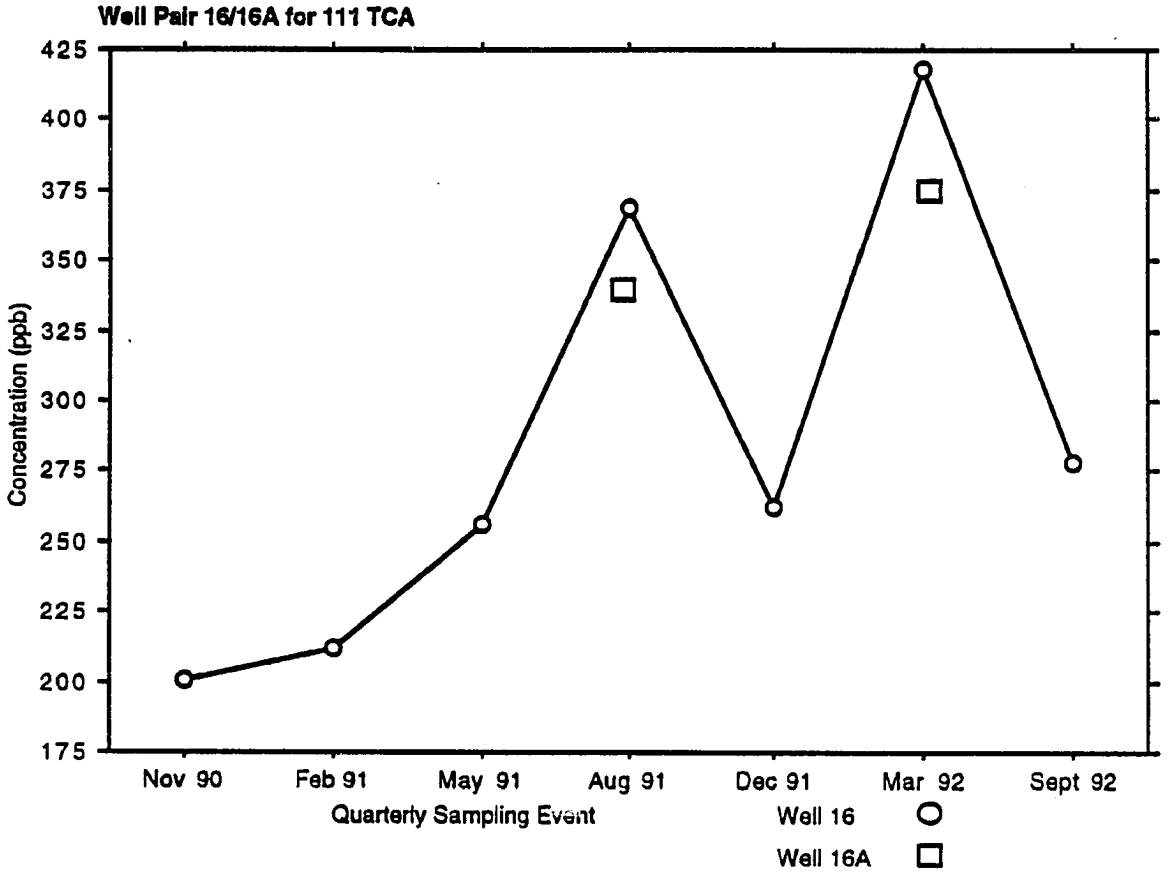


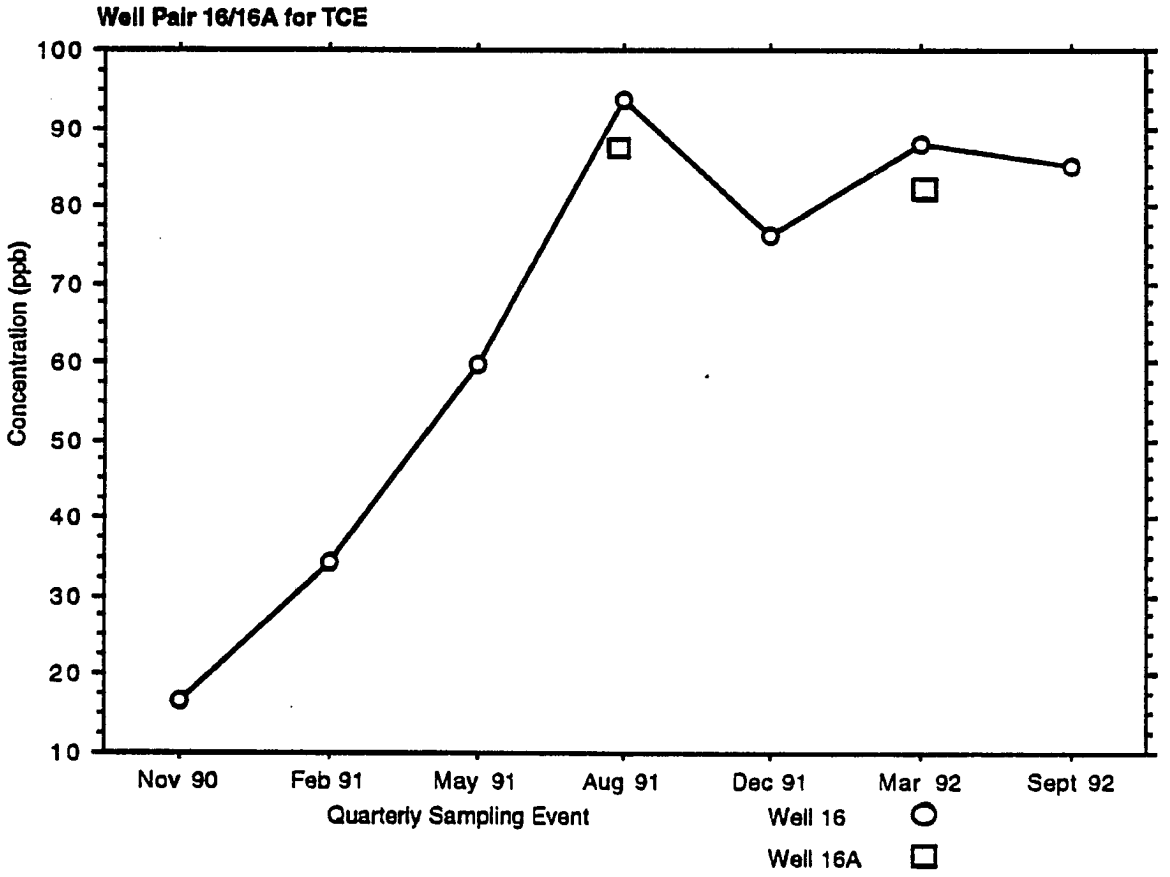


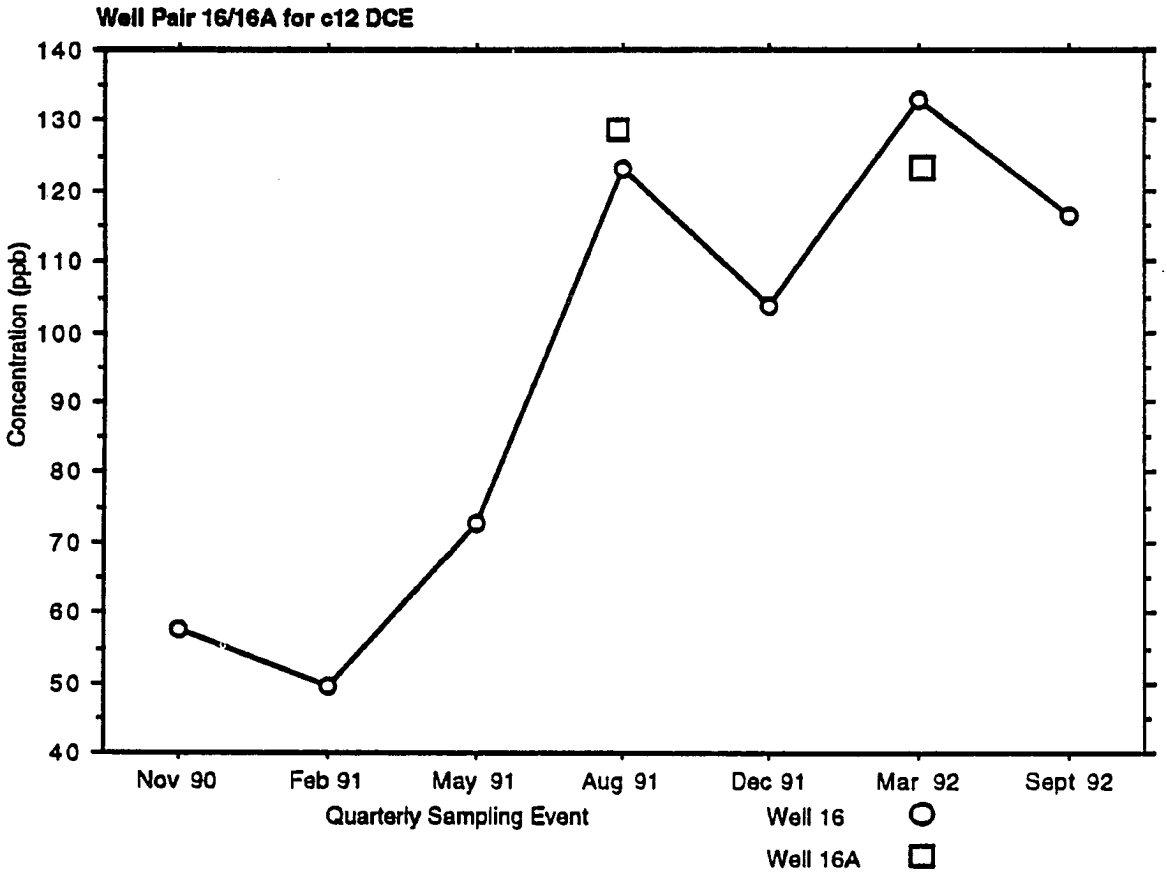


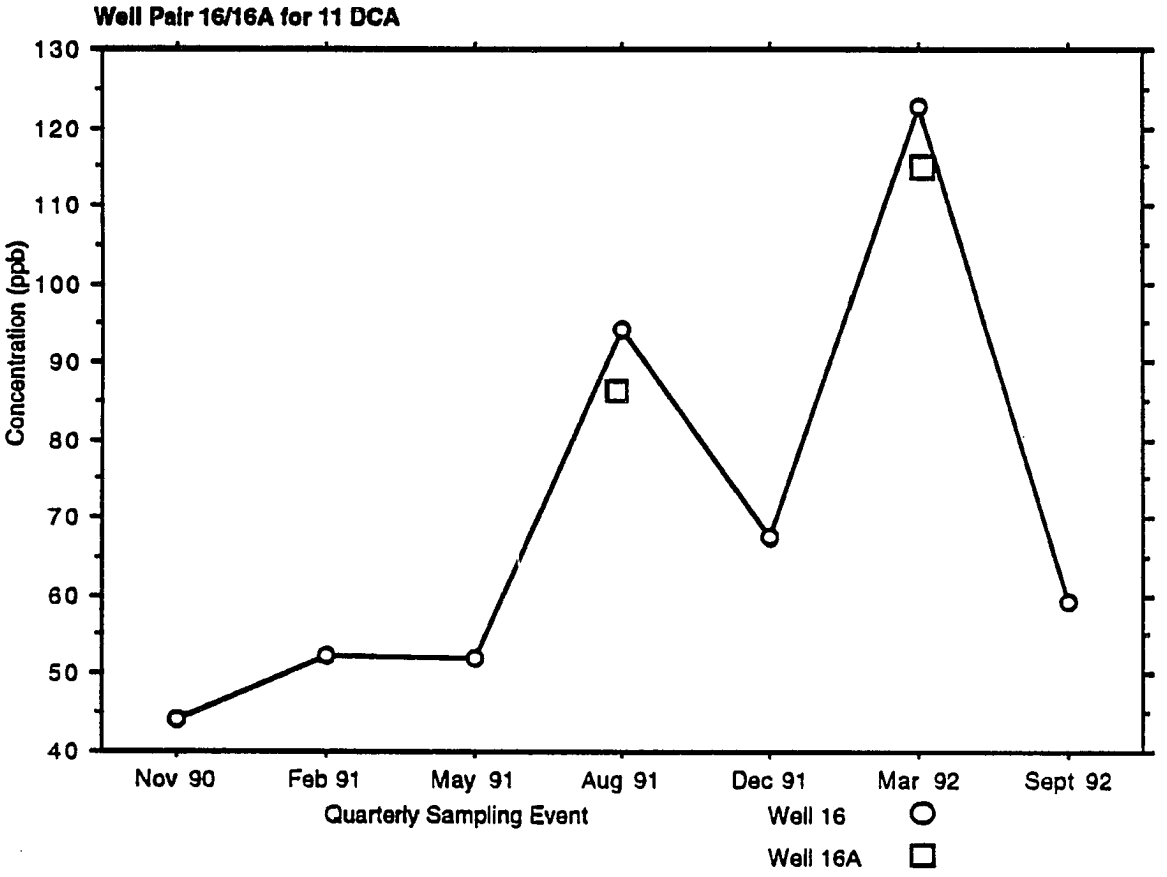
Appendix D

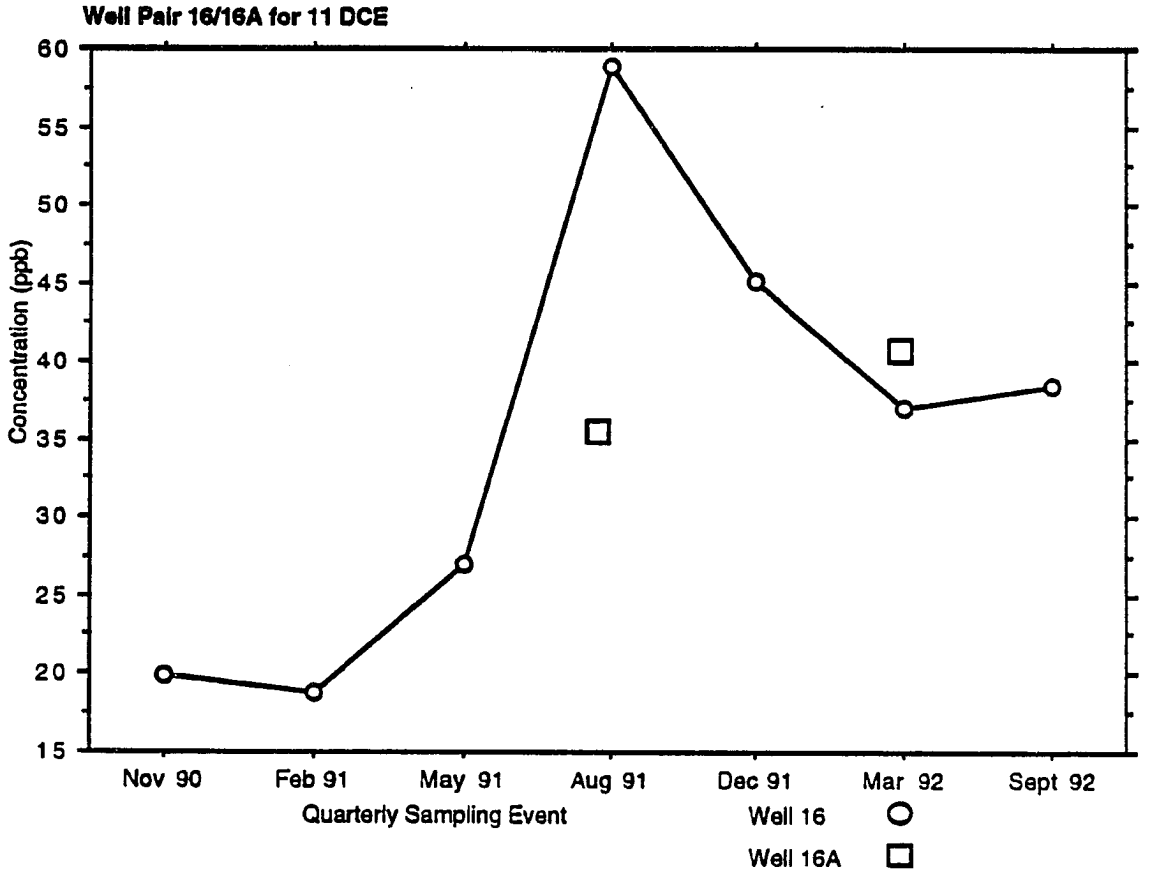
Well Pairs

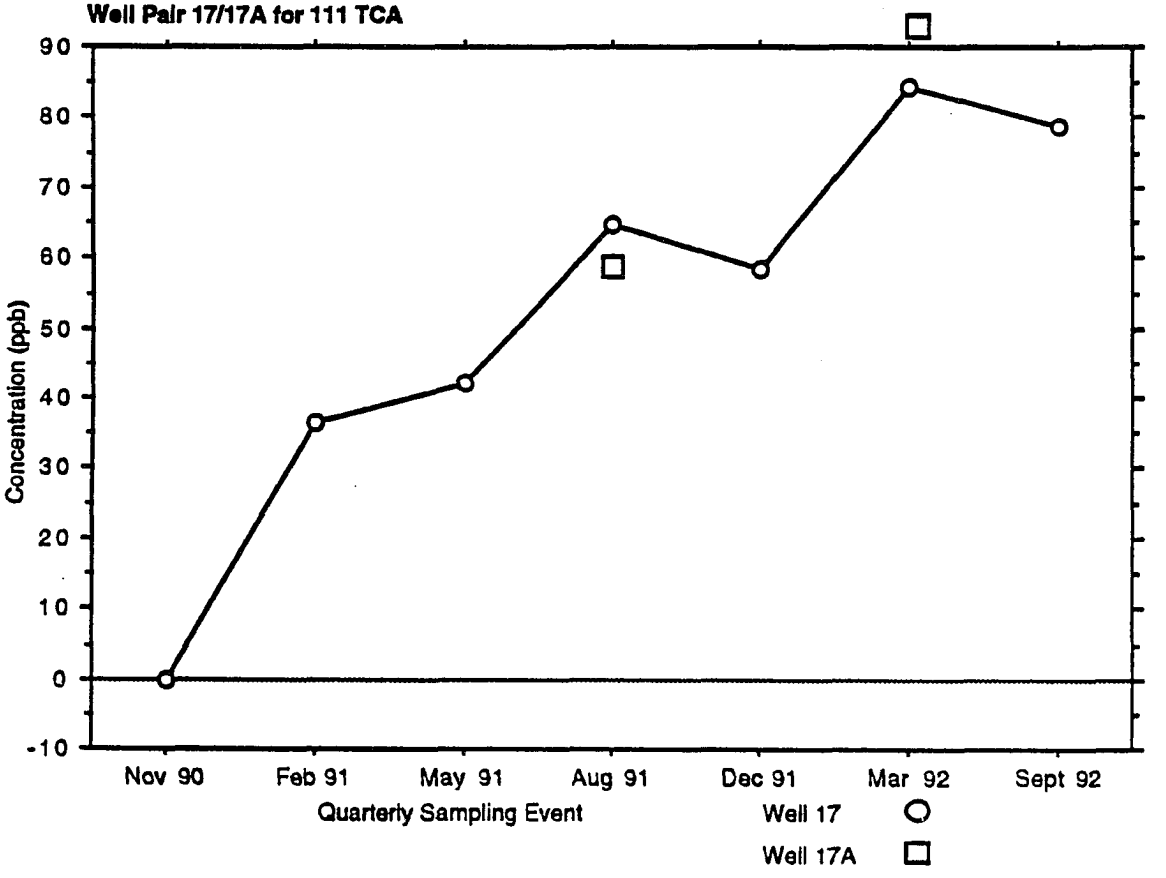


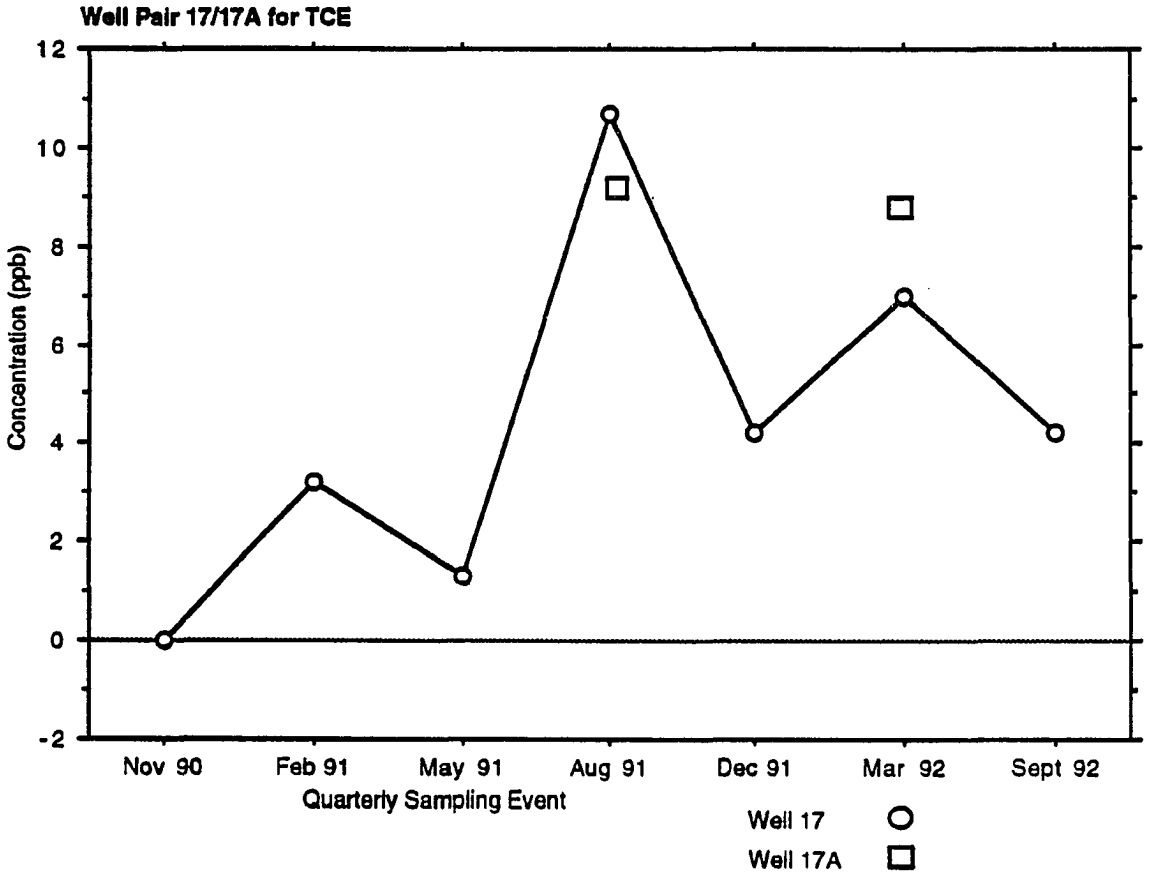


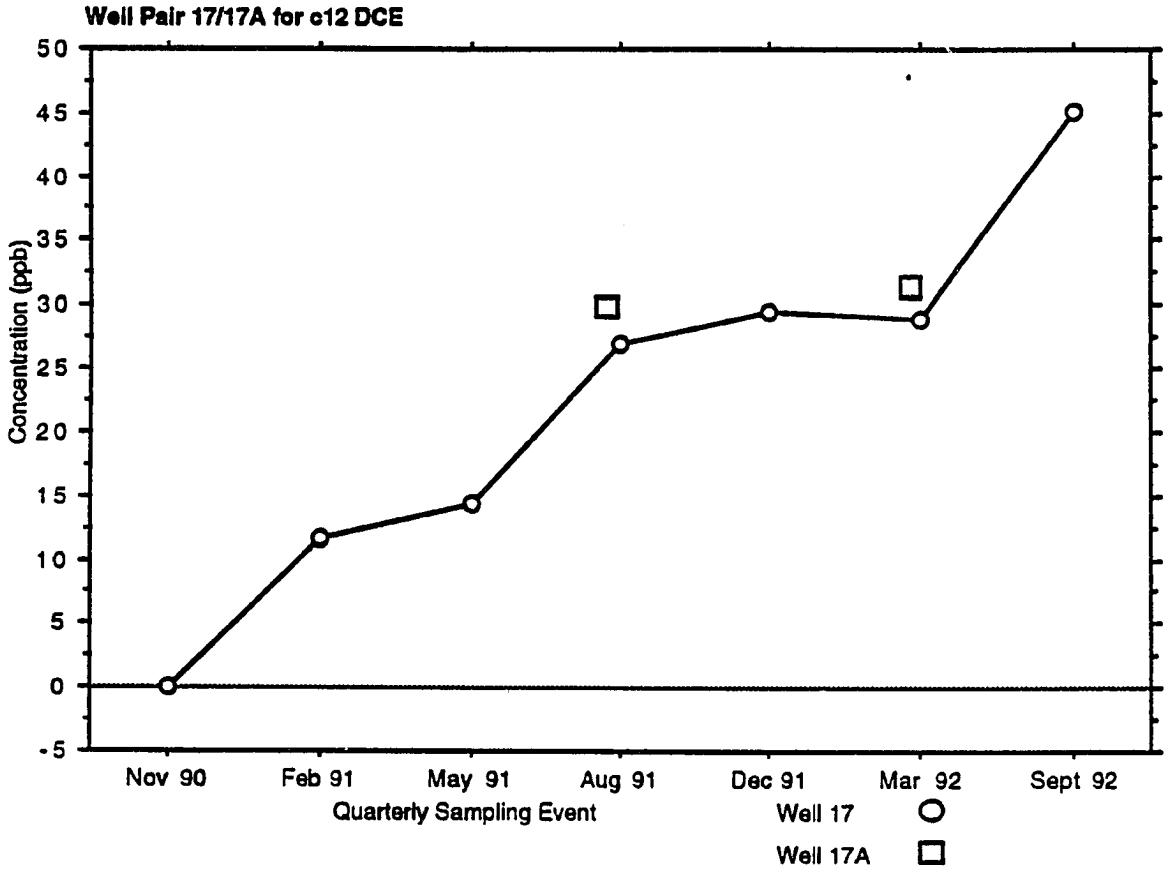


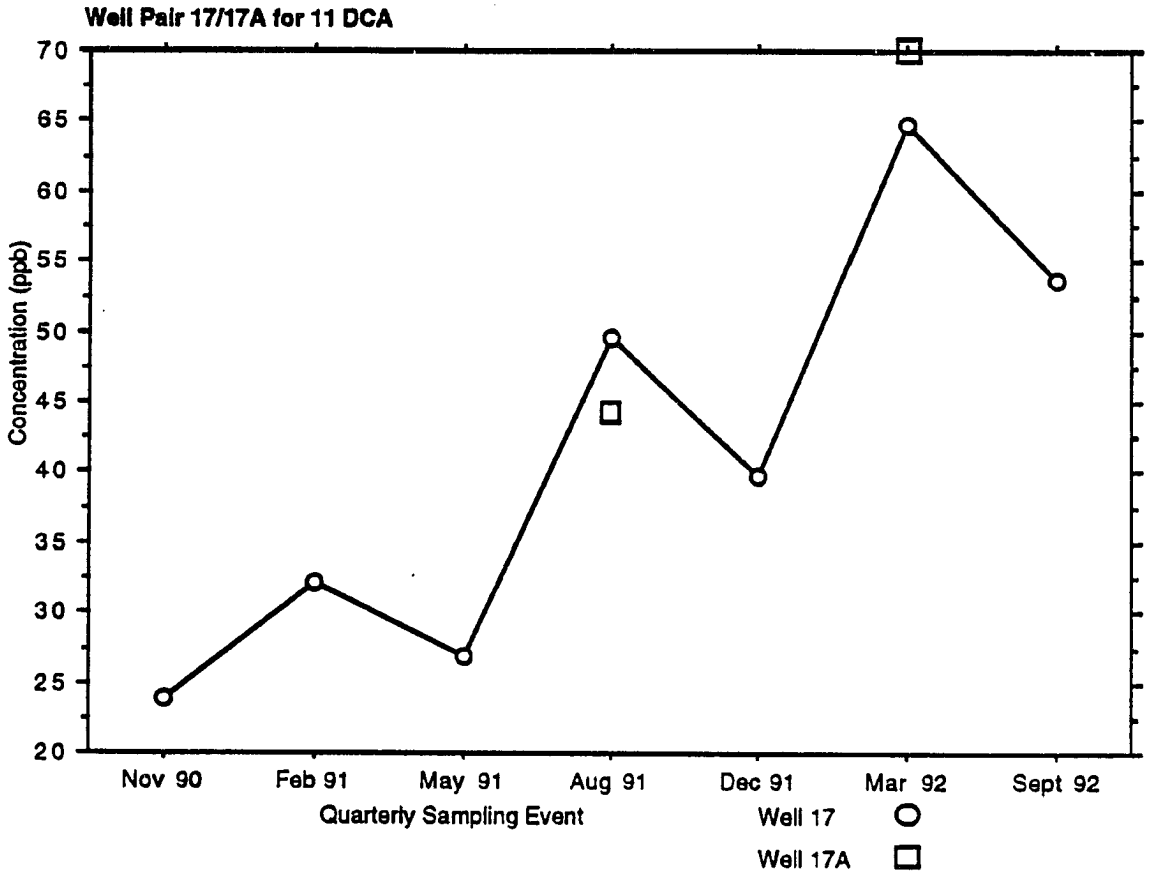


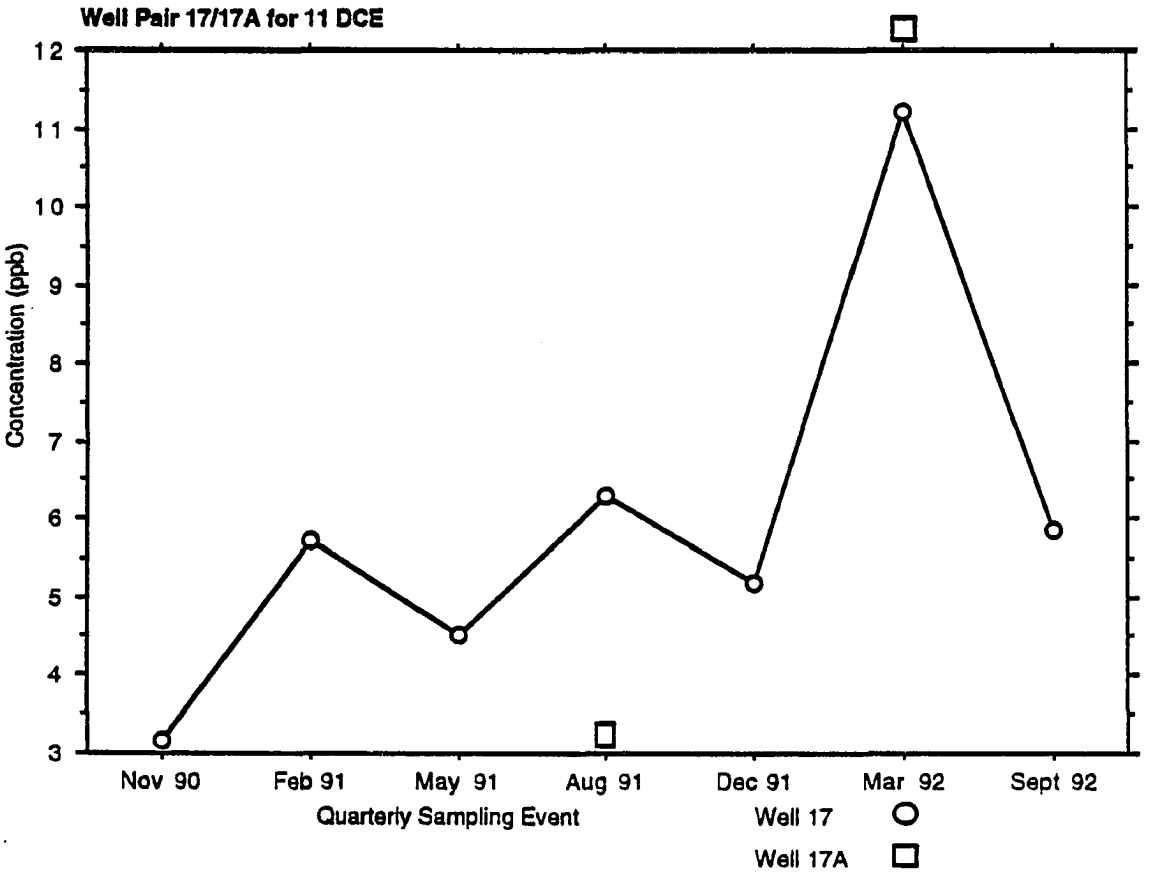


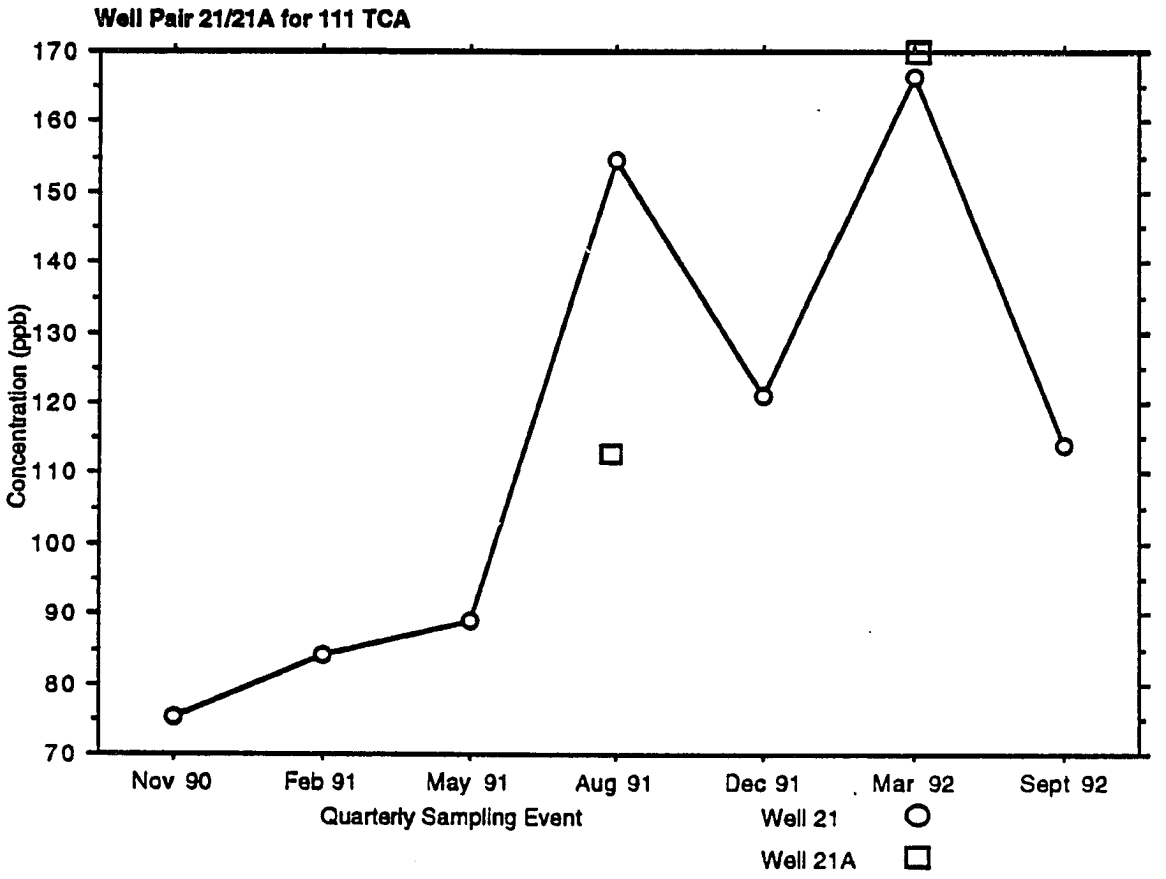


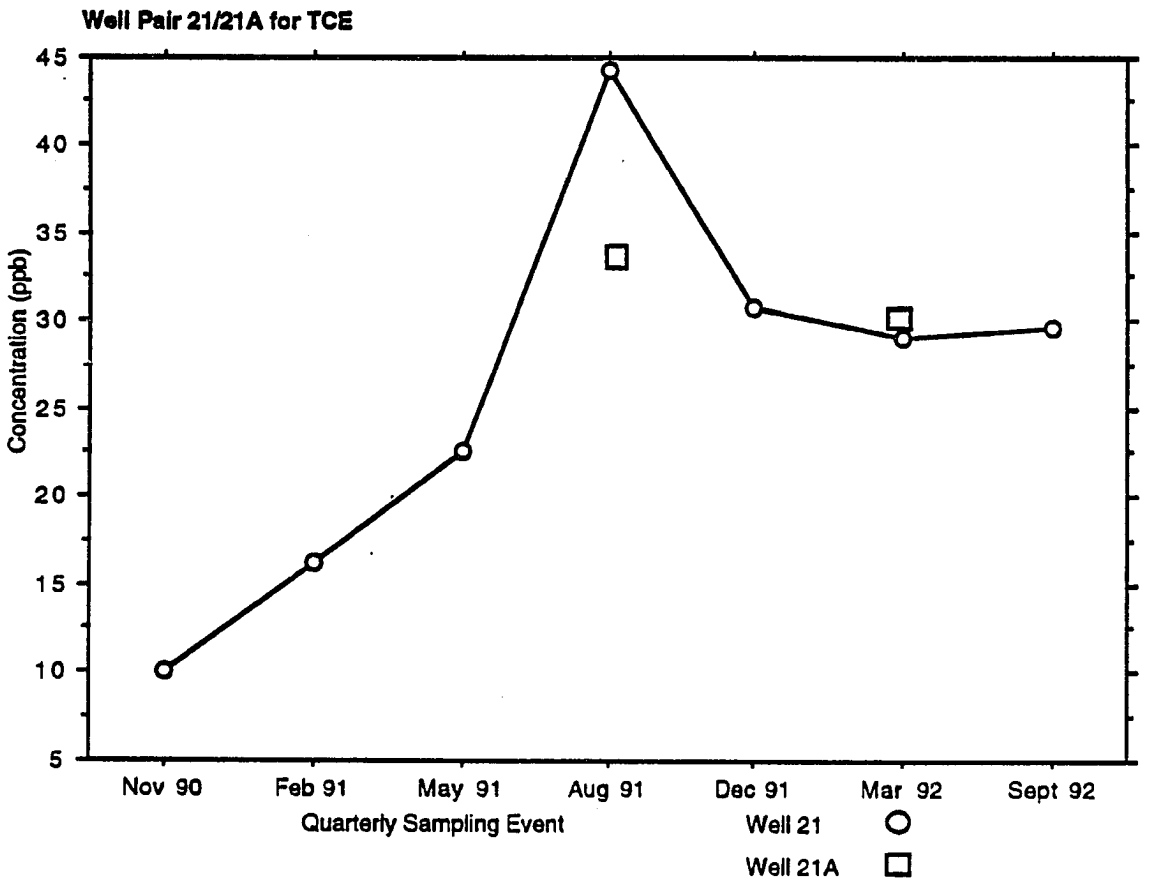


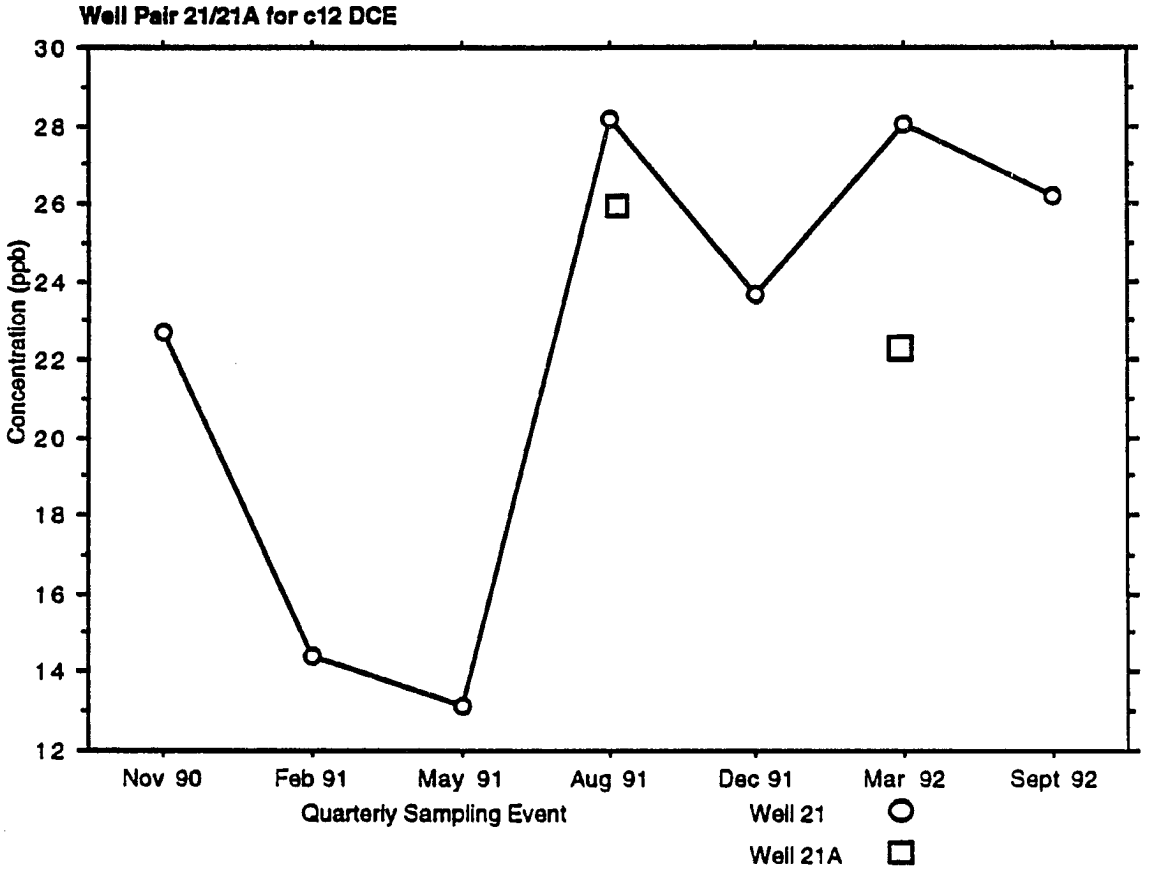


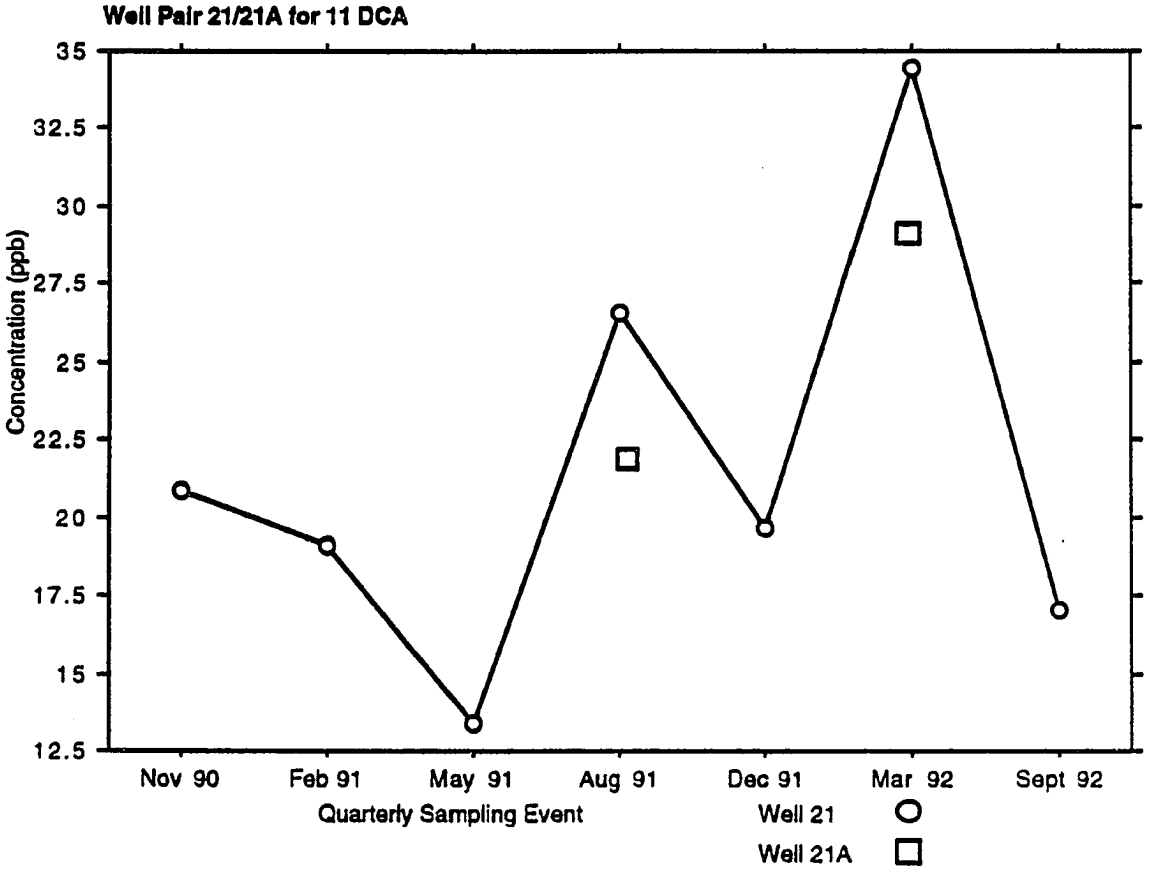


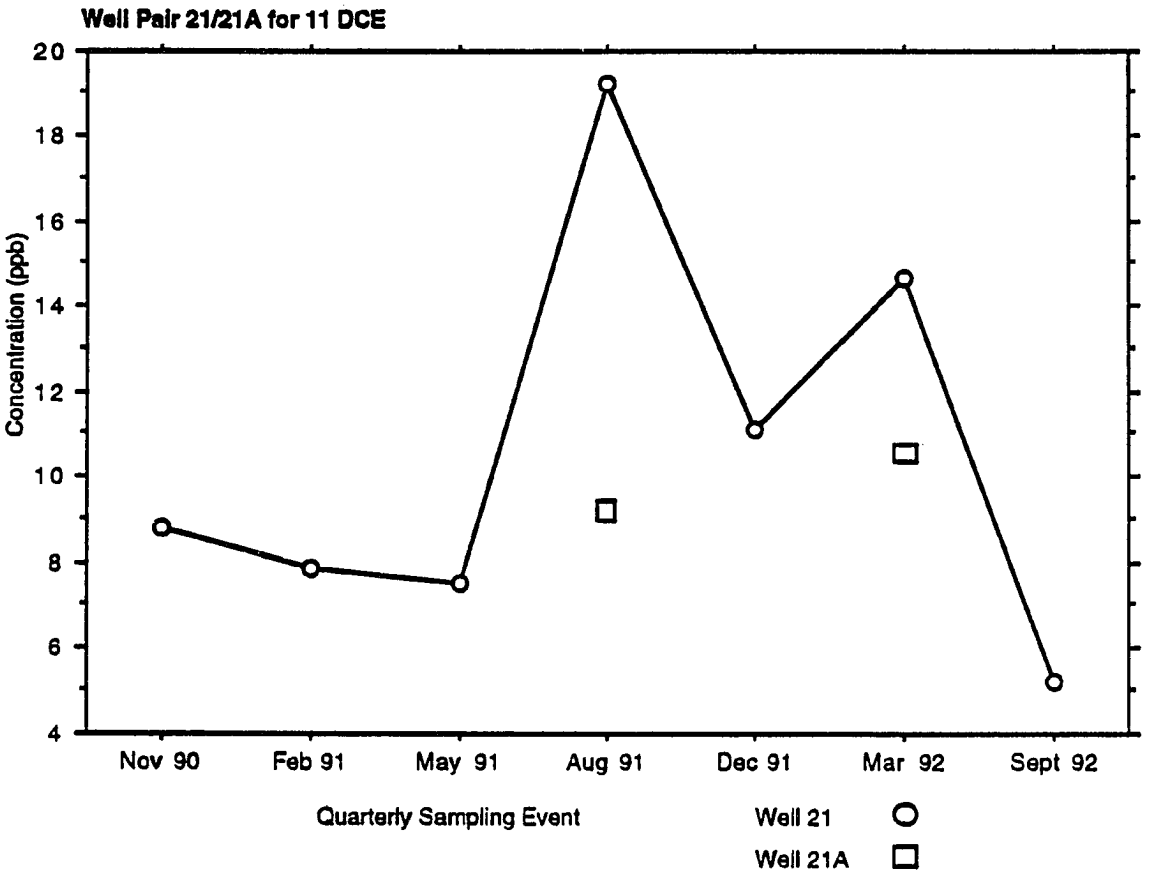












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