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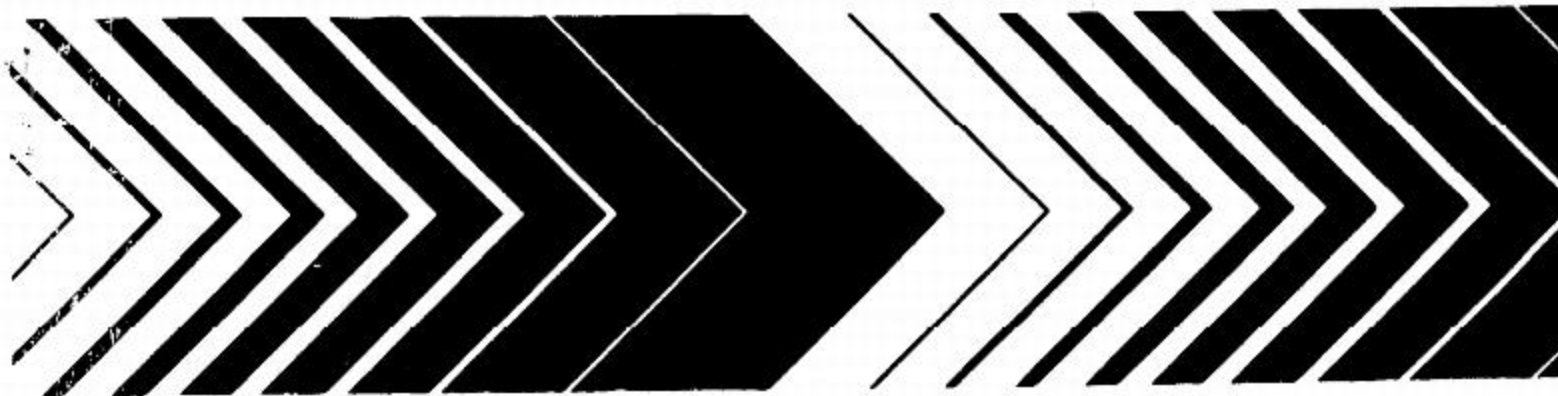
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# Sampling Frequency for Ground-Water Quality Monitoring





SAMPLING FREQUENCY FOR GROUND-WATER QUALITY MONITORING

by

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## ABSTRACT

The primary goals of this project were to collect a benchmark water-quality dataset and evaluate methods to optimize sampling frequency as a network design variable. Ground water was collected biweekly for 18 months from twelve wells at two sites in a shallow sand and gravel aquifer in Illinois. Sampling and analyses were conducted for twenty-six water quality and geochemical constituents with careful quality control measures to allow statistical analysis of variability in ground-water quality data. The results demonstrate that natural variability over time can exceed the variability introduced into the data from sampling and analysis procedures. Natural temporal variability and the highly autocorrelated nature of ground-water quality data seriously complicate the selection of optimal sampling frequency and the identification of seasonal trends in ground-water quality variables. Quarterly sampling frequency is a good initial starting point for ground-water quality monitoring network design, though bimonthly frequency may be preferred for reactive chemical constituents. Analysis of data collected during this project suggests that the collection of a long-term (i.e., more than two years) dataset is necessary to determine optimal sampling frequency and to identify seasonal trends in ground-water monitoring results. This report was submitted in fulfillment of Cooperative Agreement Number CR812165-02 by the Water Survey Division of the Illinois Department of Energy and Natural Resources under the partial sponsorship of the U.S. Environmental Protection Agency. This report covers a period from May 1, 1985 to Sept. 30, 1988; and work was completed as of May 19, 1989.







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## SECTION 1

### INTRODUCTION

This study was designed to address the effects of temporal variability on the reliability of ground-water quality monitoring results. It was initiated in May of 1985 as a logical extension of previous research which established a basis for the identification and control of sampling error in ground-water monitoring network designs.

The primary goals of the project were to collect a benchmark water-quality dataset and to evaluate methods to optimize sampling frequency as a network design variable. The density of sampling points and the frequency of sampling are the principal cost multipliers in the design and operation of monitoring networks. The optimization of sampling frequency can reduce the costs involved in monitoring network operation without affecting the information return.

There are two principal sources of variability in ground-water quality data, "natural" variability and variability resultant from the network design and operation. The components of "natural" variability arise from temporal or spatial variability related to hydrologic processes such as pumpage, recharge or discharge, as well as influences of these processes on the release and distribution of chemical constituents from a variety of chemical sources. The sources may be natural mineral assemblages, precipitation and percolation through the unsaturated zone, in addition to numerous point and non-point sources of chemical contaminants. In general, "natural" sources of variability cannot be controlled although they may be quantified through effective monitoring network design.

Water-quality data variability may also arise from the sampling and analytical components of monitoring network design. Sampling variability includes variations due to the selection of the locations and construction of sampling points in space, sampling frequency, well purging and the execution of the sampling protocol. The sampling protocol consists of the procedures used to collect, handle, preserve, and transport water samples to the analytical laboratory. Elements of the sampling protocol have been evaluated for their relative contributions to variability or errors in water-quality data in previous research (1-6).

Analytical variability in water-quality data arises principally from the errors involved in analytical methods and the subsequent data processing steps. These errors can be controlled once suitable water-quality indicators or chemical constituents have been selected and a thorough data quality assurance/quality control program has been designed and executed.



This study was planned to control the sources of variability in water quality data which result from network design components such as sampling location, frequency, sampling methods and analytical procedures. The sampling frequency was held constant at a biweekly interval between sample collection dates. The benchmark dataset that resulted from this experimental design could then be analyzed to determine the optimal sampling frequency for selected water-quality variables at both uncontaminated and contaminated study sites. The objectives of this analysis are enumerated below:

1. Establish the degree of natural variability in both physical and chemical parameters under known hydrologic conditions.
2. Determine the statistical reliability of annual water quality trends derived from biweekly, monthly, bimonthly, and quarterly data sets.
3. Assess the impact of natural variability, serial correlation (persistence) and seasonal trends on the sensitivity of simple parametric statistical tests to detect water quality changes.
4. Identify optimum sampling frequencies for annual mean and minimum detection sensitivity for selected conservative and reactive chemical constituents under known hydrologic conditions.
5. Analyze available water quality data from other studies which may allow the extension of the conclusions to other hydrogeologic situations.
6. Explore the effect which the geochemical variability of ground water in unconfined aquifers has on the utility of chemical speciation models for the selection of waste-specific indicator parameters.

Optimization of sampling frequency in ground-water quality monitoring networks should provide sufficient sensitivity for chemical constituent detection and adequate characterization of average chemical conditions. This should be accomplished with a minimum number of sampling dates. It was not within the scope of this work to provide an integrated discussion of the hydrologic and chemical processes which give rise to natural variability in the benchmark dataset. Some introductory and background material has been presented to place the project results in proper perspective.

## VARIABILITY IN GROUND-WATER QUALITY

### Hydrologic Transience in Ground-Water Systems

The impact of the sources of variability mentioned above will be influenced by the hydrology of the ground-water system. It is important to understand that although aquifer hydraulic properties may not vary significantly at a single measurement point over time, spatial variability may be substantial. This is a very active area of research with application to monitoring network design (7,8,9,10,11).

Temporal and spatial variations in ground-water elevation may affect ground-water flow rate and the direction of movement. Such changes may influence the quality of the ground water in the vicinity of a sampled well by directing water from a different upgradient area or changing the velocity with which dissolved constituents move along a flow path. Examples abound in the literature detailing ground-water response (i.e., elevation change) to a wide variety of influences. In addition to seasonal fluctuations produced in response to short-term (i.e., months to one year) events, ground-water levels also reflect changes in long-term (i.e., years to decades) conditions. Table 1 presents a number of natural and artificial (man-induced) influences which can cause changes in ground-water elevation (the parenthetical sign denotes whether the water table would be expected to rise or fall due to the listed cause).

**TABLE 1. CAUSES FOR TEMPORAL VARIATIONS IN GROUND-WATER ELEVATION**

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---

Infiltration/recharge (+)
Natural -- rainfall, snowmelt, flood (bank storage)
Artificial -- pipe or tank leakage, injection, irrigation
Aquifer loading on confined & semi-confined aquifer systems (+ or -)
Barometric changes -- air pressure changes
Concentrated loads -- trains, automobiles, etc.
Other external loads -- earthquakes, tides
Discharge (-)
Natural -- evaporation, transpiration, surface water interaction
Artificial -- pumpage

---

---

### **Infiltration/Recharge**

Atmospheric water falling to the earth's surface in its various forms is the principal source of ground-water recharge. Numerous studies have investigated the mechanisms of natural recharge (12,13,14,15,16,17) and recharge rates through various geologic materials (18,19). Factors affecting recharge include: 1) the character and thickness of the soil and other deposits above and below the water table, 2) topography, 3) vegetal cover, 4) land use, 5) antecedent soil moisture content, 6) depth to the water table, 7) the intensity, duration and seasonal distribution of rain-

fall, 8) the form of precipitation (i.e., snow, rain, sleet, etc.), and 9) the air temperature, wind velocity, humidity, and other meteorologic and climatologic factors (18,20).

In most areas of the U.S., particularly the subhumid Midwest, natural, shallow ground-water recharge generally occurs during limited times of the year, commonly in the spring and late fall. During these periods, rainfall tends to be of the long-duration, low intensity form. Cool weather and lack of vegetative growth are conducive to low evapotranspiration rates and contribute to greater antecedent soil moisture conditions thus enhancing the potential for recharge to occur. Alternatively, high evapotranspiration rates caused by growing plants and hot weather during the summer months may eliminate ground-water recharge. During the winter, when the ground is frozen, recharge is almost nonexistent.

Artificial recharge may occur in any location where man returns water to the subsurface environment. Methods of artificial recharge can be generally divided into three categories: 1) land application (e.g., spray irrigation, land flooding, surface impoundments), 2) subsurface percolation (e.g., septic system drainfields, cesspools, leaking sewers), and 3) subsurface injection (e.g., injection wells). Recharge can be intentional as with the case of recharge pits and injection wells (21,22,23) or inadvertent as with leaking sewers, and waste treatment lagoons (24,25). However the recharge is realized, local hydraulic gradients will be affected. Suter and Harmeson (21) documented rises from 5 to 15 feet (1.5 to 4.5 m) in wells near recharge pits along the Illinois River in Peoria. Morton et al. (25) noticed a rise of nearly 8 feet (2.4 m) beneath a septic waste impoundment during its early stages of operation. A number of papers have described mathematically the growth of ground-water mounds beneath areas where water has been applied to the land surface (26,27,28,29).

#### Aquifer Loading

Water levels in artesian wells, and to a lesser degree in some water-table wells, have been shown to respond to changes in atmospheric pressure and other external loads (30,31). Such responses are due to changes in fluid pressure and stress in the aquifer matrix. Roberts and Romine (32) observed a change of over 0.5 foot (0.15 m) in the piezometric surface of a well in central Illinois as the barometric pressure increased about one foot (0.3 m) for a barometric efficiency of approximately 0.5. Barometric efficiencies generally have been found to fall in the range from 0.20 to 0.75 (33). Atmospheric effects have been observed to a lesser degree in water table aquifers and have been attributed to the presence of entrapped air (34,35). Atmospheric pressure changes caused water table fluctuations from 0.6 to 2.4 inches (0.02 to 0.06 m) in a fine-grained aquifer in Utah (36).

Water level fluctuations in wells in confined aquifer systems have been attributed to a variety of other causes including concentrated loads such as trains (32,37,38) and shocks caused by earthquakes (39,40,41). Again, water level response is related to changes in fluid pressure and stress in the aquifer matrix. As might be expected, the magnitude of water level response

is a function of the magnitude of the load (or shock), the elastic properties of the aquifer, and the degree of confinement (41). Roberts and Romine (32) reported short-term fluctuations up to 0.06 (0.02 m) foot in response to a passing train in central Illinois. Jacob (38) reported a similar response to a passing train on Long Island.

Scott and Render (41) discussed the water level fluctuations in several wells in Canada due to the 1964 earthquake in Alaska. The earthquake registered 8.5 on the Richter scale and caused water level fluctuations throughout the conterminous United States as well as Hawaii. For the wells in confined aquifers that they discussed, water levels fluctuated from approximately 0.5 to 0.8 foot (0.15 to 0.24 m) as the shock wave passed. Residual increased water levels were on the order of 0.1 foot (0.03 m); these residuals dissipated or were assimilated into the ground-water trend within several hours to days. A hydrograph of water levels in a well in an unconfined aquifer showed an initial increase of 0.2 foot (0.06 m) followed by a decline of 1.1 feet (0.33 m). It took 4 days to recover to its pre-shock level. This dramatic change was attributed to an increase in ground-water discharge due to the initial shock followed by a reduction of water in storage. Thomas (40) found similar responses (up to 0.87 feet, 0.26 m) in wells in Utah, California, and New Mexico to two earthquakes in Alaska and Chile.

#### Ground-Water Discharge

Diurnal variations in water table elevation have been well documented (31,42,43). Most of these fluctuations have been attributed to evapotranspiration losses, but some fluctuations may also be due to daily atmospheric pressure changes (36). Diurnal fluctuations appear as small "waves" upon the regional ground-water trend. The change in water level occurs as ground-water storage is reduced to meet the water needs of plants and to satisfy soil evaporation requirements. Drawdown generally is greatest during the daylight hours; the maximum rate of drawdown occurs near midday. The magnitude of the fluctuation is relatively small and depends upon weather conditions and plant water requirements. Fluctuations are generally greater during the height of the growing season (July) than they are later in the season (August). Water level fluctuations due to evapotranspiration are essentially negligible after killing frosts. Typical daily fluctuations documented in investigations conducted in the United States (31), Canada (42), and Sweden (43) were on the order of 0.1 foot (0.03 m).

In areas of ground-water withdrawals, ground-water level changes caused by pumpage are superimposed on seasonal and long-term fluctuations produced by natural ground-water recharge and discharge. When a well is pumped, water levels decline, forming a characteristic cone of depression. The shape and depth of this cone depend on the amount, rate, and duration of withdrawal, the hydraulic characteristics of the well structure, and the hydraulic properties of the aquifer. Water level declines are directly proportional to pumpage and inversely proportional to the distance from the withdrawal point. The hydraulic properties of an aquifer remain essentially unchanged over time; however, pumpage normally exhibits seasonal variations in response to water supply demands.

## **Water Quality Variability and Network Design**

Ground-water quality monitoring networks are designed for a number of purposes, including ambient resource studies, contaminant detection and assessment, Contaminant source evaluation, litigation, and research investigations. The effective design of virtually any such network, regardless of purpose, depends on knowledge of the hydrogeologic system of interest, an indication of the presumed contaminants or preferred water quality indicators and an assessment of the relative contributions of sources of variability. These aspects of monitoring network design have been addressed previously in the literature (44,45,46,47,48,49). The common recommendations in these works are that background information must be supplemented with the results of a preliminary sampling experiment to progressively refine the network design to account for error and variability in the chemical results.

Variability in the analytical results for particular ground-water chemical constituents may arise due to "natural" causes such as nonhomogenous spatial distributions of the constituents and temporal variability in recharge. Variability may also arise due to network design-related variables such as well design, sampling devices and sampling protocols. The apparent sources of variability in water-quality data which are often attributed to natural (i.e., temporal and spatial) effects include hydrologic transience, the fluctuations in contaminant source strength and composition and the interactions between reactive chemical, biochemical and mineral constituents in recharge water and ground water. Our understanding of the interdependence of hydrologic, biological and chemical processes in the subsurface is limited. However, it may not be necessary to fully understand the relationship between these processes, contaminant sources and the resultant chemical distributions in order to monitor potential contaminant releases.

The temporal and spatial variability which is observed in water quality results over time at discrete monitoring points is the result of the processes noted in the preceding discussion as well as the sample collection and measurement errors inherent to network design and operation. This variability, or "noise", in the data embodies the stochastic distribution of possible values for particular chemical constituents and the effects of both determinate (i.e., systematic) and indeterminate (i.e., random) error. Determinate error can be measured as inaccuracy or bias if the "true value" is known. Indeterminate error can be estimated as imprecision or irreproducibility if a sufficient number of replicate determinations can be made to faithfully estimate the mean or the "true" value. In practice, determinate errors can only be estimated and controlled by careful quality assurance/quality control measures exercised over appropriate sampling and analytical procedures because the true value in environmental distributions is unknown and some disturbance of the subsurface is inevitable in ground-water quality work. Identifying and controlling these design-related errors have been the focus of much of our recent research (1,3,50,51,52).

Statistical measures of short-term temporal variability include seasonal effects (e.g., consequences of recharge or temperature effects) which can be assigned to the seasons of the year, periodic effects (e.g., consequences of anthropogenic contaminant sources or pumping effects) and serial correlation or dependence effects which tend to make data points following maxima or minima in temporal data series higher or lower, respectively, than one would attribute to random processes alone. Trends in data, on the other hand, are long-term variations compared to those which may occur within a hydrologic year (53). This categorization of temporal effects is somewhat artificial in that the combination of seasonal, periodic or correlative components may result in a water-quality time series which cannot be differentiated quantitatively. It must be recognized then, that the identification of short- or long- term trends in water quality is conditional on some knowledge of the proximity of the sampling location to the location and time of chemical release as well as the statistical characteristics of ground-water quality variables.

Statistical measures of temporal variability have been reviewed recently by Loftis et al. (54), Montgomery et al. (55) and Harris et al. (56). They cite numerous examples of both short- and long- term temporal variability which supplement the earlier reviews of Porter and Trautman (53) and Colchin et al. (57).

Loftis et al. (54) note in their review that although there are numerous reports of apparent seasonality or periodic effects in ground-water quality data, very few long-term datasets exist at sufficiently high sampling frequency (i.e., more frequent than quarterly) to statistically distinguish these effects from those of serial dependence or autocorrelation. These characteristics of the limited ground-water quality datasets, together with the fact that the quality variables are frequently not normally distributed, constrain the use of simple parametric statistical tests of significance to compare means or identify trends (55). The development of benchmark ground-water quality datasets at high sampling frequency (i.e., monthly or biweekly) for time periods in excess of one year would be most useful in determining minimum statistical criteria for cost-effective network design. This type of dataset would also be very useful in the identification of applicable statistical methods for trend analysis and for significance testing of comparisons of background versus contaminated water quality conditions (56).

Spatial and temporal variability in ground-water quality may affect the sensitivity of contaminant detection and the estimation of mean chemical concentrations. To some extent, spatial chemical data collected at discrete points along a horizontal flow path may be quite similar to data collected over time at a single point in the path. This supposition is, of course, dependent on a number of factors related to hydrologic conditions as well as the nature of the chemical source, reactivity and mobility constraints. The substitution of spatially intense samples for use in temporal variability studies could be applied to studies of ambient concentrations of conservative chemical species for regional assessments in rather unique hydrologic situations.

## SECTION 2

### CONCLUSIONS

1) Sampling and analytical errors can be controlled to within about +20% of the annual mean inorganic chemical constituent concentration in ground water if the protocols are properly designed and executed. The use of previously published guides for ground-water monitoring can provide reproducible, accurate results for such studies. The effects of sampling and analytical errors may be far more serious for trace organic contaminants.

2) The results of the study concentrate mainly on inorganic chemical constituents in ground water. The statistical characteristics of the time-series data for reactive chemical constituents (e.g., Fe(II), sulfide,  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$  and  $\text{NO}_2^-$ ) disclose that temporal variability is often lower than the magnitude of concentration changes observed during purging of stagnant water prior to sampling. This means that improper well purging can result in gross errors and the introduction of artifacts into ground-water quality datasets.

3) In agreement with the results of previous studies, distributions of ground-water quality variables show little consistent tendency towards either normality or nonnormality, and values within a time-series exhibit significant autocorrelation or serial dependence. Autocorrelation effects detected within datasets of relatively short duration (i.e., less than one or two years) suggest that it is very difficult to quantify seasonality or time-trends under stable hydrologic and steady contaminant source release conditions. The potential implications for the design of source detection and contamination assessment monitoring systems may be serious. Sampling more frequently than quarterly may result in significantly reduced information return for the cost and effort involved in data collection. The actual magnitude of this "loss of information" will be dependent on both the sampling frequency and the proposed duration of the monitoring effort. A relatively long-term data collection period may be required for reasoned decision-making in judging plume capture or cleanup efficiencies, since high sampling frequencies may not yield significant increases in information.

4) Temporal variability in ground-water quality which is seasonal in nature (i.e., duration or cycle of less than one year) may not be easily identified, given the highly correlated statistical distribution of chemical parameter values and the sensitivity of results to purging and pumping. It may be necessary, therefore, to have five- to ten-year background datasets before seasonal components can be distinguished statistically. Quarterly sampling frequency represents a good initial choice for monitoring network designs. The frequency should be reevaluated as site-specific data are collected and with respect to the duration of the program. Background

water quality datasets collected in a single year may only be snapshots of the actual conditions prevalent during the sampling period.

5) Regional changes in water quality (i.e., short-term variations or long-term trends) may be easily recognized in datasets from wells upgradient from contaminant sources while source contributions may mask any such changes in downgradient wells. This observation complicates simple parametric statistical comparisons of upgradient and downgradient contamination effects in ground water.

6) Major ionic constituents (i.e.,  $\text{Na}^+$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{HCO}_3^-$ , etc.) were also major components of the waste stream at the Beardstown site. Under these conditions, the extent of natural or geochemical variability imposed no significant constraints on chemical speciation model results for identifying waste-specific indicators.



## SECTION 3

### RECOMMENDATIONS

1) Several ground-water research sites should be established to collect long-term (i.e., in excess of five years) water quality datasets under known hydrologic conditions in order to permit the quantitative treatment of seasonality and serial dependence effects in the data.

2) Given the fact that natural variability of major ionic constituents of ground water exceeds the errors involved in reliable sampling and analytical protocols, it is recommended that network design efforts emphasize longer term monitoring of natural and contaminant-related variability rather than high frequency (i.e., more frequent than biweekly or monthly) intensive sampling activities.

3) Research into the statistical characteristics of the inorganic water quality variables should be extended to include organic constituents where few long-term datasets exist and the sources of variability inherent to network design and operations may be much greater than natural variability.

4) Reliable methods for statistical analysis of "trend" data are needed, particularly where gaps exist in temporal datasets. The dataset collected in this study provides a sound basis for the design of further research in the detection of water quality trends.

5) The sensitivity of overall variability in ground-water quality results to purging procedures prior to sampling needs to be addressed in a series of experiments which integrates hydrologic and chemical data collection methods.

6) The integration of chemical and hydrologic data collection and interpretation should be encouraged in future research and regulatory data analysis efforts. The use of models which incorporate solute transport and reaction components could be quite useful in determining hydrologic versus chemical control over the natural variability in ground-water quality constituents.

## SECTION 4

### EXPERIMENTAL DESIGN AND PROCEDURES

#### REGIONAL LOCATION AND DESCRIPTION OF FIELD SITES

One of the principal objectives of this study was to assess the relative contributions of natural and network-design-related variability to ground-water quality monitoring results. Two sites were chosen to enable the isolation of the effects of network design variables from those due to natural or contaminant-related sources. To maximize the potential for temporal variability, the chosen sites were located over water table aquifers of moderate to high yield. One site was in a pristine environment far removed from any sources of contamination. The other site was in an industrial environment under the influence of a leaking anaerobic waste impoundment.

The two field sites are located in west-central Illinois (Figure 1) on a wide, sandy outwash plain known as the Havana Lowland region. The "clean" site is in Sand Ridge State Forest at the widest part of the Lowland several miles south of Peoria. The contaminated site is near the city of Beardstown at the southern boundary of the Lowland approximately 40 miles (64 km) down the Illinois River from the Sand Ridge site. As shown in Figure 1, the Lowland quickly broadens south of Peoria to a width of over 20 miles (32 km) and then gradually narrows to about 10 miles (16 km) at Beardstown.

#### Regional Geology

The Havana Lowland region is a section of the broad Pennsylvanian Lowland that covers most of Illinois and much of Indiana. It was formed during pre-glacial times at the convergence of the ancient Mississippi and Teays Rivers and other smaller tributaries (58). In the area of Sand Ridge State Forest, the ancient river channel cut through the Pennsylvanian shales, sands tones, and limestones into Mississippian limestones, shales, and dolomites. The channel continued to the south of Beardstown, eventually eroding into formations of Devonian, Silurian, and Ordovician age before joining the present Mississippi River about 20 miles (-32 km) north of the Missouri River at St. Louis. The modern Illinois River joins the channel of the ancient Mississippi at a point just west of Sand Ridge State Forest.

During the early Pleistocene period, the Havana Lowland was filled with sand and gravel outwash which was later at least partially removed and continually reworked, covering the outwash plain with successional terraces of sand and gravel valley train or outwash fans (59). These sand and gravel deposits reach a depth of about 200 feet (61 m) in the deepest portions of the now-buried ancient valley. The major physiographic areas of the Havana Lowland are shown in Figure 2.

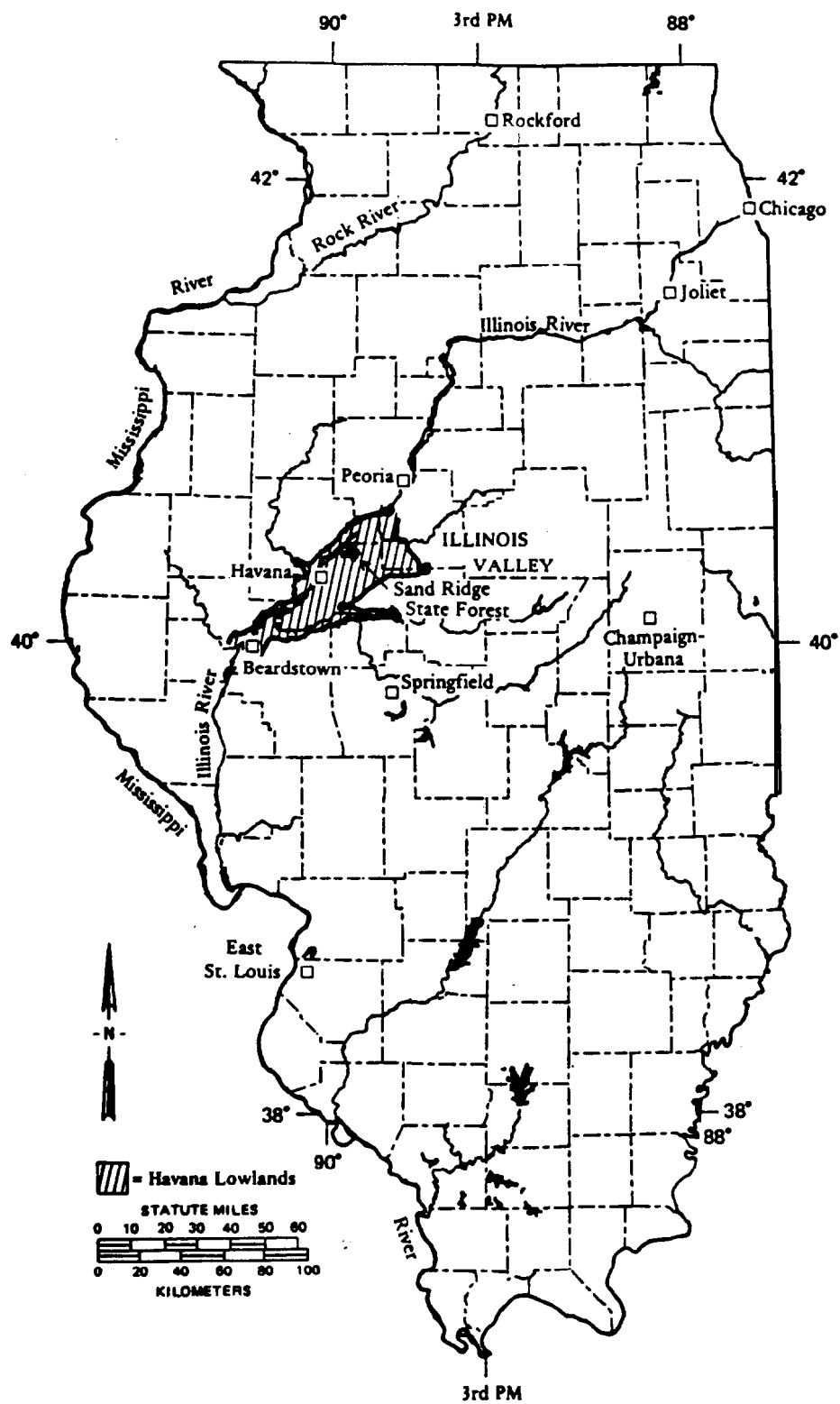
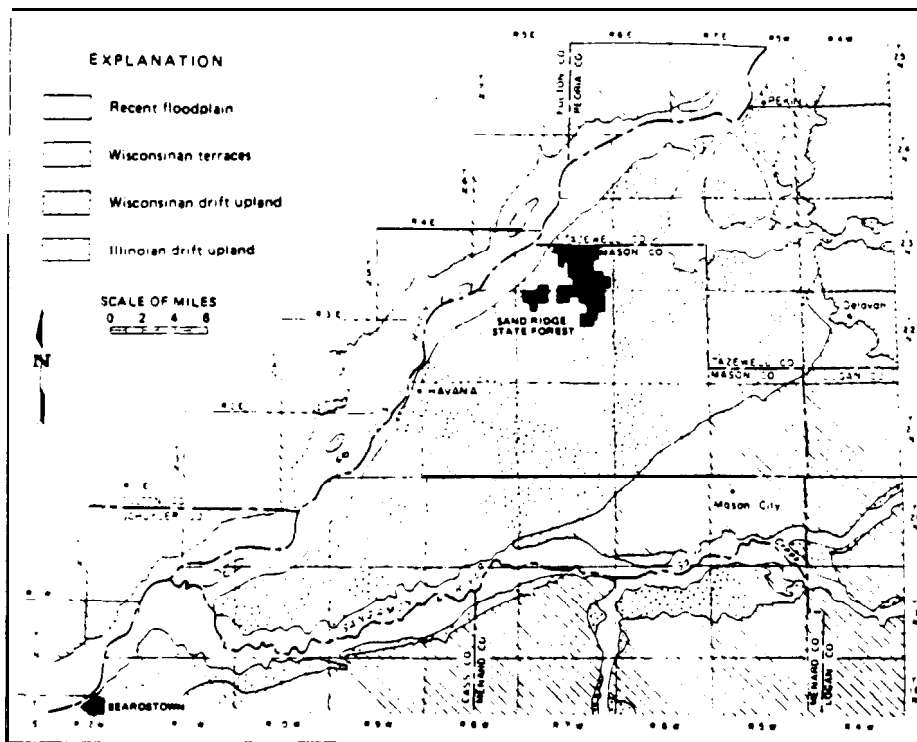
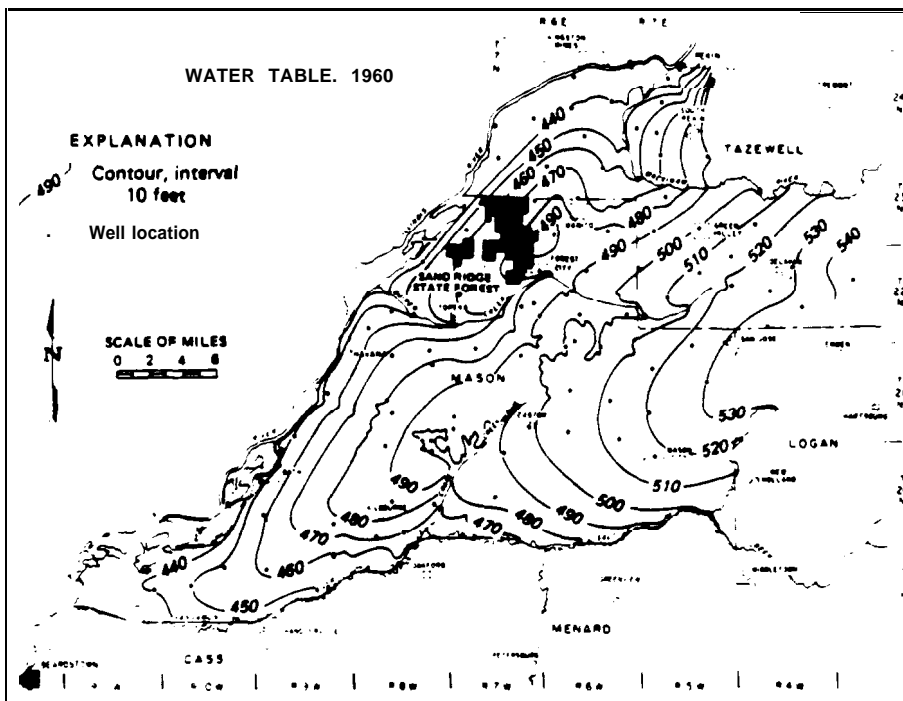


Figure 1. Location map of the two field sites at Sand Ridge State Forest and Beardstom, Illinois.



**Figure 2. Surficial geology map of the Havana Lowland region.**



**Figure 3. Water table contour map of the Havana Lowland region (1960).**

## Regional Hydrology and Climate

The saturated thickness of the sand and gravel aquifer in the Havana Lowland ranges from 50 feet (15 m) or less along the Illinois River to more than 200 feet (61 m) in areas east of Sand Ridge State Forest. Greater than 100 feet (31 m) of saturated deposits underlie both field sites. A water table contour map drawn in 1960 for the Havana Lowland is shown in Figure 3. Contours were not plotted at the Beardstown area, but the 440 and 450 foot (134-137 m) contour levels should continue to follow the Illinois River to the south of the Sangamon River through Beardstown. More limited coverage, recent data indicate that the present water table topography is similar to the 1960 map. Regional ground-water flow has a stable directional component toward the Illinois River, although recent pumpage for a state fish hatchery near Sand Ridge State Forest has influenced water levels locally.

The Illinois River is a major shipping route between Chicago and St. Louis. It is controlled through levee and lock structures and does not usually flood large areas of the adjoining land. The average annual discharge rate of the river is approximately 15-22 cubic feet per second (cfs) [0.42-0.62 m<sup>3</sup>/s] with a record low of about 1.5 cfs (0.04 m<sup>3</sup>/s) and record highs of 90 cfs (2.5 m<sup>3</sup>/s) at Havana and 125 cfs (**3.5** m<sup>3</sup>/s) at Beardstown (60).

Mean annual precipitation in the Havana Lowland area is approximately 35.5 inches (0.9 m). Total monthly precipitation recorded at Havana, midway between the two field sites, for the period 1983 through 1987 is shown in Figure 4. As shown, seasonal variations can be great, with the greatest amounts of precipitation occurring typically in the spring and fall months. An anomalously high monthly rainfall occurred in November 1985, shortly before the start of the biweekly sampling period, when nearly 11 inches (**0.3** m) of rain fell.

Ground-water levels have been continuously recorded by the Illinois State Water Survey (ISWS) at Snicarte (located between Havana and Beardstown) since 1958. A well hydrograph for the period 1983 through 1987 at Snicarte appears as Figure 5. The well is situated in an area remote from pumping centers and, therefore, should reflect only natural fluctuations in shallow ground-water levels caused by seasonal and long-term responses to precipitation and climatologic conditions. Annual fluctuations of 3 to 4 feet (0.9 to 1.2 m) are common. Recharge typically occurs during the spring and late fall months. A shift in the timing of peak ground-water levels can be seen in the two-year period from 1985 to 1987. Ground-water level highs occurred in the late fall and early winter of those years rather than in the spring as had occurred in previous years. This shift is apparently the result of low snowfall during the winter and less rainfall during the spring months of those years. Note the severe decline in ground-water levels during 1987 when the total annual rainfall was only 29 inches (0.7 m), about 20% below normal. The greatest amounts of rain occurred in June, August, and December which are usually low recharge months. Similar declines were found in monitoring wells and piezometers at the two field sites.

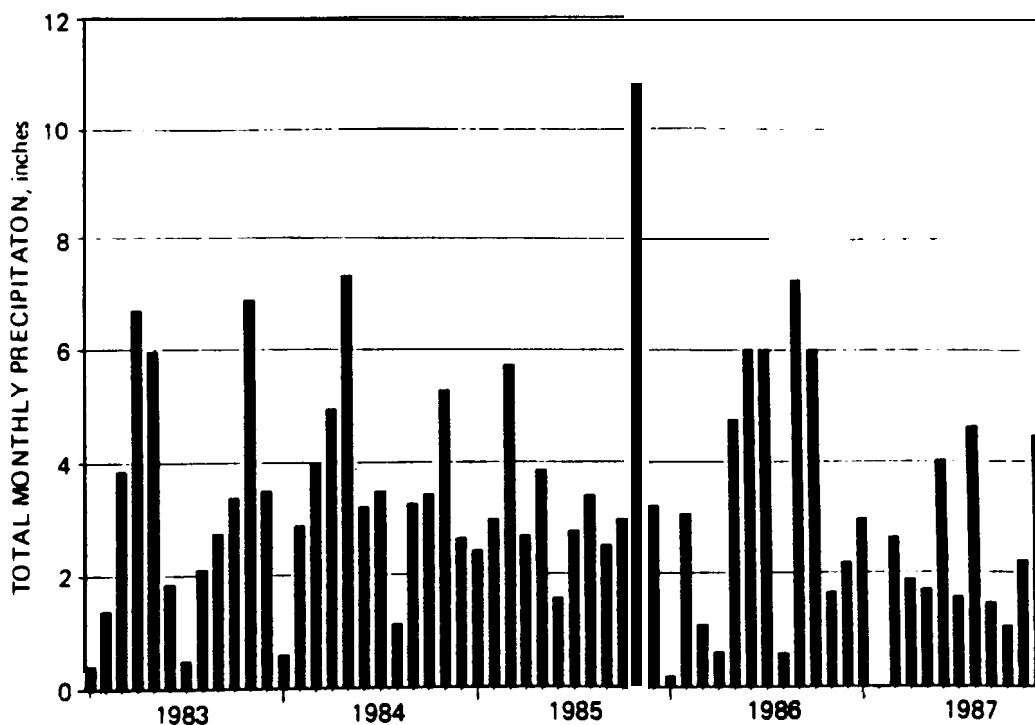


Figure 4. Monthly precipitation recorded at Havana, IL, 1983-1987.

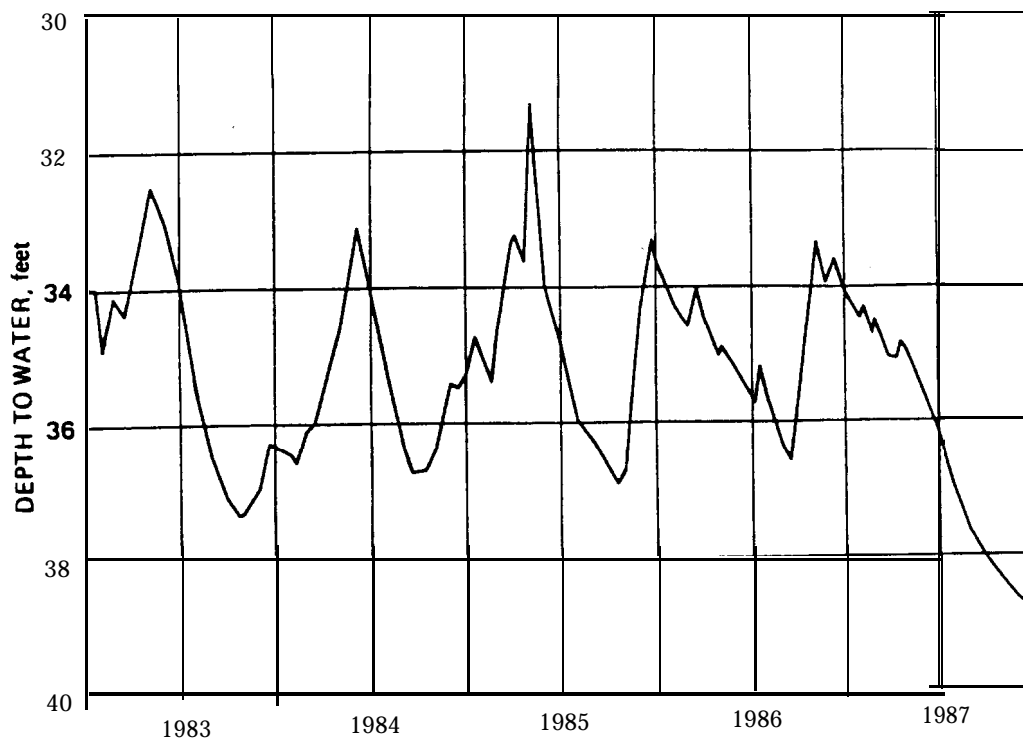


Figure 5. Depth to ground water recorded at Snicarte, IL, 1983-1987.

Studies by O'Hearn and Cibb (61) and Walton (62) indicate that during years of normal precipitation, ground-water baseflow to streams in the Havana Lowland area ranges from 4 to 5 in/yr (0.1-0.13 m/yr or approximately 11-14% of mean annual precipitation). O'Hearn and Gibb (61) estimated ground-water baseflow to streams in this area for low ( $Q_{90}$ ) and high ( $Q_{10}$ ) streamflows as 1.8 in/yr (0.04 m/yr) and 13.6 in/yr (0.34 m/yr), respectively. Walton (62) also estimated that recharge to the aquifer, based on the water table map of 1960 (Figure 3), was 10 inches (or 0.25 m, 29% of the mean annual precipitation).

## **General Site Descriptions**

### **Sand Ridge State Forest**

Sand Ridge State Forest is an Illinois Department of Conservation (IDOC) facility located 5 miles (**8** km) southeast of the Illinois River in the north-central Havana Lowland. The Illinois State Water Survey's experimental field site is located in the middle of the State Forest near the center of Section 34, T23N, R7W, 3rd PM, Mason County, Illinois.

The land surface is dominated by rolling sand dunes covered with oak, hickory, and pine. Within the forest, several areas have been cleared for growing grains that provide cover and food for wildlife during the winter months. The absence of any nearby source of ground-water contamination and the ability to work in a remote, open site led to the choice of one of the cleared areas as our "pristine" field site.

Privately-owned land surrounding the State Forest is used primarily as farm land on which cash grain crops such as corn and soybeans are grown. Center-pivot irrigation systems are used extensively throughout the area to maintain high crop yields on the sandy soils. In 1983, a state fish hatchery near the Illinois River in the northwest corner of the State Forest began operation. Water is supplied to the hatchery by 9 wells located one mile (1.6 km) north of the field site used in this study. Pumpage at the hatchery has averaged over 9 million gallons per day (0.4 m<sup>3</sup>/s), with occasional lows of about 7 million gallons per day (0.3 m<sup>3</sup>/s). The influence of this well field on the local ground-water flow domain at the field site is described later in this report.

Three distinct horizons comprise the unconsolidated deposits at Sand Ridge: at the surface is 30 feet (9 m) of dune sand (the Parkland sand); from 30 feet (9 m) to a depth of 55 feet (17 m) is the Manito Terrace of the Wisconsin outwash, consisting of a sometimes silty, sometimes coarse sand to medium gravel; and from 55 feet (17 m) down to bedrock below 110 feet (**34** m), and possibly as deep as 150 feet (46 m), is the medium sand to fine gravel of the Sankoty sand (Kansan outwash). Illinoian deposits are missing. The bedrock beneath the site is probably early Pennsylvanian limestone, shale, or dolomite.

Depth to the water table is greater than 30 feet (9 m) below the ground surface. Ground-water movement is generally toward the Illinois River. The hydraulic gradient measured at the site in 1983 was approximately 0.0016

(63). Aquifer tests conducted on the water supply wells at the state fish hatchery indicate that the hydraulic conductivity of the sand and gravel at approximately 100 feet (30 m) depth (in the Sankoty sand) is about 2000 gpd/ft<sup>2</sup> (0.094 cm/sec). Tracer experiments conducted in 1983 (63) indicated smaller hydraulic conductivities (from 250 to 1900 gpd/ft<sup>2</sup>, 0.01 to 0.09 cm/sec) may be experienced in shallower materials. Hydraulic conductivity values of 350 to 900 gpd/ft<sup>2</sup> (0.02 to 0.04 cm/sec) were obtained by empirical methods of analysis based on the grain size distributions of shallow aquifer samples (63). In that same study, the porosity of the saturated terrace materials was found to be 25%.

#### Beardstown

The "contaminated" field site is located in the vicinity of several liquid waste impoundments serving a pork slaughtering facility approximately 1 mile (1.6 km) southeast of Beardstown (in the SE corner, Sec. 23, T18N, R12W, 3rd PM, Cass County, Illinois). Beardstown is situated at the southern end of the broad Havana Lowland where the Illinois River turns southward on its way to the Mississippi River.

While the field site lies two miles southeast of the river, it is only about 5 feet (1.5 m) higher than the floodplain. Farmland and wooded areas surround the facility. The unconsolidated deposits lying above the bedrock consist of the clayey sands of the Beardstown Terrace on the Wisconsin outwash plain. The bedrock surface is of Mississippian age and lies at about 100 feet (30 m) below the ground surface.

Facility memos and consultant's reports provided preliminary information on ground-water conditions at the site. Owing to land surface elevation changes, depth to water varies from about 5 to 15 feet (1.5 to 4.5 m) below the ground surface. Similar to the Sand Ridge site, regional ground-water flow is toward the Illinois River (hydraulic gradient, 0.002). However, the influence of several waste treatment impoundments on ground-water elevations at the site had not been evaluated. Due to the presence of silt and clay, the aquifer is less permeable than it is at the Sand Ridge site. One falling head permeability test produced a hydraulic conductivity value of only 130 gpd/ft<sup>2</sup> ( $6 \times 10^{-3}$  cm/sec). However, this value may represent the lower end of hydraulic conductivities at the Beardstown facility as a slug test on another well on-site could not be conducted because of "an inability to fill the well with water" (64). While it is unclear from the report exactly how the well was being filled, it is clear that the aquifer could accept water faster than it was being applied to the well. This suggests a hydraulic conductivity greater than that calculated for the other well.

#### FIELD SITE INSTRUMENTATION

##### Well Construction Details

Each field site contained: 1) a network of piezometers to describe local ground-water conditions, 2) nested sampling wells, to define the



ground-water quality variability, and 3) real-time hydrologic monitoring systems that have provided a continuous record of selected hydrologic and meteorologic parameters since mid-1987. The placement and construction of these structures and instruments within the field site were critical to the study. This was particularly true at the Beardstown site where placement of sampling wells upgradient and within a contaminant plume downgradient of an anaerobic waste impoundment was vital to the project objectives. The monitoring devices (sampling wells, piezometers, and hydrologic monitoring systems) were constructed in a similar manner at both field sites. A description of general construction details is provided here before discussing each site in detail. Previous research investigations (1,2,3,4) provided the basis for the design and construction of the monitoring wells and selection of pumping mechanisms.

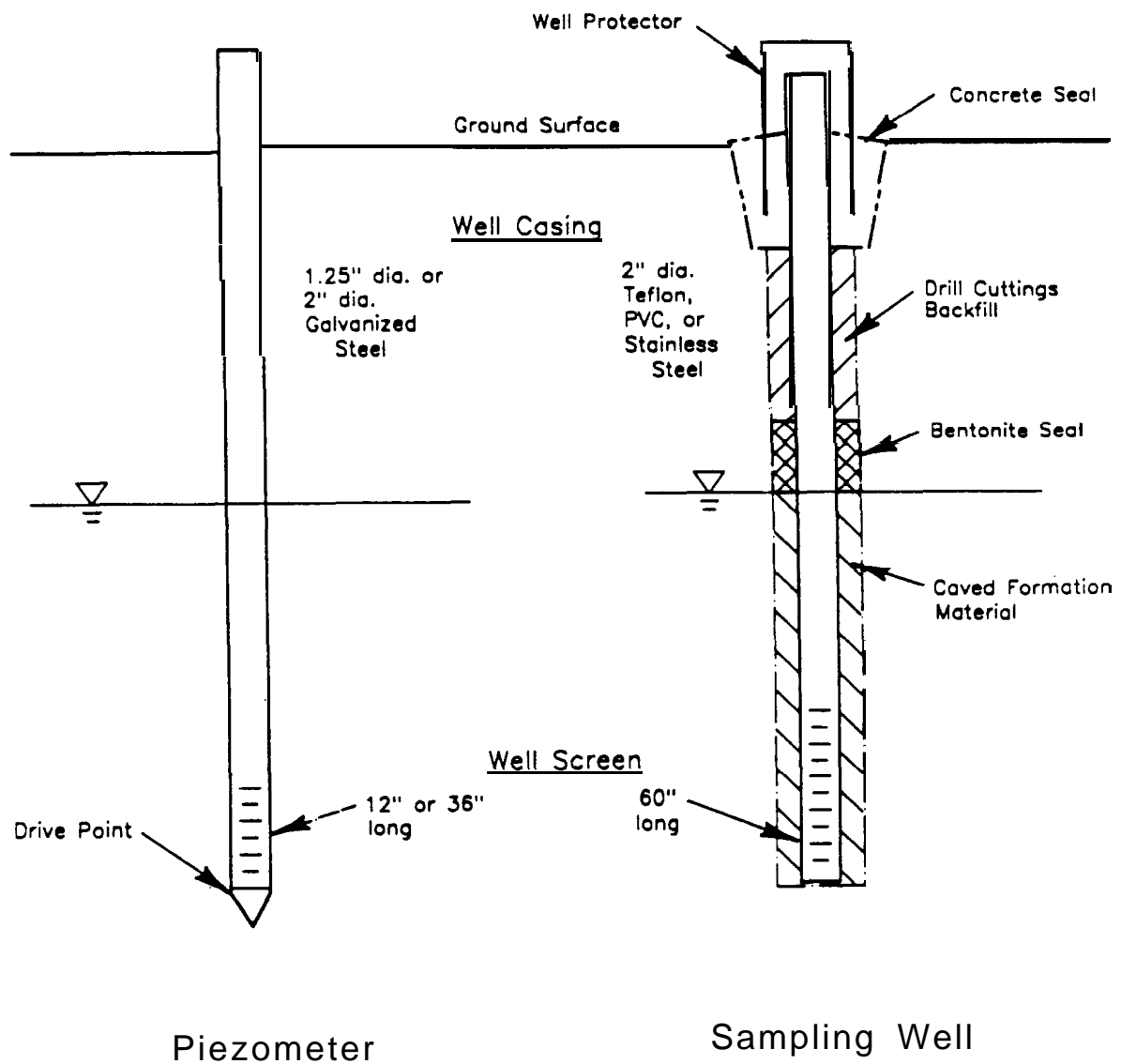
## Monitoring Wells

Bore holes for construction of all monitoring wells were drilled with a 4.25-inch (11 cm) inside diameter (I.D.) hollow-stem auger. Prior to drilling at each location, all auger flights and aquifer solid samplers were steam cleaned thoroughly. Steam cleaning was not done when moving between successively deeper holes at the same site but was done when moving to a different site (e.g., moving from areas downgradient to upgradient of the anaerobic impoundments at Beardstown). In addition, all well casing materials and well protectors were steam cleaned immediately before placement in the bore hole.

Due to the sandy environment, it was necessary to use water to maintain an open hole as auger flights were added. Only water taken from nearby water wells with similar water quality to that of the upgradient wells was used. No drilling mud or other method of bore hole stabilization was used. Casing lengths and the screen were screwed together as they were placed down the inside of the auger flights before the flights were removed to ensure that the sandy materials would not collapse in the bore hole after drilling. All casings and screens were 2-inch (5 cm) I.D. In every case, the saturated formation collapsed around the casing and screen as the auger string was removed, leaving an open bore hole only above the water table. A plug of bentonite pellets two to three feet thick was placed in the annulus directly above the top of the caved material. Drill cuttings (principally sand) were backfilled above the bentonite seal to within three feet of land surface. A concrete plug approximately 3 feet (0.9 m) deep and 2 feet (0.6 m) in diameter was placed around the well casing at the ground surface to prevent surface drainage from moving down the well casing. A six-inch (15 cm) diameter steel well protector with locking cap was installed over the protruding well casing to complete the well.

The construction details of the sampling wells (Figure 6) at both sites are identical in all ways other than the length of casing and casing materials in two wells at Beardstown. One well at Beardstown was constructed of stainless steel (SS) and one other of polyvinylchloride

All of the other sampling wells at both sites were constructed with polytetrafluoroethylene (PTFE-Teflon<sup>®</sup>, DuPont). All wells have 2-inch



**figure 6.** Typical piezometer and sampling well construction for the Sand Ridge and Beardstown field sites.

(5 cm) I.D. flush-threaded casing. Screens were 5 feet (1.5 m) long with 0.01-inch (0.02 cm) slot openings.

Dedicated tubing and positive displacement bladder pumps (Well Wizard<sup>®</sup>, QED Environmental Systems) were permanently installed in each sampling well with pump intakes positioned 2 feet (0.6 m) below the top of the screen in each well. Each bladder and all tubing were made of PTFE, but the pump housings and fittings were made of the same material as that of the well casing in which they were installed (i.e., PTFE pumps in PTFE wells, PVC pump in PVC well, and SS pump in SS well).

Well development was performed within hours of well installation by evacuating the water in the casing with compressed air. Surging to first evacuate the casing, then allowing complete recovery of the water in the well was the best available method to obtain water movement through the well screen to remove fine materials from the permeable sands and gravels. Development times from 30 minutes to one hour were required until the discharge was free of sediment. Steady development with a constant stream of compressed air was equivalent to a pumping rate of 20 to 30 gallons per minute (1 to 2 l/s) at both sites.

Following development, hydraulic conductivities at all sampling wells were determined by slug tests performed through a casing pressurization technique similar to that detailed by Prosser (65). The casing pressurization technique was used because these highly permeable aquifers possess very rapid (less than one minute) recovery times. A microcomputer-controlled data acquisition system was used at the two field sites to allow collection of up to 100 data points (depth-to-water measurements) per second (66). Casing pressurization tests could not be performed at the Sand Ridge well DO35 (#1 in Figure 7) because the height of the water column over the well screen was insufficient to allow for significant displacement of water.

### Piezometers

The piezometers at both sites (Figure 6) consisted of drive points constructed of galvanized steel casing. Screens on the drive points were either 12 inches (30.5 cm) or 36 inches (91.4 cm) long and had slot widths of 0.01 inches (0.02 cm). Casing diameters were either 1.25 inches (3.2 cm) or 2 inches (5 cm).

### Hydrologic Monitoring Systems

Data logging systems for continuous recording of selected hydrologic and meteorologic parameters were installed late in the project to provide more information on the timing of recharge events at both sites. Instrumentation included:

- 1) submerged pressure transducers to measure ground-water levels in a piezometer nest,
- 2) a tipping-bucket rain gauge to measure rainfall timing and intensity,

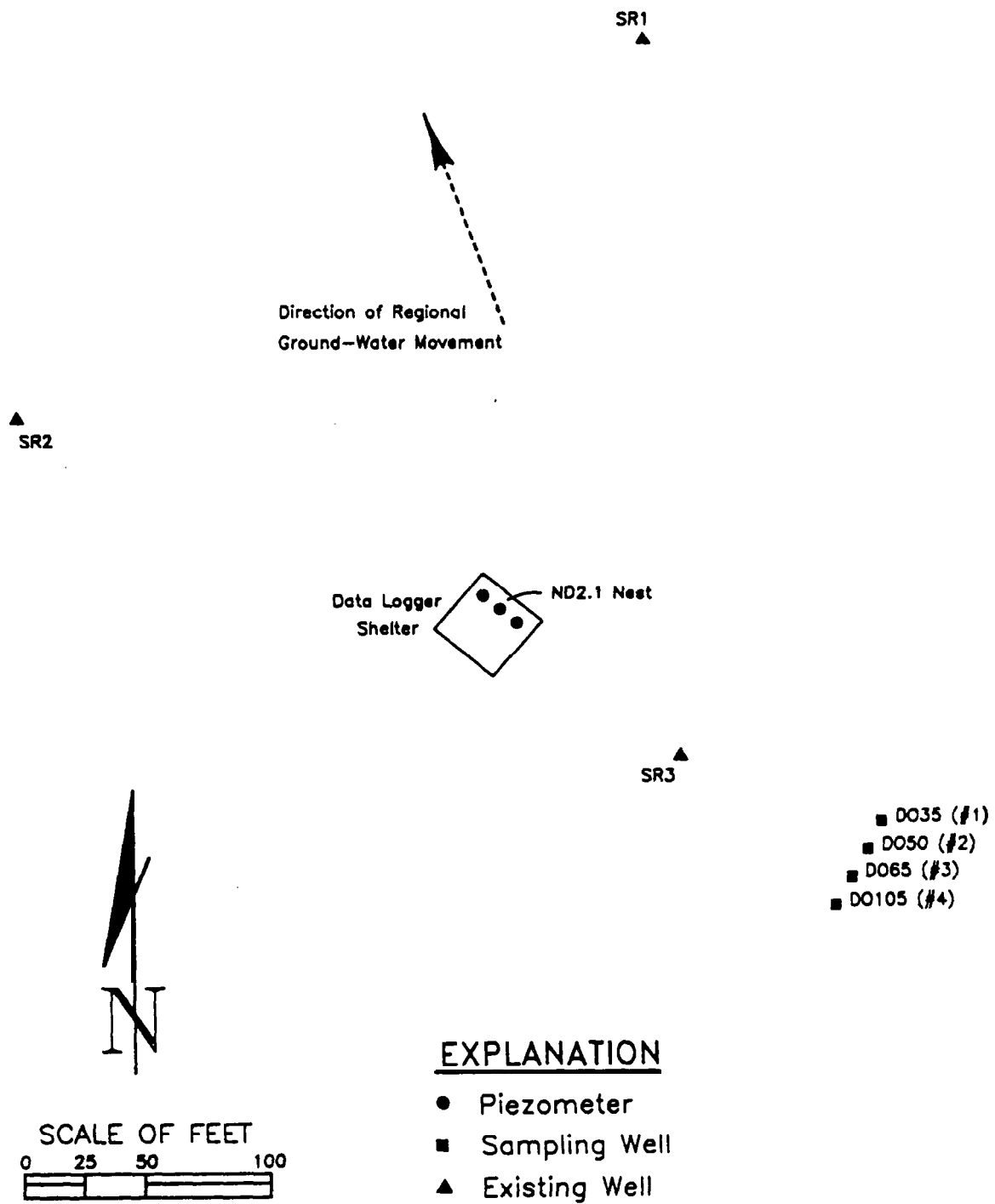


Figure 7. Sampling well and piezometer network for the Sand Ridge field site.

- 3) a temperature probe to measure ambient air temperature, and
- 4) a barometric pressure sensor to measure atmospheric pressure.

Parameters sensed by these instruments were recorded on a multichannel, battery-operated, portable data logging system (Easylogger<sup>(R)</sup> Omnidata). This particular data logging system provided a means to record sensed data every 15 minutes for a period in excess of thirty days without downloading the recorded data. Data were stored on 128 kilobyte nonvolatile EPROM (erasable programmable read only memory) storage packs. Storage packs were capable of being replaced in the field, brought back to the office, and downloaded to transfer the stored data to a microcomputer.

## **SAND RIDGE STATE FOREST**

### **Background**

The placement of sampling wells for the purpose of evaluating natural variations in ground-water quality at this "clean" site was not as critical as at the "contaminated" Beardstown site. The site at Sand Ridge has been used in previous (63) and other current (67) State Water Survey experiments, so the hydrogeology of the site was well known. In particular, the depth to water and the direction and rate of ground-water movement had been documented.

One principal concern for this site was the construction of the shallowest sampling well. To evaluate shallow ground-water quality changes, it was important to complete a well as near to the water table as possible. The risk of a shallow well completion was that of the well going dry during the study period and the subsequent loss of that data collection point. Since 1982, the water table had been falling principally as a result of water use by the nearby fish hatchery. Consideration was given to both natural ground-water fluctuations and the maximum drawdown that could be expected from the fish hatchery's production wells.

A second concern at this site was to avoid the potential influence of residual dye tracers used in experiments conducted in 1983 (63). Information from previous and ongoing research at the site provided excellent information to determine a location upgradient from such potential influences. A summary of the well construction details for the Sand Ridge site appears in Table 2.

### **Piezometer Network**

Many of the piezometers at this site have been in place since 1982 and have provided a record of water level fluctuations since that time. Wells SR1, SR2, and SR3 (Figure 7) are 40 feet (12 m) deep with 20-foot (6 m) screens that intersect the water table. Ground-water elevation data from these wells were used to calculate the gradient and direction of flow at the

TABLE 2. SAND RIDGE WELL CONSTRUCTION DETAILS

Well name	Well type <sup>a</sup>	Date completed	Measuring point elev. <sup>b</sup> (ft)	Bottom elev. <sup>b</sup> (ft)	Well depth (m)	Well riser <sup>c</sup> (m)	Screen length (m)
SR1	5 cm PVC	1982	993.59	951.6	12.0	0.73	6.1
SR2	5 cm PVC	1982	991.78	949.8	12.1	0.61	6.1
SR3	5 cm PVC	1982	991.73	949.7	12.1	0.64	6.1
ND2.1.1	3.2 cm SP	1982	991.29	956.3	10.0	0.58	0.6
ND2.1.2	3.2 cm SP	1982	991.31	952.3	11.2	0.58	0.6
ND2.1.3	3.2 cm SP	1982	991.32	947.3	12.8	0.58	0.6
DO35 (#1)	5 cm PTFE	10/84	992.43	955.3	10.7	0.64	1.5
DO50 (#2)	5 cm PTFE	10/84	992.44	940.2	15.2	0.67	1.5
DO65 (#3)	5 cm PTFE	10/84	993.33	925.1	19.8	0.67	1.5
DO105 (#4)	5 cm PTFE	10/85	992.09	885.0	32.0	0.64	1.5

<sup>a</sup> PVC, polyvinyl chloride; SP, sand point; PTFE, Teflon<sup>(R)</sup>

<sup>b</sup> Elevations in feet relative to 1000-foot datum, not mean sea level

<sup>c</sup> Height of well above land surface

site. Nested wells ND2.1.1, ND2.1.2, and ND2.1.3 are 1.25 inch (3.2 cm) diameter drive points with 12 inch (30.5 cm) long, 0.01-inch (0.02 cm) slotted screens completed at depths of 33, 37, and 42 feet (i.e., 10, 11, and 12.5 m), respectively.

### **Monitoring Wells**

The sampling wells, #1, #2, #3, and #4, are located as close to the upgradient boundary of the field site as possible (Figure 7). The wells were placed upgradient of well sites used in the previous tracer experiments according to ground-water level information collected from the SR wells. The sampling wells were completed at depths of 35, 50, 65, and 105 feet (11, 15, 20, and 32 m) below ground. Wells #1, #2 and #3 were completed in October of 1984. Well #4 was completed in September, 1985. All four wells have PTFE casing and screen.

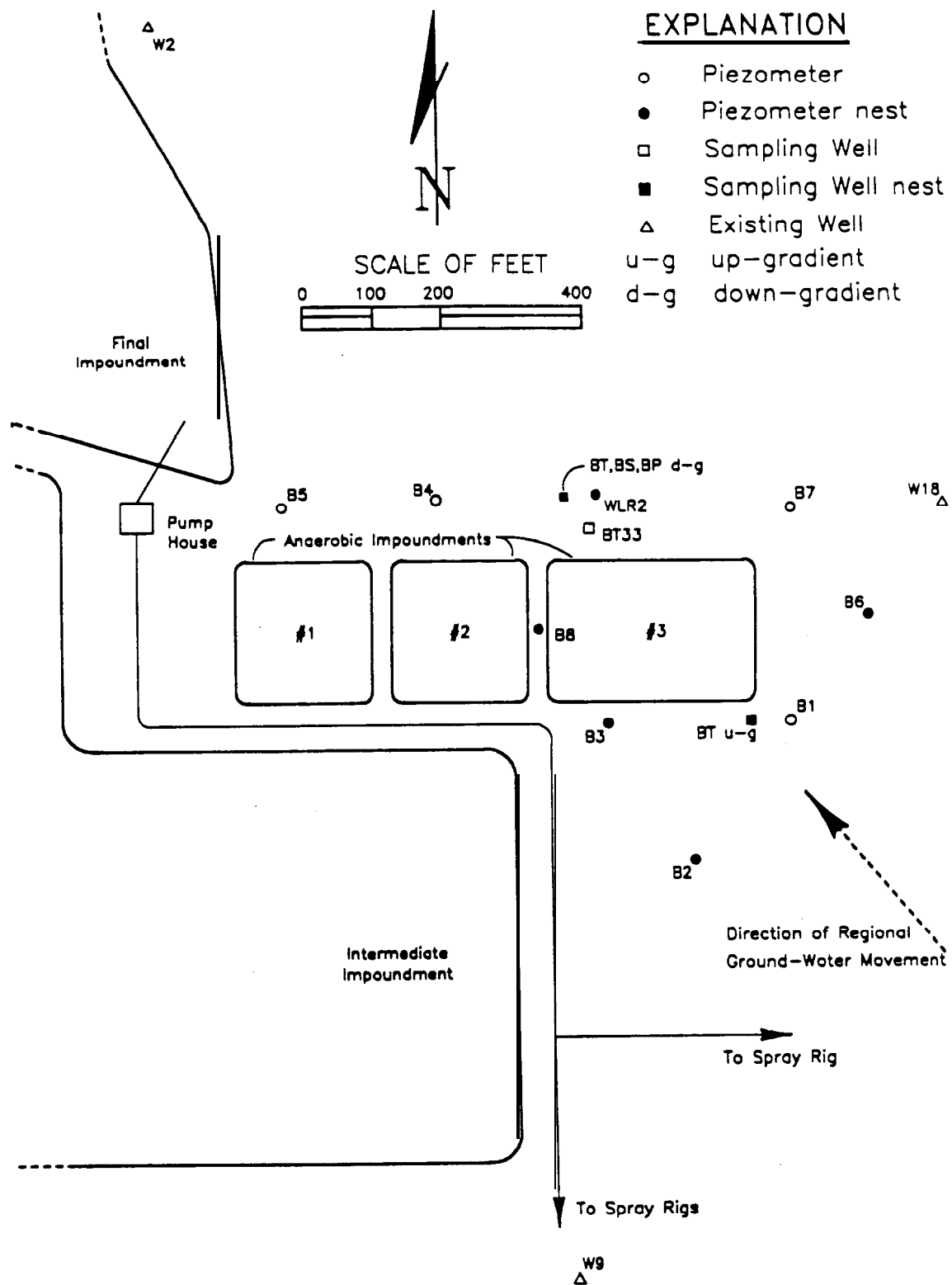
### **Hydrologic Instrumentation**

The data logging system for this site was installed inside a walk-in shelter built around the ND nest of wells. The system was designed to monitor: a) water levels in the 3 ND wells by means of 3 submerged pressure transmitters, b) precipitation in a tipping-bucket rain gauge, c) ambient air temperature from a temperature probe, and d) atmospheric pressure from a barometric pressure sensor. Installation of these instruments did not occur until August, 1987. The usefulness of data from the instruments was greatly reduced due to the lack of measurable recharge during the remainder of the sampling period.

## **BEARDSTOWN**

### **Background**

The Beardstown site is located on the property of a commercial pork processing operation. The average plant waste discharge for this facility is approximately 1.1 million gallons per day ( $0.05 \text{ m}^3/\text{s}$ ). The wastewater is composed of animal slaughtering wastes, processing wastes, and a small volume of sanitary sewage. Treatment of the wastewater is accomplished by a three-stage series of impoundments (Figure 8). Waste flow from the plant is initially sent to a set of three small anaerobic impoundments. These three impoundments are arranged in parallel and cover a total of approximately 3.2 acres (1.3 ha). Discharge from these impoundments is sent to a 30-acre (12 ha) intermediate impoundment capable of storing approximately 29 million gallons ( $110,000 \text{ m}^3$ ). Five floating aerators in the intermediate impoundment provide oxygen to the water to enhance treatment. Wastewater is sent from the intermediate impoundment to another 30-acre (12 ha) impoundment for contact chlorination treatment. Discharge from the final impoundment is accomplished by three 1400 gpm ( $0.09 \text{ m}^3/\text{s}$ ) pumps which deliver the water to four central-pivot spray irrigation systems. The irrigation systems provide water to 400 acres (160 ha) of cropland situated southeast of the liquid waste impoundments. Discharge of water through the irrigation system occurs throughout the year whenever the final impoundment becomes full.



**Figure 8. General plan of the Beardstown field site.**



The process of selecting specific well locations at Beardstown was much more involved than at the Sand Ridge site. The local hydrogeology and chemistry of the ground water near the impoundments were unknown in any great detail at the beginning of the project. Very few ground-water data for the Beardstown area were available. No data existed to describe the influence of the impoundments on local ground-water flow and quality. Therefore, the design of the piezometer and sampling well networks progressed in stages with the goals of, first, accurately describing the regional gradient and direction of flow, and second, defining the location (vertically and horizontally) of the contaminant plume presumed to be emanating from the three anaerobic treatment impoundments.

Based on a consultant's report (64) regarding regional gradient and direction of flow, a triangular array of piezometers was placed south of the easternmost anaerobic impoundment (Figure 8) for the purpose of providing more site-specific information. Later, more piezometers and piezometer nests were installed at several locations around and between the impoundments to determine the presence and magnitude of vertical gradients caused by mounding of water beneath the impoundments (Figure 9). The data obtained from these piezometers were used to establish the positions of the upgradient and downgradient nests of sampling wells on a line parallel to the regional ground-water flow path passing beneath anaerobic impoundment 3.

Before designing and installing the sampling well network, it was necessary to find the horizontal and vertical position of the leachate plume presumed to be emanating from the anaerobic impoundments. In July of 1985, small diameter sand points were driven at several locations along the downgradient side of the easternmost anaerobic impoundment (#3). At each 5 foot (1.5 m) depth interval, the well point was bailed until the discharge was clear of sediment. A sample was subsequently collected and tested for electrical conductance. Higher electrical conductivity indicated the presence of greater dissolved solids concentrations that would accompany a contaminant plume at this site. The highest conductivity readings occurred in a 15-foot (4.6 m) thick zone between depths of 20 and 35 feet (6.1 to 10.6 m). This zone was chosen for the position of the downgradient sampling wells. Aquifer solid samples taken from the formation at the depth of the sampling well screens indicated that the zone of interest consisted of a silty medium-grained sand. A summary of the well construction details at the Beardstown site appears in Table 3.

### **Piezometer Network**

Most of the piezometers at this site were installed specifically for the purposes of the project, and their locations are shown in Figure 9. Well W18 had been drilled previously and formed part of a larger sampling network used by facility consultants. Piezometers WLR2.1 and WLR2.2 are nested 2-inch (5.1 centimeter) diameter sand point wells that were monitored continuously by the data logger at this site. All other piezometers with names beginning with a "B" are 1.25-inch (3.2 centimeter) diameter sand points.

TABLE 3. BEARDSTOWN WELL CONSTRUCTION DETAILS

Well name	Well type*	Date completed	Measuring point elev. (ft MSL)	Bottom elev. (ft MSL)	Well depth (m)	Well riser** (m)	Screen length (m)
B1	3.2 cm SP	6/25/85	450.92	433.9	4.2	0.91	0.91
B2.1	3.2 cm SP	6/25/85	450.55	433.5	4.3	0.88	0.91
B2.2	3.2 cm SP	10/29/85	450.52	423.5	7.3	0.88	0.91
B3.1	3.2 cm SP	6/25/85	451.71	434.7	4.3	0.85	0.91
B3.2	3.2 cm SP	6/25/85	451.79	421.8	8.2	0.88	0.91
B4	3.2 cm SP	6/26/85	458.20	430.2	7.5	0.94	0.91
B5	3.2 cm SP	6/26/85	460.55	431.5	8.0	0.75	0.91
B6.1	3.2 cm SP	10/29/85	453.67	435.7	4.6	0.85	0.91
B6.2	3.2 cm SP	10/30/85	453.51	425.5	7.7	0.82	0.91
B7	3.2 cm SP	10/30/85	458.82	434.8	6.4	0.91	0.91
B8.1	3.2 cm SP	10/30/85	462.60	435.6	7.3	0.88	0.61
B8.2	3.2 cm SP	10/30/85	462.62	425.6	10.3	0.91	0.61
B8.3	3.2 cm SP	4/7/87	462.54	442.6	5.2	0.88	0.61
WLR2.1	5 cm SP	10/30/85	458.68	430.7	7.6	0.88	0.91
SLR2.2	5 cm SP	10/30/85	458.47	425.5	9.2	0.82	0.91
BT18 (#5)	5 cm PTFE	10/10/85	450.99	431.0	5.6	0.45	1.52
BT23 (#6)	5 cm PTFE	10/10/85	451.20	426.2	7.1	0.45	1.52
BT25 (#8)	5 cm PTFE	10/9/85	457.48	430.5	7.7	0.45	1.52
BT30 (#9)	5 cm PTFE	10/9/85	457.56	425.6	9.2	0.45	1.52
BT35 (#10)	5 cm PTFE	10/9/85	457.72	420.7	10.8	0.45	1.52
BS30 (#11)	5 cm SS	10/9/85	458.04	426.0	9.2	0.45	1.52
BP30 (#12)	5 cm PVC	10/9/85	457.70	425.7	9.2	0.45	1.52
BT33 (#13)	5 cm PTFE	10/9/85	458.74	423.7	10.2	0.45	1.52
W18	5 cm GS	4/19/82	457.52	439.5	5.2	0.30	1.52

\* SP, sand point; PTFE, Teflon<sup>(R)</sup>; SS, stainless steel; PVC, polyvinyl chloride;  
GS, galvanized steel

\*\* Height of well above land surface

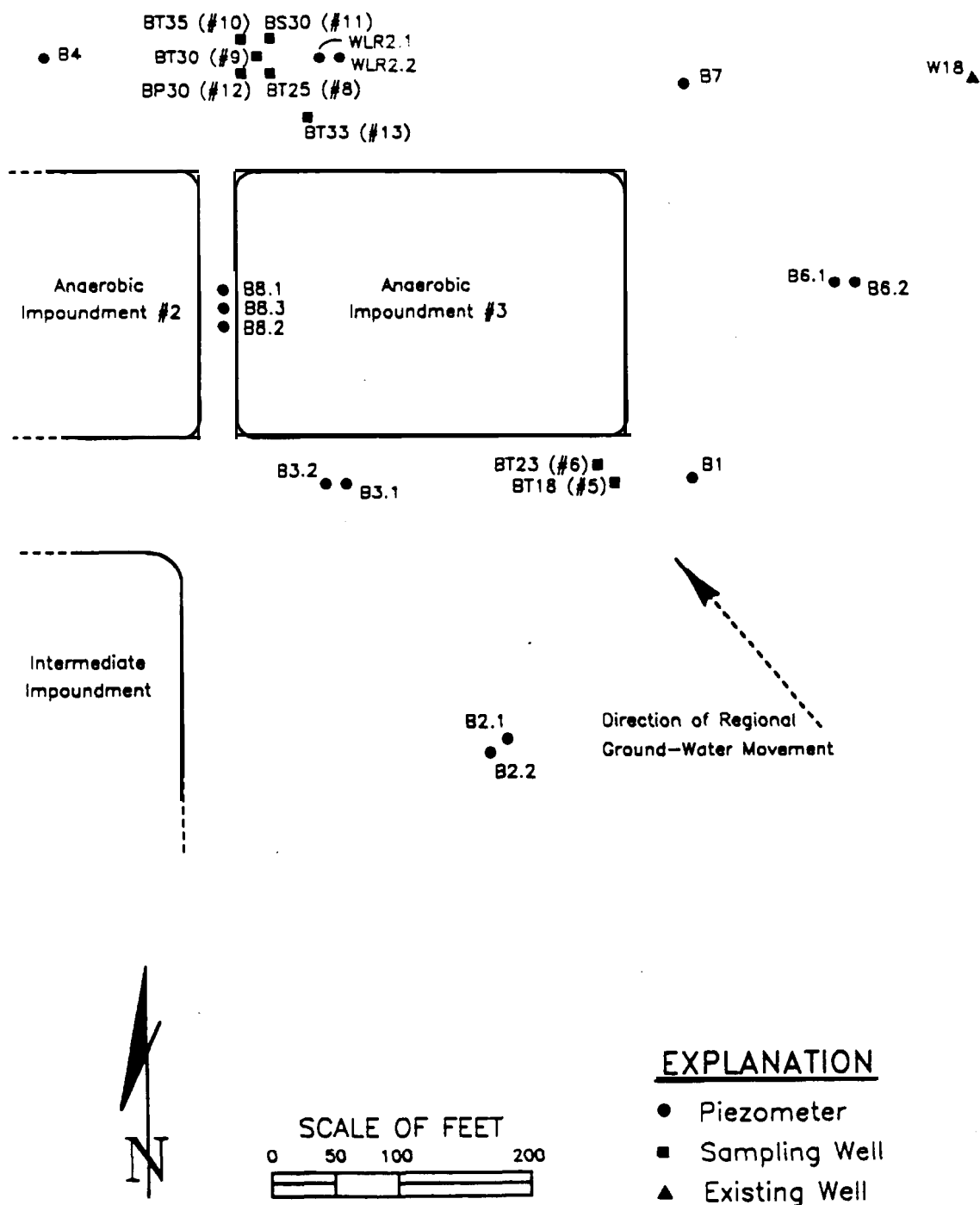


Figure 9. Detailed view of the sampling well and piezometer network at the Beardstown field site.

The piezometers were installed in a pattern that facilitated the drawing of potentiometric surface maps at three different levels beneath the impoundments. The deepest Well in each nest, Bn.2, monitors the regional gradient and direction of flow. The shallow wells, Bn or Bn.1, indicate the effect of mounding under the impoundments. Piezometer B8.3 was installed on the berm between the impoundments as a means of locating the top of the ground-water mound formed by water leaking beneath impoundments 2 and 3.

### **Monitoring Wells**

The downgradient nest of sampling wells (Figure 9) contained three PTFE wells, #8, #9 and #10, with screens placed at three discrete 5-foot (1.5 m) intervals. The wells were completed at 25 feet (8 m), 30 feet (9 m), and 35 feet (11 m) below ground surface, respectively. These three wells were located in such a way as to be parallel to the regional ground-water flow path, while two other 30-foot (9 m) wells, #11 and #12, (one SS and the other PVC) were placed on either side of the 30-foot (9 m) PTFE well, #9, in a line perpendicular to regional ground-water flow.

The two upgradient wells, #5 and #6, were completed at 18 feet (5.5 m) and 23 feet (7 m). The wells were placed at the foot of the impoundment berm on a cross section parallel with the regional ground-water, flow and through the downgradient wells #8, #9, and #10. Wells #5 and #6 also were constructed of PTFE. Sampling well #13 was completed at a depth of 33 feet (10 m) and was placed along the same cross section as the other sampling wells at a point mid-way between the impoundment and the downgradient nest of wells. Because of land surface elevation changes, the screened sections of wells #6, #9 and #13 are approximately the same depth below the water table.

### **Hydrologic Instrumentation**

The data logging system at Beardstown recorded water levels in the piezometer nest WLR2.1 and WLR2.2, precipitation, barometric pressure and ambient air temperature. Installation of this system was completed in April 1987.

## **FIELD ACTIVITIES**

### **Sampling Trip Logistics**

Biweekly sampling was the highest frequency which would permit sample analysis within the recommended holding times for each constituent and allow preparation for the next run on a routine basis. It was necessary to carefully consider the timing of each step of the operation to maintain the sampling frequency within a day of the biweekly timing. The sampling crew was charged with establishing a sample collection routine which would work within the travel, sampling and analytical constraints. The schedule outlined in Table 4 was used during this project.

The travel involved in this schedule proved to be quite manageable, even in inclement weather, provided the sampling itself could be completed.

**TABLE 4. PROJECT SAMPLING RUN SCHEDULE**

**Day 1**

7:00 AM	Depart Champaign
9:30 AM	Arrive Manito, IL; purchase ice for sample coolers
9:45 AM	Arrive Sand Ridge State Forest
10:00 AM	Set up; measure ground-water levels in monitoring wells; insulate pump output lines and calibrate field measurement equipment
<b>10:30 AM</b>	Begin well purging procedures and flow measurements
11:00 AM	Measure ground-water levels in piezometers; purge and sample PTFE wells #1-4 in order. Field determinations of alkalinity and dissolved oxygen are made as samples are collected.
2:30 PM	Take blank samples for Day 1 (well #7) and prepare to leave for Beardstown site
4:30 PM	Arrive at Beardstown upgradient well site; repeat setup, ground-water level measurement, calibration and purging procedures
5:30 PM	Sample upgradient monitoring wells #5 and 6 in order and perform alkalinity and dissolved oxygen determinations; prepare to leave site

**Day 2**

8:00 AM	Purchase ice and refuel vehicle, if necessary
9:00 AM	Arrive at Beardstown downgradient well site; repeat setup, ground-water level measurement, calibration and purging procedures; measure ground-water levels in piezometers
10:30 AM	Sample nested PTFE wells #8, 9, 10 in order, then complete wells #11, 12 and 13; perform alkalinity and dissolved oxygen determinations as samples are collected
2:00 PM	Take blank samples for Day 2 (well #14); prepare to leave site
4:30 PM	Arrive Champaign; unload samples from van, sort and select two wells for duplicate analyses and two wells for spiking
5:30 PM	Spike and split samples appropriately and transfer to refrigerators and freezers for storage prior to analysis

The most critical holding periods for specific analytes (i.e. sulfide, ferrous iron, methane and ammonia) could still be met even if road closures or other problems necessitated an additional overnight stay prior to returning to Champaign.

### **Use of the Van**

In order to establish control over the conditions of purging, sampling, and field determinations, a sampling vehicle was designed, purchased, and outfitted. Built on a 20-foot (6 m) stock van chassis, it was equipped with a 6.5 kw generator, heating and air-conditioning, a refrigerator, and a 1 HP on-board air compressor to supply drive gas for the sampling pumps. The van also has approximately 12 linear feet (3.6 m) of bench space for field determinations. It seats three individuals which make up the foul-weather sampling crew. The vehicle was received in mid-October of 1985 from the manufacturer.

### **Field Parameters and Sampling Protocols**

Sampling and analytical protocols are detailed descriptions of the actual procedures used in sample retrieval, handling, storage and transport, subsampling and analysis. Given the results of our previous research involving ground-water sampling, we were confident in our selection of reliable sampling and purging techniques (1,2,3,4,5,6). The basis of the sampling protocol was to obtain chemically and hydrogeologically representative samples for volatile organic compounds. It was expected that a suitable protocol for the collection of volatile organic compounds would be more than adequate for the other, less error-prone chemical constituents. Therefore, purging would be done at flow rates well below those used during well development. The actual sampling of the ground water would be done at flow rates of approximately 100 mL/min. Wells at both sites showed very good yields, with hydraulic conductivities in excess of 400 gpd/ft<sup>2</sup> (0.02 cm/s). From rough computations (3), it was clear that greater than 95% aquifer water could be obtained from pumps set at the top of the well screen in ten minutes or less by pumping at 1-2 L/min. Thus, all of the wells could be pumped at a relatively low rate, ensuring hydrologic representativeness. This was verified for each well at the time of sampling by monitoring the well purging parameters: pH, temperature, conductivity, redox potential and dissolved oxygen. The remainder of the sampling protocol for the chemical constituents of interest involved Agency recommended procedures for sample handling and preservation (68,69).

The sample handling scheme followed in the field is shown in Figure 10, referenced to the notes below:

- A. Once the variabilities of the well purging parameters had stabilized to less than about 10% (i.e.,  $\pm 0.05$  pH,  $\pm 5$   $\mu\text{S}\cdot\text{cm}^{-1}$ ,  $\pm 0.1^{\circ}\text{C}$ , and  $\pm 5$  mv) over two successive well volumes, unfiltered samples were taken first for organic compound determinations. The sample containers were 40 mL (TOC, VOC) or 500 mL (TOX) glass bottles with PTFE-lined caps. After flushing the sample bottles with the aquifer

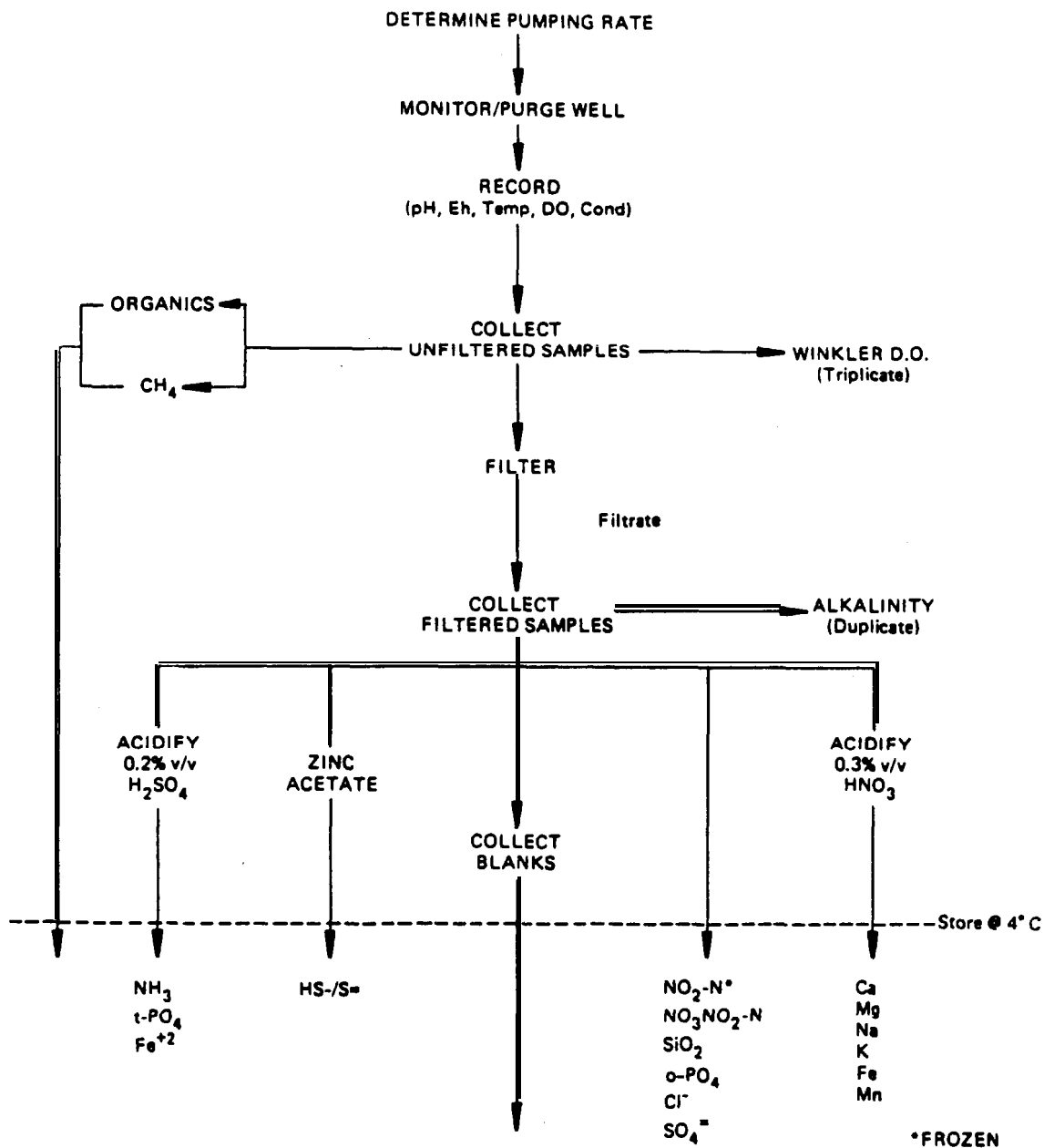


Figure 10. Sample handling flow diagram.

water, samples were taken devoid of headspace and refrigerated. Methane samples were obtained by filling 25 mL gas tight polyethylene syringes. These were also refrigerated.

- B. Triplicate field samples of unfiltered water (Wells #1 - 3 only) were collected in clean, 300 mL glass BOD bottles for dissolved oxygen determinations. The Azide Modification of the Winkler Method was used (70).
- C. A SS and PTFE in-line filter holder with 0.4  $\mu\text{m}$  polycarbonate membranes was used for sample filtration, with the dedicated sampling pumps providing the pressure. At least one liter of water was filtered and discarded in order to flush the filter holder and wash the membrane before any samples were taken. Samples for various analyses were treated as shown in Table 5 (e.g., samples for metals determinations were taken in acid cleaned, 500 mL high-density polyethylene bottles and acidified with  $\text{HNO}_3$ ).
- D. Duplicate field samples of filtered water were taken in clean polyethylene bottles for alkalinity determinations.
- E. At the end of each day, field blanks of double deionized water were taken as well numbers 7 and 14 for each inorganic parameter and preserved accordingly. Double distilled-in-glass water was used for the organic parameter blanks.

Replicate samples were taken from each well for all analytes except methane. Two samples from two individual wells (one from each site) were selected for duplicate analyses. Similarly, two samples were chosen for spiking with suitable standards for the inorganic species.

In order to expedite the sample handling procedures, all sample bottles were brought into the field thoroughly cleaned and labelled for individual analyses or similarly preserved analytes. An example set of labels is shown in Figure 11. The labels contain project-specific information such as ID# (well or blank), date of collection, means of preservation, handling precautions (if any), as well as the determinations to be done on subsequent subsamples. Details of how this information was used in sample tracking are provided in sections to follow.

## LABORATORY ACTIVITIES AND ANALYTICAL PROTOCOLS

### Sample Preparation

Polyethylene bottles to be used for field collection were initially washed in a 5% Contrad 70<sup>(R)</sup> detergent solution. The bottles were then rinsed with deionized water, followed by a rinsing with 50% HCl. The final



**TABLE 5. SAMPLE HANDLING, PRESERVATION AND ANALYSIS ACCORDING TO PARAMETER**

Chemical parameter	Container type <sup>1</sup>	Means of preservation <sup>2</sup>	Maximum holding <sup>3</sup>	Approximate time to analysis <sup>4</sup>
Alkalinity	HP	4°C	24 hours	Immediate
Winkler DO	B	Fix on site, store dark	8 hours	Immediate
NH <sub>3</sub>	HP	4°C, 0.2% v/v H <sub>2</sub> SO <sub>4</sub>	28 days	<3 days
NO <sub>3</sub> NO <sub>2</sub> -N	HP	4°C	8 hours	<3 days
S <sup>=</sup>	V	4°C, Zinc Acetate	7 days	<3 days
SiO <sub>2</sub>	HP	4°C	28 days	<3 days
o-PO <sub>4</sub>	HP	4°C	48 hours	<4 days
NO <sub>2</sub> -N	HP	Frozen	48 hours	<4 days
TOC	V	4°C, Gas Tight	24 hours	<4 days
VOC	V	4°C, Gas Tight	24 hours	<4 days
t-PO <sub>4</sub>	HP	4°C, 0.2% v/v H <sub>2</sub> SO <sub>4</sub>	28 days	<5 days
CH <sub>4</sub>	S	4°C, Gas Tight	24 hours	<1 week
Cl <sup>-</sup>	HP	4°C	28 days	<1 week
Ca	HP	4°C, 0.3% v/v HNO <sub>3</sub>	6 months	<2 weeks
Fe	HP	4°C, 0.3% v/v HNO <sub>3</sub>	6 months	<2 weeks
Fe(II)	HP	4°C, 0.3% v/v HNO <sub>3</sub>	8 hours	<2 weeks
K	HP	4°C, 0.3% v/v HNO <sub>3</sub>	6 months	<2 weeks
Mg	HP	4°C, 0.3% v/v HNO <sub>3</sub>	6 months	<2 weeks
Mn	HP	4°C, 0.3% v/v HNO <sub>3</sub>	6 months	<2 weeks
Na	HP	4°C, 0.3% v/v HNO <sub>3</sub>	6 months	<2 weeks
SO <sub>4</sub> <sup>=</sup>	HP	4°C	28 days	<2 weeks
TOX	G	4°C, Gas Tight		<2 weeks

Footnotes:

1. High density polyethylene (HP), glass septum vial (V), amber glass with PTFE-lined cap (G), polyethylene syringe (S), BOD bottle (B).
2. Sample preservation performed immediately upon collection.
3. Samples analyzed as soon after collection as possible.  
The times listed are the maximum times that samples may be held before analysis and still considered valid. Some samples may not be stable for the maximum time period given (68,69).
4. Approximate time to analysis includes two days of field storage and transport.

SAMPLE TRACKING ID	SF 01 1950	DATE: 03/10/86	← COLLECTION DATE
	UNFILTERED	40 mL GLASS VIAL	
	GAS TIGHT		
	DET: VOLATILES		
SAMPLE ID	SF 01 1951	DATE: 03/10/86	
	UNFILTERED	40 mL GLASS VIAL	← STORAGE VESSEL
	GAS TIGHT		
	DET: TOC		
PROJECT	SF 01 1952	DATE: 03/10/86	
	UNFILTERED	500 mL AMBER GLASS	
PRECAUTION	GAS TIGHT		
	DET: TOX		
	SF 01 1953	DATE: 03/10/86	
	FILTERED	125 mL POLYETHYLENE	
	FROZEN		
	DET: NO2-		
	SF 01 1954	DATE: 03/10/86	
	FILTERED	500 mL POLYETHYLENE	
	0.3% V/V HNO3		
ANALYTE(S)	DET: Ca Mg Na K Fe Mn		
	SF 01 1955	DATE: 03/10/86	
	FILTERED	500 mL POLYETHYLENE	
	UNPRESERVED		
	DET: NO3 SiO2 o-PO4 CL- SO4=		
	SF 01 1956	DATE: 03/10/86	
	FILTERED	500 mL POLYETHYLENE	
	0.2% V/V H2SO4		
	DET: NH3 Fe(II) t-PO4		

Figure 11. Typical set of sample bottle labels.

step in bottle preparation was a complete rinsing with double-deionized water (resistivity > 17.8 megohms). Glass bottles for organic analyses were washed as above and then muffled at 450°C for 4 hours. All Teflon-lined bottle caps and septa were rinsed in methanol following the detergent washing procedure. Double deionized water was used for all cleaning, rinsing, blank and standard preparation for the inorganic parameters. Double distilled-in-glass water was used for the solutions and rinsing procedures for organic parameters.

Standard solutions for calibration of inorganic analyses were prepared by serial dilution with class-A volumetric glassware. Stock solutions were obtained from commercial vendors if available, or prepared by dilution of pre-measured ampules or a high-purity analytical salt of the desired constituent. All stock and calibration standards were verified by comparison to NBS or USEPA reference standards, as well as by comparison to previous lots of standard. Analytical standard solutions were prepared for sample spiking and the control standards prepared for submission as "field standards".

When samples were returned from the field, they were separated into analytical groups for spiking. The method of spiking varied with the set of constituents to be analyzed. Initially, for nitrite samples, an aliquot of nitrite standard was added to the field duplicate of each well chosen for spiking. This procedure proved to be inadequate for several reasons. Beginning with Run 25, the samples were spiked immediately in the field, prior to freezing, using a micropipette and a class-A volumetric flask. For sulfide samples, a glass microliter syringe was used to inject 50  $\mu$ L of the spike solution through the septum into the field duplicate sample of the two spike-designated wells. For all other inorganic constituents, an aliquot of spike solution was added directly to the appropriate duplicate sample bottle. This procedure was made more rigorous after Run 6, in which a 25 mL aliquot of stock spike solution was added to 475 mL of sample in a 500 mL volumetric flask. All spiked sample results were corrected for the dilution of the sample and spike volumes.

All field duplicate samples from wells which were not designated to be spiked or duplicated were put into refrigerated storage. Samples for atomic absorption analysis were not refrigerated prior to analysis because it was noted that the samples became turbid. The working analytical dilutions done by air-displacement pipettes were more accurate when used on samples which were at room temperature.

The sample processing scheme used for the project is illustrated in Figure 12, which includes the computer databases where the analytical values were recorded. The data processing aspects of the study will be covered in more detail in a later section of the report.

### Sample Tracking

The first step in the sample tracking process involved the pre-labeling of all sample bottles prior to each sampling trip, as described previously. All of the information from these labels was then entered into the sample

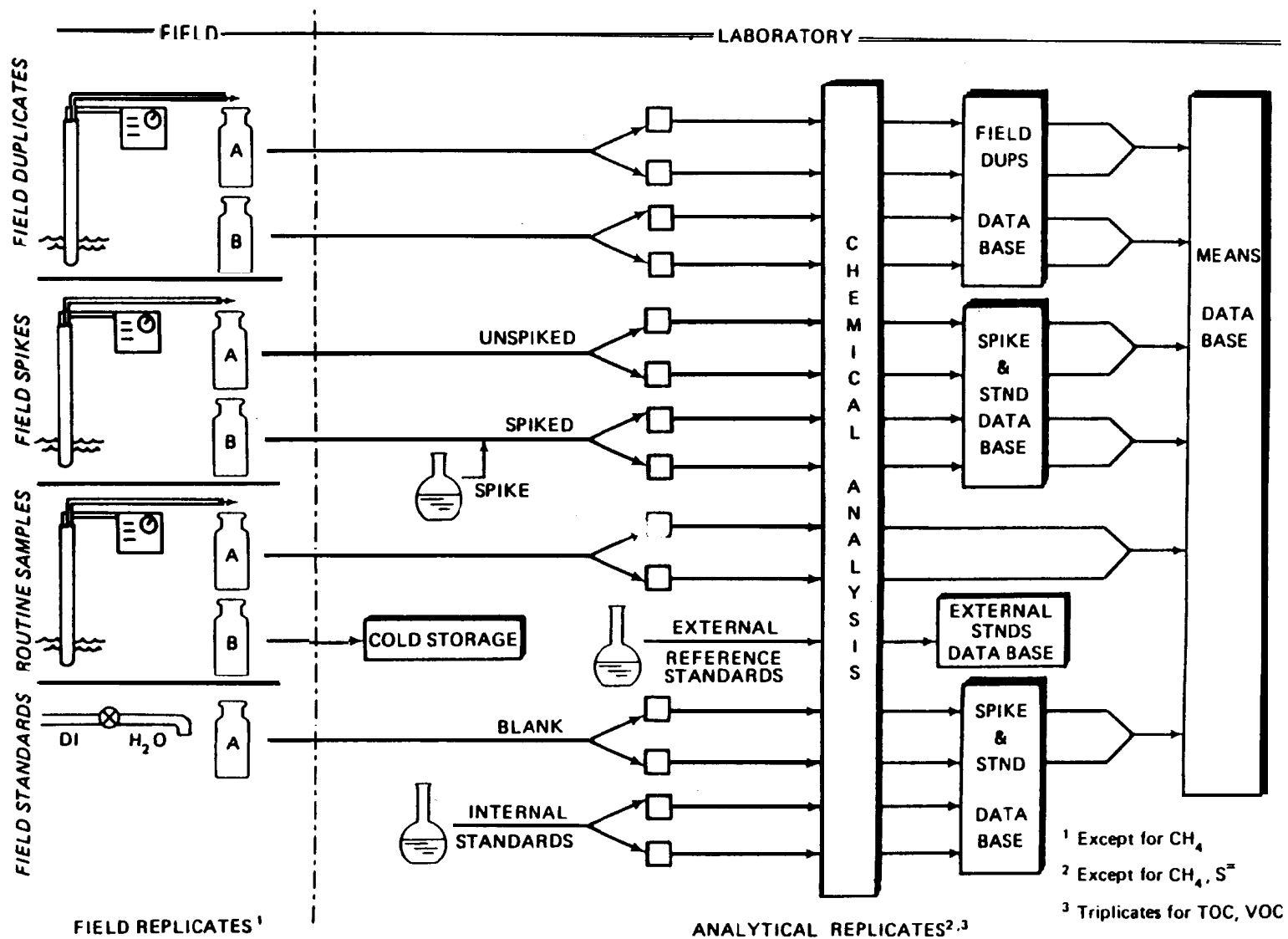


Figure 12. Project sample processing scheme.

tracking system, which was maintained as a Lotus 1-2-3<sup>(R)</sup> spreadsheet. In this way, even before Samples were collected, sample numbers had already been assigned. Once the samples arrived at the laboratory and had been sorted and spiked, determinations of the most sensitive constituents were begun. Each individual sample or subsample was also indexed by a laboratory identification number. As each sample was analyzed for specific constituents, the analyst noted the date, his or her initials, and any comments on difficulties relevant to that analysis. This information also was noted for those parameters which were measured in the field. Figure 13 is an example of the first sheet of the sample tracking system used for this project.

### **Analytical Protocols**

The analytical methods employed in the study are summarized in Table 6. Most of the test procedures involved the use of well-established methods, with necessary refinements or adjustments only for the particular analytical instruments available.

It was important to optimize the analytical protocols and minimize the time for sample processing given the variety of parameters and the number of corresponding instrumental methods. For the most part, standard methods were used for the basis of each determination without major modification (68,71,72). Ammonia, methane, sulfate, and metals determinations required special consideration. Ammonia determinations were made after neutralization of the H<sub>2</sub>SO<sub>4</sub>-preserved sample by 10 N NaOH by the method of Ivancic and Degobbis (73). In comparison with standard methods this method gave superior results over the wide concentration range observed between the ground-water samples at the two sites. Sulfate was determined by an automated potentiometric titration method using lead nitrate titrant. This was developed specifically for the project because of analytical interferences in the water samples from the downgradient Beardstown location. Total dissolved metals were determined by the single-solution modification (76) of the standard atomic absorption spectrophotometric method (68). In this modification, lanthanum (ionization suppressant) and cesium (releasing agent) were added at concentrations of 5 and 2 g/L, respectively.

A list of analytical instruments used by the laboratory for the study is given in Table 7. The analytical aspects of the project were performed as would be expected in a routine monitoring program. Research tasks, such as optimization of some of the methods for detectability, precision, or minimization of bias due to the sample matrix, could not be performed within the scope of the project. However, some problems with established procedures that prevented any reliable data collection were investigated to improve method performance. These investigations are discussed in detail in Section 5.

A large part of the analytical work load was the overall Quality Assurance (QA) effort, which included the use of calibration standards, external Quality Control (QC) standards (USGS, USEPA, NBS), field standards and blanks, field spikes, field duplicates and analytical duplicates. Analytical duplicates were performed on those samples and QC solutions for which duplication was possible. The samples themselves accounted for less

Lab ID	Proj ID	WELL NO	Date taken	PRESERV	FILTER	comment	D.O.	analyst	Alk	analyst
	FIELD	1	24-Aug-87	UP	0.1	DO/con/pH/Eh/Temp Unfiltered	24-Aug-87	JK	24-Aug-87	JK
	FIELD	2	24-Aug-87	UP	0.1	DO/con/pH/Eh/Temp Unfiltered	24-Aug-87	JK	24-Aug-87	JK
	FIELD	3	24-Aug-87	UP	0.1	DO/con/pH/Eh/Temp Unfiltered	24-Aug-87	JK	24-Aug-87	JK
	FIELD	4	24-Aug-87	UP	0.1	DO/con/pH/Eh/Temp Unfiltered	24-Aug-87	JK	24-Aug-87	JK
	FIELD	5	24-Aug-87	UP	0.1	DO/con/pH/Eh/Temp Unfiltered	24-Aug-87	JK	24-Aug-87	JK
	FIELD	6	24-Aug-87	UP	0.1	DO/con/pH/Eh/Temp Unfiltered	24-Aug-87	JK	24-Aug-87	JK
703298	SF-0109780	1	24-Aug-87	VIAL	uf					
703299	SF-0109781	1	24-Aug-87	VIAL	uf					
703300	SF-0109782	1	24-Aug-87	AMB GL	uf					
703301	SF-0109783	1	24-Aug-87	FROZEN	0.1					
703302	SF-0109784	1	24-Aug-87	HNO3	0.1					
703303	SF-0109785	1	24-Aug-87	UP	0.1					
703304	SF-0109786	1	24-Aug-87	H2SO4	0.1					
703305	SF-0109787	1	24-Aug-87	ZnAce	0.1					
703306	SF-0209788	2	24-Aug-87	VIAL	uf					
703307	SF-0209789	2	24-Aug-87	VIAL	uf					
703308	SF-0209790	2	24-Aug-87	AMB GL	uf					
703309	SF-0209791	2	24-Aug-87	FROZEN	0.1					
703310	SF-0209792	2	24-Aug-87	HNO3	0.1					
703311	SF-0209793	2	24-Aug-87	UP	0.1					
703312	SF-0209794	2	24-Aug-87	H2SO4	0.1					
703313	SF-0209795	2	24-Aug-87	ZnAce	0.1					
703314	SF-0309796	3	24-Aug-87	VIAL	uf					
703315	SF-0309797	3	24-Aug-87	VIAL	uf					
703316	SF-0309798	3	24-Aug-87	AMB GL	uf					
703317	SF-0309799	3	24-Aug-87	FROZEN	0.1					
703318	SF-0309800	3	24-Aug-87	HNO3	0.1					
703319	SF-0309801	3	24-Aug-87	UP	0.1					
703320	SF-0309802	3	24-Aug-87	H2SO4	0.1					
703321	SF-0309803	3	24-Aug-87	ZnAce	0.1					
703322	SF-0409804	4	24-Aug-87	VIAL	uf					
703323	SF-0409805	4	24-Aug-87	VIAL	uf					
703324	SF-0409806	4	24-Aug-87	AMB GL	uf					
703325	SF-0409807	4	24-Aug-87	FROZEN	0.1					
703326	SF-0409808	4	24-Aug-87	HNO3	0.1					

Figure 13. Example of the lead sheet of the sample tracking system.

TABLE 6. ANALYTICAL METHODS USED IN THE PROJECT

Parameter	Type of method*	Reference Method**			
		Std. Methods (71)	USEPA (68)	USGS (72)	Other***
pH	E				5
Conductance	E				5
TOC/VOC	P	505b	415.1		
TOX	APT	506			
Total Alkalinity	PT				5
Chloride	PT	407C			
(NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> )-N	AS		353.2		
SO <sub>4</sub> <sup>=</sup>	AS, PT	426D			(see text)
SiO <sub>2</sub>	AS			00955	
o-PO <sub>4</sub> <sup>=</sup>	S		365.3		
t-PO <sub>4</sub> <sup>=</sup>	S		365.3		
Ca	AAS				76
Mg	AAS				76
Na	AAS				76
K	AAS				76
Eh	E				5
DO	RT, E	421B, 421F			
Fe(II)	S				75
Fe(total)	AAS				76
Mn	AAS				76
NH <sub>3</sub>	S				73
CH <sub>4</sub>	GC-FID				74
S <sup>=</sup>	S	427			
NO <sub>2</sub> <sup>-</sup> -N	S	419			

\* Types of methods: AAS = atomic absorption spectrophotometric; APT = adsorption-pyrolysis, titrimetric; AS = automated spectrophotometric; E = electrometric; GC-FID = gas chromatographic - flame ionization detection; P = persulfate, oxidation; PT = potentiometric titration; RT = redox titration; S = spectrophotometric

\*\* Method number corresponding to, or most closely to, that used in this project.

\*\*\* See reference or text for discussion.

**TABLE 7. INSTRUMENTATION USED FOR ANALYTICAL DETERMINATIONS**

Parameters	Instrument
Ca, Mg, Na, K, Fe, Mn	GBC 903 Atomic Absorption Spectrophotometer (with D2 background correction for Fe, Mn, Mg)
Na, K	Allied Analytical Systems; Video 11E Atomic Absorption Spectrophotometer*
SiO <sub>2</sub> , (NO <sub>3</sub> <sup>-</sup> + NO <sub>2</sub> <sup>-</sup> )-N, NO <sub>2</sub> <sup>-</sup> -N, SO <sub>4</sub> <sup>=</sup> (Wells 1-4)	Technicon AAI system with Orion AS-150 autosampler and chart recorder
Cl <sup>-</sup> , SO <sub>4</sub> <sup>=</sup> (Wells 8-13), Fe(II) and S <sup>=</sup> standardizations	Metrohm E-636 Titroprocessor
NO <sub>2</sub> <sup>-</sup> -N, S <sup>=</sup> , NH <sub>3</sub> , Fe(II), O-P0 <sub>4</sub> , t-P0 <sub>4</sub>	Beckman DBG UV/VIS Spectrophotometer Beckman DU UV/VIS Spectrophotometer With Updatel <sup>(R)</sup> electronics
TOC, NVOC, POC	Oceanographic International Model 700 TOC analyzer
CH <sub>4</sub>	Varian 3740 Gas Chromatograph Hewlett-Packard 3390 Integrator
TOX	Dohrmann DC-20 TOX Analyzer
All inorganic calibration curves and calculations	IBM PC/XT, IBM PC/AT, or PC Designs Et 286i microcomputers using least-squares first or second-degree linear regressions done with RS/1 <sup>(R)</sup> ** software

\* Used as a backup for some of the metal analyses in other runs.

\*\* Trademark; Bolt, Beranek and Newman, Inc.



than 22% of all inorganic constituent determinations, with the exception of sulfide. A summary of the entire QA/QC analysis effort is given in Figure 14.

### **Reporting and Verification of Analytical Data**

Once a set of analytical determinations was completed and the analyst had made the appropriate entries in the sample tracking log, the results were reported in a summary which included:

1. Calibration curve with slope,  $r^2$ , intercept and the coefficients of the first- or second-degree linear equation fitted to the calibration points (sensitivity was included for atomic absorption and other spectrophotometric methods),
2. Instrument response readings (e.g., absorbance, peak height),
3. Dilution factors, if any,
4. Computed values for the calibration standards and all QC samples using the regression equation,
5. Predicted concentrations for each unknown, and
6. True values for all calibration standards and QC samples, with **bias** calculated as a percent recovery.

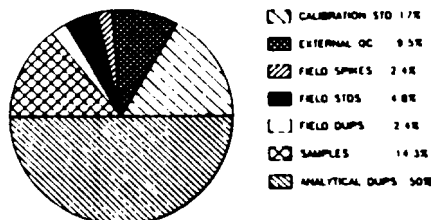
In order to maintain complete and accurate analytical records, each analyst was responsible for keeping backup copies of their results in a lab notebook, computer file, or both.

The chemical data generated from each sampling trip were recorded on master data sheets according to sample type (primary water sample, internal spikes and standards, field duplicates and external standards). The composition of these subsets, from collection to data handling, is shown in Figure 12.

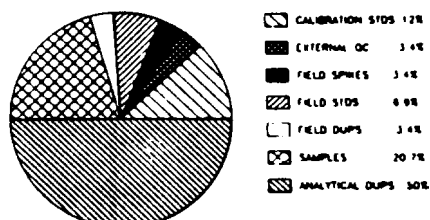
Replicate analytical subsampling (triplicate for some analytes) and the resulting magnitude of each biweekly data set required that the project data base be kept in the most manageable form possible. Thus, for the primary water samples (including the two field blanks), only mean values were recorded. The results of all field determinations were also recorded with the "means." Missing data were marked with either "NA" (not available or lost) or "ERR" (error in value obtained). A complete explanation or statement of the problem was noted in a separate data validation notebook.

The internal spike and standard data subset contained all reported values from the two field blanks (called Wells 7A and 14A), the two field standards (called Wells 7B and 14B) and the two wells chosen for spiking (as well as their unspiked counterparts). Mean values were used in computing percent recovery of each spike and standard.

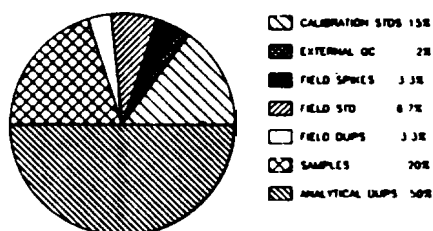
QUALITY CONTROL SUMMARY  
for Na, K, Ca, Ma, T-Fe, Ma



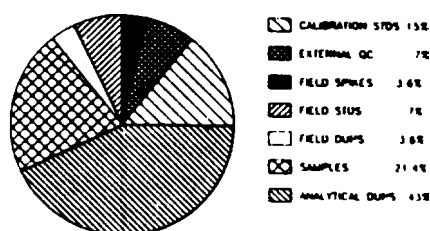
QUALITY CONTROL SUMMARY  
FOR CHLORIDES



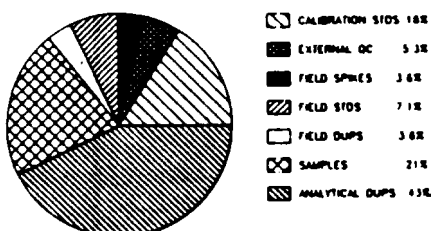
QUALITY CONTROL SUMMARY  
FOR Fe2+



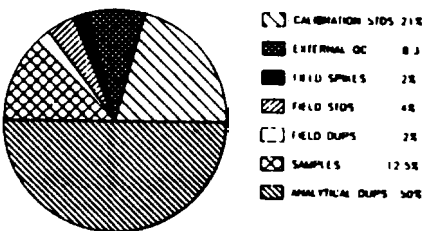
QUALITY CONTROL SUMMARY FOR SULFATE  
(POTENTIOMETRIC TITRATION)



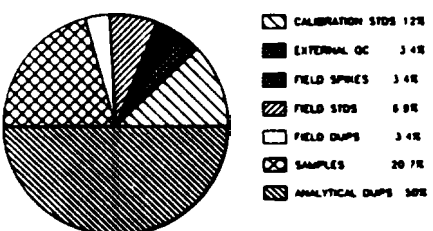
QUALITY CONTROL SUMMARY  
for NH3, T-PO4, O-PO4



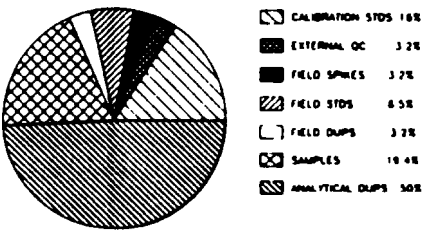
QUALITY CONTROL SUMMARY  
for SULFATE (AUTOANALYZER)



QUALITY CONTROL SUMMARY  
FOR SIUCA



QUALITY CONTROL SUMMARY  
FOR NO2-N & (NO3+NO2)-N



QUALITY CONTROL SUMMARY  
FOR SULFIDE

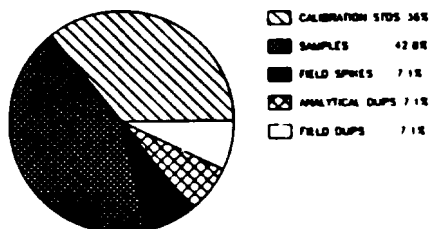


Figure 14. Summary of the quality assurance contribution to the analytical workload.

Finally, additional data sheets were used to record all values obtained from the two wells designated as field duplicates. With replicate subsampling, as many as four values could be reported for a given parameter. For those analytes which were subsampled in triplicate, only the first two reported values were recorded.

The original analytical results were filed after the mean analytical results were recorded onto the appropriate master data sheets.

Ion balances for each of the 12 monitoring wells were computed using a modified version of the WATEQF (77) chemical equilibrium speciation model. Data could be entered interactively or through ASCII files derived from the master means database. Data which did not agree to within  $\pm 5\%$  were examined more closely to determine the possible source(s) of error (i.e., a particular analysis out of control). Ion balance results (expressed as a relative percent) were then recorded on the master data sheets along with the primary water sample data. An outline of the flow of data as well as the relationships among the individual databases is shown in Figure 15.

The next step in data handling involved transcription of the data from the paper data sheets to computer files. Again, the data were kept according to sample type. Lotus 1-2-3<sup>(R)</sup> was selected as the database management package because of its simplicity, in addition to its graphical and statistical capabilities. By converting a Lotus worksheet to an ASCII file, other software packages could be used as well.

The task of data verification was an ongoing process, beginning with entry into the 1-2-3<sup>(R)</sup> spreadsheets. Data outliers and unexplained gaps in the data on the master data sheets were checked against the original results. Changes then were noted in the data validation notebook. Once the data had been entered, the following checks were made to insure agreement among the various databases:

1. Averages were computed for all replicate values in the field duplicates database and compared with the value recorded in the "means" database.
2. Averages were computed for all replicate values of unspiked samples and compared to those values recorded in the "means" database.

Quality control charts were also employed in the data verification effort. Reported values for each parameter were plotted as a function of time (run number). Lines also were drawn showing the average and control limits of two and three standard deviations. Values which fell outside of the three standard deviation limit from the mean were noted, as were successive values which differed by more than two standard deviations. All notations regarding data outliers were recorded in the data validation notebook. This same procedure also was used for the spike and standard data by plotting percent recoveries on control charts.

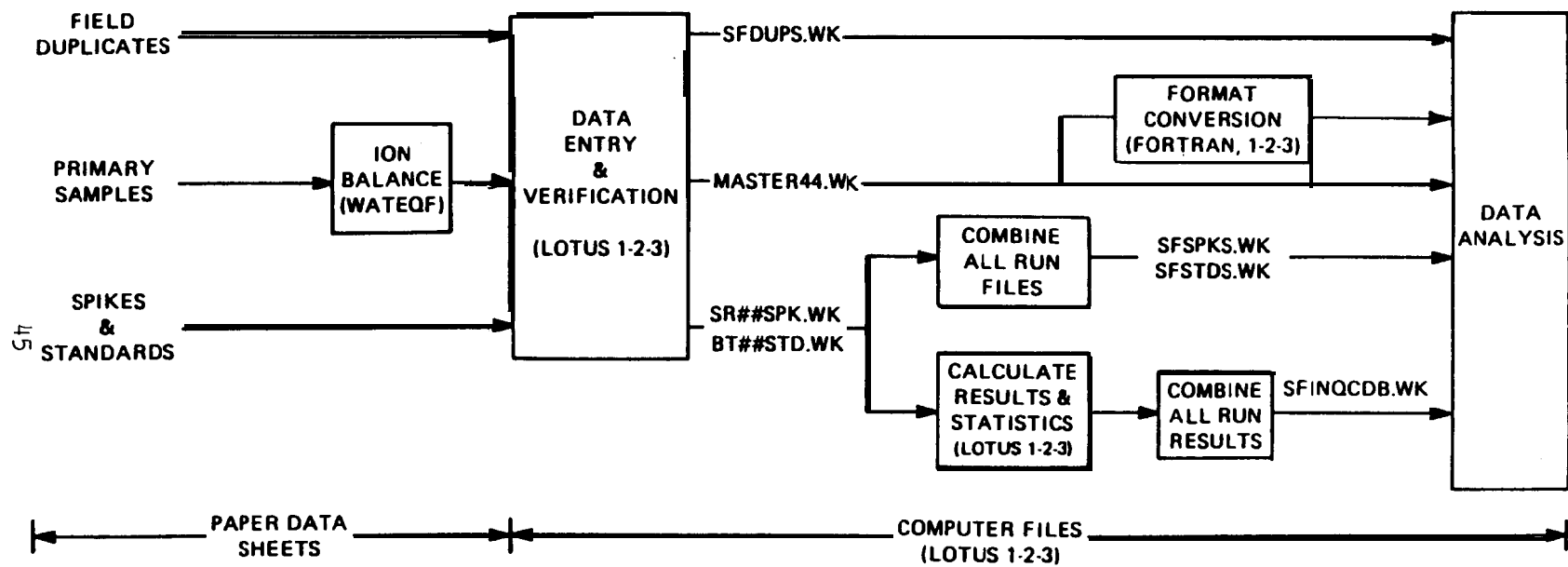


Figure 15. Data handling flow chart.

## **SECTION 5**

### **RESULTS AND DISCUSSION**

#### **FIELD ACTIVITIES**

##### **Routine Activities**

Five preliminary sampling runs were completed between November 1985 and March 1986. Then thirty-nine biweekly sampling trips were conducted during the period of March 10, 1986 through August 25, 1987. These field activities involved purging and sampling the monitoring wells 526 times and measuring more than 2,000 ground-water levels. Only two wells were missed out of the 528 sampling opportunities. The 105 ft (32 m) well (#4) at Sand Ridge was not sampled on January 26, 1987 because of a compressor breakdown which was complicated by a cold weather failure of an air line fitting at the well-head. The well was again operational by the end of that week. The other instance also occurred at Sand Ridge on August 10, 1987. Faulty air seals in the pump of well #3 could not be corrected in the field, even after replacing the bladder and all gaskets. The pump was returned to the manufacturer but a replacement was not obtained until after the last regular sampling trip. Samples were collected from well #3 on that last trip using a PVC pump.

Despite the replacement of one of our most experienced field and laboratory personnel and the need to move our entire laboratory operation twice, the 14-day interval between sampling dates was maintained, although Run #18 was delayed by one day due to an engine problem with the sampling van.

##### **Major Difficulties**

Although a near-perfect sampling record was established over the course of this project, minor problems invariably occurred in the field. Broken probe/meter cables, worn tubing fittings, dead batteries, leaking pump bladders, erratic monitoring probes and other such difficulties were, for the most part, quickly solved. The van was stocked with the proper tools and adequate replacement parts and supplies. A backup was kept for nearly every piece of equipment, from pump assemblies to pipettes. Even with regular equipment maintenance, however, many of the backups were used at one time or another.

The most significant problem regarding field equipment involved the mobile van's air compressor system. From the time of the first breakdown, mentioned in the preceding section (January 26, 1987), the compressor ran rough and erratically, often tripping its circuit breaker. The compressor was down through mid-August and during this time a portable backup was used.

A new pressure switch (the second one during the project period) was installed in March, but that did not improve the compressor performance. The compressor itself was finally sent out for servicing in June but no problems were diagnosed. No further problems occurred after the unit was reinstalled in June 1987.

Well temperature data from July through September of 1986 were not obtained due to a faulty thermistor probe and cable. The length of new cable required (140 ft, 43 m) had to be back ordered, causing the inordinate gap in the data.

The battery operated digital buret used in the field for alkalinity titrations was sent out for repair during the period of November through December of 1986. During this span, the Sand Ridge and upgradient Beardstown samples were titrated in the field using an Eppendorf micro-pipette (100-1000 microliters). The downgradient Beardstown samples, however, required a titrating resolution less than 0.1 mL. Therefore, these samples were refrigerated upon collection and titrated after return to the laboratory.

Problems with the calibration and response of the electrometric dissolved oxygen probe resulted in missing or partial data on 8 of the 39 biweekly sampling trips. This problem did not present itself in a specific period, but appeared sporadically over the entire project period. Although the membrane/electrolyte modules were replaced when necessary, the age of the probe assembly itself was probably the largest factor causing this difficulty.

## **LABORATORY ACTIVITIES**

### **Routine Activities**

The laboratory activities generally went very well despite the fact that the entire laboratory operation was moved twice during the sampling phase of the project. This achievement was due to the dedication and commitment of the project staff. They put in frequent night, weekend, and holiday hours to complete the work from one sampling run prior to arrival of samples from the next run. More than 95% of the individual analytical determinations were completed within the prescribed Agency holding and storage periods. Exceptions to this level of performance were documented in a logbook.

### **Difficulties**

A number of analytical and instrument difficulties were encountered during the project. In most cases, alternative instrumentation or methods (i.e., manual vs. automated) were used to complete the work in a timely fashion. Analytical problems were more difficult to deal with, particularly due to the differing background matrices represented in water from Sand Ridge versus that from Beardstown.

Foremost among the analytical problems was the inability of the automated methyl thymol blue procedure for sulfate to yield measurable results for many of the downgradient Beardstown samples. The interference manifested itself as a sudden drop in the spectrophotometer signal baseline whenever downgradient samples were introduced into the autoanalyzer reaction train. The peak heights of affected samples were inconsistent with those from either the calibration standards or quality controls. This meant that even if the baseline could be brought back on scale, quantitative interpretation was impossible. The interference presumably was due to the organic contaminants in that system. Dilution could not be used to reduce the interference because the sulfate levels were too low to remain detectable. The interference did not affect all downgradient wells to the same degree, and it was inconsistent over time. Attempts were made to remove the interference by oxidative pretreatment with hydrogen peroxide and by adding a carbon adsorption column in line, but they were unsuccessful. Several alternative automated sulfate procedures could not be investigated because of cost and time constraints. Tests of a manual and automated turbidimetric method revealed poor precision and accuracy for the Beardstown downgradient sample group, so they were not used.

These problems led to the development of a potentiometric titration procedure for sulfate, which employed the Metrohm E-636 Titroprocessor for analysis and endpoint detection. Calibration was done by analyzing standards containing various amounts of sulfate covering the concentration range of the samples. The titration results were used to compute the sample sulfate values by linear regression calibrated on sulfate standards (78).

A method that combined attributes of several published procedures was developed (78,79,80,81,82) to avoid serious inorganic interferences to potentiometric sulfate techniques (such as orthophosphate, copper, and hardness ions). The first step in the procedure was the addition of lanthanum nitrate solution to the aliquot of sample taken for analysis, in order to precipitate orthophosphate. The treated sample was mixed and then held for ten to fifteen minutes until precipitation was complete. It was then vacuum filtered through a 0.45  $\mu\text{m}$  pore-size cellulose acetate membrane filter. The samples were then passed through a strong acid cation exchange column (i.e., Dowex 50W-X8; 20-50 mesh). Then 25 mL of sample was mixed with an equal volume of methanol solution, which contained 3 to 4 drops per liter of formaldehyde as an antioxidant. If the sulfate concentration of the sample aliquot was below about 0.5 mg  $\text{SO}_4^{2-}/\text{L}$ , the solution was spiked with 2 mL of 1000 mg/L sulfate standard. One drop of bromcresol green/methyl red indicator was then added to the sample, and the pH was adjusted to approximately 7 with 2 N NaOH. Approximately one drop of 10% volume/volume (v/v) perchloric acid solution then was added, reducing the pH to between 5.5 and 6, and the sample was titrated with 0.010 M lead nitrate solution. The indicator electrode for the titration was a PbS solid-state ion-selective electrode (ISE) and the reference electrode was a double-junction electrode with a 10%  $\text{KNO}_3$  outer filling solution. Frequently, the lead electrode had to be cleaned between titrations with a mildly abrasive polishing strip.

The ammonia analysis method was another source of analytical problems. Although samples were preserved with 0.2% v/v  $\text{H}_2\text{SO}_4$  in the field per USEPA recommendations (69), the standard manual ammonia procedures (i.e., indophenol blue method, etc.) were designed for unpreserved samples. Hence, the procedure did not contain an adequate pH buffer for the optimum pH of the color-forming reaction (i.e., pH 10.5-11). The high alkalinity and the presence of the sulfuric acid caused erratic results which could not always be identified by the external standards, field spikes, or field standards. Manual neutralization was performed before reagent addition to overcome this problem, but the test was very sensitive to the performance of the analyst. Problems were particularly serious during Runs 18-22, and in the five preliminary runs. There were additional difficulties in obtaining ammonia-free double deionized water due to ambient contamination from laboratory operations and the influence of nearby sheep, swine, corn, and soybean farming operations on the outside air ducted into the laboratory.

Nitrite-N analyses were performed initially by a manual procedure (Table 6), but time and staff considerations prompted an attempt to use the standard USEPA automated procedure (68). This method was used from Runs 23 to 32. Inconsistent instrument performance and poor detection limits relative to sample levels prompted a return to the manual procedure at Run 33. Concentrations in the samples were uniformly lower than 0.05 mg/L which is very close to the reported detection limit. During the course of troubleshooting the nitrite-N problems, it was found that once the frozen samples were thawed, the nitrite-N levels quickly deteriorated. Therefore, samples could not be refrozen if there were analytical problems, and once the duplicate samples were used (which did not allow for backups for the field spike and field duplicate samples), further reanalyses were not possible.

The preservation technique for the sulfide samples was tested using standard solutions before the initiation of field collection. The analytical results showed that the preservation technique was effective and gave reliable quantitative recoveries for at least two days after collection.

Titration of samples from the Beardstown sites with the highest alkalinities showed that more than 1.5 mL of concentrated nitric acid might be necessary to lower the pH of the samples to pH <2 on many occasions (69). Therefore, a concentration of 3 mL/L (0.3% v/v) nitric acid was used for the metals samples. Tests also were made of the accuracy of total iron determinations using sulfuric acid preserved samples against standards made up in nitric acid. The tests showed that the results would be in error by a factor of approximately 2 to 3. All atomic absorption standards were made up in this acid solution in order to match the matrix of the samples.

Staff analytical task assignments were made in order to attain the holding-time goals (Table 5) and to avoid conflicts in instrument usage. Analysts had backup assignments to cover absences of primary responsible persons and maintain the necessary turn-around time. Following Run 22, weekly or biweekly Analytical Support Group Meetings were introduced in order to review all data as a group and to try to resolve analytical problems. Problems could not always be resolved immediately for the current or immediately following runs. The meetings were, however, important in



identifying the generation of potentially bad data from sources such as spike or standard preparation problems, building water system and contamination problems, test interferences, or instrument malfunctions. These sources of error were resolved routinely before tests became out of control for extended periods.

## **DATA QUALITY EVALUATION**

### **Method Performance**

There are numerous ways in which to assess the performance of the analytical procedures, using different aspects of the overall QA/QC program. The detection limits attained in practice were computed by pooling replicate analytical results of the lowest calibration standard used for each analytical run. An additional low standard was analyzed in duplicate for this procedure. For trace constituents (iron, manganese, sulfide, etc.), the lowest calibration standard was close to the actual detection limit, and was easily within the factor of 10 suggested by the American Chemical Society (ACS) procedure (83). For the major constituents, whose concentrations were higher than the routine accepted detection limits by a factor of 100 or more, no attempt was made to optimize method or instrumental sensitivity. In these cases an extra low calibration standard was included to compute an approximate detection limit by the ACS procedure (83).

Detection limits were computed for several randomly distributed runs before pooling the data from the low calibration standards over all of the runs. This was done to see if detection limits were consistent for the duration of the study. That assumption was valid.

The detection limits computed for various inorganic constituents by the above procedure are presented in Table 8. For spectrophotometric procedures, the sensitivities (the concentration producing 0.0044 absorbance units) were computed for each calibration to monitor method consistency. In accordance with the ASTM procedure for the reporting of low-level data (84), all computed concentrations were recorded in the database. This was done rather than following common practice of censoring the data distribution by reporting low values as "less than" a detection limit or as zero. No detection limits are reported for some analytical determinations, such as  $\text{Cl}^-$ , potentiometric  $\text{SO}_4^{=}$ , and total alkalinity, where the detection limit is as much a function of sample size as instrumental performance factors or reagent concentrations.

Three different types of quality control samples were used in this investigation as a control for methodological accuracy. These control samples were "blind" or field standards, spiked samples, and external reference standards.

A summary of the mean percent recoveries and one standard deviation for "blind" standards is presented in Table 9. These standards were prepared by field sampling personnel, as described in Section 4. A separate standard

TABLE 8. DETECTION LIMITS FOR SELECTED INORGANIC CONSTITUENTS  
COMPUTED FOR REPETITIVE ANALYSES OF LOW CALIBRATION STANDARDS

Analyte	Detection limit (mg/L)
NH <sub>3</sub>	0.012
(NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> )-N	0.030
NO <sub>2</sub> <sup>-</sup> -N	0.002
Sulfide	0.003
Sulfate (autoanalyzer)	1.5
SiO <sub>2</sub>	0.98
o-PO <sub>4</sub>	0.008
t-PO <sub>4</sub>	0.009
Ca	0.21
Mg	0.10
K	0.047
Na	0.30
Fe(total)	0.032
Fe(II)	0.015
Mn	0.013

was prepared for each type of preservation method (e.g., atomic absorption metals, sulfate + chloride + nitrate + orthophosphate, etc.). Two field standards were submitted with samples for each run, one representing concentrations similar to wells #1-6 and the other similar to wells #8-13. Computations of the mean accuracy for the field standards in Table 9 indicated a hypothesis of 100% recovery could be accepted at the 95% confidence interval for all constituents except calcium, potassium, orthophosphate, and nitrite-N.

The mean percent recoveries and standard deviations for spiked samples are summarized in Table 10. Like the field standards, spiked samples were prepared by field personnel. A sample from one well for each of the collection days was selected to be spiked with a known laboratory standard solution. This procedure provided a total of two spiked samples per run. The preparation of the spiked samples was described in Section 4. The apparently large relative standard deviations resulted in part because computed recoveries were the product of the two field standard mean values. Each of the means included a certain level of analytical imprecision. Also each spiked control sample was a field duplicate of the unspiked one. Standard error propagation formulas were used to monitor the reasonableness of the percentage errors given the analytical data for each run. Then the error values were incorporated into the spike and standard spreadsheets. By this criterion, all constituents could be considered to represent 100% recovery at the 95% confidence interval, except for total iron (atomic absorption) and total sulfide which tended to be systematically low. The increased variation in iron values was a problem because it was necessary to compute Fe(III) by difference, using the Fe(II) analytical result and total iron concentration data.

The third type of control samples used to assess the accuracy of the analysis methods were USEPA, U. S. Geological Survey (USGS) and National Bureau of Standards (NBS) reference standards. The USEPA standards contain a known mass of the analyte of interest and were diluted or concentrated (made up in less volume) to be more similar to project samples. The NBS trace metal standards have "certified" reference values. The U.S. Geological Survey "Standard Reference Water Samples" have mean concentrations and standard deviations computed from a critical evaluation of laboratory results from "round robins" of participating analytical laboratories.

A summary of the percent recoveries and relative standard deviations for the external reference standards that were included in replicate in each analysis set is presented in Table 11. These samples were analyzed more than 10 times over the course of the sampling and analytical period of the project. The accuracy and precision of analysis of these standards were excellent. This **was true** even for iron and manganese concentrations near the detection limit of the instrumental procedure. External stable standards do not exist, or are of questionable validity (due to preservation and stability problems), for several constituents of interest, such as ferrous iron, sulfide and nitrite-N. These standards generally showed higher accuracy and better precision than did the field standards and spikes. Part of this result may be attributed to the consistency of preparation of the control solutions by laboratory personnel. Matrix variability in the samples

TABLE 9. SUMMARY OF THE MEAN ACCURACY AND PRECISION  
(ONE STANDARD DEVIATION) OF FIELD STANDARDS  
(Expressed in Percent)

Param.	Overall		Sand Ridge		Beardstown	
	Acc.	Prec.	Acc.	Prec.	Acc.	Prec.
NH <sub>3</sub>	95.90	23.49	91.99	29.80	100.09	12.54
T-PO <sub>4</sub>	99.64	8.60	100.95	9.28	98.24	7.56
Fe(II)	96.07	18.80	NA*	NA	96.07	18.80
NO <sub>2</sub> <sup>-</sup> -N	82.17	36.29	81.07	35.00	83.27	37.50
Sulfide	NA	NA	NA	NA	NA	NA
(NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> )-N	100.35	10.27	98.85	7.82	101.97	12.17
SiO <sub>2</sub>	99.47	5.03	100.21	2.97	98.71	6.41
o-PO <sub>4</sub>	103.44	15.38	106.54	20.77	100.12	2.32
Cl <sup>-</sup>	105.78	32.59	112.01	46.55	100.18	1.52
SO <sub>4</sub> <sup>=</sup>	95.77	21.85	94.73	6.58	97.24	33.07
Ca	98.36	3.88	98.65	3.76	98.07	3.98
Mg	99.15	8.70	99.90	10.72	98.42	6.03
Na	101.69	12.17	103.51	16.16	99.95	5.87
K	97.85	5.17	99.10	5.15	96.63	4.89
Fe	99.22	5.80	100.34	7.20	98.04	3.46
Mn	101.04	6.46	101.28	8.17	100.79	3.92

\* No field standard used due to low concentration in monitoring wells.

TABLE 10. SUMMARY OF THE MEAN ACCURACY AND PRECISION  
(ONE STANDARD DEVIATION) OF FIELD SPIKES (Expressed in Percent)

Param.	Overall		Sand Ridge		Beardstown	
	Acc.	Prec.	Acc.	Prec.	Acc.	Prec.
$\text{NH}_3$	98.08	28.32	97.62	31.52	98.54	24.80
T- $\text{PO}_4$	99.44	25.11	97.78	29.48	100.99	20.08
Fe(II)	102.82	27.59	102.12	18.18	103.33	32.75
$\text{NO}_2^-$ - N	101.29	26.55	102.44	25.83	100.23	27.15
Sulfide	90.32	13.97	89.08	16.20	91.44	11.48
$(\text{NO}_2^- + \text{NO}_3^-)$ - N	104.74	28.06	100.59	13.04	108.70	36.66
$\text{SiO}_2$	97.09	14.19	99.00	11.50	95.41	16.01
o- $\text{PO}_4$	101.75	30.11	100.54	6.12	102.88	41.38
$\text{Cl}^-$	111.86	59.07	123.71	72.06	101.95	42.97
$\text{SO}_4^{=}$	105.05	43.92	94.02	20.63	118.57	58.66
Ca	105.43	41.46	101.44	15.39	109.11	55.30
Mg	96.80	17.22	95.85	14.66	97.67	19.25
Na	96.47	31.41	87.79	19.76	104.93	37.71
K	96.88	13.02	96.20	12.57	97.55	13.41
Fe	86.61	17.01	86.08	19.85	87.12	13.67
Mn	95.99	12.16	96.92	12.80	95.07	11.42

TABLE 11. PERCENT RECOVERIES AND RELATIVE STANDARD DEVIATIONS OF EXTERNAL QUALITY CONTROL STANDARDS.  
(Concentrations in mg/L)

Standard	Ca			Mg			Na			K		
	TV <sup>1,2</sup>	% R	RSD	TV	% R	RSD	TV	% R	RSD	TV	% R	RSD
USEPA 882-1 (+10)	4.06	99.0	2.62	0.84	99.3	4.85	4.65	100.3	4.05	0.98	99.3	3.36
USEPA 882-1 (+2)	--	--	--	--	--	--	--	--	--	--	--	--
USEPA 882-2	5.4	98.1	2.89	1.8	99.4	3.44	8.20	100.8	3.34	2.10	99.9	2.77
USGS M-76 (+25)	7.48	99.1	7.05	4.80	103.1	2.67	6.36	102.8	3.26	--	--	--
USGS M-86 (+10)	7.15	100.3	3.15	2.83	98.8	2.27	7.77	100.5	2.77	--	--	--
USGS M-86	--	--	--	--	--	--	--	--	--	4.62	96.6	4.21
USGS M-2 (+10)	6.25	103.3	3.45	2.80	101.6	1.64	6.52	103.7	1.69	--	--	--
USGS M-2	--	--	--	--	--	--	--	--	--	3.70	96.2	3.17
USGS M-84 (+10)	8.67	102.1	2.82	5.18	101.8	1.33	7.97	99.4	2.44	--	--	--
USGS M-84	--	--	--	--	--	--	--	--	--	4.74	93.1	3.57
USGS M-88 (+20)	7.21	101.2	4.33	2.72	98.0	3.11	6.02	100.1	1.66	--	--	--
USGS M-88	--	--	--	--	--	--	--	--	--	5.07	99.9	3.22
USGS M-100 (+25)	7.20	100.2	2.09	3.92	97.6	2.12	11.24	99.4	2.55	--	--	--
USGS M-100	--	--	--	--	--	--	--	--	--	4.48	93.0	1.92
USGS M-82	--	--	--	--	--	--	--	--	--	1.89	91.9	2.91
USGS M-54	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-6	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-2 (+2)	--	--	--	--	--	--	--	--	--	--	--	--
USEPA 384-1	--	--	--	--	--	--	--	--	--	--	--	--

continued on next page

<sup>1</sup> TV = True or reference value; % R = % recovery; RSD = % relative standard deviation

<sup>2</sup> TV = Reference concentration for USGS standards is the mean of round robin results

TABLE 11. (CONTINUED)

Standard	Fe (tot)			Mn		
	TV	% R	RSD	TV	% R	RSD
USEPA 284-1	0.021	112.1	51.28	0.0129	102.6	45.6
USEPA 284-2	0.797	99.5	2.10	0.348	100.6	2.35
USEPA 284-2 (x2)	1.580	99.1	3.09	0.696	102.1	2.64
USEPA 284-2 (x4)	3.188	99.0	3.28	1.392	100.9	3.42
USEPA 284-2 (+2)	0.399	99.1	4.66	0.174	100.5	10.76
USEPA 386 (x4)	0.400	99.6	4.00	0.400	102.9	3.38

continued on next page

TABLE 11. (CONTINUED)

Standard	Cl <sup>-</sup>			SO <sub>4</sub> <sup>=</sup> (autoanalyzer)			SO <sub>4</sub> <sup>=</sup> (potentiometric)			SiO <sub>2</sub>		
	TV	% R	RSD	TV	% R	RSD	TV	% R	RSD	TV	% R	RSD
USEPA 882-1 (+10)	--	--	--	--	--	--	--	--	--	--	--	--
USEPA 882-1 (+2)	--	--	--	23.5	93.9	14.0	--	--	--	--	--	--
USEPA 882-2	17.8	105.0	4.37	--	--	--	--	--	--	--	--	--
USGS M-76	--	--	--	--	--	--	--	--	--	9.76	108.8	5.03
USGS M-76 (+25)	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-86 (+10)	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-86	44.4	99.4	4.52	--	--	--	--	--	--	13.3	98.6	2.27
USGS M-2 (+10)	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-2	32.0	100.0	2.77	--	--	--	--	--	--	--	--	--
USGS M-84 (+10)	--	--	--	34.7	98.5	3.53	--	--	--	--	--	--
USGS M-84	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-88 (+20)	--	--	--	27.3	95.60	5.52	--	--	--	--	--	--
USGS M-88	37.1	99.8	2.33	--	--	--	--	--	--	--	--	--
USGS M-100 (+25)	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-100	79.0	101.9	0.63	--	--	--	--	--	--	--	--	--
USGS M-82	--	--	--	--	--	--	--	--	--	--	--	--
USGS M-54	--	--	--	--	--	--	--	--	--	11.2	102.4	3.31
USGS M-6	--	--	--	--	--	--	74.5	99.0	3.33	--	--	--
USGS M-2 (+2)	--	--	--	--	--	--	105.4	94.6	1.29	--	--	--
USEPA 384-1	80.8	99.6	1.29	--	--	--	95.3	95.5	1.80	--	--	--

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TABLE 11. (CONCLUDED)

[illegible]

contributed to the poorer precision of the spikes. Sources of the slight discrepancies between the variability in the external reference standards and the field standards include differing reagent sources and techniques for preparation of the control solutions from outside agencies and our laboratories.

The external QC standards covered a broad concentration range. Plots of observed standard deviation versus true or reference concentration were evaluated by unweighted first-degree linear regression to see if there was a trend in precision with concentration. Significance tests for the slope of the regression line were performed with the RS/1<sup>(R)</sup> statistical and graphical software package. A summary of these results and the concentration ranges covered for each analyte are shown in Table 12. Note that in most cases, the equations of the lines only give an approximation of the standard deviations of a given concentration because of inherent regression uncertainty. A statistical summary of the chemical constituent concentrations over the study period for each well is provided in Appendix A. Detailed time-series graphs of the actual mean data for each well are provided in Appendix B.

Another way used to estimate analytical method precision was to pool the duplicate laboratory analysis data from the database of field duplicate samples (84,85). Outliers were removed by application of the Grubbs test (86). The results are presented in Table 13. This is a reasonable approach when samples are grouped by similarity of matrix and approximate concentration. It could be used further to estimate the variance attributable to sampling when combined with the overall sample variance. For Eh and total alkalinity, the precision was calculated using all analytical data.

In general, small variations in accuracy and precision were randomly distributed throughout the sampling and analytical period. The major exception was ammonia, which suffered from a particular period of probable inaccuracy. Some of the quality controls also tended to support a low bias in the atomic absorption iron determinations and in the determination of total phosphate. The latter problem may be due in part to the difficulty in properly controlling the acidity of digested samples and standards that had been acid-preserved because the method is extremely sensitive to sample acidity.

Analytical performance was verified to be within acceptable limits (or samples were identified for reanalysis) by several techniques:

1. Comparison to previous data from the same location
2. Ion balance computations
3. Computation of alkalinity from the major ion composition
4. Examination of QC and/or calibration data for each analytical run

**TABLE 12. ANALYTICAL PRECISION ESTIMATES FROM EXTERNAL  
REFERENCE QUALITY CONTROL STANDARDS**

Analyte	Calibration range (mg/L) <sup>a</sup>	Equation <sup>b</sup>		P(slope) <sup>c</sup>	pooled s <sup>d</sup>
		A	B		
NH <sub>3</sub>	0-3	0.1464	-0.0381	0.020	--
T-PO <sub>4</sub>	0-3.5	0.0768	-0.0125	0.004	--
(NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> )-N	0-2	0.0197	+0.0067	0.013	--
SiO <sub>2</sub>	5-15	--	--	0.59	0.41
o-PO <sub>4</sub>	0-1.6	--	--	0.74	0.046
Cl <sup>-</sup>	0-100	--	--	0.71	1.09
SO <sub>4</sub> <sup>=</sup> (AA)	10-40	--	--	0.48	1.23
SO <sub>4</sub> <sup>=</sup> (AA)	50-550	0.0587	-4.0845	0.02	--
SO <sub>4</sub> <sup>=</sup> (P)	10-110	--	--	0.57	1.89
Ca	0-7.5	0.0845	-0.2695	0.078	--
Mg	0-7.5	0.0115	0.0396	0.099	--
Na	0-15	0.0239	+0.0342	0.051	--
K	0-5	0.0363	-0.0071	0.001	--
Fe	0-5	0.0309	+0.0046	0.001	--
Mn	0-0.5	--	--	--	0.012
Mn	0.3-1.4	0.0350	-0.0023	0.005	--

<sup>a</sup> All samples were analyzed in this range, after appropriate dilution.  
For example, 70 mg/L calcium sample would be analyzed after a tenfold dilution, so the actual analysis precision would be 10 times that computed with the equation or pooled s given here.

<sup>b</sup> Precision ( $S_{est}$ ) =  $AC + B$ , where C is the analyzed concentration.

<sup>c</sup> Significance of the slope (0.05 or smaller is highly significant)

<sup>d</sup> For analytes showing no significant dependence of analytical precision on concentration, this is the precision estimate using all standards.

**TABLE 13. POOLED ANALYTICAL PRECISION BASED ON REPLICATE  
LABORATORY ANALYSES OF FIELD DUPLICATE SAMPLES.\*  
(STANDARD DEVIATION VALUES IN MG/L)**

Parameter	Wells		
	(1-4)	(5-6)	(8-13)
NH <sub>3</sub>	0.004	0.006	4.9
T-PO <sub>4</sub>	0.006	0.004	0.36
Fe(II)	0.02	0.11	0.02
NO <sub>2</sub> <sup>-</sup> -N	0.00	0.00	0.00
(NO <sub>2</sub> <sup>-</sup> + NO <sub>3</sub> <sup>-</sup> ) - N	0.006	0.00	0.00
SiO <sub>2</sub>	0.59	--	0.08
o-PO <sub>4</sub>	0.005	0.009	0.35
cl <sup>-</sup>	0.11	0.16	0.62
SO <sub>4</sub> <sup>=</sup>	0.92	--	1.2
Ca	0.70	0.67	0.95
Mg	0.22	0.33	0.33
Na	0.05	0.86	1.87
K	0.01	0.05	0.50
Fe	0.01	0.04	0.04
Mn	0.003	0.080	0.008
T O C	0.03	0.02	0.12
TOX (micrograms/L)	1.2	1.9	3.2
VOC	0.002	0.00	0.18
Total alkalinity	3.59	1.08	6.30
Eh (volts)	0.020**	0.011**	0.019**

\* Pooled on the basis of matrix similarity

\*\* Wells 1-3, 4-6, 8-13, respectively

5. Computation of pH with the geochemical computer equilibrium model PHREEQE, using analytical concentrations and historical saturation index information as inputs (87).

Questionable data were noted in a log of sample verification notes when reanalyses provided data that still seemed to be unusual, or when reanalyses could not be done (e.g., pH, Eh,  $\text{NO}_2^-$ -N, sulfide). For the purpose of this project, the remaining questionable values were not deleted, although they might be in future studies of the geochemistry of the test sites.

### **Sample Data Quality**

During the course of the study, more than 55,000 analytical determinations were made on blanks, standards and samples. The final dataset was 96% complete, that is, 96% of the maximum possible number of samples and subsequent analytical determinations were successfully completed. Outliers were screened successively at  $\pm 3$  and  $\pm 2$  standard deviations from the mean levels. In most cases, this screening revealed apparent errors in calculations, calibration, or data entry which were corrected prior to data analysis. For all wells and constituents, the maximum number of samples which were identified as possible outliers and for which no documented error was identified was four percent of the total. No adjustment was made to apparent outliers for which no documented error could be identified. Some other screening methods are given in the immediately preceding section.

Mean ion balance errors for the complete dataset are reported in Figure 16. The error bars represent one standard deviation from the mean. The mean error for all wells was less than  $\pm 2\%$ . There tended to be a slight positive bias in the Beardstown downgradient samples. This may reflect complexation of divalent metals by unidentified organic ligands or the influence of ammonia determinations that appeared to be erroneously high for several runs. It is important to note that the project analytes appear to cover virtually all charged species present in significant concentrations and that the average performance on Beardstown downgradient samples was comparable to that for the wells in the uncontaminated environments. The larger standard deviations for the downgradient wells (#8-#13) most likely reflect the imprecision in the ammonia analyses (Tables 9 and 10) from run to run. This effect is also evident in the larger standard deviations from wells #5 and #6, at Beardstown relative to the Sand Ridge results. Since  $\text{Na}^+$ ,  $\text{Ca}^{++}$ ,  $\text{SO}_4^-$  and  $\text{Cl}^-$  made up a large proportion of the total ionic solids in samples from wells #5 and #6 the analytical precision alone translates into a higher relative error in the ion balance.

Analyses were performed on the quality assurance/quality control (QA/QC) data to determine if there was evidence of temporal variability in the blanks and standards or field standard recoveries and to determine if there was a concentration-related dependence in the accuracy or precision of these datasets. A time series was constructed for the field and laboratory QA/QC samples (i.e., field standards and blanks). Missing values were removed to create a complete series of lower total sample size. A linear regression was then fit to the series with time as the independent variable.

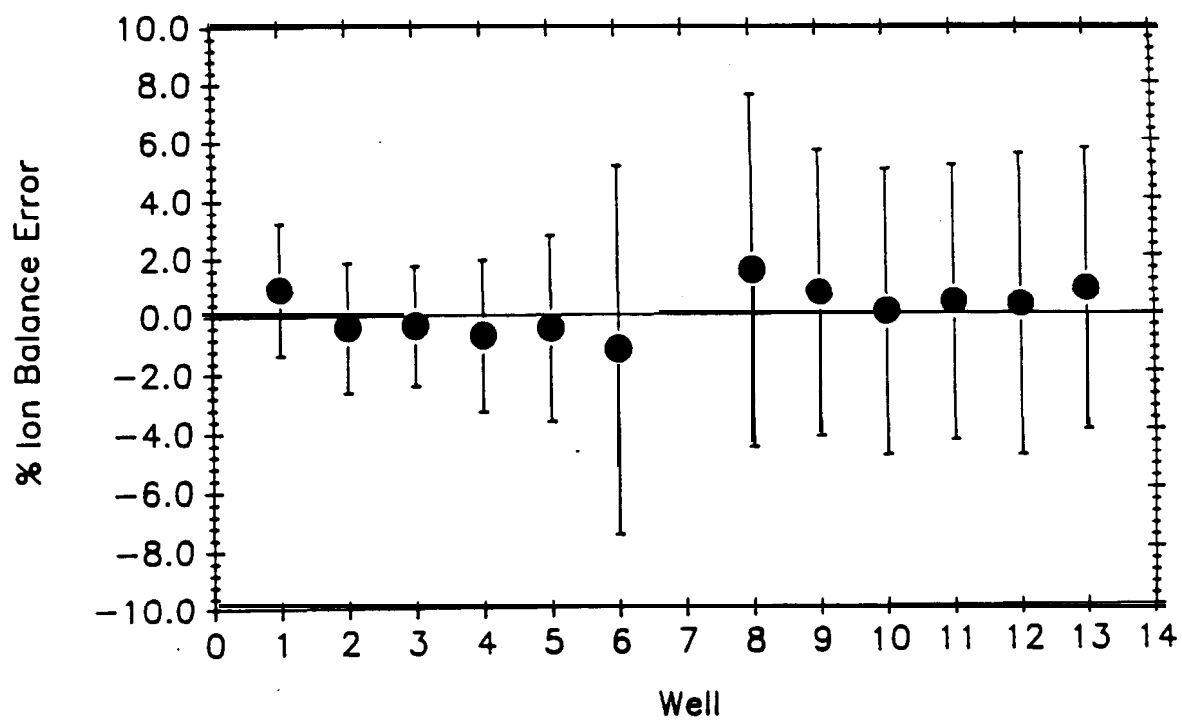


Figure 16. Ion balance error summary.

The significance of the slope (time coefficient) was tested at the 0.05 significance (95% confidence level). No cases were found in which the slope was significant. This result was somewhat surprising since the expected number of rejections of the null hypothesis (that the slope is zero) is 0.05 times the number of analyses, or approximately seven. This result may be explained by the lack of correlation in the data (especially blanks) and perhaps by nonnormality or outliers, all of which may make the true significance level less than the nominal value of 0.05 and hence, reduce the number of rejections. The test should be powerful enough, however, to detect trends over long periods of time in the laboratory and field procedures. The absence of significant trends may be taken as evidence that there was no significant temporal trend in the blanks and standards which might bias the sample dataset over time.

The procedure outlined above also was applied to the sample percent recoveries for three groupings of the wells: 1) the uncontaminated Sand Ridge site (wells #1-#4), 2) the upgradient wells at the Beardstown contaminated site (wells #5 & #6) and 3) the downgradient wells at this site (wells #8-#13). Time series were formed for each of two sets of determinations for each chemical for each group of wells. The first reflects laboratory error only (i.e., two replicate determinations were performed on samples spiked within the laboratory), while the second incorporates both laboratory and field error (two replicate determinations were performed on actual samples). Separate time series also were constructed from the mean, median, and standard deviation of the percent recovery data.

No significant trends were found in field or laboratory recoveries for any chemicals in the Sand Ridge wells. Significant increasing recovery trends with time in the mean, median, and standard deviation of the percent recoveries were found in  $\text{NH}_3$  (laboratory and field),  $\text{SO}_4^{=}$  (field only), Fe(II) (laboratory Only) and  $\text{Mn}_T$  (laboratory only) for the Beardstown wells. The apparent recovery trends were due largely to difficulties encountered in the five preliminary sampling runs of the study between November 1985 and March of 1986 when the biweekly sampling began. When these early samples were eliminated, the time trends were no longer statistically significant. As in the blank and standards analysis, the number of significant trends was less than would be expected based on chance.

The average overall analytical accuracy and precision values for the chemical constituents were given in Tables 9, 10, 12, and 13. The levels of overall accuracy and precision achieved during the project were routinely within acceptable limits for the laboratory analytical methods (Table 6). Exceptions to this level of performance were noted for constituents which were consistently present at or near analytical detection limits (e.g., precision of Fe(II), sulfide and  $\text{Cl}^-$ ). The QA/QC data analyses demonstrate that the sampling and analytical protocols employed in the study were in control.

## CHARACTERIZATION OF GROUND-WATER HYDROLOGY

In addition to chemical determinations, measurement of hydrologic parameters was performed to provide a basis for the interpretation of variability in the ground-water chemistry due to hydrologic processes. The hydrologic data collection was not an original objective of the study, but it is a necessary part of the benchmark dataset. It will provide a basis for future interpretations of coupled hydrologic and geochemical processes. Ground-water elevation measurements in piezometers and sampling wells were the principal data collected at the two sites. Ground-water level hydrographs and contour maps were prepared from these data to provide information on ground-water response to recharge, the direction of ground-water movement, and the rate of ground-water movement. A summary discussion of the ground-water hydrology of each site follows.

### **Sand Ridge State Forest**

A five-year hydrograph of ground-water levels recorded at Sand Ridge Well SR3 and precipitation recorded at Havana appears in Figure 17. The five-year hydrograph depicts natural, seasonal variations in the water table as well as the effects produced by ground-water withdrawals at the nearby State Fish Hatchery. Annual maxima in the hydrograph are indicative of seasonal recharge which typically occurs in the late fall and spring. Superimposed on this yearly cycle is a ground-water level recession beginning with the start of pumping for the fish hatchery in September of 1983. Ground-water levels have dropped at a rate of approximately 1.2 feet (0.37 m) per year since the hatchery started operations.

Hydrographs of sampling wells #1 (D035) and #4 (D0105), prepared from water level measurements made every two weeks during sampling runs, along with precipitation recorded at Sand Ridge for the study period, are shown in Figure 18. Elevations of water levels in sampling wells #2 (D050) and #3 (D065) at the Sand Ridge site usually fell between wells #1 and #4, denoting a slight upward gradient from the deeper well #4. Downward gradients from well #1 to wells #2 and #3 were observed occasionally. However, the head in well #4 was always above the other three wells. [Note: Because no nearby benchmark was available from which to survey a level circuit, the elevations shown in Figures 18 and 19 were calculated from a benchmark created on-site and given an arbitrary datum of 1000 feet. Therefore, the elevations shown on the figures should not be considered as feet above mean sea level. Actual ground-water elevations are known to be approximately 460 feet above mean sea level in this area (see Figure 3).] Examination of Figure 18 shows little obvious correlation between rainfall and ground-water levels. From March through October 1986, ground-water levels declined approximately one foot (0.3 m), even though 4.7 and 8.1 inches (12 and 20 cm) of rain fell in June and July, respectively. These rains were probably responsible for a slight decrease in the rate of ground-water level declines, but an extremely low August rainfall caused the recession to proceed. Fall and winter precipitation caused water levels to rise approximately 0.6 foot (0.2 m) by March 1987. This rise, however, left water levels nearly 0.5 foot (0.15 m) below the previous year's high. Fortunately, even though ground-water levels fell through the remainder of the study period, sampling well #1,



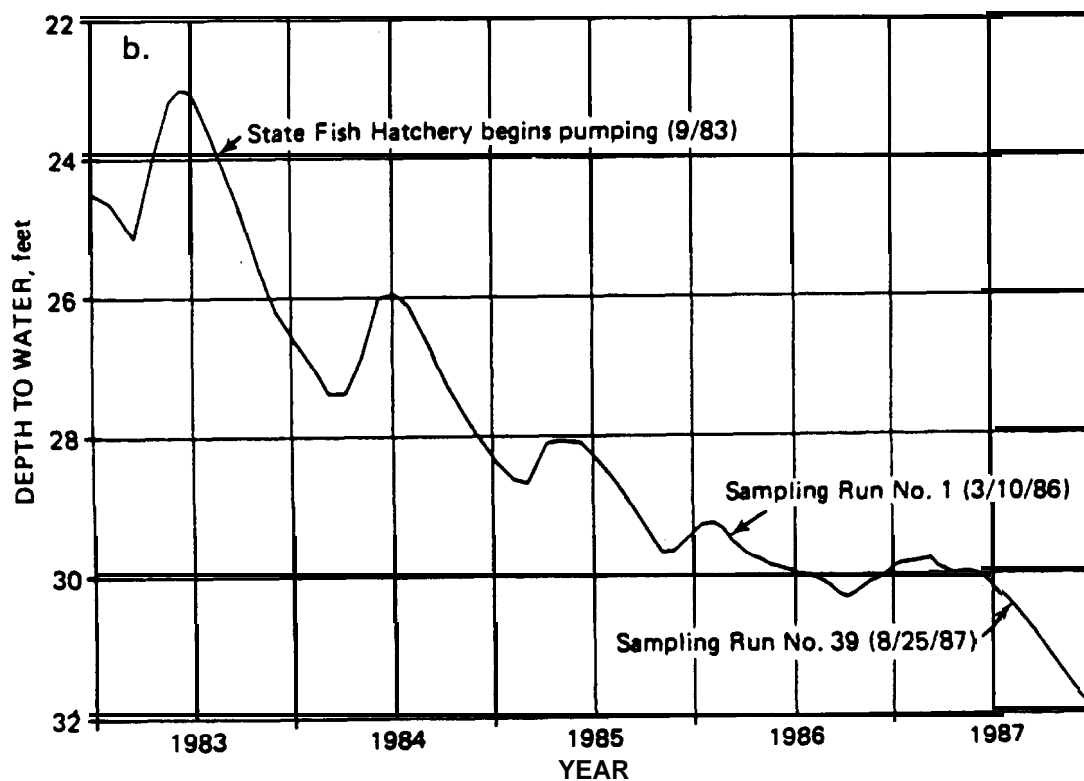
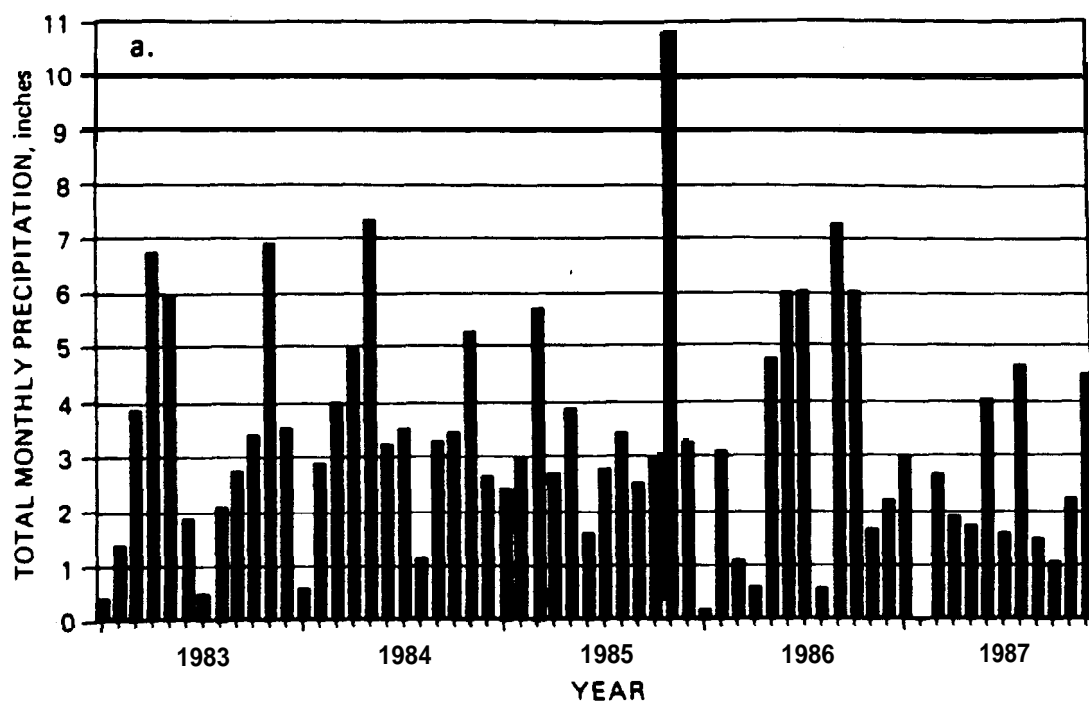
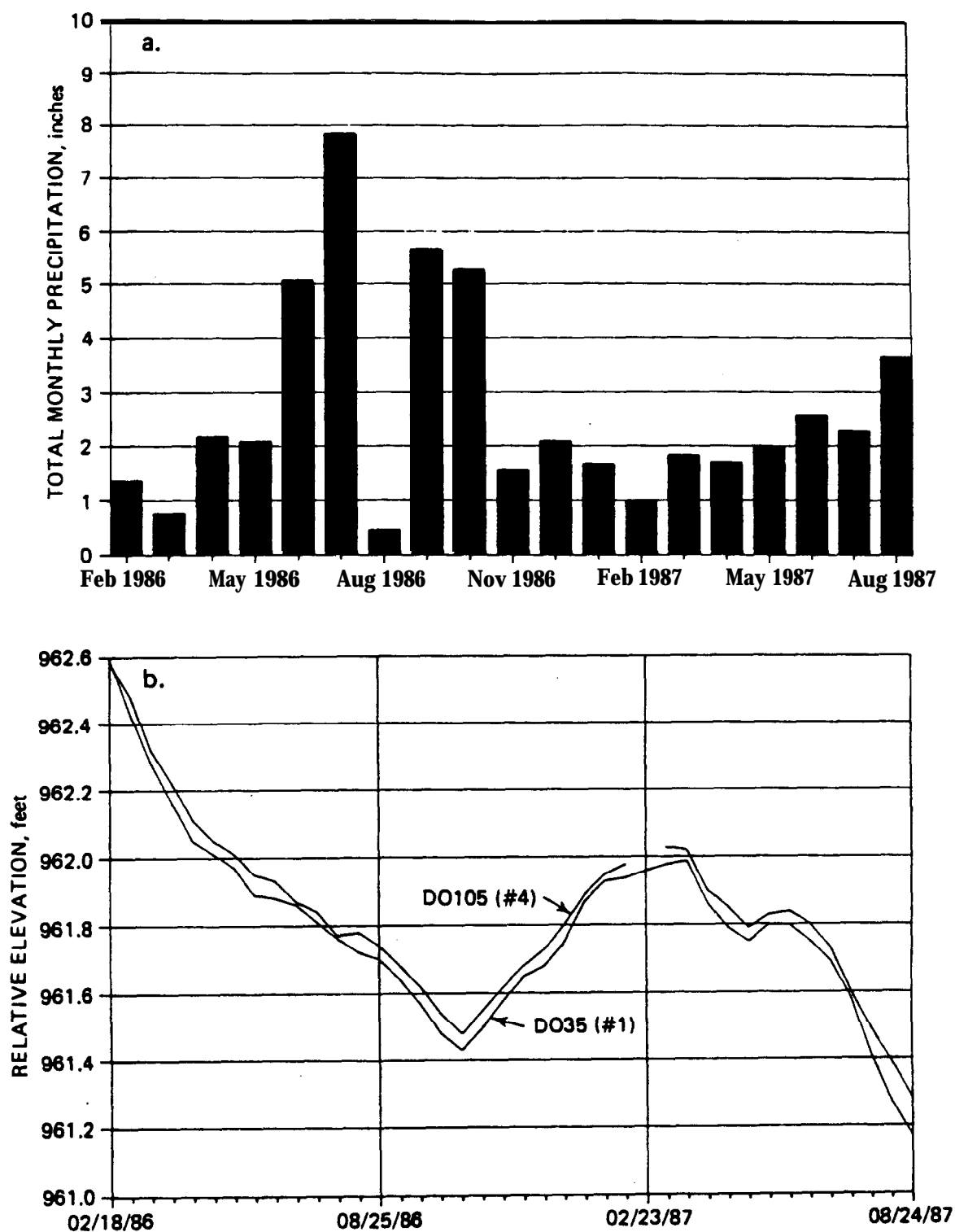


Figure 17. Monthly precipitation recorded at Havana (a) and depth to ground water in Well SR3 at Sand Ridge field site (b) for the period 1983-1987.



**Figure 18.** Monthly precipitation recorded at Sand Ridge State Forest (a) and **relative** ground-water elevations in Wells DO35 and DO105 at Sand Ridge field site (b) during the field sampling period. (Elevations in feet relative to a 1000-foot datum)

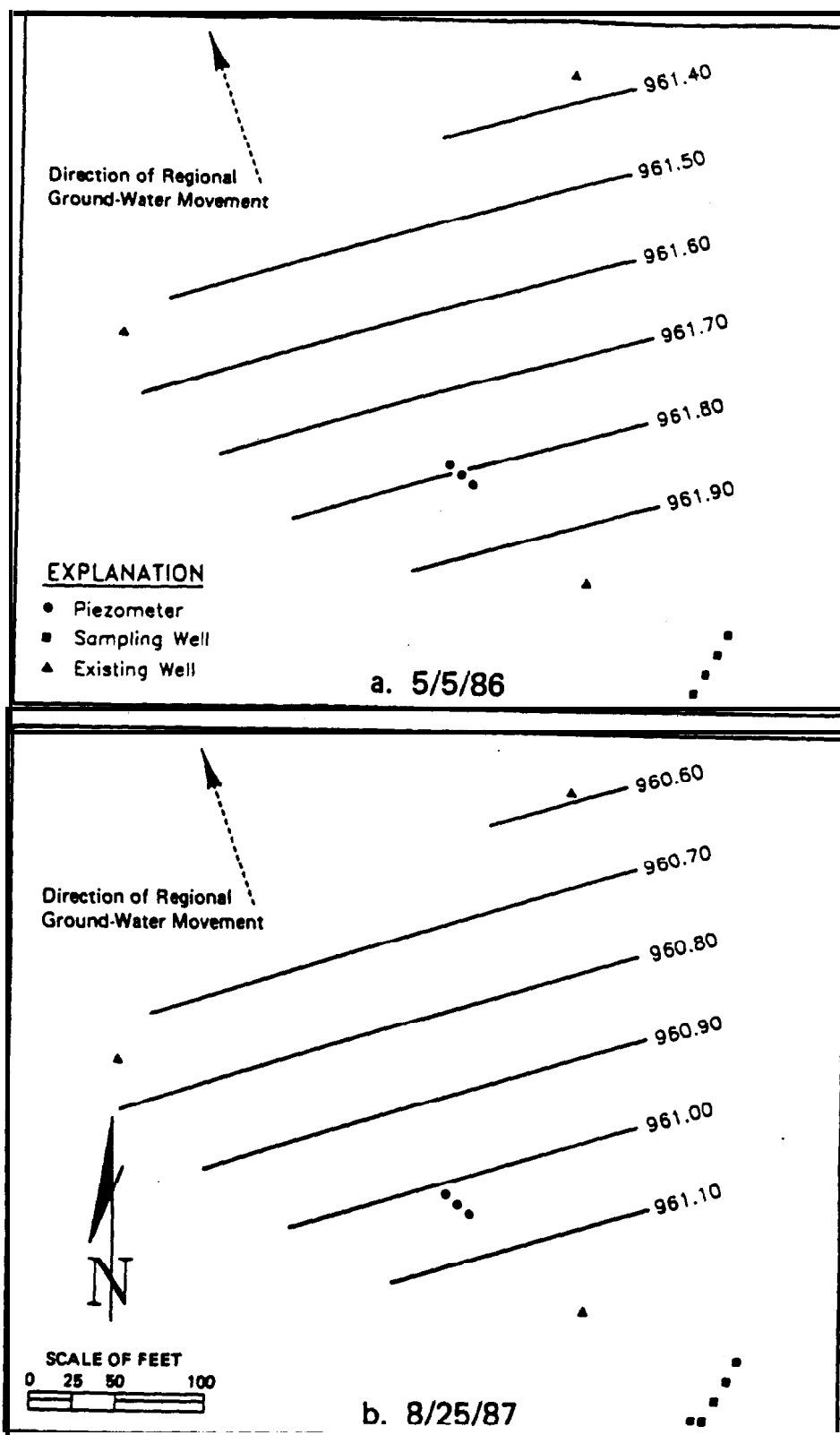
completed at a depth of 35.1 feet (11 m) below ground, did not have water levels drop below the top of the 5-foot (1.5 m) well screen.

Only slight vertical variations in head were observed at this site. As shown in Figure 18(b), the head difference between the shallowest (35 ft, 11 m) and deepest (105 ft, 32 m) nested sampling wells was fairly constant. The gradient was always upward throughout the study period. The largest head difference observed between the two wells was 0.1 foot (0.03 m) for an upward vertical gradient of 0.0014 ft/ft. While gradient reversals were observed between wells #1, #2 and #3, the timing and duration of the gradient changes could not be resolved with the biweekly frequency of observations. A data logging system was installed- at the site to continuously record water levels in three nested piezometers located within 100 feet of the sampling wells. However, the installation of the recording instruments occurred late in the project (April 1987)) and transient vertical ground-water gradient reversals were not observed before the end of the sampling period in August.

Although ground-water levels generally declined, the direction of ground-water flow did not change significantly. Potentiometric surface maps prepared from water level measurements at the SR wells on each sampling run show that the direction of flow remained in a northwesterly direction. Potentiometric surfaces prepared from data collected on May 5, 1986 and August 24, 1987 are shown in Figure 19. Even though ground-water elevations dropped approximately 0.8 feet (0.24 m) during that time period, the direction of flow remained the same. The horizontal hydraulic gradient was computed to be 0.002 for both surfaces.

Results of casing pressurization tests performed on sampling well #2 revealed that the hydraulic conductivity of the sand at 50 feet (15 m) depth at Sand Ridge is approximately 600 to 750 gpd/ft<sup>2</sup> (0.028 to 0.035 cm/s). These results were lower than might be expected for the clean, medium sand found at this site. "Underdamped" responses in water level recovery, indicative of a very rapid ground-water level response to induced changes in head, were experienced in the deeper sampling wells #3 (65 ft, 20 m) and #4 (105 ft, 32 m). Such water level responses cannot be directly analyzed by typical Hvorslev methods (88) but are indicative of hydraulic conductivities greater than the 600 to 750 gpd/ft<sup>2</sup> calculated.

Substitution of a hydraulic conductivity of 750 gpd/ft<sup>2</sup> (0.035 cm/s), a hydraulic gradient of 0.002, and an effective porosity of 0.23 into Darcy's equation produces a ground-water velocity of only 0.9 ft/d (0.3 m/d). Tracer experiments conducted at this site in 1983 (63) indicated the ground-water velocity approaches 2 ft/d (0.6 m/d). Given the same hydraulic gradient and porosity, a hydraulic conductivity of 1700 gpd/ft<sup>2</sup> (0.08 cm/s) would be necessary to yield this velocity. Such a hydraulic conductivity is possible in these materials and may account for the underdamped water level recoveries experienced in the two deeper wells. Estimated rates of ground-water movement fell within a range of 1 to 2 ft/d (0.3-0.6 m/d).



**Figure 19.** Potentiometric surface at Sand Ridge field site on May 5, 1986 (a) and August 24, 1987 (b).  
(Elevations in feet relative to a 1000-foot datum)

## **Beardstown**

Ground-water hydrographs of all piezometers and sampling wells at Beardstown were prepared using water level measurements collected every two weeks during sampling runs. Hydrographs of sampling wells #6, #13, #8, and #10 generally plotted parallel with each other. The hydrographs appear along with the monthly precipitation record at Beardstown in Figure 20a & b. The hydrographs of the nested B8 piezometers located between anaerobic impoundments 2 and 3 appear in Figure 20c (note that B8.3, the most shallow piezometer, was installed in April of 1987). Strikingly similar patterns are evident in the hydrographs for wells up- and down-gradient from, as well as between, the anaerobic impoundments.

Figure 20 shows clearly that water levels rose and fell during the course of the study in response to rainfall events. Ground-water level fluctuations were more frequent and of greater amplitude at the Beardstown site than at Sand Ridge, possibly because the water table is closer to the land surface at the Beardstown site (5 to 15 feet deep, 1.5-4.5 m, as compared to 30 feet, 9 m, at Sand Ridge). An extremely wet July was experienced in 1986 with over 10 inches (25 cm) of rainfall, and ground-water levels rose more than one foot (0.3 m) shortly thereafter. Low August 1986 rainfall resulted in a decline of over one foot (0.3 m). Rains in September and October 1986 contributed to a rise of approximately 2 feet (0.6 m). Generally low rainfall throughout the remainder of the study period resulted in a decline in ground-water levels, with slight recovery experienced during the spring and early summer of 1987.

Information collected from the hydrologic monitoring system revealed that ground-water levels in the silty water-table aquifer beneath the Beardstown site responded to changes in atmospheric pressure. An example of this response is shown in Figure 21. The figure displays data recorded every 15 minutes for the barometric pressure, the water level in piezometer WLR2.1, and daily precipitation for the month of March 1988. The figure shows that increases in atmospheric pressure often were accompanied by corresponding drops in water level. Similarly, decreases in atmospheric pressure were accompanied by increases in water level. Changes in water level are not always easily attributed to atmospheric pressure changes because of the interference of rainfall recharge. Barometric efficiencies calculated for the data shown in Figure 21 ranged from 13 to 83 percent with a mean of 36 percent.

Because of the presence of the wastewater impoundments, the ground-water flow pattern at the Beardstown site was much more complex than at the Sand Ridge site. Potentiometric surface maps were prepared from water level measurements collected at all sampling wells and piezometers to describe three surf aces (upper, middle, and lower) according to the depth of the well used. Figure 22 shows the three potentiometric surfaces for two dates following the installation of piezometer B8.3, which was used to define the top of the mound created beneath anaerobic impoundment 3. April 21, 1987 (sampling run #30) was chosen to represent a period where ground-water levels were high and August 25, 1987 (sampling run #39) was chosen to represent a period when ground-water levels were low.

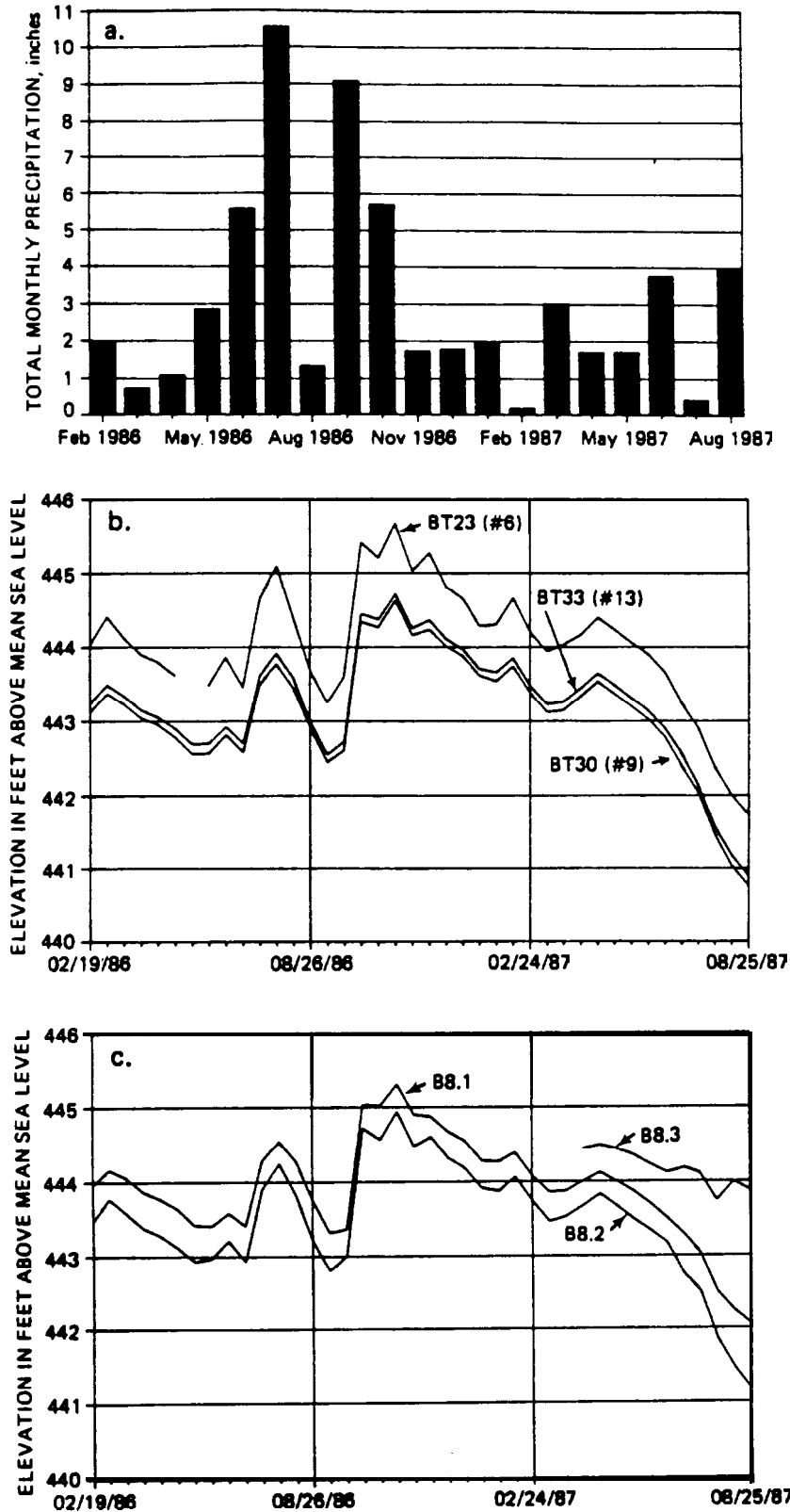


Figure 20. Monthly precipitation recorded at Beardstown (a), ground-water elevations in Wells BT23, BT30, and BT33 (b), and ground-water elevations in the B8 piezometer nest (c) at Beardstown field site during the field sampling period.

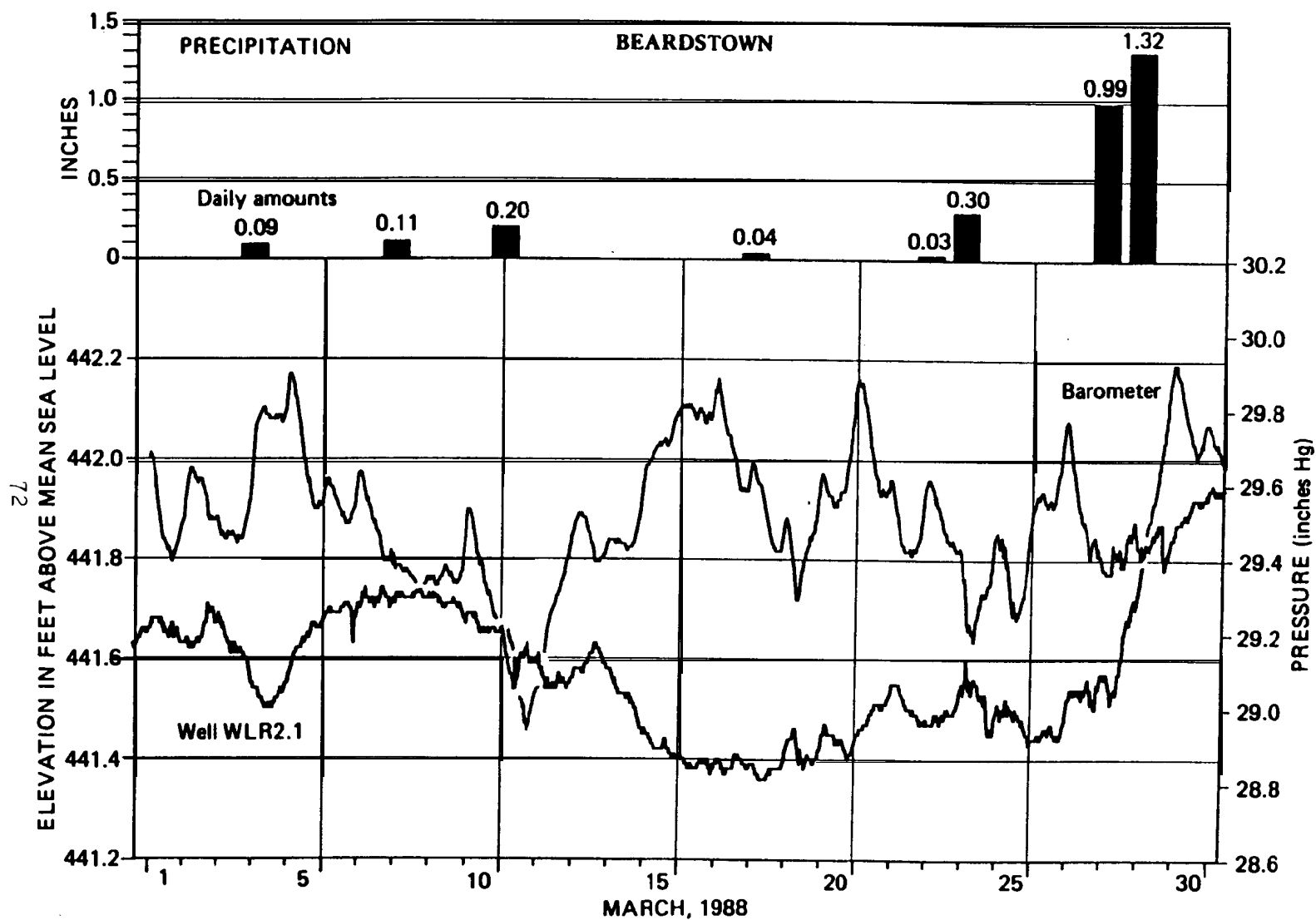


Figure 21. Precipitation, barometric pressure, and ground-water elevation in piezometer WLR2.1 recorded at the Beardstown field site in March, 1988.

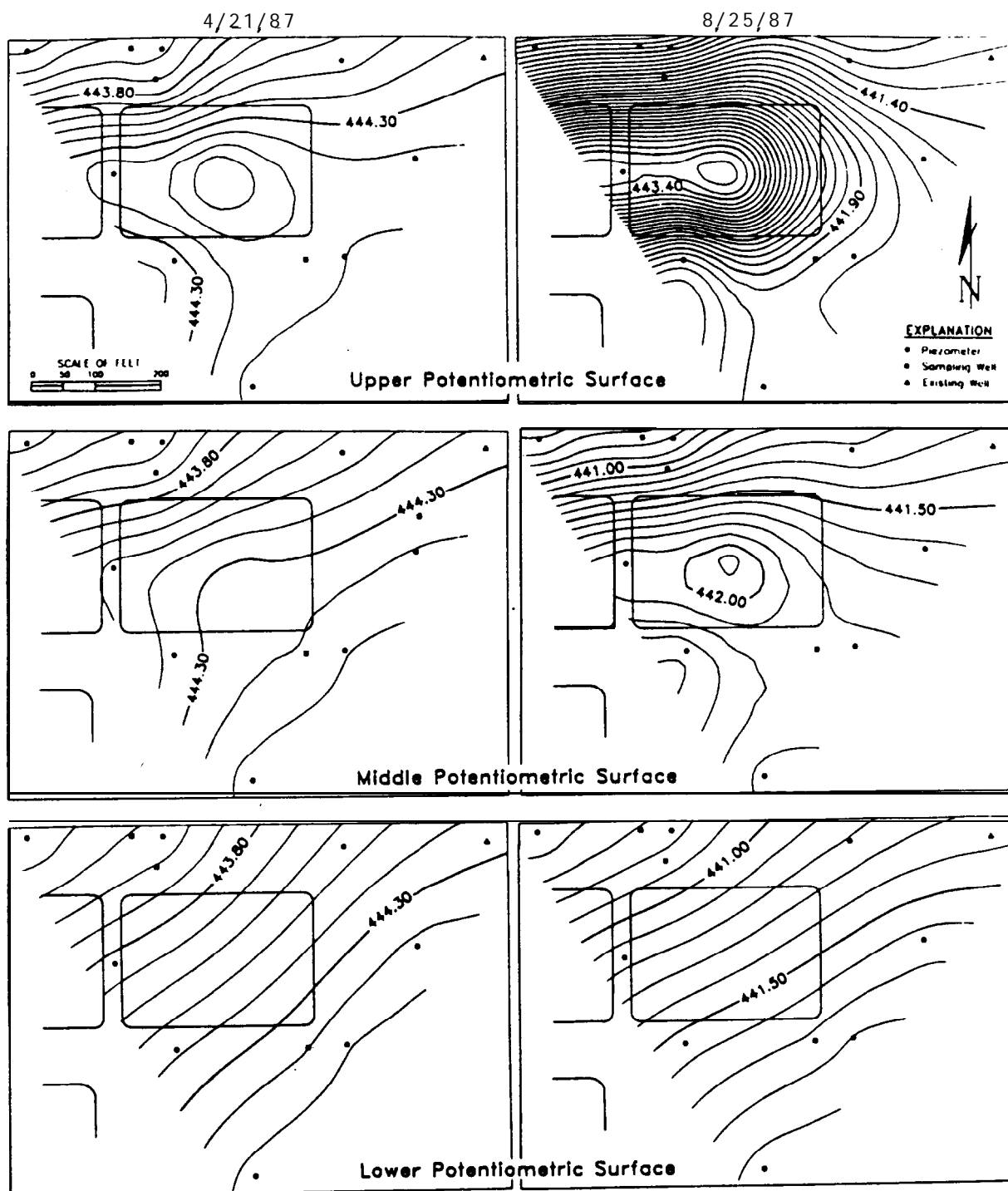


Figure 22. Upper, middle, and lower potentiometric surfaces at the Beardstown field site on April 21, 1987 and August 25, 1987.



The upper and middle potentiometric surfaces in Figure 22, show that a ground-water mound formed beneath the anaerobic impoundments. The B8 piezometers placed between the anaerobic impoundments 2 and 3 gave a clear indication that a vertical gradient existed beneath the impoundments. A hydrograph of the B8 piezometer nest (Figure 20c) shows the vertical gradient which was present between anaerobic impoundments 2 and 3. For mapping purposes, the elevation of the ground-water surface beneath the impoundments was estimated to be slightly higher than the elevation of the surface at B8.3 because no piezometers were placed in the impoundments. Further, vertical gradients beneath the center of impoundment 3 were assumed to be the same as those at the B8 piezometers located between anaerobic impoundments 2 and 3 (Figure 9).

The height of the mound above regional water levels and the change in height in comparison to regional ground-water levels were of considerable interest. Figure 22 shows that the height of the mound (on the upper potentiometric surface) above regional ground-water elevations (on the lower potentiometric surface) changed significantly between April and August. Over this period, ground-water levels fell approximately 2.7 feet (0.8 m) on the lower surface. However, ground-water elevations on the upper surface directly beneath the impoundment fell only 1 foot (0.3 m).

Regional ground-water elevations appear to be predominantly affected by rainfall recharge. Regional ground-water elevation declines can be attributed largely to a lack of rainfall (almost 40% below normal for the April to August period). The height of the mound, however, appeared to be affected not only by the rate of impoundment leakage but also by the magnitude of the leakage in comparison to the regional ground-water discharge rate. This hypothesis is supported by surface and ground-water level measurements made through the course of the project.

Staff gage readings of the water surface in the anaerobic impoundments, made during every sampling run, indicated that the volume of water stored in the impoundments was fairly stable throughout the study period. Water levels in each anaerobic impoundment were controlled by a fixed-elevation circular weir. In controlling the water levels within the impoundments, heads on the impoundment bottoms were held within a range of 1 to 2 feet, (0.3 to 0.6 m). It is likely that leakage through the bottom of each impoundment was reasonably constant.

If the rate of leakage from the impoundment was constant, it would be expected that the leakage rate would be proportionately smaller in comparison to the regional discharge when regional ground-water levels were high. The result might then be observed as the assimilation of the ground-water mound into the regional flow field. This effect is shown by the April 21 potentiometric surfaces in Figure 22. When regional ground-water levels were low, regional ground-water discharge is less and the constant leakage rate from the impoundment would be expected to be greater in proportion to the regional discharge. The ground-water mound then would be expected to be more pronounced as shown by the August 25 potentiometric surfaces in Figure 22.

**TABLE 14. VERTICAL HYDRAULIC GRADIENTS AT THE B8 PIEZOMETER NEST**

Between piezometers	Vertical gradient		Relative change
	April 21, 1987	August 25, 1987	
B8.3 & B8.1	0.03	0.09	3x
B8.1 & B8.2	0.05	0.26	5x

The mounding effect was exemplified further by the vertical gradients induced beneath the impoundment. Vertical gradients beneath the impoundment are seen most easily in the hydrographs of the B8 piezometers (Figure 20c). The head difference between the shallowest and deepest piezometers, B8.3 and B8.2, was less than 1 foot for most of the period in which water levels were recorded in B8.3. However, as water levels fell during the summer, the head difference between piezometers gradually increased to over 2.5 feet (0.76 m). The changes in the vertical gradients between piezometers B8.3 and B8.1 and between piezometers B8.1 and B8.2 for the two dates are shown in Table 14. Vertical gradients increased by a factor of 3 to 5 over this four-month period.

The mound had an effect on the wells located down-gradient, and potentially "upgradient," from anerobic impoundment 3. Equipotential lines drawn on a vertical cross section parallel to the regional ground-water flow path beneath anaerobic impoundment 3 and through the sampling wells are shown in Figure 23. The equipotential lines shown are interpretations of the head data collected from the piezometers and sampling wells at the site on April 21, 1987 (Figure 23a) and August 25, 1987 (Figure 23b). These are the same dates for which potentiometric surfaces are shown in Figure 22. Ground-water elevation data from the B8 piezometers were used to draw the contours beneath the impoundment (see Appendix C). The equipotential lines are considered conceptual because head values at depth in the aquifer were not available and no flow modeling was conducted to provide a mass balance of the regional and impoundment fluxes.

The conceptual cross sections provide a reasonable interpretation of ground-water movement beneath the impoundment. The cross sections show that water moving out from the bottom of the impoundment forces "regional" ground water (ground water from an upgradient direction) downward as it approaches the impoundment. Water from the impoundment would move through the screens of the downgradient sampling wells as it was diverted into the regional flow system. At certain times, particularly when the regional water table was low (or when the regional flow was low compared to the impoundment leakage) as in Figure 23b, water leaking from the impoundment also may be expected to move toward the upgradient sampling wells #5 and #6. Therefore, while the downgradient wells always received water which originated in the impoundment, the upgradient wells may have been affected only periodically depending on the strength of the regional flow system. This may have caused ground-water quality changes in wells #5 and #6.

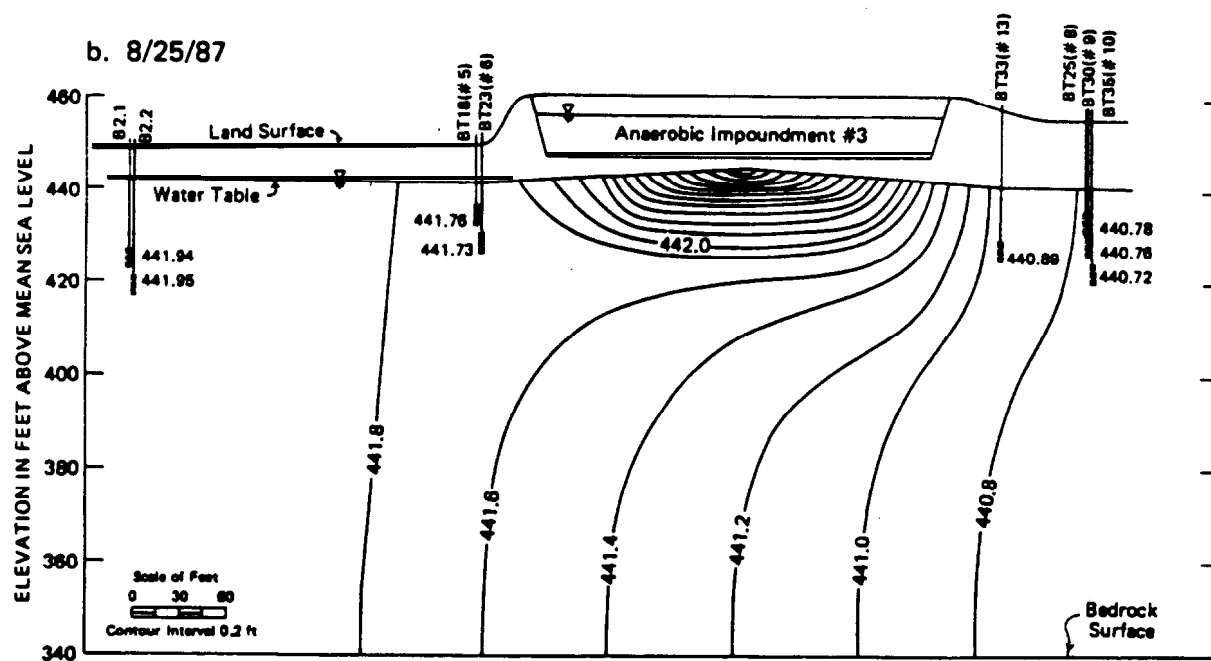
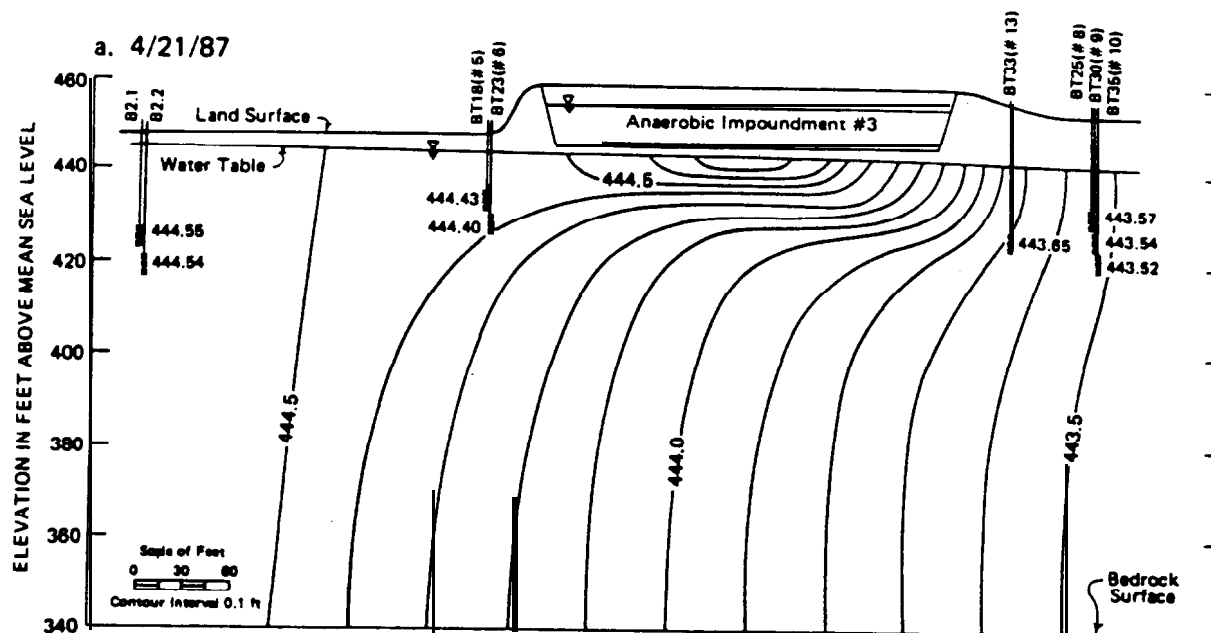


Figure 23. Equipotential lines beneath anaerobic impoundment 3 at the Beardstown field site on April 21, 1987 (a) and August 25, 1987 (b).

Results of casing pressurization tests performed on selected sampling wells at Beardstown are shown in Table 15. Two variations of the Hvorslev (88) method of analysis were used. The first method is an approximation based on a well point extended in uniform soil (Hvorslev's Case 8) and is also the method commonly outlined in ground-water texts (e.g., Freeze and Cherry, 33). The second method is an approximation for a well point extended through a permeable layer between impervious strata (Hvorslev's Case 9). This method was used for comparison with the first method because it was felt that the siltiness of layers above and below screened sections may cause the horizontal hydraulic conductivity to govern ground-water movement. As shown in Table 15, the hydraulic conductivity ranged from 2.4 to  $3.0 \times 10^{-2}$  cm/s for Hvorslev's Case 8 method and from 3.1 to  $4.2 \times 10^{-2}$  cm/s for Hvorslev's Case 9 method. Basically, results from the second method were 1.3 times greater than those from the first. It is not possible at this time to determine which values are more accurate. These values are within a range reasonable for a silty to clean sand (33) and are quite similar to those observed at the Sand Ridge site. The differences between the results for the two methods at the Beardstown site may reflect differences in hydraulic conductivity between the developed bore hole and that of the natural geologic material.

The potentiometric surfaces in Figure 22 indicate that the slope of the potentiometric surface varied greatly with location and with time. This is in marked contrast to the constant slope of the potentiometric surface observed at the Sand Ridge site.

Because of the large vertical head differences near the impoundment, hydraulic gradients and ground-water velocities were calculated in three space dimensions according to a method outlined by Abriola and Pinder (89). The method is based on the differentiation of a three-dimensional linear interpolation of hydraulic heads at four irregularly spaced points to derive hydraulic gradients in three dimensions. Substitution of the calculated x-, y-, or z-gradient into Darcy's law provides the ground-water velocity in the respective direction.

**TABLE 15. HYDRAULIC CONDUCTIVITIES (IN  $10^{-2}$  CM/S)  
AT SELECTED BEARDSTOWN WELLS**

Method of calculation*	BT18 (#5)	BT23 (#6)	BT25 (#8)	BT35 (#10)	BS30 (#11)	BP30 (#12)	BT33 (#13)
Hvorslev #8	3.0	3.2	3.0	3.0	2.5	2.5	2.4
Hvorslev #9	3.9	4.2	3.8	3.8	3.3	3.2	3.2

\* Hvorslev's Case 8 and Case 9, see reference 88.

For this site, the magnitude Of the three-dimensional gradients (and velocities) calculated by this method depended on the choice of the four wells used in the computation. This was particularly true in areas where infiltration from the impoundment had a profound effect on vertical gradients. Four areas were chosen to more closely examine the nature of ground-water velocity changes across the site. These were: 1 ) upgradient from the anaerobic impoundment, utilizing head differences and distances between piezometers B1, B2.1, B3.1, and B3.2, 2) downgradient from the anaerobic impoundment, utilizing head differences and distances between wells WLR2.1, BT33 (Well #13), BT30 (Well #9), and BT35 (Well #10), 3) beneath the impoundment on the "upgradient" side, utilizing head differences and distances between piezometers B8.1, B8.2, B3.1, and sampling well BT18 (well #5), and 4) beneath the impoundment on the downgradient side, utilizing head differences and distances between piezometers B8.1, B8.2 and sampling wells BT33 (well #13), and BT25 (well #8). Water level data from B8.3 were not used in these calculations because a full length of record over the entire sampling period was not available.

A summary of the ranges and means of the hydraulic gradients and ground-water velocities calculated for the four areas around anaerobic impoundment 3 is presented in Table 16. The values in the table represent the range and means calculated from observed heads measured at the site during the 39 biweekly sampling runs conducted between March 11, 1986 and August 25, 1987. A horizontal hydraulic conductivity ten times the vertical value was used in the calculation of ground-water velocities because of the siltiness and layering of the aquifer materials.

Resultant ground-water velocities calculated over the length of the project for these four areas are shown in Figure 24. Shallow ground-water velocities upgradient of the impoundment (mean, 0.22 m/d) were slightly less than downgradient of the impoundment (mean, 0.30 m/d). This was due to the presence of the ground-water mound beneath the impoundment. Velocities decreased as the mound was approached and increased again after the mound was passed. Ground-water velocities beneath the impoundment were much greater than the upgradient and downgradient velocities. This was due principally to the large vertical gradients created within the mound. Vertical gradients beneath the impoundment were 10 to 25 times greater than vertical gradients outside the boundary of the impoundment. Resultant velocities beneath the impoundment on the downgradient side of the mound (mean, 1.15 m/d) were greater than those on the upgradient side of the mound (mean 0.65 m/d).

Velocities computed for upgradient and downgradient locations beneath the impoundment paralleled each other because of the use of head data at piezometers B8.1 and B8.2 for both locations. The strong vertical gradient between these two piezometers had a large influence on the calculated velocities for these two areas. The steep increase in velocities over the last five sampling runs was further indication of the influence of the vertical gradient on ground-water velocities. As mentioned previously, when regional water levels fell over the course of the summer of 1987, the mound beneath the impoundment gradually became more pronounced. This caused both

TABLE 16. HYDRAULIC GRADIENTS AND GROUND-WATER VELOCITIES AT BEARDSTOWN\*

Location	Parameter	X-Direction		Y-Direction		Z-Direction		Resultant velocities	
		Range	Mean	Range	Mean	Range	Mean	Range	Mean
Upgradient of Impoundment 3	Gradient (m/m)	0.00083 to 0.0017	0.0011	-0.0025 to -0.00065	-0.0012	0.00051 to 0.0029	0.0017		
	Velocity (m/d)	-0.23 to -0.11	-0.15	0.09 to 0.34	0.16	-0.04 to -0.007	-0.025	0.16 to 0.42	0.22
Beneath Impoundment 3 on "Upgradient" side	Gradient (m/m)	0.0011 to 0.0020	0.0015	-0.00093 to 0.0045	0.0013	0.026 to 0.085	0.042		
	Velocity (m/d)	-0.27 to -0.15	-0.20	-0.63 to 0.13	-0.18	-1.17 to -0.36	-0.58	0.42 to 1.35	0.65
Beneath Impoundment 3 on "Downgradient" Side	Gradient (m/m)	0.0020 to 0.0110	0.0056	-0.0069 to -0.0031	-0.0042	0.028 to 0.092	0.046		
	Velocity (m/d)	-1.54 to -0.49	-0.78	0.42 to 0.95	0.57	-1.27 to -0.38	-0.63	0.76 to 2.20	1.15
Downgradient of Impoundment 3	Gradient (m/m)	-0.000096 to 0.0013	0.00057	-0.0033 to -0.0012	-0.0021	0.00035 to 0.0089	0.0039		
	Velocity (m/d)	-0.17 to 0.009	-0.077	0.16 to 0.45	0.28	-0.12 to -0.005	-0.054	0.20 to 0.46	0.30

\* Velocities calculated using horizontal hydraulic conductivities,  $K_x$  &  $K_y = 27$  m/d; vertical hydraulic conductivity,  $K_z = 0.1 K_x = 2.7$  m/d; and effective porosity,  $n = 0.2$ . Ranges given are the extremes (most negative to most positive) from 39 biweekly sampling runs conducted between 3/11/86 and 8/25/87. For velocity vectors, positive X-direction is east, positive Y-direction is north, and positive Z-direction is upward.

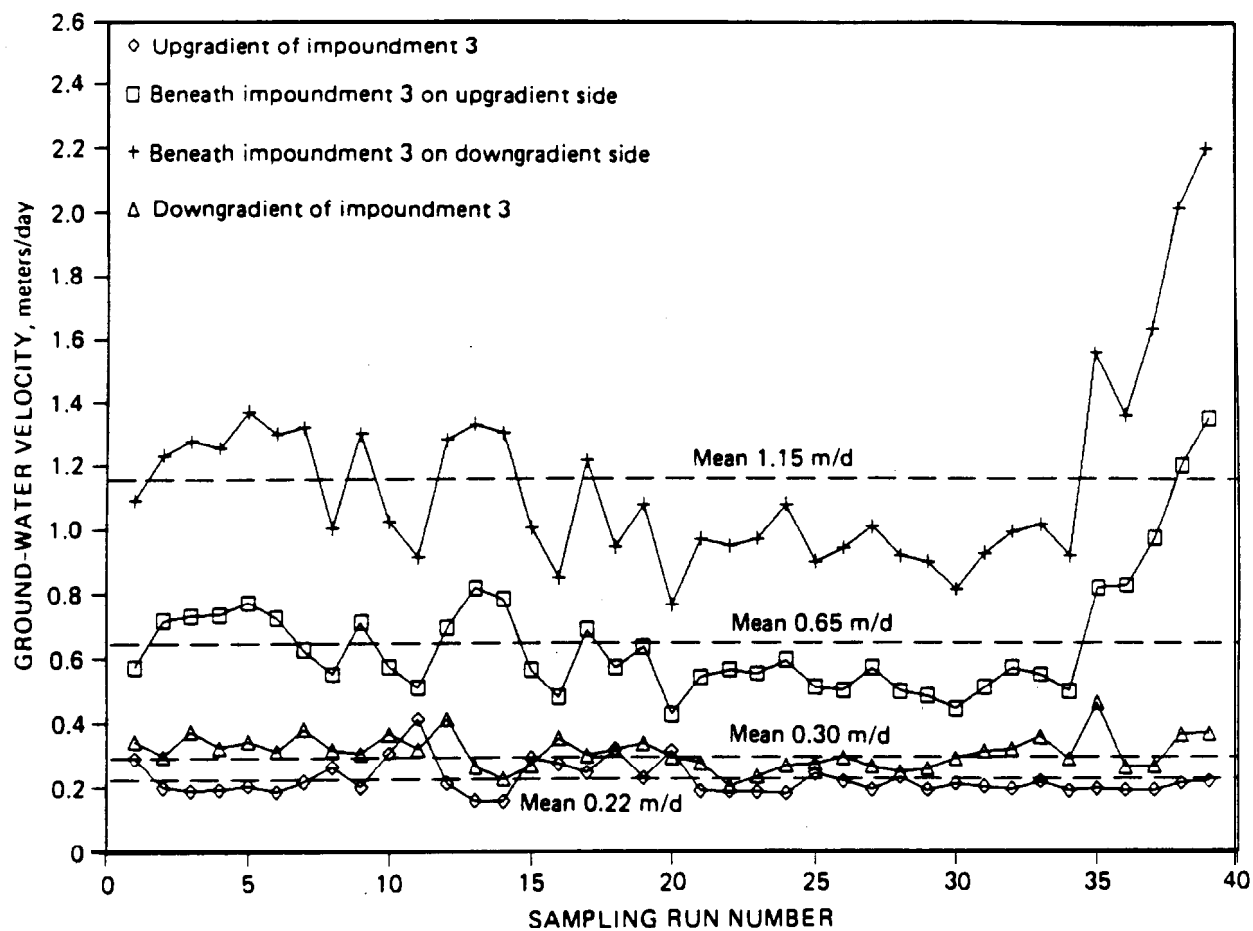


Figure 24. Calculated ground-water velocities for four areas in the vicinity of anaerobic impoundment 3 at the Beardstown field site.

the vertical hydraulic gradients and ground-water velocities to increase as a result.

The ground-water velocities and hydraulic gradients observed at the Beardstown site were indicative of a much more complex flow system than at Sand Ridge. Water level response to rainfall at Beardstown was much more rapid and of greater amplitude than at Sand Ridge. The response to changes in atmospheric pressure, even under water table conditions, was apparent at the Beardstown site. The leaking impoundments coupled with a shallower, more responsive water table and more variable geologic materials at Beardstown comprised a more transient hydrologic system than at Sand Ridge.

According to individual well hydrographs, ground-water levels fell a maximum of over three feet (0.9 m) at Beardstown during the field sampling period but less than two feet (0.6 m) at the Sand Ridge site. This was despite the fact that the Sand Ridge site was within the influence of a continuously pumping well field. In spite of the pumpage, the direction and rate of movement of ground water at Sand Ridge remained remarkably constant throughout the study period as shown in the potentiometric surfaces in Figure 19. Conditions at Beardstown, however, changed markedly and are best exemplified by the potentiometric surfaces shown in Figure 22. Vertical hydraulic gradients, created by the leaking impoundments at Beardstown, were particularly large and the principal cause for velocity changes. However, at locations distant from the immediate vicinity of the impoundments, ground-water velocities (and hydraulic gradients) remained relatively constant (Figure 24). This information is consistent with the ground-water chemistry of each site as will be related in the following sections.

## **CHEMICAL DATA CHARACTERISTICS**

The completed sampling at the uncontaminated site extended over more than 2.5 years (1020, days) with field and laboratory determinations of 26 chemical and physical parameters at established intervals over the time period. The sampling and analysis at the contaminated site were conducted over 1.8 years (600 days) for the same suite of major parameters. Figure 25 shows graphically the relative fractions of anions or cations present, on the average, for each well. For these summaries, the mean inorganic concentrations for each well (Appendix A) were processed by the WATEQ4F computerized aqueous chemical speciation model (90). Ion pairs and complexes (e.g.,  $\text{CaHCO}_3^+$ ,  $\text{MgHCO}_3^+$ ,  $\text{CaSO}_4^0$ ,  $\text{MgCO}_3^0$ , etc.) were counted with their anionic and cationic components for simplicity in these figures. The vertical order of the ligand represents the order of the components in each of the bars.

Ground water at the Sand Ridge site contained calcium, magnesium, and bicarbonate components introduced during recharge through the soil zone. Small amounts of sodium, sulfate and silica were also present. Calcium was consistently higher (i.e., approximately 1.5 times) than magnesium on a molar basis. Calcium, magnesium, and bicarbonate decreased distinctly with depth. The decrease corresponded approximately to the relative ages of the ground water (i.e., oldest = deepest) determined by tritium ( $^3\text{H}$ ) dating.



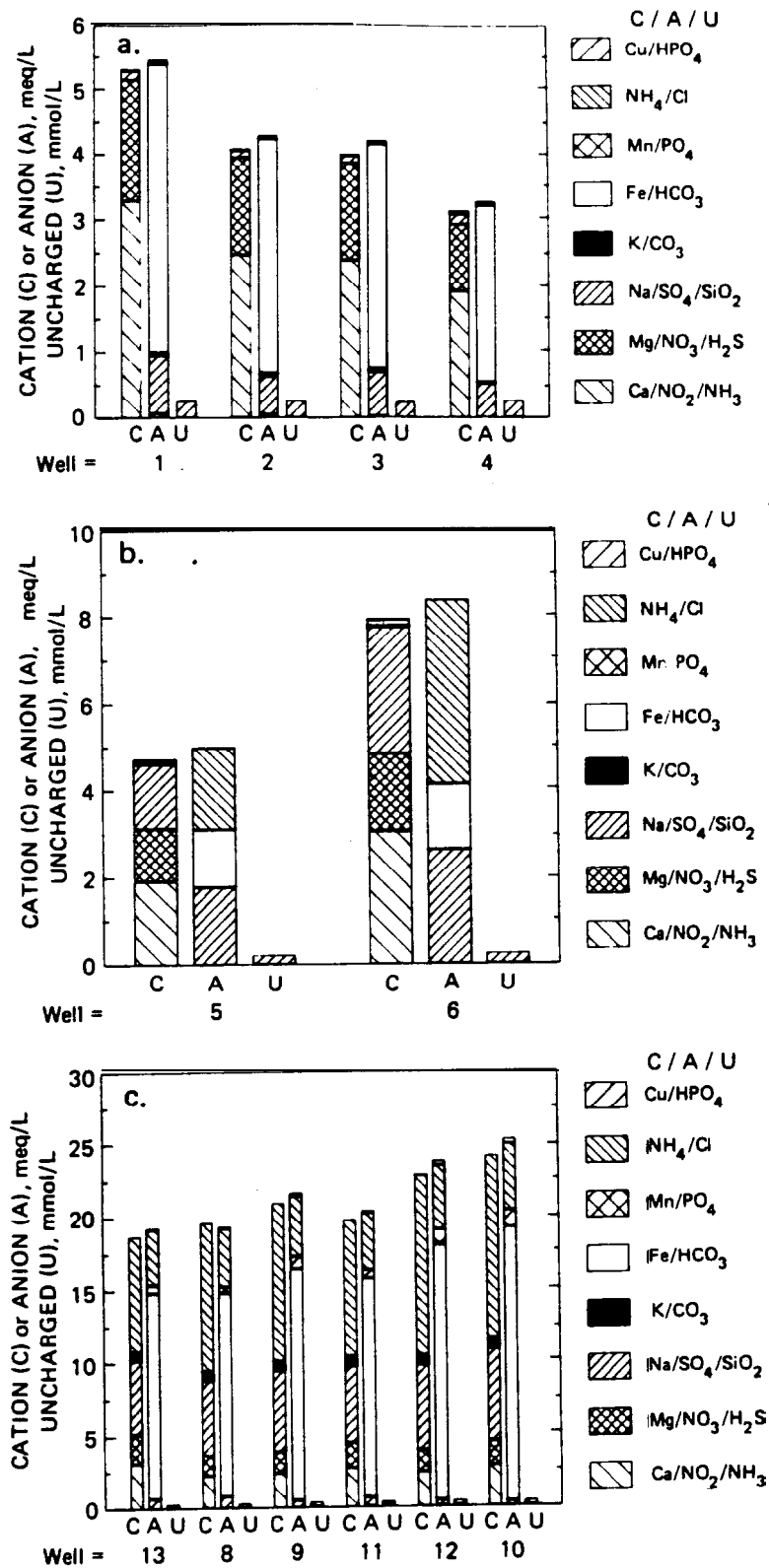


Figure 25. General chemical characteristics for the Sand Ridge wells, (a), the upgradient wells at Beardstown (b), and the downgradient wells at Beardstown (c).

Comparison of the results for water samples from wells #1 and #4 (i.e., the shallowest and deepest wells, respectively, at Sand Ridge) provides a measure of the difference between fully oxidized and suboxic subsurface redox conditions. Average profiles of  $O_2$ , Eh and Fe(II) with depth at the Sand Ridge site are shown in Figure 26 (a two standard deviation range is included for each parameter). Very strong oxygen concentration and redox potential gradients were present and were reflected by average concentrations of ferrous iron. These chemical gradients were very stable during the study. It is likely that the dissolved oxygen levels measured in water from well #4 at Sand Ridge represented an upper limit of concentration since oxygen diffusion through the PTFE tubing alone could increase the apparent  $O_2$  levels by 0.2 to 0.3  $mg \cdot L^{-1}$  (91).

Samples of the uncontaminated ground water from Beardstown upgradient wells were similar to each other in relative proportions of components, but were considerably different in ionic strength. The water from well #5 had strength similar to the Sand Ridge wells (0.007 versus 0.005-0.008), but sodium accounted for approximately one-third of the equivalents of cations present. Sodium was present at about twice the molar concentration of calcium. Water from well #6 had the same general ionic character as well #5, but contained proportionally more of all components. The average ionic strength of water from well #6 was 0.011 compared to 0.007 for well #5, and the ferrous iron in well #6 was 3.5 times the average level in well #5. For both wells, chloride and sulfate made up the bulk of the anionic composition on a charge basis with chloride 1.5 to 3 times the bicarbonate and sulfate concentrations on a molar basis.

The effect of the lagoon seepage on downgradient ground-water composition was striking. The average ionic strengths of water from the downgradient wells were 2 to 4 times as high as wells #5 and #6. Ammonium ion and sodium were the dominant cations, with potassium approximately seven times the upgradient levels on a molar basis. The sodium concentration was consistently 9 to 10 times the potassium concentration. The molar ratio of  $Ca^{2+}$  to  $Mg^{2+}$  was consistently 1.5. Ion pairing and complexation of  $Ca^{2+}$  and  $Mg^{2+}$  by  $HCO_3^-$ ,  $HPO_4^{2-}$ ,  $SO_4^{2-}$  and  $CO_3^{2-}$  accounted for approximately 10-20% of the dissolved metal species in samples from these wells. The ferrous iron concentrations were twice the upgradient concentrations, but they remained insignificant in the overall constituent balance, relative to the other cations. Bicarbonate was by far the dominant anionic constituent, making up approximately three-quarters of all anions on a charge basis. Chloride was consistently the next most important anion in concentration (about 0.25 that of bicarbonate), with  $SO_4^{2-}$ ,  $HPO_4^{2-}$  and  $PO_4^{3-}$  the remaining significant anionic forms.

The results for the ground-water samples from Beardstown showed the marked differences one would expect between locations upgradient and downgradient from a leaking anaerobic treatment impoundment. Dissolved oxygen levels at both upgradient and downgradient locations (Tables A-5 through A-12) were consistently at or near the detection limit for oxygen electrode measurements and below the corresponding limit for iodometric titration by the Winkler method. Ground-water quality conditions were changed markedly at downgradient locations by the leakage of leachate from the anaerobic

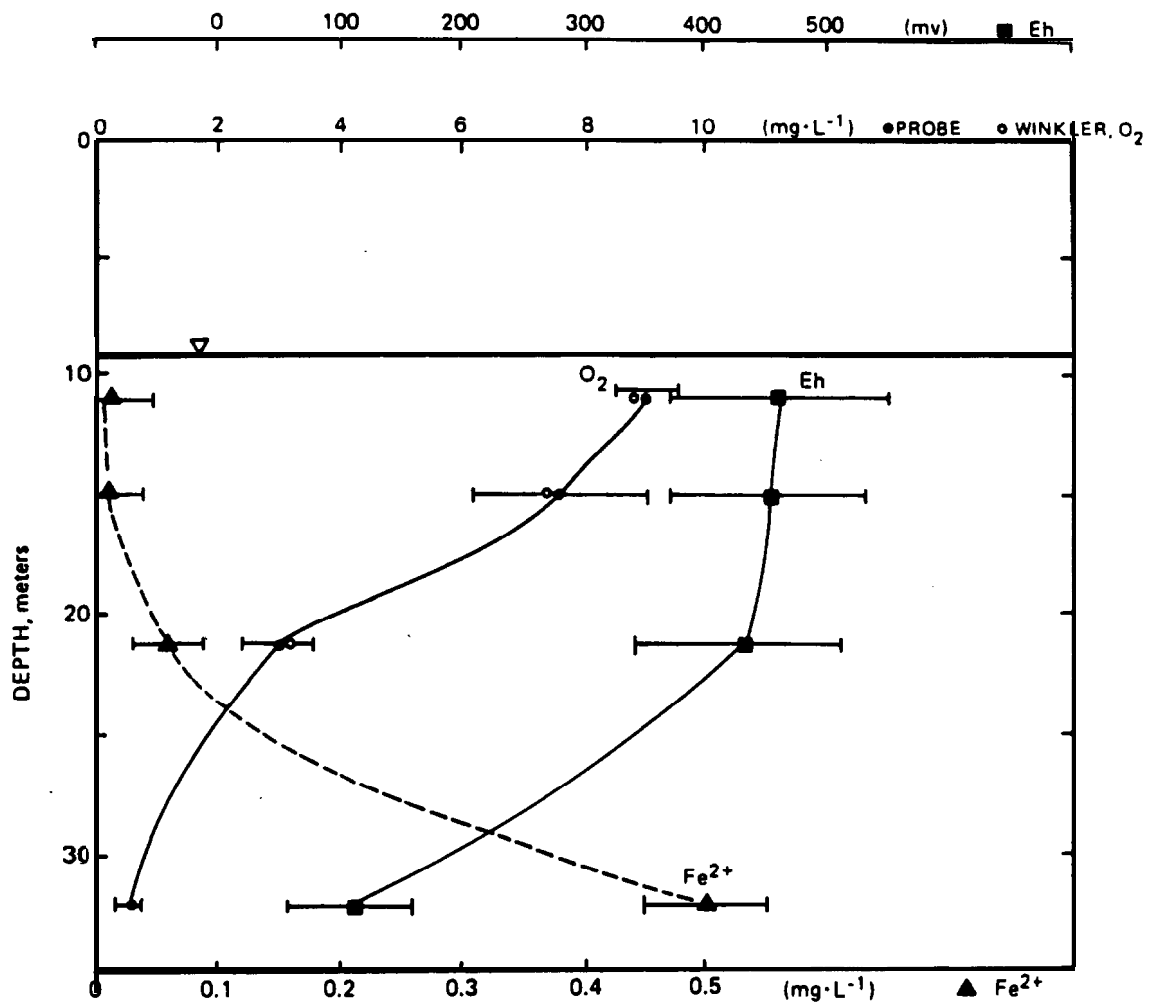


Figure 26. Profiles of Eh, dissolved oxygen, and ferrous iron with depth at the Sand Ridge field site.

impoundment. The downgradient ground-water samples were generally much higher in dissolved solids, temperature, total organic carbon, methane, alkalinity, ammonia, sulfide, iron, chloride, sodium and potassium than were samples from upgradient positions.

The average results of water analyses for redox-related species and Eh in samples from wells at the Beardstown site are shown in Figure 27. The results from the upgradient nested wells (i.e., #5 and #6) showed some increase in ferrous iron and sulfide concentrations with depth but no significant change in Eh or concentrations of dissolved oxygen and methane. The downgradient wells along a flow path from the impoundment accessed progressively more reducing ground water, judging from average methane, dissolved oxygen, sulfide and Eh measurements. Ferrous iron values did not increase or decrease significantly downgradient. This observation may be explained in part by iron mineral controls on ferrous iron solubility. Saturation indices for common ferrous-carbonate, -phosphate and -sulfide minerals were all at or above saturation for ground-water samples from the downgradient wells, using the equilibrium speciation model (90).

The analytical results from samples from the three wells finished at 30 ft (10 m) depth, only 1 to 1.5 m apart and constructed of dissimilar materials (i.e., #9 -PTFE; #11 -SS; and #12 - PVC) are shown in Tables A-8, A-10, and A-11. The results reflect the sensitivity of the iron and sulfide systems to well casing material effects and presumed differences in the geochemical microenvironment near the wells. A more detailed discussion of these results appears in Barcelona et al. (92).

Table 17 gives a summary of the saturation indices computed for several minerals of interest using mean values of the chemical analyses over the course of the project. The indices suggest an approach to calcium carbonate equilibrium from initial oversaturation at the Sand Ridge site. The deepest well (#4) represents water closest to that of the regional base flow, which would have an "age" since recharge takes place on the order of decades. The shallower wells would be expected to have younger water (on the order of days to years in age) containing CO<sub>2</sub> picked up from the overlying soil and calcium, magnesium, and carbonate leached from surrounding materials. As the CO<sub>2</sub> gas is depleted with depth, the water approaches equilibrium with calcite. The ground water at Sand Ridge tended to be near saturation with respect to chalcedony, a cryptocrystalline form of quartz. This phenomenon may represent the product of reactions of the recharge water with clay minerals in the soil zone and weathering reactions of silicate minerals in the aquifer materials.

In the Beardstown downgradient wells, there appears to be a trend towards equilibrium with calcium carbonate from upgradient to downgradient positions. Insufficient calcium is introduced from the waste plume to reach saturation, so the driving force towards equilibrium appears to be the generation of bicarbonate from organic material decomposition. Increases in temperature due to microbial activity also favor this change. Iron concentrations may be controlled by ferrous carbonate (siderite). The uncertainty in the equilibrium constants for many sulfide and phosphate minerals and their slow precipitation rates or uncertain stoichiometries make their role

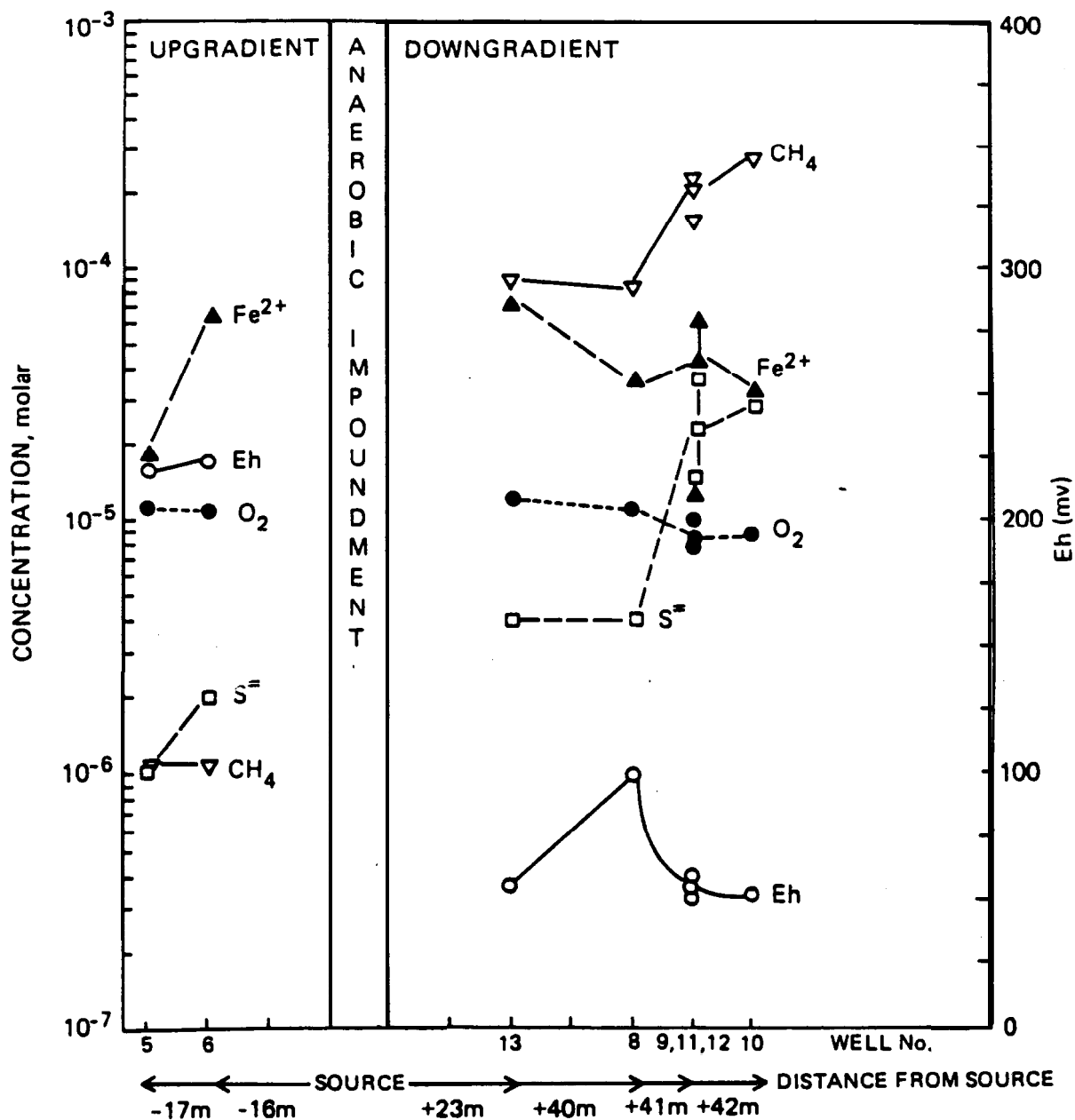


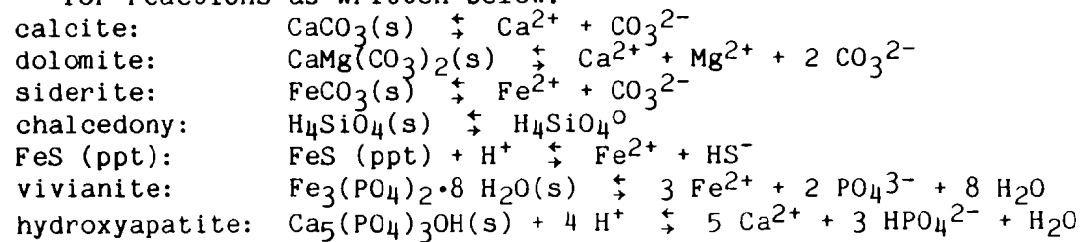
Figure 27. Average concentrations of redox-active chemical species with distance from contaminant source. (Concentration is on a logarithmic scale, Eh is on a linear scale and distances from source are schematic and not to scale)

TABLE 17. MEAN SATURATION INDICES\* FOR SELECTED MINERALS  
IN GROUND WATER FROM THE PROJECT WELLS

Well	Calcite	Dolomite	Siderite	Chalcedony	FeS (ppt)	Vivianite	Hydroxyapatite
1	0.32	0.27	-1.78	0.09	--	-8.62	-2.85
2	0.33	0.32	-1.85	0.09	--	-8.28	-1.82
3	0.36	0.39	-0.73	0.06	--	-4.28	-0.70
4	-0.02	-0.42	-0.14	0.09	--	-1.61	-1.23
5	-1.68	-3.65	-1.43	0.02	-1.18	-4.93	-9.16
6	-1.78	-3.89	-1.21	0.07	-1.09	-4.39	-10.03
8	-0.28	-0.81	0.25	0.14	0.28	1.74	0.30
13	-0.18	-0.58	0.49	0.14	0.92	2.51	0.97
9	-0.22	-0.68	0.27	0.19	0.94	2.16	1.12
11	-0.20	-0.63	0.46	0.15	0.95	2.50	0.83
12	-0.18	-0.59	-0.03	0.20	0.77	1.35	1.46
10	-0.11	-0.48	-0.16	0.20	0.92	1.92	1.75

\* Saturation Index =  $\log \left| \frac{IAP}{K_{sp}} \right|$  where IAP = ion activity product and  
K<sub>sp</sub> = solubility constant

for reactions as written below.



(if any) difficult to assess. Sulfide may be controlled by precipitation with ferrous iron, which is suggested by the relative consistency of the saturation index for ferrous sulfide.

The principal dissolved contaminants at the Beardstown site were major ionic constituents of the anaerobic leachate which seemed to be at or near chemical equilibrium with the aquifer materials. The usefulness of any of these constituents as waste-specific indicators under similar conditions would not appear to be constrained significantly by assumptions of chemical equilibrium and the use of speciation models.

## STATISTICAL STRUCTURE AND TEMPORAL VARIABILITY

### Estimation of Sources of Variation

In order to insure that monitoring resources are optimally allocated, it is important to identify the sources of natural (i.e., spatial and temporal) and sampling and analytical variance. The general statistical approach to reducing the effect of any source of variation is to randomize and collect replicates. Therefore, the effects of natural variability can only be reduced by increasing the sample size (that is, either the sampling frequency or the length of the data collection series). For instance, increasing the sample size has the effect of reducing the component of the variance of the long-term mean attributable to field and lab errors. In addition, if the component of the total variance due to laboratory and/or field errors is large, it can be reduced by taking more than one field or laboratory replicate at each sampling occasion. Whether or not collection of laboratory or field replicates is cost effective depends on the fraction of the total variance attributable to each source. The conceptual model used to estimate sources of variation was:

$$\sigma_t^2 = \sigma_n^2 + \sigma_l^2 + \sigma_f^2$$

where:  $\sigma_t^2$  = total variance

$\sigma_n^2$  = natural variance

$\sigma_l^2$  = laboratory analytical variance

$\sigma_f^2$  = field sampling variance

Generally, the natural variations in water quality time series are of interest. For instance, the difference between the time series of a given contaminant at a downgradient and an upgradient well may give an indication of whether contaminant release has occurred. However, the difference series is inevitably corrupted by errors in the field data collection and laboratory analysis procedures, both of which introduce what may be considered "noise" into the time series. Each of these noise processes has a variance, and the total variance is the sum of the three variance terms. This model assumes that the three sources of variation are statistically independent, which is a reasonable assumption because the sources are physically

independent. A possible exception is that the magnitude of the field and laboratory errors may depend on the true value of the chemical concentration. This consideration is addressed below.

The sources of variation were estimated as follows. First, the laboratory analytical variance was estimated by taking the difference of the laboratory calibration standards series, since each standard was subjected to two replicate analytical determinations. Each difference was normalized by the (known) true value of the standard. Then, a normalized standard deviation was computed using the inner-quartile differences (i.e., 75th minus 25th percentiles) multiplied by an adjustment factor appropriate to the normal distribution. The use of the adjustment factor for the normal distribution does not imply that the distributions are in fact normal (most are not); it is only a convenience. Next, a similar procedure was applied to the field replicate series. Because the field replicates include the effect of laboratory analytical variability as well, the analysis of the field replicates provided estimates of the sum of the normalized laboratory and field sampling variance. The normalized field sampling variance was then estimated by subtraction. This subtraction occasionally gave negative values, which were reported as "NA". An alternative procedure would be to simply set these values (i.e., the normalized field variance) to zero. Finally, the normalized total variance was estimated from the entire time series for each well, and for each chemical constituent where the normalization was by the median for the given well. The normalized natural variance was then estimated by subtraction.

The results are summarized in Table 18 for the three groups of wells. For almost all of the groups, and for almost all of the chemical constituents, a high fraction of the total variation was natural. In fact, with the exceptions of calcium, magnesium and potassium which showed little or no natural variability and manganese which was usually near detection limits, the combined lab and field variances were generally below ten percent of the total variance. This is consistent with the QA/QC data analyses, which showed that the data collection errors were generally quite small. The entries in the table have been separated into water quality parameters and chemical parameters of geochemical interest. The results confirm that if careful sampling and analytical protocols are used, the analytical and sampling errors can be held to less than about 20%. Therefore, the natural variability in the major ion chemistry of the system can be identified. For TOC and TOX it is clear that "natural"<sup>1</sup> sources of variability are greater than the combined lab and field variance. However, the level of overall variability in TOX results was quite large in comparison to the mean values for each well. The significance of these determinations at the microgram per liter concentration level is doubtful.

A similar attempt to estimate sources of variations in ground-water quality data was performed by Summers et al. (93). These workers analyzed data from two sources on related ground-water samples collected in the vicinity of power plant waste disposal impoundments. They reported that, in general, combined sampling and analytical variability was less than the natural variability. They noted that combined sampling and analytical variability was usually less than about 15% of the total variability which



**TABLE 18. PERCENTAGE OF VARIANCE ATTRIBUTABLE TO LABORATORY ERROR, FIELD ERROR, AND NATURAL VARIABILITY BY CHEMICAL AND SITE**

Type of parameter	Sand Ridge			Beardstown (upgradient)			Beardstown (downgradient)		
	lab	field	nat	lab	field	nat	lab	field	nat
<u>Water Quality</u>									
NO <sub>3</sub> <sup>-</sup>	0.0	0.0	100.0	0.1	NA*	99.9	0.2	NA	99.8
SO <sub>4</sub> <sup>=</sup>	0.0	0.0	100.0	0.2	NA	99.8	1.4	0.1	98.6
SiO <sub>2</sub> <sup>=</sup>	0.0	NA	100.0	0.0	20.0	80.0	0.0	6.8	93.2
o-PO <sub>4</sub> <sup>=</sup>	1.2	1.2	97.6	0.0	0.0	100.0	0.0	0.0	100.0
T-PO <sub>4</sub> <sup>=</sup>	0.0	NA	100.0	2.8	NA	97.8	0.9	NA	99.1
Cl <sup>-</sup>	7.2	NA	92.8	0.0	3.3	96.7	0.0	17.2	82.8
Ca	0.0	45.7	54.3	0.0	2.3	97.7	0.0	3.6	96.4
Mg	0.0	20.0	80.0	0.0	2.2	97.8	0.0	2.8	97.2
Na	0.0	NA	100.0	0.0	0.3	99.7	0.0	7.1	92.9
K	0.0	NA	100.0	33.9	NA	66.1	87.1	NA	12.9
<u>Geochemical</u>									
NH <sub>3</sub> <sup>-</sup>	0.0	0.0	100.0	0.0	0.0	100.0	0.0	0.0	100.0
NO <sub>2</sub> <sup>-</sup>	NA	NA	NA	0.1	NA	99.9	0.3	NA	99.7
S <sup>=</sup>	NA	NA	NA	NA	NA	NA	NA	NA	NA
Fe <sup>2+</sup>	NA	NA	NA	0.0	0.1	99.9	0.0	5.9	94.1
Fe <sub>T</sub>	0.0	NA	100.0	0.0	0.0	100.0	0.0	NA	100.0
Mn <sub>T</sub>	0.0	NA	100.0	0.0	40.1	59.9	0.0	73.6	26.4
<u>Contaminant</u>									
<u>Indicator</u>	<u>lab + field</u>			<u>lab + field</u>			<u>lab + field</u>		
TOC**	15.4		84.6	29.9		70.1	40.6		59.5
TOX**	0.0		100.0	12.5		87.5	24.6		75.4

\* NA indicates that the number of observations on which the estimated variance was based was less than 5, or the estimated variance was negative.

\*\* True field spiked standards not available for these constituents, demanding combined estimates of laboratory and field variability.

is consistent with the results of the present study. Summers et al. did report exceptions in the cases of  $\text{NO}_3^-$ , silicate, and Zn where the combined sampling and analytical variance exceeded 30% of the total variance. The potential sensitivity of these constituents to well construction and sampling errors was not discussed in their report.

The implication of the results discussed above and those of this study is that network design optimization efforts should focus primarily on the natural variability. The use of field and laboratory replication for purposes other than QA/QC will be difficult to justify as long as the sampling and analytical protocols are in control. This conclusion must be qualified, however. The chemical constituents present at appreciable concentrations (i.e.,  $\text{mg}\cdot\text{L}^{-1}$ ) at either site were the major cations and anions and general water quality indicators. The analytical and sampling variances for trace organic contaminants would be expected to be higher, and their analytical recoveries are frequently found to be a function of concentration. For such contaminants, the field and laboratory variations may not be independent, which would violate a basic assumption in this model.

The field and analytical data were collected with very careful QA/QC in the course of this research project. It is unlikely that combinations of different laboratories and field sampling crews would be able to achieve and maintain such low levels of error. Further, the sites used in this study provided fairly stable conditions of ground-water flow rates and direction as well as a steadily leaking source of contamination. In addition, the contaminant source itself was of fairly uniform composition. The effect of these conditions would be to minimize natural variability making the degree of sampling and analytical control all the more critical.

### **Temporal Variations in Ground-Water Quality**

There are numerous examples of both short- and long-term variability in ground-water quality, in the literature. Recent reviews by Loftis et al. (54) and Montgomery et al. (55) pointed out the need for very careful selection of statistical methods and for qualified interpretations of existing datasets. The well-documented cases of both short- and long-term temporal variability in ground-water quality have been tabulated in Tables 19 and 20, respectively. These observations cover temporal variability caused by agricultural and nonagricultural sources in high-volume water supply production wells and in low-volume observation, monitoring, and shallow private wells all in a variety of hydrogeologic settings. The concentration variations are noted mainly as multiples above and below an arbitrary baseline or background concentration. In a few instances, where the trends were clearly very long-term or cyclic (i.e., due to alternate pumping and nonpumping conditions), the variations have been entered in concentration units. Although the details of purging, sampling, filtration/preservation, and analysis were frequently lacking in the reports, quite substantial variability has been documented over time-frames ranging from minutes to decades. Significant short-term temporal concentration variability has been observed in low yield wells (i.e., monitoring and observation wells) largely resulting from purging effects (6,101). Similar variations from one to ten times the initial or background concentrations have been noted in samples from

TABLE 19. OBSERVATIONS OF TEMPORAL VARIATIONS IN GROUND-WATER QUALITY: SHORT-TERM VARIATIONS

	Constituents (concentration variation)	Nature of variability		Reference
		Period	Probable cause	
Agricultural Sources	Se ( $\pm 2 \text{ mg} \cdot \text{L}^{-1}$ )	Monthly	Irrigation/return/ indeterminate	94
	$\text{NO}_3^-$ (1-3X) $\text{SO}_4^{=}$ (3-7X)	Minutes	Pumpage/head changes and leaching from unsaturated zone	95
	$\text{NO}_3^-$ (1-4X)	Minutes	Pumpage/vertical stratification	96
	$\text{NO}_3^-$ (1-10X) $\text{SO}_4^{=}$ (1-1.5X)	Monthly	Irrigation/fertilizer applications/ leaching; locational differences apparent	97
	$\text{NO}_3^-$ (0.5-2X) Atrazine (1-5X)	Hours to weeks	Surface runoff recharge	98
92 Non-Agricultural or mixed sources	$\text{H}_2\text{S}$ (1-5X) $\text{SO}_4^{=}$ (1-1.2X) $\text{NH}_3$ (1-3X)	Minutes to hours	Pumping rate and well drilling	57
	$\text{NO}_3^-$ (1-13X) $\text{SO}_4^{=}$ (1-2X)	Minutes to hours	Pumping rate and purging	99
	Fe (1-3X) Mn (1-1.5X)	Minutes	Purging	100
	PCE, TCE, 1,2-t-DCE (1-10X)*	Minutes	Pumping rate and purging	101
	TCE (2-10X) $\text{Fe}^{2+}$ (1-110X) $\text{S}^{=}$ (1-15X)	Monthly to weekly	Pumping rate and development of cone of depression	102
	Volatile halocarbons (1-8X)	Minutes	Purging	6

\* PCE = perchloroethylene, TCE = trichloroethylene, 1,2-t-DCE = 1,2 trans-dichloroethylene

TABLE 20. OBSERVATIONS OF TEMPORAL VARIATIONS IN GROUND-WATER QUALITY: LONG-TERM VARIATIONS

	Constituents (concentration variation)	Nature of variability		Reference
		Period	Probable cause	
Agricultural Sources	Cl <sup>-</sup> (+1.5X)	Decades	Irrigation/recharge	103
	SO <sub>4</sub> <sup>=</sup> (2-4X)			
	NO <sub>3</sub> <sup>-</sup> (3-6X)	Seasonal	Irrigation/precipitation	104
	SO <sub>4</sub> <sup>=</sup> (3-7X)			
	NO <sub>3</sub> <sup>-</sup> ( $\pm 48$ mg·L <sup>-1</sup> /yr)	Seasonal	Leaching/recharge	105
	NO <sub>3</sub> <sup>-</sup> (1-12X)	Seasonal	Irrigation/fertilizer applications	97
	SO <sub>4</sub> <sup>=</sup> (1-1.5X)			
Non-Agricultural or Mixed Sources	NO <sub>3</sub> <sup>-</sup> (1-5X)	Seasonal	Recharge/fertilizer applications	106
	NO <sub>3</sub> <sup>-</sup> (1-1.5X)	Years-seasonal	Infiltration/recharge	98
	Pesticides (1-1.5X)			
	Conductance (2-3X)	Seasonal	H <sub>2</sub> O level fluctuations	107
	SO <sub>4</sub> <sup>=</sup> (1-3.5 X)		freezing/thawing	
	Hardness (2-6X)		recharge	
	Conductance (+2,000 $\mu$ S·cm <sup>-1</sup> )	Decades	Irrigation/upconing of saline water	108
	NO <sub>3</sub> <sup>-</sup> ( $\pm 55$ mg·L <sup>-1</sup> /yr)	Seasonal	Sewage/fertilizer recharge and applications	109
	Cl <sup>-</sup> (1-3X)	Seasonal	Oil field brine/recharge	110, 111
	PCE ( $\pm 1$ -20X)*	Seasonal	Infiltrated surface water quality variations	112
	TCE ( $\pm 1$ -3X)*	Seasonal	Pumping rate and patterns in well field	102

\* PCE = perchloroethylene, TCE = trichloroethylene

high-volume production wells due to pumping rate, initial pumping after periods of inactivity and cone of depression development (57,95,96,102,103).

In general, the major ionic chemical constituents determined in this study showed differences between their overall maximum and minimum values from the mean for each well on the order of one or two times the mean value (see Appendices A and B). One or two times the mean value places the variability noted in this study in the same range as the long-term, seasonal variability noted in Table 20. The magnitude of overall long-term variations observed in this study and the literature (Table 20) is often much lower than those noted for short-term variations due to pumping and local recharge effects. The magnitude of short-term concentration variations noted in the literature strongly suggests that the analysis of ambient resource, water quality datasets must be undertaken with careful attention to the pumping procedures used in purging and sample collection. This observation is particularly Critical in relatively sparse datasets where annual "mean" concentrations may be determined from programs with low sampling frequency (i.e., annually, biannually, etc.). Similar cautions in interpretations of long-term datasets apply in the analysis of trends at varying or unequal sampling frequencies due to the relatively short duration of the records in comparison to the length of apparent annual to multi-year variations.

It was expected that the high sampling frequency (i.e., biweekly) and consistent purging and sampling procedures employed in this study would permit the identification of optimal frequencies for monitoring water quality variations under stable hydrologic and contaminant source conditions. For this reason, field sampling and laboratory analytical protocols were carefully controlled.

### **Sampling Frequency**

The primary purpose of the project was to investigate the optimal sampling frequency for ground-water quality monitoring. Strictly speaking, there is no minimum sampling frequency. However, there is a relationship between the information content of the data and the sampling frequency. The term "information" is sometimes used loosely, but in a statistical context, it can be given a more precise definition, depending on the use of the data. The most common definition of information (e.g., in the Fisher sense) is in terms of the variance of the mean,  $\text{Var}(\bar{x}) = \sigma^2/n$ , where  $\bar{x}$  is the sample mean,  $n$  is the sample size, and  $\sigma^2$  is the variance of the data. The reciprocal of the variance of the mean is a measure of the information content of the data. If the  $\sigma^2$  is large, or the sample size small, the information content is low. While this definition of information applies to estimation of the mean, the power of trend detection (in space or time) is related to the variance of the mean as well.

As noted in the preceding discussion, the total variance is made up of the natural variance and the variance attributable to the sample collection process (field sampling and laboratory error). Most monitoring programs are intended to discriminate some effect (e.g., the long-term mean in the case of baseline sampling, or the difference in the mean between upgradient and

downgradient wells in the case of RCRA sampling) from the total variation in the time series. The effect of sample collection variance might be reduced by replicate sampling. Although, as shown in the previous section, the sample collection variance made up such a small fraction of the total variance that it probably would not be worthwhile for data similar to that described here. The effect of natural variation can only be quantified by increasing the number of samples (increased sampling frequency or length of sample collection). Increasing the number of samples also reduces the effect of the sampling variance. Seemingly, the information content of the data could be increased arbitrarily, since it depends linearly on the sample size. In practice, though, ground-water quality data are correlated in time (autocorrelated), and the autocorrelation increases with the sampling frequency. When the data are autocorrelated, the variance of the mean can be reexpressed as  $\text{Var}(\bar{x}) = \sigma^2/n_{\text{ef}}$ , where  $n_{\text{ef}}$  is an effective independent sample size, which depends on the autocorrelation. The value of  $n_{\text{ef}}$  is always less than  $n$ , the actual sample size, if the autocorrelation is positive, as it usually is in practice. If the model that describes the autocorrelation is the lag-one Markov process,  $n_{\text{ef}}$  approaches an upper limit as the sampling frequency increases, regardless of how large  $n$  becomes. The lag-one process has been found to provide a reasonable description of many water quality time series as detailed by Lettenmaier (113). It is often difficult to extend the analysis of water quality data beyond lag-one because the autocorrelation function becomes excessively noisy.

The ratio  $n_{\text{ef}}/n$  can be considered to be a measure of the loss of information due to autocorrelation in the data. Although  $n_{\text{ef}}$  always increases with  $n$  for positive autocorrelation,  $n_{\text{ef}}$  may increase quite slowly if the autocorrelation is high. For this reason, one of the analyses conducted was to estimate a model of the serial dependence (i.e., autocorrelation) in the observed chemical series. A description of the procedure used follows.

First, all missing values were removed to form a series of lower total sample number with no missing values. This procedure is straightforward, but it has the disadvantage that the interval between observations is not constant (i.e., is greater than two weeks) when there are missing observations. The effect of this approach, as compared to a much more laborious procedure that would concurrently estimate the missing data and the time series model, is to bias the autocorrelation estimates downward slightly (113). The practical effect is minimal so long as the number of missing observations is small, which was usually the case for the chemical constituents determined in this study.

Second, an outlier screening test was applied, as described in the preceding discussion on data quality. Finally, a lag one autoregressive (lag-one Markov) model was fit to the data. Diagnostic procedures described in Box and Jenkins (114) were applied to check the model fit. Specifically, Portmanteau's test and Anderson's test were applied to the estimated model residuals. The number of cases which failed the diagnostic tests was only slightly larger than would be expected by chance. In most of those cases that failed the diagnostic test, there was apparent strong seasonality in the data, as described below. In all cases, the estimated lag one

correlation was retained and averaged with the other estimates for the same chemical in the given well group.

Seasonality and long-term trends in the data presented a major complication in the analysis. There are well-structured methods for handling seasonality in time series, but none are applicable to the relatively short (i.e., in terms of total duration) chemical time series that were available for analysis. The problem is that, to properly estimate a seasonal model, a relatively large number of seasonal cycles (e.g., at least 10) are required; this corresponds to, say, ten years of data, which greatly exceeds the length of the sampling horizon. Ignoring the seasonality tends to inflate the estimate of the autocorrelation coefficient, as does the existence of trends in the data. There is no completely satisfactory solution to this problem. Our approach was to identify series with apparent strong seasonality or long-term trends subjectively (seasonality in some variables, such as temperature, is apparent, and can be argued from first principles). Table 21 identifies those series for which there was apparent strong seasonality, as well as the number of violations of the diagnostic checks for each variable and well group. The maximum possible number of violations for each variable was twice the number of wells in the group, since two tests were applied. Subsequent results for series showing a high number of rejections, or for which there was strong apparent seasonality or long-term trends, should be interpreted with caution. However, these problems were not an issue for a large number of series. By summarizing the results over well groups, and to a more limited extent, over chemical constituents, it is possible to give a general picture of the sampling frequency dependence of the effective independent sample size, which is relatively unaffected by the peculiarities of individual variables or sites.

Table 22 gives the average lag one correlation for each variable and well group, ordered by the sum of the ranks over all well groups. Variables at the top of the list tended to have the lowest autocorrelation, while variables at the bottom were most highly autocorrelated. Also given is the average autocorrelation over all three well groups. Autocorrelations tended to be stronger at the Beardstown wells than at Sand Ridge and were higher at the Beardstown upgradient wells than at the downgradient wells. The latter effect may be due to randomness introduced by the release, migration and transformation of the contaminants. Autocorrelations for almost all variables, even those with no apparent trends or seasonality, were quite high, suggesting that there was considerable redundancy in the data at a biweekly sampling frequency.

To illustrate the effect of the autocorrelation on sampling frequency, we solved for the sampling interval, in weeks, that would result in ratios  $n_{\text{eff}}/n = 0.5, 0.8, \text{ and } 0.9$  using equation 13 of Lettenmaier (113). Alternatively, these can be interpreted as relative losses of information due to autocorrelation in the data of 50, 20, and 10 percent. The results are given in Table 23. At Sand Ridge, the implied loss of information was about 50 percent for many variables at a weekly sampling frequency, 20 percent for many variables at sampling intervals in the range of 4-8 weeks, and 10 percent for the majority of variables at a sampling interval of 8 weeks or more. At the Beardstown wells, the loss of information at high sampling

**TABLE 21. SUBJECTIVE ESTIMATE OF STRENGTH OF SEASONALITY  
OR TREND IN VARIABLES BY LOCATION**

	Sand Ridge (1-4)	Beardstown (upgradient)	Beardstown (downgradient)	Number of violations
pH				0
Cond	*	+	+	2
Temp C	+	+	+	6
Temp W	+	+	+	4
Eh				1
Probe O <sub>2</sub>				0
Wink O <sub>2</sub>				0
Alkalinity	*	+	*	1
NH <sub>3</sub>				3
NO <sub>3</sub> <sup>-</sup> N				1
NO <sub>3</sub> <sup>-</sup> NO <sub>2</sub> <sup>-</sup> N				0
HS <sup>-</sup>			*	0
SO <sub>4</sub> <sup>=</sup>		*	*	0
SiO <sub>2</sub>		*		0
o - P O <sub>4</sub> <sup>=</sup>			*	1
T-PO <sub>4</sub>			*	1
Cl <sup>-</sup>		*	+	2
Fe <sup>2+</sup>			*	3
Ca	*	*	+	1
Mg	*	*		2
Na		*	*	3
K		*	*	3
Fe <sub>T</sub>				0
Mn <sub>T</sub>		*	+	0
TOX				2
VOC				6
NVOC			*	4
TOC			*	3

+ Indicates strongly seasonal

\* Indicates apparent trend or possible seasonality

TEMP C = Flow cell temperature, TEMP W = temperature reading in well

TOC = VOC + NVOC; Total Organic Carbon = Volatile Organic Carbon +  
Nonvolatile Organic Carbon

Cond = Conductance



**TABLE 22. RANKING OF AVERAGE LAG ONE CORRELATION OVER ALL SITES, FROM SMALLEST TO LARGEST**

	Sand Ridge (1-4)	Beardstown (5-6)	Beardstown (8-13)	Summed rank	Average (over all three well groups) (rho)
$\text{NO}_2^- \text{N}$	.27	.42	.37	17	.35
$\text{Fe}_2$	.01	.86	.56	18	.48
pH	.51	.47	.20	25	.39
$\text{S}^=$	.16	.36	.67	26	.40
$\text{NH}_3$	.29	.82	.26	28	.46
$\text{SiO}_2$	.37	.76	.24	28	.46
$\text{Mn}_T$	.51	.47	.20	28	.39
Probe $\text{O}_2$	.41	.66	.44	30	.51
$\text{T-PO}_4^=$	.06	.20	.86	32	.37
$\text{o-PO}_4^=$	.10	.19	.91	33	.40
Eh	.46	.60	.60	34	.55
$\text{NO}_3\text{NO}_2^- \text{N}$	.75	.35	.42	36	.51
TOC	.46	.60	.60	37	.55
$\text{SO}_4^=$	.59	.53	.52	39	.55
$\text{Fe}_T$	.21	.90	.66	40	.59
K	.31	.89	.71	46	.64
Ca	.45	.92	.66	50	.68
Mg	.49	.91	.65	50	.68
$\text{Cl}^-$	.19	.96	.75	54	.63
Na	.47	.95	.65	56	.69
Alkalinity	.73	.69	.76	62	.73
Ion balance	.73	.69	.76	62	.73
Temp C	.54	.92	.79	69	.75
VOC	.54	.92	.79	70	.75
Cond	.80	.94	.75	73	.83
TOX	.80	.94	.75	74	.83
Temp W	.66	.97	.78	76	.80
NVOC	.66	.97	.78	77	.80

**TABLE 23. SAMPLING INTERVALS (IN WEEKS) FOR GIVEN RATIO OF EFFECTIVE TO INDEPENDENT SAMPLE SIZE, BASED ON THE ESTIMATED LAG ONE MARKOV MODEL**

	0.5	$n_{ef}/n$ 0.8	0.9
<b><u>Sand Ridge</u></b>			
NO <sub>2</sub> <sup>-</sup> N	2	4	5
Fe <sup>2+</sup>	1	1	2
pH	4	7	9
S <sup>=</sup>	2	3	4
NH <sub>3</sub>	2	4	5
SiO <sub>2</sub>	3	5	6
Mn <sub>T</sub>	4	7	9
Probe-0 <sub>2</sub>	3	5	7
T-PO <sub>4</sub> <sup>=</sup>	1	2	3
O-PO <sub>4</sub> <sup>=</sup>	1	2	3
Eh	3	6	8
NO <sub>3</sub> NO <sub>2</sub> <sup>-</sup> N	8	16	21
SO <sub>4</sub> <sup>=</sup>	3	6	8
Fe <sub>T</sub>	5	9	12
K	2	3	4
Ca	2	4	5
Mg	3	6	8
Cl <sup>-</sup>	4	7	9
Na	2	3	4
Alkalinity	3	6	8
Ion	7	14	19
balance	7	14	19
Temp C	4	8	10
VOC	4	8	10
Cond	10	20	27
TOX	10	20	27
Temp W	6	11	15
NVOC	6	11	15
<b><u>Beardstown Upgradient</u></b>			
NO <sub>2</sub> <sup>-</sup> N	3	6	7
Fe <sup>2+</sup>	15	29	39
pH	3	6	8
S <sup>=</sup>	3	5	6
NH <sub>2</sub>	11	22	30
SiO <sub>2</sub>	8	16	22
Mn <sub>T</sub>	3	6	8
Probe 0 <sub>2</sub>	6	11	15
T-PO <sub>4</sub> <sup>=</sup>	2	3	4
o-PO <sub>4</sub> <sup>=</sup>	2	3	4

continued on next page

**TABLE 23. (continued)**

	0.5	$n_{ef}/n$ 0.8	0.9
Eh	5	9	12
$\text{NO}_3\text{NO}_2^- \text{N}$	3	5	6
TOC	5	9	12
$\text{SO}_4^-$	4	7	10
$\text{Fe}_T$	21	42	56
K	19	38	51
Ca	26	53	71
Mg	23	47	62
$\text{Cl}^-$	53	107	144
Na	42	85	114
Alkalinity	6	12	16
Ion balance	6	12	16
Temp C	26	53	71
VOC	26	53	71
Cond	35	71	95
TOX	35	71	95
Temp W	71	143	192
NVOC	71	143	192

**Beardstown Downgradient**

$\text{NO}_2^- \text{N}$	3	5	6
$\text{Fe}^{2+}$	4	8	11
pH	2	3	4
$\text{S}^-$	6	11	15
$\text{NH}_3$	2	4	5
$\text{SiO}_2$	2	4	5
$\text{Mn}_T$	2	3	4
Probe $\text{O}_2$	3	6	8
$\text{T-PO}_4^-$	15	29	39
$\text{o-PO}_4^-$	23	47	62
Eh	5	9	12
$\text{NO}_3\text{NO}_2^- \text{N}$	3	6	7
	5	9	12
$\text{SO}_4^-$	4	7	9
$\text{Fe}_T$	6	11	15
K	7	13	18
Ca	6	11	15
Mg	5	11	14
$\text{Cl}^-$	8	16	21
Na	5	11	14
Alkalinity	8	16	22

concluded on next page

**TABLE 23. (concluded)**

	0.5	$\frac{n_{ef}}{n}$ 0.8	0.9
Ion balance	8	16	22
Temp C	10	19	25
<b>VOC</b>	10	19	25
Cond	8	16	21
TOX	8	16	21
Temp W	9	18	24
NVOC	9	18	24

frequencies was much greater. At the upgradient wells, which had the highest autocorrelation, the inferred loss of information of 50 percent occurred for Several variables at a sampling interval of over 26 weeks. Information loss of between 20 and 10 percent was inferred for some variables at sampling intervals exceeding one year. This effect was particularly evident for  $\text{Na}^+$ ,  $\text{Cl}^-$  and well-head temperature (TEMPW) which showed an increasing trend over the study period.

The results of the study indicate that, for the major chemical constituents (i.e., water quality or contaminant indicator), quarterly sampling represents a good starting point for a preliminary network design. Some estimated ranges of sampling frequency to maintain information losses below ten percent are shown in Table 24. This frequency, of course, must be evaluated with respect to the purpose and time-frame over which the network will be conducted. Under the conditions of this study, sampling four to six times per year would provide an estimated information loss below 20% and minimize redundancy. The results for reactive, geochemical constituents suggest that bimonthly sampling frequency would be a good starting point if chemical reactivity and transformation are of concern.

It is clear that for common chemical constituents, a suggested sampling frequency of bimonthly or quarterly would represent a reasonably efficient monitoring design for evaluation of general water quality. The wide ranges of sampling frequencies shown in Table 24 for geochemical and trace-level reactive constituents are in some measure a reflection of random analytical and natural variability. This is particularly true for species like dissolved oxygen,  $\text{NH}_3$ ,  $\text{NO}_2^-$ , sulfide and ferrous iron under oxidizing or suboxic conditions where their concentrations were expected to be at or near detection limits. Determinations of these species can be diagnostic of oxidation-reduction intensity situations in ground water and have major implications for the design of remedial action activities predicated on microbial transformations or chemical reactions to encourage contaminant removal (67,115,116,117). Determinations of total organic halogen (TOX) are probably not relevant to uncontaminated situations because the variability represented in these values in this study was very nearly all analytical.

A subsampling experiment was performed to evaluate the usefulness of the estimated sampling frequencies for ambient average or unusual event detection (i.e., 90th percentile excursions) of selected types of chemical constituents (Table 24). The procedure has been fully described elsewhere (119). Reduced sampling frequency subsets were derived from the 39 run biweekly base dataset. In this experiment it was assumed that the base dataset represented the "true" existing ground-water quality conditions at the two sites. This assumption was made for the sake of practicality, and one should recognize that ambient ground-water quality is the result of stochastic processes. Conclusions drawn from this analysis are diagnostic and should be used only as preliminary design parameters.

The base dataset was broken down by F sequential sampling intervals (in weeks) and N subsets, as follows:

**TABLE 24. ESTIMATED RANGES OF SAMPLING FREQUENCY (IN MONTHS) TO  
MAINTAIN INFORMATION LOSS AT <10% FOR SELECTED TYPES OF  
CHEMICAL PARAMETERS**

Type of parameter	Pristine background conditions	Contaminated	
		Upgradient	Downgradient
<u>Water Quality</u>			
Trace constituents ( $<1.0 \text{ mg} \cdot \text{L}^{-1}$ )	2 to 7	1 to 2	2 to 10
Major constituents	2 to 7	2 to 38	2 to 10
<u>Geochemical</u>			
Trace constituents ( $<1.0 \text{ mg} \cdot \text{L}^{-1}$ )	1 to 2	2	1 to 5
Major constituents	1 to 2	7 to 14	1 to 5
<u>Contaminant Indicator</u>			
TOC	2	3	3
TOX	6 to 7	24	7
Conductivity	6 to 7	24	7
pH	2	2	1

<u>F</u>	<u>N</u>	<u>Description</u>
2	1	base dataset of 39 runs
4	2	1 subset of runs, 1 of 19 runs
6	3	subsets of 13 runs
8	4	3 subsets of runs, 1 of 9 runs
12	5	4 subsets of runs, 1 of 7 runs
24	3	subsets of 12 runs
78	1	subset of 39 runs

These consecutive sampling intervals corresponded to 2-week, 1-month, 1.5-month, 2-month, quarterly, semiannual and 1.5-year sampling frequency. The base dataset and the subsets were then each rank ordered. The mean, median and the 90th percentile statistics were calculated then for the base dataset as well as the subsets. At a given sampling frequency a measure of the "error" of the subset statistics relative to the "true" statistic from the base dataset was defined as the average percent deviation from the "true" value. The acceptable sampling frequency for a particular parameter was then selected as the lowest frequency for which the average percent deviation fell below an arbitrary cutoff of 10 percent. This type of approach (i.e., distribution-free, nonparametric method for percentile estimation) has been used in previous studies of water quality variability (118, 119, 120) when assumptions of normality and independence in the data are inappropriate.

Under the conditions of this study there were several apparent trends in the results of the subsampling experiment which are of note. The minimum sampling frequencies to estimate the means of selected types of chemical parameters within  $\pm 10$  percent are provided in Table 25. Similar to the results in Table 24, it is clear that a quarterly frequency represents a conservative estimate for an initial sampling interval for determining the major ionic constituents as well as pH, TOC and conductivity. These results, therefore, support the regulatory minimum sampling frequency for those parameters. Reactive and trace level constituents seem to require a somewhat more frequent sampling interval for adequate estimation of the "true" mean. Within the limits of this subsampling experiment, the minimum sampling frequencies to estimate the median (i.e., 50th percentile) base dataset values within  $\pm 10$  percent were not much different from that of the mean. The minimum sampling frequency necessary to estimate extreme values (i.e., 90th percentile) was usually more frequent than quarterly under the range of hydrogeochemical conditions of the study.

Caution must be exercised in interpretation of these results due to the effects of seasonality and long-term trends. However, it should be clear that there is considerable redundancy in the data at the two-week sampling interval, and that, at similar sites and for most of the variables studied, operational sampling programs would be inefficient at sampling intervals more frequent than bimonthly. The practical implication of this is that, for many operational monitoring programs, a relatively long time horizon (e.g., on the order of ten years) may be required to obtain adequate information for decision-making purposes, given that high frequency sampling will not yield much increase in information.

**TABLE 25. MINIMUM SAMPLING FREQUENCY (IN MONTHS) TO ESTIMATE THE MEAN OF THE BASE DATASET WITHIN 10 PERCENT**

Type of parameter	Pristine background conditions (Wells #1-4)	Contaminated conditions	
		Upgradient (Wells #5,6)	Downgradient (Wells #8-13)
<u>Water Quality</u>			
Trace constituents ( $<1.0 \text{ mg}\cdot\text{L}^{-1}$ )	<1	6	3
Major constituents	3	26	26
<u>Geochemical</u>			
Trace constituents ( $<1.0 \text{ mg}\cdot\text{L}^{-1}$ )	<1	<1	<1
Major constituents	<1	<1	3
<u>Contaminant Indicator</u>			
TOC	6	6	6
TOX	<1	1	<1
Conductivity	>6	6	>6
pH	>6	3	6



It is important to emphasize that the information from sampling depends on the effective independent sample size, not just the ratio  $n_{ef}/n$ . Therefore, if the autocorrelation is large so that a relatively low sampling frequency is necessary to avoid sampling redundancy, the total length of the sampling period must be increased to achieve sufficient information return. These results cannot simply be interpreted to mean, for instance, that quarterly sampling is adequate, unless that interpretation is couched in terms of the time horizon of the sampling program. This conclusion of the study has been supported recently by the work of Bell and DeLong (121) who reported the results of an eight-year long, monthly data evaluation for tetrachloroethylene in ground water. They noted that the tetrachloroethylene concentration data showed no evidence of seasonality, normality or serial correlation in the first three years of monthly sampling, but some definable trends appeared in the fourth through eighth years of sampling. Their work supports our general recommendation of quarterly sampling frequency as an initial design parameter in network design and underscores the need to collect long-term datasets in order to define temporal trends in chemical constituent concentrations.

## SECTION 6

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## **SECTION 7**

### **APPENDICES**

- A. Summary of Analytical Results for Sampling Wells. (Constituent concentrations are expressed in  $\text{mg}\cdot\text{L}^{-1}$  except as noted.)
- 5. Time series of individual constituent concentrations for biweekly sampling runs for each well at the Sand Ridge Site (Wells #1, #2, #3 and #4) and the Beardstown site (Wells #8, #9, #10, #11, #12, and #13).
- C. Ground Water Elevations Measured During Each Biweekly Sampling Run at the Sand Ridge and Beardstown Sites. (Elevations at the Sand Ridge Site are in feet relative to an arbitrary 1000 foot reference point. Elevations at Beardstown are in feet relative to mean sea level.)

# APPENDIX A

## SUMMARY OF ANALYTICAL RESULTS FOR SAMPLING WELLS (CONSTITUENT CONCENTRATIONS ARE EXPRESSED IN mg•L<sup>-1</sup> EXCEPT AS NOTED.)

**TABLE A-1. SUMMARY OF ANALYTICAL RESULTS FOR WELL 1**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	41	359.27	10.569	381.00	340.00	358.00	8
pH (pH units)	44	7.75	0.532	9.70	6.80	7.62	5
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	44	3.65	5.011	26.70	0.00	2.40	5
TOC	44	0.85	0.260	1.77	0.00	0.83	5
Temperature (°C)	37	1.98	0.924	14.60	10.50	12.00	12
Alkalinity	44	216.26	11.582	245.80	184.10	218.95	5
Chloride	44	2.19	0.707	5.74	1.36	2.09	5
(NO <sub>3</sub> + NO <sub>2</sub> )-N	44	0.95	0.200	1.25	0.62	1.02	5
Sulfate	44	36.18	5.761	49.90	20.60	36.95	5
Ortho-PO <sub>4</sub>	44	0.02	0.015	0.08	-0.01	0.02	5
Total PO <sub>4</sub>	44	0.04	0.048	0.31	-0.00	0.02	5
Silica	43	15.54	0.315	16.15	14.85	15.60	6
Calcium	44	65.85	3.344	78.40	60.55	65.33	5
Magnesium	44	22.58	1.226	26.20	21.07	22.15	5
Sodium	43	3.17	0.265	3.72	1.80	3.16	6
Potassium	42	0.70	0.037	0.77	0.61	0.71	7
Eh (volts)	44	0.47	0.090	0.68	0.30	0.49	5
Electrode DO	38	9.00	0.503	9.93	7.85	8.93	11
Winkler DO	42	8.83	0.875	11.90	7.17	8.9	7
Iron	43	0.01	0.037	0.12	-0.05	0.01	6
Iron(II)	22	0.01	0.031	0.12	-0.03	0.01	27
Manganese	44	0.00	0.009	0.03	-0.01	0.00	5
Ammonia	44	-0.01	0.014	0.02	-0.06	-0.01	5
Sulfide	44	0.00	0.005	0.01	-0.01	0.00	5
Nitrite-N	43	0.00	0.002	0.01	-0.00	0.00	6
Methane	39	-0.12	0.788	0.16	-4.91	0.00	10
VOC	44	0.20	0.566	3.66	0.01	0.07	5
NVOC	44	0.74	0.183	1.16	0.18	0.75	5
Ion Balance (%)	44	0.93	2.280	6.62	-2.50	0.99	5

**TABLE A-2. SUMMARY OF ANALYTICAL RESULTS FOR WELL 2**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	40	280.40	19.002	300.00	245.00	288.00	9
pH (pH units)	43	7.95	0.351	8.95	7.42	7.90	6
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	41	3.17	3.689	19.80	0.00	2.30	8
TOC	43	0.53	0.202	1.37	0.08	0.51	6
Temperature ( $^{\circ}\text{C}$ )	36	11.75	0.189	12.00	11.10	11.80	13
Alkalinity	43	175.15	13.894	195.20	151.30	179.10	6
Chloride	43	1.54	0.712	4.47	0.91	1.36	6
( $\text{NO}_3 + \text{NO}_2$ )-N	43	0.74	0.067	0.87	0.62	0.74	6
Sulfate	43	24.08	4.013	31.75	16.20	25.50	6
Ortho- $\text{PO}_4$	43	0.03	0.015	0.09	0.00	0.03	6
Total $\text{PO}_4$	42	0.06	0.061	0.38	0.02	0.04	7
Silica	42	15.37	0.421	16.05	14.50	15.45	7
Calcium	43	49.38	4.258	55.76	39.80	50.53	6
Magnesium	43	18.03	1.491	20.75	15.20	18.35	6
Sodium	42	2.43	0.225	3.01	1.98	2.48	7
Potassium	41	0.61	0.038	0.67	0.53	0.61	8
Eh (volts)	43	0.46	0.083	0.66	0.30	0.48	6
Electrode DO	38	7.61	1.421	14.20	5.88	7.55	11
Winkler DO	41	7.36	1.576	13.80	5.35	7.63	8
Iron	40	0.02	0.040	0.18	-0.04	0.01	9
Iron(II)	20	0.00	0.020	0.05	-0.02	0.00	29
Manganese	43	0.00	0.009	0.03	-0.01	0.00	6
Ammonia	43	-0.01	0.016	0.01	-0.06	-0.01	6
Sulfide	43	-0.00	0.008	0.01	-0.04	0.00	6
Nitrite-N	42	0.00	0.002	0.01	-0.00	0.00	7
Methane	38	-0.06	0.376	0.09	-2.31	0.00	11
VOC	43	0.19	0.54	3.46	0.01	0.06	6
NVOC	43	0.42	0.119	0.59	0.00	0.45	6
Ion Balance (%)	43	-0.41	2.251	6.13	-6.83	-0.29	6

**TABLE A-3. SUMMARY OF ANALYTICAL RESULTS FOR WELL 3**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	46	276.22	15.463	299.00	205.00	279.00	3
pH (pH units)	49	8.01	0.269	8.82	7.48	7.98	0
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	2.77	3.496	18.55	0.00	1.85	6
TOC	46	0.47	0.192	1.17	0.00	0.44	3
Temperature ( $^{\circ}\text{C}$ )	42	11.79	0.370	12.80	11.00	11.90	7
Alkalinity	49	166.86	8.986	196.40	147.00	166.60	0
Chloride	46	1.68	0.655	3.79	0.88	1.46	3
( $\text{NO}_3 + \text{NO}_2$ )-N	48	0.32	0.067	0.41	0.11	0.34	1
Sulfate	46	28.20	3.159	35.45	19.10	29.41	3
Ortho- $\text{PO}_4$	49	0.07	0.015	0.12	0.03	0.07	0
Total $\text{PO}_4$	49	0.08	0.053	0.42	0.04	0.07	0
Silica	44	14.64	0.372	15.20	13.80	14.72	5
Calcium	46	47.65	2.437	53.50	43.20	47.36	3
Magnesium	46	17.87	0.922	21.00	15.80	17.83	3
Sodium	44	2.75	0.234	3.45	2.20	2.79	5
Potassium	43	0.60	0.030	0.69	0.50	0.61	6
Eh (volts)	49	0.45	0.085	0.64	0.26	0.45	0
Electrode DO	42	2.98	0.630	4.07	1.73	3.12	7
Winkler DO	46	3.05	0.702	4.05	1.21	3.27	3
Iron	47	0.02	0.042	0.20	-0.04	0.01	2
Iron(II)	48	0.06	0.287	1.99	-0.03	0.01	1
Manganese	49	0.00	0.009	0.03	-0.01	0.00	0
Ammonia	49	-0.01	0.016	0.01	-0.06	-0.01	0
Sulfide	46	0.00	0.006	0.02	-0.01	0.00	3
Nitrite-N	43	0.00	0.002	0.01	-0.00	0.00	6
Methane	39	-0.01	0.056	0.15	-0.30	0.00	0
VOC	46	0.17	0.496	3.26	0.01	0.05	3
NVOC	46	0.37	0.117	0.59	0.00	0.39	3
Ion Balance (%)	46	-0.35	2.078	5.98	-3.77	-0.95	3

**TABLE A-4. SUMMARY OF ANALYTICAL RESULTS FOR WELL 4**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	45	225.44	11.587	248.00	207.00	220.00	4
pH (pH units)	48	7.81	0.364	8.80	6.93	7.83	1
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	41	3.07	3.948	22.38	0.00	2.10	8
TOC	45	0.62	0.398	2.89	0.00	0.58	4
Temperature ( $^{\circ}\text{C}$ )	39	12.13	0.336	12.50	11.10	12.30	10
Alkalinity	48	132.32	5.379	146.70	121.10	132.40	1
Chloride	45	1.66	0.715	4.94	0.75	1.48	4
( $\text{NO}_3 + \text{NO}_2$ )-N	48	-0.02	0.026	0.04	-0.07	-0.01	1
Sulfate	45	22.34	4.652	31.85	15.10	20.80	4
Ortho- $\text{PO}_4$	48	0.11	0.023	0.20	0.06	0.11	1
Total $\text{PO}_4$	48	0.13	0.048	0.40	0.09	0.12	1
Silica	43	15.78	0.334	16.45	15.05	15.80	6
Calcium	45	38.42	2.373	45.50	34.70	38.00	4
Magnesium	45	12.27	0.613	14.20	11.43	12.10	4
Sodium	43	3.62	0.317	4.32	3.00	3.60	6
Potassium	42	0.72	0.045	0.83	0.59	0.72	7
Eh (volts)	48	0.13	0.071	0.34	0.08	0.10	1
Electrode DO	41	0.62	0.264	1.81	0.05	0.55	8
Winkler DO	1	0.42	--	0.42	0.42	0.42	48
Iron	47	0.44	0.096	0.53	0.05	0.46	2
Iron(II)	46	0.50	0.076	0.73	0.33	0.50	3
Manganese	48	0.15	0.026	0.18	-0.00	0.16	1
Ammonia	48	0.06	0.039	0.20	-0.05	0.06	1
Sulfide	45	0.00	0.004	0.01	-0.01	0.00	4
Nitrite-N	42	0.00	0.001	0.00	-0.00	0.00	7
Methane	38	0.01	0.084	0.36	-0.31	0.00	11
VOC	45	0.13	0.323	2.03	0.01	0.05	4
NVOC	45	0.56	0.394	2.86	0.00	0.52	4
Ion Balance (%)	45	-0.70	2.613	5.85	-5.18	-0.96	4



TABLE A-5. SUMMARY OF ANALYTICAL RESULTS FOR WELL 5

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	41	374.95	96.759	578.00	252.00	400.00	8
pH (pH units)	44	6.48	0.352	7.45	5.42	6.45	5
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	6.26	4.593	22.90	0.10	4.60	6
TOC	44	3.08	0.745	5.75	0.52	3.06	5
Temperature ( $^{\circ}\text{C}$ )	37	12.49	2.690	17.20	8.70	11.60	12
Alkalinity	44	65.45	5.662	78.50	51.60	66.20	5
Chloride	44	66.60	38.943	140.20	19.37	68.81	5
( $\text{NO}_3 + \text{NO}_2$ )-N	44	-0.02	0.023	0.01	-0.07	-0.01	5
Sulfate	44	76.76	13.132	127.00	49.20	77.87	5
Ortho- $\text{PO}_4$	44	0.06	0.029	0.16	0.02	0.05	5
Total $\text{PO}_4$	44	0.10	0.047	0.35	0.05	0.09	5
Silica	43	13.31	1.090	15.60	11.80	13.20	6
Calcium	44	38.50	8.592	56.65	27.20	35.21	5
Magnesium	44	14.72	3.134	20.35	10.80	13.50	5
Sodium	43	33.99	11.986	54.40	16.40	30.60	6
Potassium	42	2.88	0.826	4.04	1.38	2.79	7
Eh (volts)	44	0.23	0.033	0.32	0.10	0.22	5
Electrode DO	38	0.36	0.134	0.95	0.08	0.34	11
Winkler DO	0	--	--	--	--	--	49
Iron	43	1.02	0.226	2.00	0.72	1.01	6
Iron(II)	43	1.04	0.176	1.42	0.70	1.02	6
Manganese	44	0.09	0.017	0.14	0.07	0.09	5
Ammonia	44	0.26	0.151	0.62	-0.05	0.28	5
Sulfide	44	0.04	0.011	0.06	0.01	0.03	5
Nitrite-N	43	0.00	0.002	0.01	-0.00	0.00	6
Methane	39	-0.00	0.036	0.11	-0.15	0.00	10
VOC	44	0.13	0.347	2.19	0.01	0.04	5
NVOC	44	3.03	0.740	5.53	0.51	3.02	5
Ion Balance (%)	43	-0.47	3.199	8.17	-8.08	-1.04	6

**TABLE A-6. SUMMARY OF ANALYTICAL RESULTS FOR WELL 6**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	43	647.88	114.828	850.00	475.00	661.00	6
pH (pH units)	46	6.19	0.389	7.26	5.02	6.15	3
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	9.19	4.925	22.25	1.20	8.50	6
TOC	46	2.32	0.487	3.37	0.34	2.35	3
Temperature ( $^{\circ}\text{C}$ )	38	12.57	1.898	15.80	10.00	11.90	11
Alkalinity	46	73.83	11.491	100.00	56.40	71.45	3
Chloride	46	149.50	40.893	231.80	91.80	154.60	3
( $\text{NO}_3 + \text{NO}_2$ )-N	46	-0.02	0.024	0.01	-0.07	-0.01	3
Sulfate	46	109.36	24.647	161.95	59.20	104.45	3
Ortho- $\text{PO}_4$	46	0.07	0.020	0.16	0.04	0.07	3
Total $\text{PO}_4$	46	0.16	0.074	0.59	0.08	0.14	3
Silica	45	15.11	0.708	16.60	13.25	15.20	4
Calcium	46	60.84	12.017	92.80	41.45	57.85	3
Magnesium	46	21.44	4.005	30.30	14.23	21.25	3
Sodium	44	66.98	30.788	111.50	22.50	74.50	5
Potassium	43	1.94	0.671	4.47	0.77	2.14	6
Eh (volts)	46	0.23	0.024	0.29	0.14	0.24	3
Electrode DO	39	0.36	0.145	0.94	0.09	0.36	10
Winkler DO	0	--	--	--	--	--	49
Iron	45	3.39	0.748	5.13	1.15	3.27	4
Iron(II)	46	3.47	0.913	5.20	0.00	3.35	3
Manganese	46	0.31	0.108	0.50	0.10	0.29	3
Ammonia	46	0.40	0.190	0.80	-0.05	0.47	3
Sulfide	46	0.06	0.009	0.08	0.04	0.06	3
Nitrite-N	43	0.01	0.005	0.01	-0.01	0.01	6
Methane	39	-0.09	0.660	0.21	-4.10	0.01	10
VOC	46	0.16	0.390	2.43	0.01	0.06	3
NVOC	46	2.23	0.485	3.21	0.00	2.25	3
Ion Balance (%)	45	-1.18	6.327	4.13	-40.58	-0.72	4

**TABLE A-7. SUMMARY OF ANALYTICAL RESULTS FOR WELL 8**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	42	1605.21	171.503	2000.00	1300.00	1600.00	7
pH (pH units)	45	6.88	0.208	7.53	6.54	6.85	4
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	10.90	7.645	49.30	0.85	9.60	6
TOC	44	6.78	1.156	11.85	4.65	6.63	5
Temperature ( $^{\circ}\text{C}$ )	37	15.61	1.612	18.30	11.20	15.20	12
Alkalinity	45	692.44	80.972	926.80	534.50	694.20	4
Chloride	45	141.35	9.997	163.60	125.32	142.67	4
( $\text{NO}_3 + \text{NO}_2$ )-N	45	1.85	2.062	8.76	0.00	1.26	4
Sulfate	36	35.48	5.534	46.60	20.97	36.78	13
Ortho- $\text{PO}_4$	45	14.84	7.760	40.63	6.93	11.80	4
Total $\text{PO}_4$	45	14.91	7.608	40.72	7.80	12.20	4
Silica	44	18.99	4.913	27.35	6.90	20.48	5
Calcium	45	44.13	7.060	75.75	34.05	43.50	4
Magnesium	45	17.49	2.155	25.20	14.20	16.90	4
Sodium	44	117.49	14.442	138.00	87.25	119.50	5
Potassium	43	22.80	2.442	27.10	18.05	23.20	6
Eh (volts)	45	0.10	0.027	0.14	0.03	0.10	4
Electrode DO	36	0.36	0.178	0.70	-0.51	0.34	13
Winkler DO	0	--	--	--	--	--	49
Iron	43	2.23	0.861	4.69	0.71	1.97	6
Iron(II)	45	2.27	0.912	4.99	0.92	1.94	4
Manganese	45	0.63	0.105	0.90	0.48	0.63	4
Ammonia	45	173.60	49.179	333.50	120.00	166.00	4
Sulfide	45	0.14	0.072	0.33	0.05	0.12	4
N i t r i t e - N	42	0.01	0.003	0.02	0.00	0.01	7
Methane	39	1.33	0.709	3.34	0.02	1.28	10
VOC	44	0.39	0.796	4.21	0.03	0.14	5
NVOC	44	6.42	0.900	9.14	4.52	6.44	5
Ion Balance (%)	45	1.53	6.086	21.14	-19.88	1.29	4

**TABLE A-8. SUMMARY OF ANALYTICAL RESULTS FOR WELL 9**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	40	1706.37	167.305	2125.00	1400.00	1700.00	9
pH (pH units)	43	6.86	0.223	7.45	6.48	6.87	6
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	11.09	6.191	39.80	1.05	10.50	6
TOC	43	8.12	1.132	11.22	5.71	7.90	6
Temperature ( $^{\circ}\text{C}$ )	35	15.83	1.353	17.70	10.50	15.50	14
Alkalinity	43	786.64	84.607	1006.90	616.20	782.70	6
Chloride	43	146.01	10.223	170.50	128.50	143.70	6
( $\text{NO}_3 + \text{NO}_2$ )-N	42	-0.01	0.035	0.14	-0.07	0.00	7
Sulfate	34	22.14	5.404	36.34	11.20	20.90	15
Ortho- $\text{PO}_4$	43	27.14	6.531	43.17	15.25	28.40	6
Total $\text{PO}_4$	43	27.03	6.163	39.85	16.00	27.50	6
Silica	41	21.47	1.303	23.30	17.30	21.80	8
Calcium	43	46.59	7.506	62.20	27.90	46.40	6
Magnesium	42	18.91	2.943	24.75	13.60	18.27	7
Sodium	43	126.48	15.516	164.00	96.25	126.00	6
Potassium	42	22.69	2.204	29.00	18.93	22.55	7
Eh (volts)	43	0.06	0.037	0.13	-0.02	0.07	6
Electrode DO	35	0.31	0.196	0.68	-0.65	0.30	14
Winkler DO	0	--	--	--	--	--	49
Iron	41	2.22	0.380	2.92	1.41	2.31	8
Iron(II)	43	2.40	0.478	3.66	1.53	2.40	6
Manganese	43	0.89	0.142	1.12	0.66	0.86	6
Ammonia	43	185.09	50.105	336.00	121.88	176.00	6
Sulfide	43	0.75	0.170	1.16	0.44	0.71	6
Nitrite-N	42	0.01	0.003	0.01	0.00	0.01	7
Methane	39	3.82	1.957	9.51	1.29	3.52	10
VOC	43	0.32	0.570	3.54	0.05	0.17	6
NVOC	43	7.81	0.953	9.94	5.58	7.69	6
Ion Balance (%)	42	0.74	4.937	16.67	-8.03	0.95	7

**TABLE A-9. SUMMARY OF ANALYTICAL RESULTS FOR WELL 10**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	40	1925.87	127.198	2200.00	1650.00	1972.50	9
pH (pH units)	43	6.85	0.171	7.26	6.50	6.85	6
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	13.07	6.917	36.50	5.30	11.20	6
TOC	42	9.19	0.980	12.30	7.92	9.00	7
Temperature ( $^{\circ}\text{C}$ )	35	15.76	0.960	16.80	11.30	15.90	14
Alkalinity	43	930.17	69.568	1103.00	785.00	941.60	6
Chloride	43	161.56	9.072	179.80	137.20	163.99	6
( $\text{NO}_3 + \text{NO}_2$ )-N	43	-0.00	0.055	0.26	-0.07	-0.01	6
Sulfate	34	15.53	9.560	50.07	6.02	12.90	15
Ortho- $\text{PO}_4$	43	37.52	5.788	51.55	28.30	37.80	6
Total $\text{PO}_4$	43	37.44	5.939	49.80	27.10	36.90	6
Silica	41	21.82	1.731	24.60	14.70	22.25	8
Calcium	43	55.72	5.864	68.10	41.60	55.30	6
Magnesium	43	21.19	2.021	26.00	17.22	21.10	6
Sodium	43	143.87	14.041	172.00	118.00	146.50	6
Potassium	42	26.67	2.047	30.80	22.60	26.98	7
Eh (volts)	43	0.05	0.040	0.11	-0.03	0.05	6
Electrode DO	35	0.27	0.192	0.46	-0.78	0.29	14
Winkler DO	0	--	--	--	--	--	49
Iron	41	1.66	0.266	2.52	1.33	1.59	8
Iron(II)	43	1.80	0.350	3.05	1.33	1.66	6
Manganese	43	0.56	0.119	0.94	0.33	0.55	6
Ammonia	43	213.29	46.908	386.00	151.00	206.20	6
Sulfide'	43	1.08	0.163	1.44	0.64	1.09	6
Nitrite-N	42	0.01	0.016	0.10	-0.01	0.01	7
Methane	39	4.62	3.492	18.10	0.65	3.50	10
VOC	42	0.40	0.737	4.22	0.05	0.17	7
NVOC	42	8.65	1.516	10.59	0.57	8.71	7
Ion Balance (%)	43	0.07	4.954	18.79	-9.02	-0.28	6

**TABLE A-10. SUMMARY OF ANALYTICAL RESULTS FOR WELL 11**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	40	1614.87	169.280	2140.00	1400.00	1582.50	9
pH (pH units)	43	6.84	0.196	7.33	6.47	6.84	6
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	11.34	6.080	31.00	1.20	11.15	6
TOC	43	7.21	1.292	11.49	5.42	6.96	6
Temperature ( $^{\circ}\text{C}$ )	35	15.80	1.236	17.70	12.00	15.40	14
Alkalinity	43	741.19	86.080	970.90	645.00	715.80	6
Chloride	43	138.62	16.702	179.90	119.50	134.20	6
( $\text{NO}_3 + \text{NO}_2$ )-N	42	0.39	0.273	1.03	-0.00	0.31	7
Sulfate	34	28.29	6.630	40.42	15.54	28.42	15
Ortho- $\text{PO}_4$	43	19.20	7.213	33.83	7.08	18.40	6
Total $\text{PO}_4$	43	19.32	7.263	32.96	6.64	18.20	6
Silica	41	19.85	2.285	22.30	10.65	20.65	8
Calcium	43	53.09	11.672	80.90	30.80	54.10	6
Magnesium	43	21.91	5.109	36.50	14.00	21.80	6
Sodium	43	119.25	13.378	152.00	96.50	118.00	6
Potassium	42	21.27	2.569	27.30	18.00	20.25	7
Eh (volts)	43	0.05	0.034	0.12	-0.01	0.06	6
Electrode DO	35	0.27	0.185	0.48	-0.72	0.29	14
Winkler DO	0	--	--	--	--	--	49
Iron	41	3.64	0.547	4.97	2.65	3.60	8
Iron(II)	41	3.79	0.478	4.73	2.99	3.80	8
Manganese	43	1.06	0.191	1.54	0.81	1.00	6
Ammonia	43	160.02	47.652	340.50	95.90	150.88	6
Sulfide	43	0.47	0.121	0.68	0.17	0.49	6
Nitrite-N	42	0.01	0.008	0.05	0.00	0.01	7
Methane	39	2.54	1.765	7.13	0.03	2.50	10
VOC	43	0.34	0.573	3.13	0.04	0.16	6
NVOC	43	6.92	1.130	10.17	5.23	6.73	6
Ion Balance (%)	43	0.40	4.746	12.47	-11.18	0.34	6

**TABLE A-11. SUMMARY OF ANALYTICAL RESULTS FOR WELL 12**

Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	39	1836.03	129.940	2100.00	1600.00	1820.00	10
pH (pH units)	42	6.87	0.169	7.30	6.56	6.87	7
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	42	12.77	5.677	28.40	4.10	12.20	7
TOC	42	8.57	1.749	11.80	0.00	8.83	7
Temperature ( $^{\circ}\text{C}$ )	34	15.91	1.160	17.50	12.70	15.55	15
Alkalinity	42	866.05	71.367	1032.90	726.10	860.70	7
Chloride	42	155.76	8.965	173.13	138.40	156.90	7
( $\text{NO}_3 + \text{NO}_2$ )-N	41	0.27	0.233	0.94	0.00	0.20	8
Sulfate	32	19.07	7.101	51.14	8.45	18.68	17
Ortho- $\text{PO}_4$	41	34.18	6.960	54.71	20.60	33.73	8
Total $\text{PO}_4$	42	33.81	7.142	51.35	19.15	33.60	7
Silica	40	22.07	1.422	23.60	16.10	22.55	9
Calcium	42	47.31	6.061	60.30	37.21	46.20	7
Magnesium	42	18.99	2.816	25.60	14.15	18.49	7
Sodium	42	132.53	12.063	163.50	111.50	131.50	7
Potassium	41	24.84	2.221	30.60	21.58	24.35	8
Eh (volts)	42	0.04	0.041	0.11	-0.04	0.05	7
Electrode DO	34	0.26	0.213	0.51	-0.86	0.29	15
Winkler DO	0	--	--	--	--	--	49
Iron	40	1.08	0.183	1.50	0.82	1.06	9
Iron(II)	40	1.24	0.480	3.78	0.83	1.10	9
Manganese	42	0.80	0.100	1.05	0.64	0.77	7
Ammonia	42	210.60	47.789	373.50	131.50	202.62	7
Sulfide	42	1.21	0.281	1.76	0.40	1.23	7
Nitrite-N	42	0.01	0.014	0.09	0.00	0.01	7
Methane	39	4.22	2.276	12.10	0.51	3.55	10
VOC	42	0.36	0.691	4.27	0.05	0.16	7
NVOC	42	8.25	1.628	11.62	0.23	8.39	7
Ion Balance (%)	42	0.30	5.218	19.67	-9.50	-0.56	7

**TABLE A-12. SUMMARY OF ANALYTICAL RESULTS FOR WELL 13**

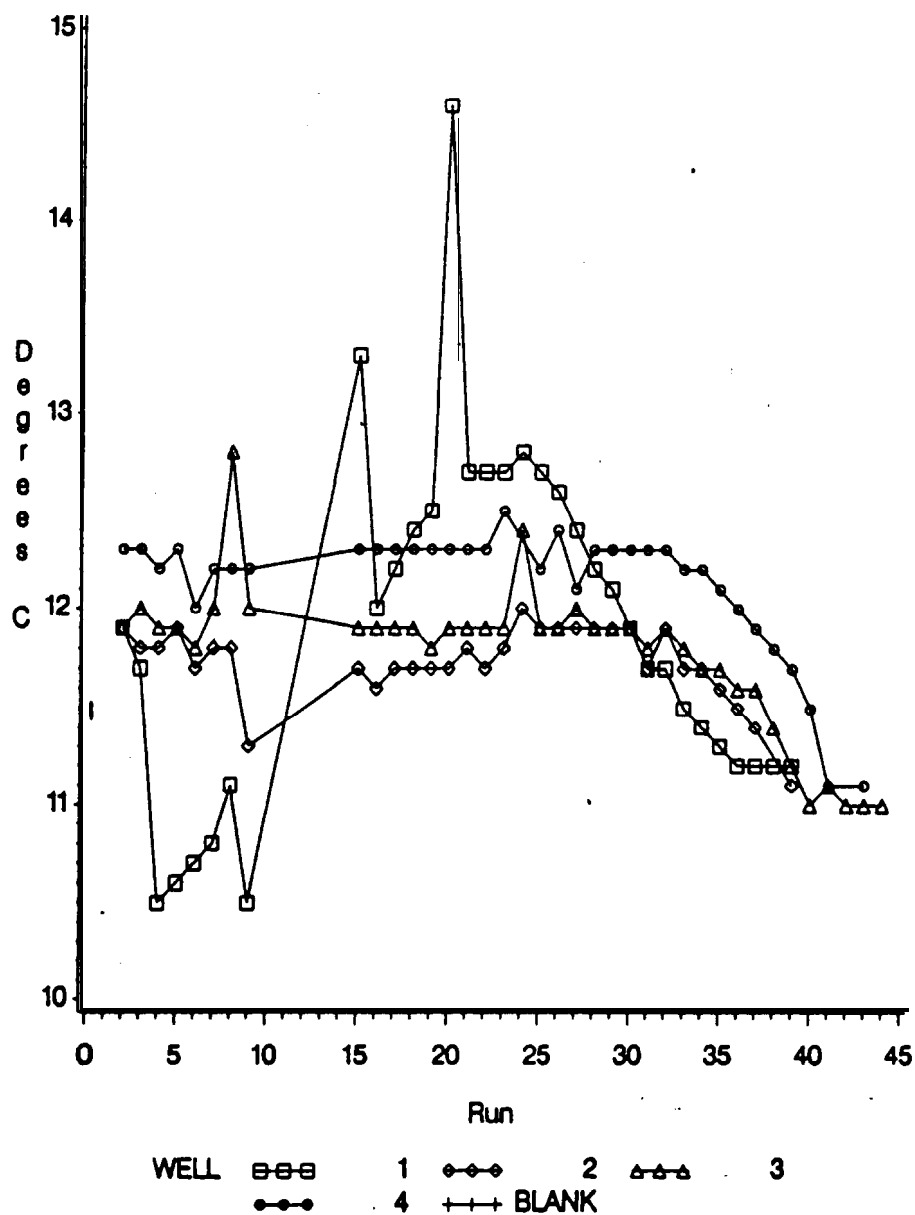
Parameter	Number	Mean	Std dev	Maximum	Minimum	Median	Missing
Conductivity ( $\mu\text{S}\cdot\text{cm}^{-1}$ )	40	1546.90	140.846	2050.00	1350.00	1510.00	9
pH (pH units)	43	6.81	0.159	7.15	6.35	6.81	6
TOX ( $\mu\text{g}\cdot\text{L}^{-1}$ )	43	10.54	7.059	33.00	0.00	8.95	6
TOC	43	6.87	0.904	10.19	5.77	6.68	6
Temperature ( $^{\circ}\text{C}$ )	34	16.61	1.121	18.00	10.90	16.80	15
Alkalinity	43	690.37	75.376	881.30	555.10	680.40	6
Chloride	43	133.49	12.141	161.65	116.72	130.90	6
( $\text{NO}_3 + \text{NO}_2$ )-N	43	0.03	0.070	0.234	-0.07	0.00	6
Sulfate	34	30.47	9.767	46.91	9.37	30.86	15
Ortho- $\text{PO}_4$	43	17.75	5.500	36.10	11.00	17.50	6
Total $\text{PO}_4$	43	17.90	5.472	34.88	10.50	16.70	6
Silica	42	19.63	1.172	22.40	17.00	19.95	7
Calcium	43	61.80	12.778	101.50	41.90	59.90	6
Magnesium	43	25.22	5.557	43.00	18.70	24.20	6
Sodium	43	114.34	10.788	141.00	94.20	114.00	6
Potassium	42	19.18	2.486	26.10	15.50	18.80	7
Eh (volts)	43	0.06	0.032	0.11	-0.01	0.07	6
Electrode DO	35	0.43	0.259	1.34	-0.53	0.41	14
Winkler DO	0	--	--	--	--	--	49
Iron	41	4.09	0.778	6.68	2.88	3.91	8
Iron(II)	41	4.16	0.801	6.96	2.27	4.06	8
Manganese	43	0.57	0.119	1.00	0.44	0.54	6
Ammonia	43	134.86	42.313	272.00	83.80	124.00	6
Sulfide	43	0.43	0.116	0.64	0.04	0.44	6
Nitrite-N	41	0.01	0.006	0.02	-0.00	0.01	8
Methane	39	1.31	0.947	3.83	0.04	1.06	10
VOC	43	0.29	0.486	2.98	0.04	0.14	6
NVOC	43	6.63	0.930	10.38	4.92	6.50	6
Ion Balance (%)	43	0.86	4.855	12.27	-11.58	1.36	6



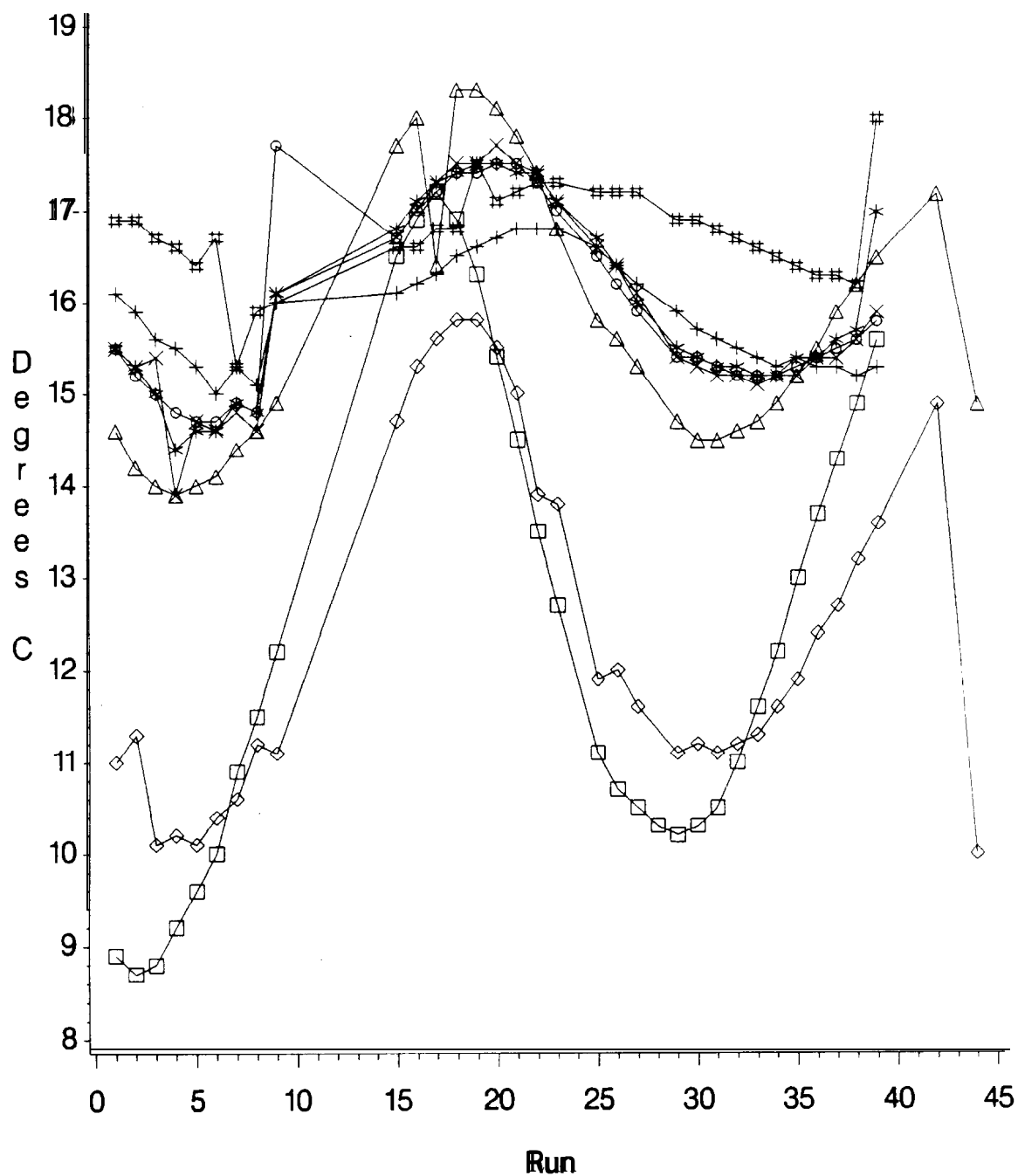
## APPENDIX B

TIME SERIES OF INDIVIDUAL CONSTITUENT CONCENTRATIONS  
FOR BIWEEKLY SAMPLING RUNS FOR EACH WELL AT THE  
SAND RIDGE SITE (WELLS #1, #2, #3 AND #4)  
AND THE BEARDSTOWN SITE (WELLS #8, #9, #10, #11, #12, AND #13)

### Well Temperature

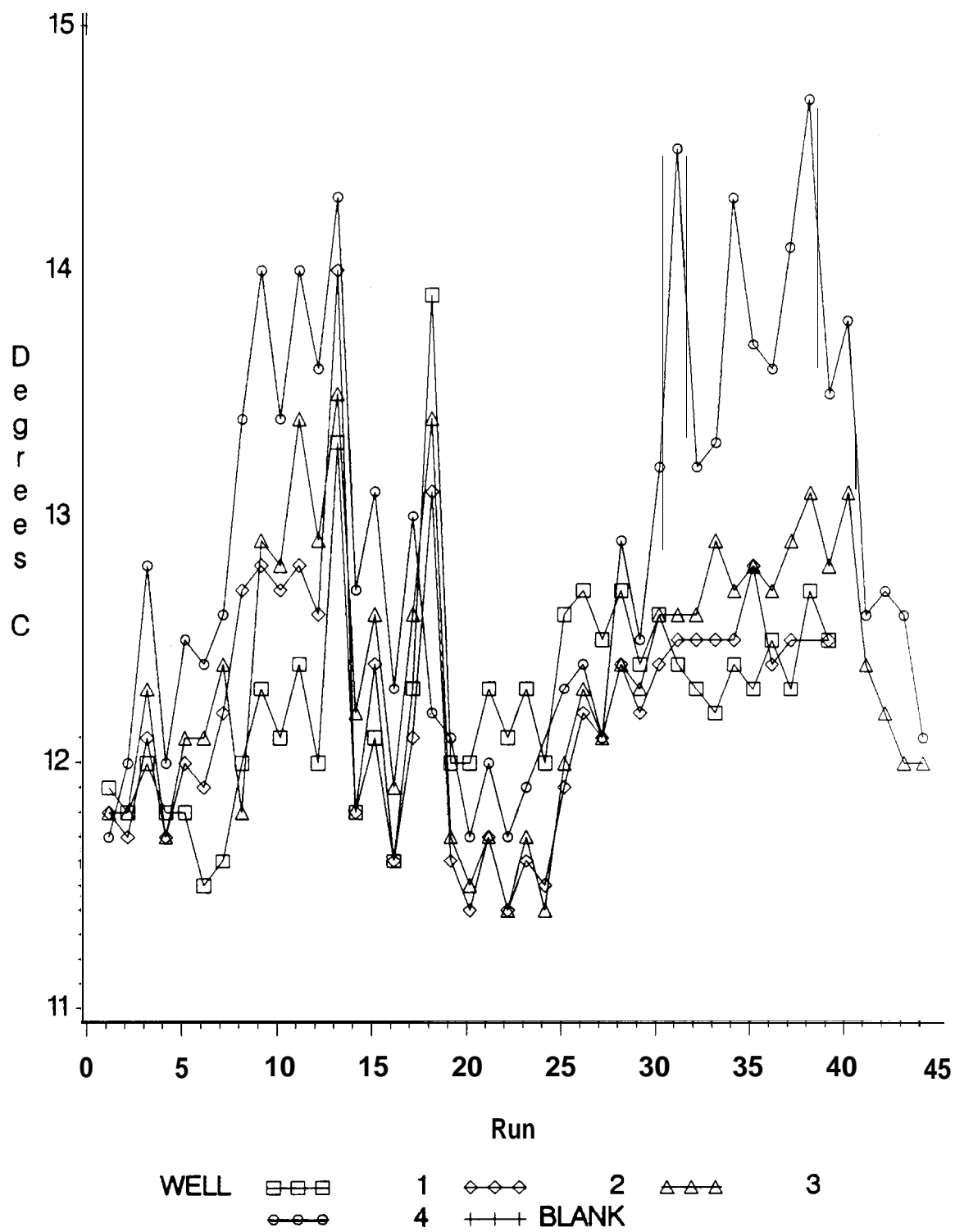


# Well Temperature

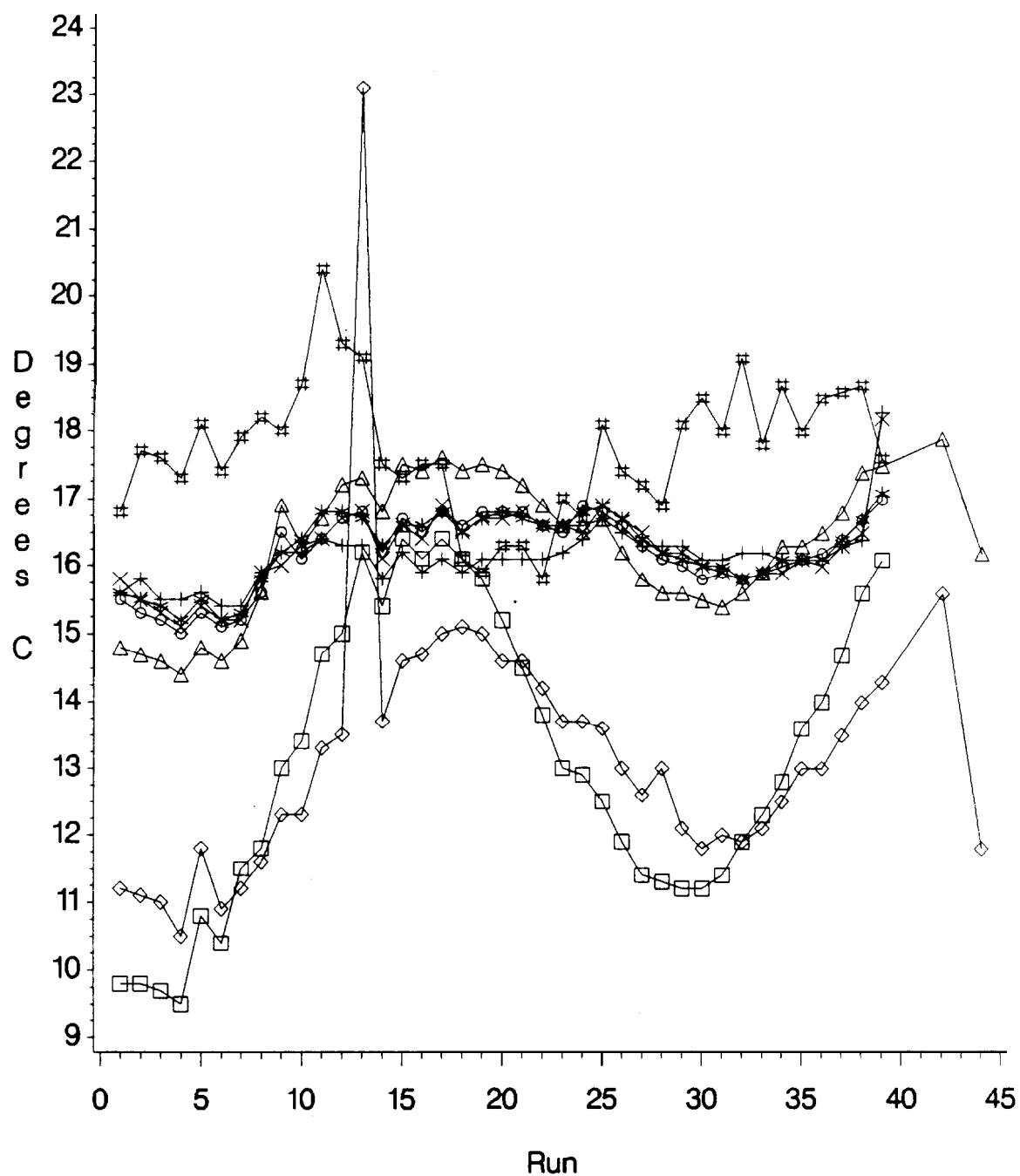


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
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	*-*-*	12	#-#-#	13	○-○-○	BLANK

# Cell Temperature

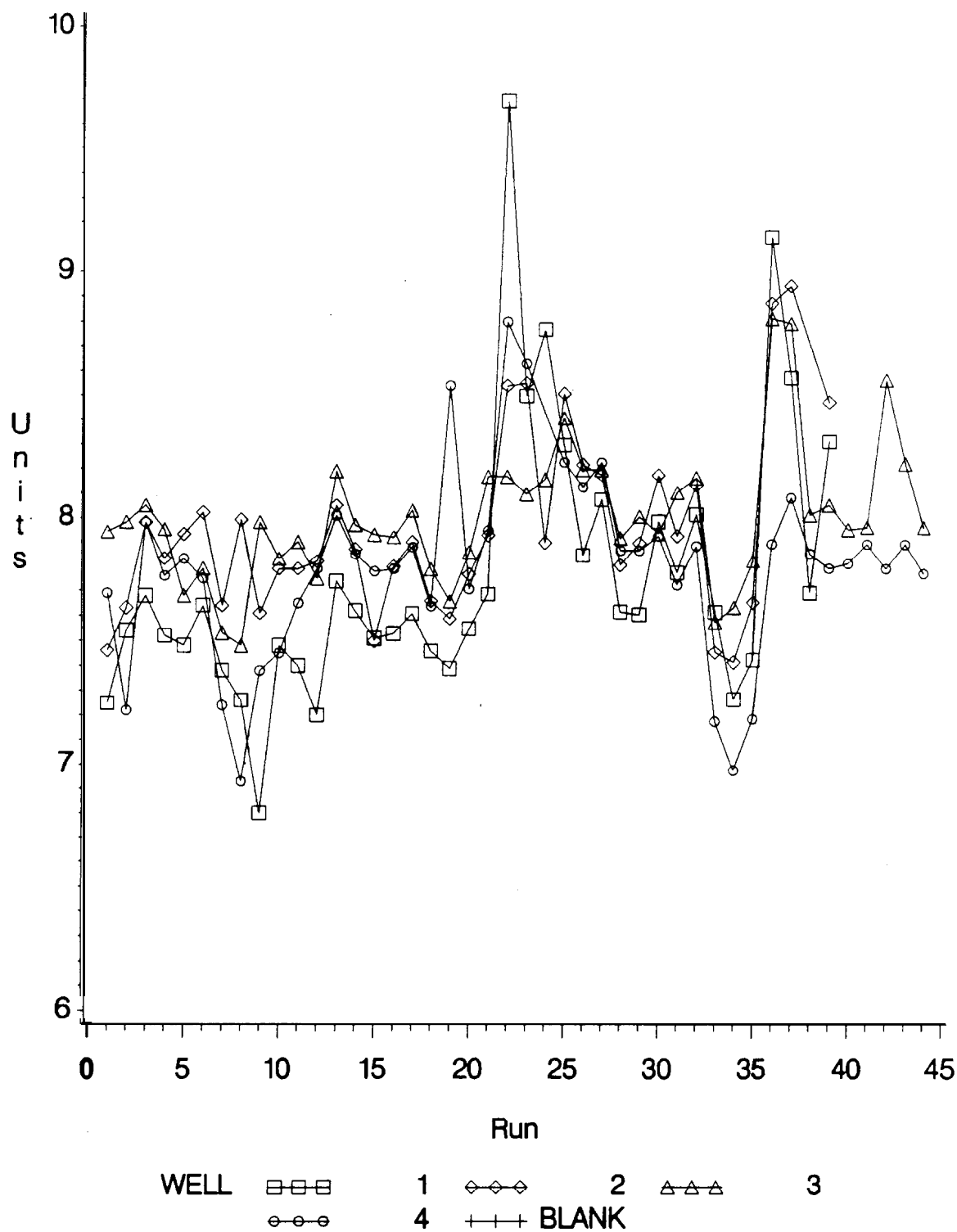


# Cell Temperature

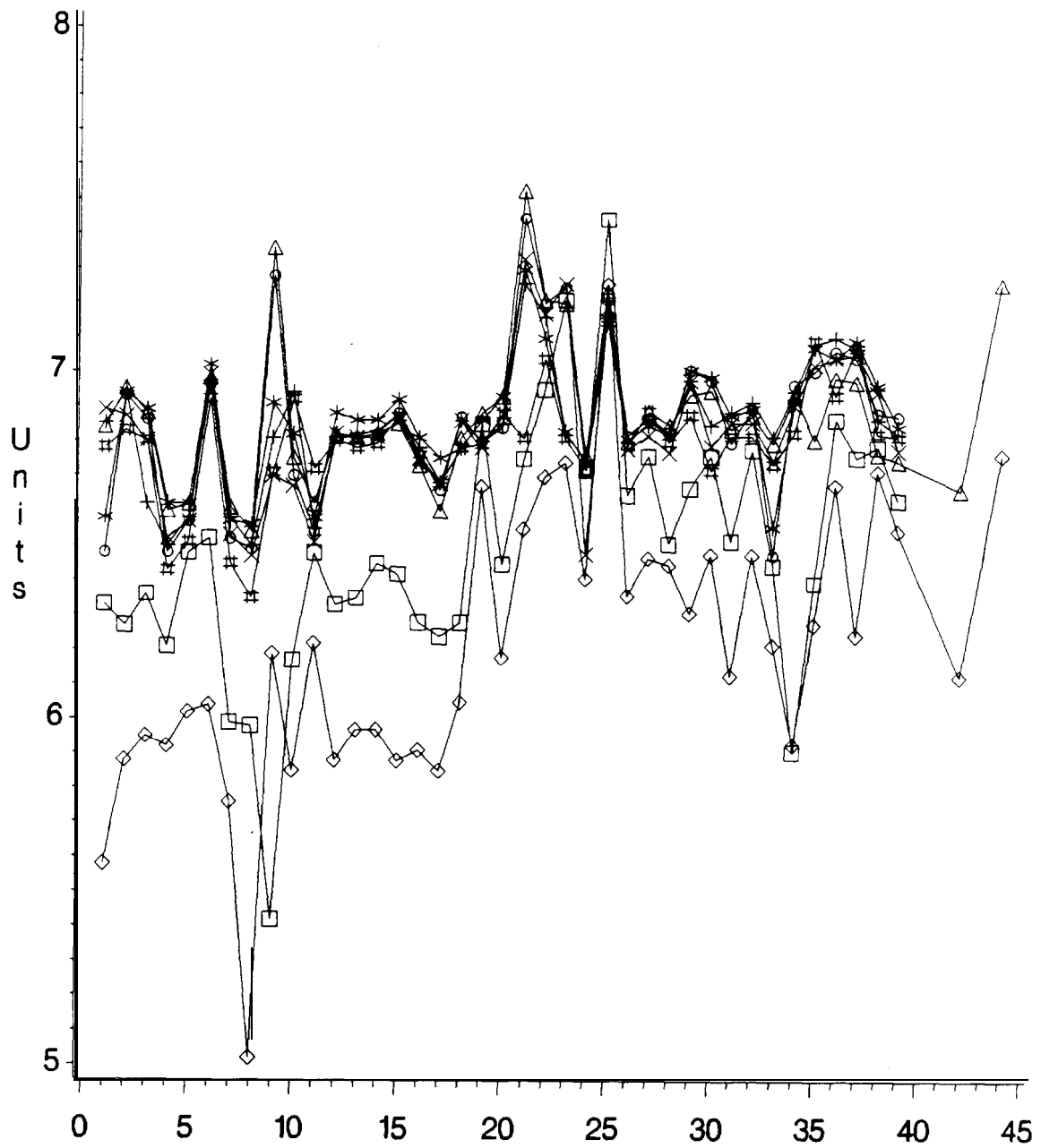


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
	○-○-○	9	+ - + - +	10	×-×-×	11
	*-*-*	12	##-##	13	○-○-○	BLANK

# PH

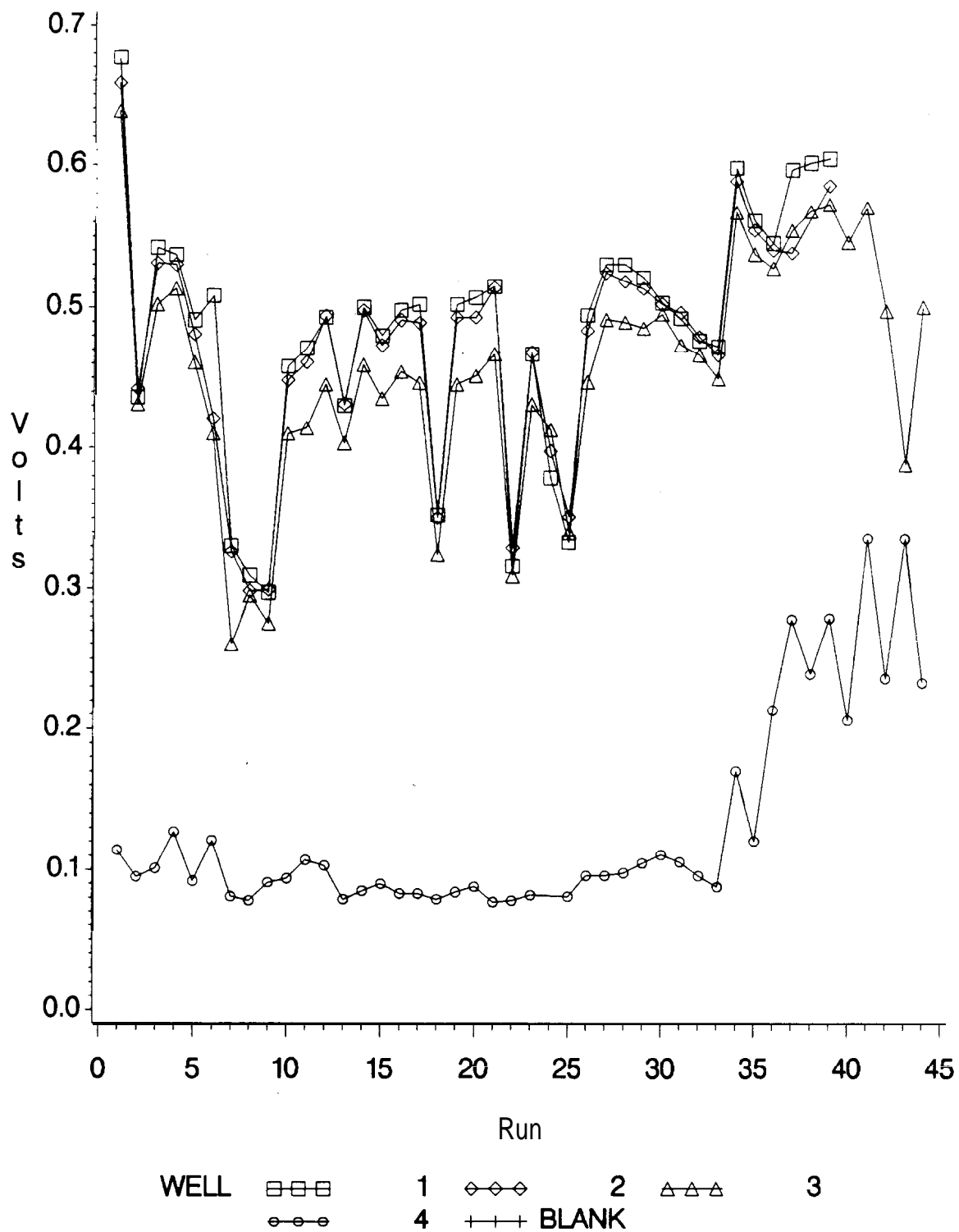


# PH

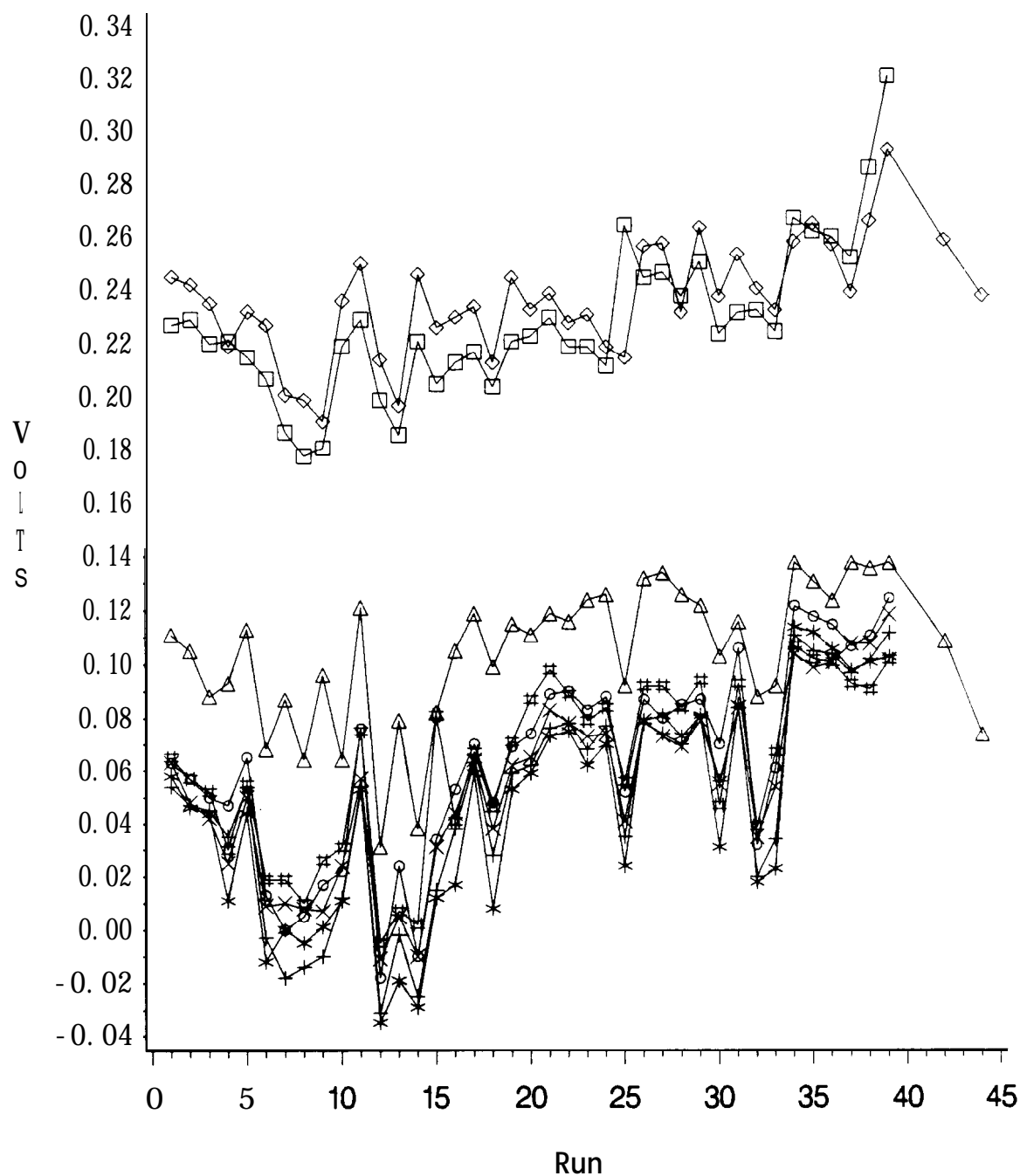


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
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	*-*-*	12	#-#-#	13	○-○-○	BLANK

Eh

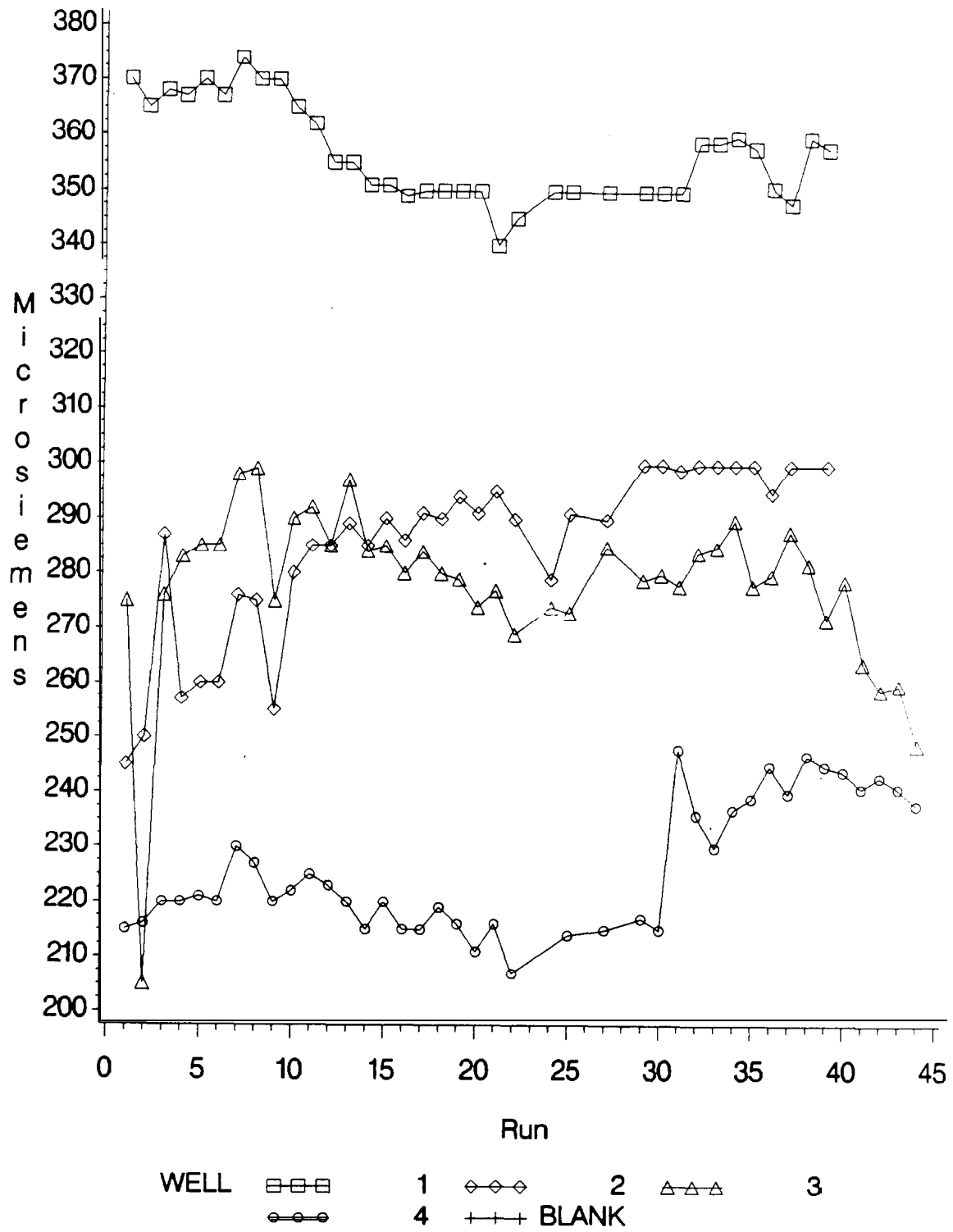


# Eh

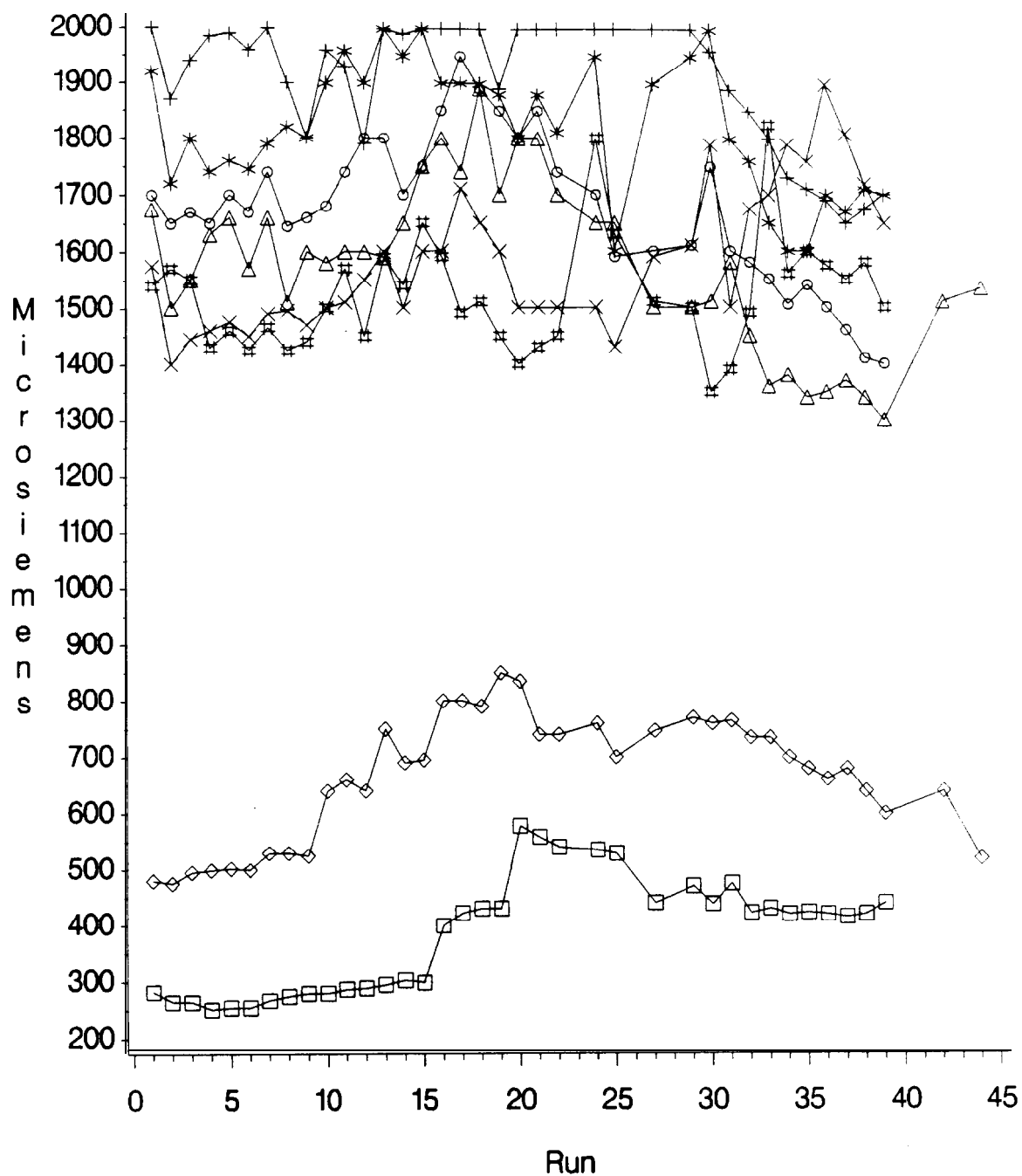




# Conductivity

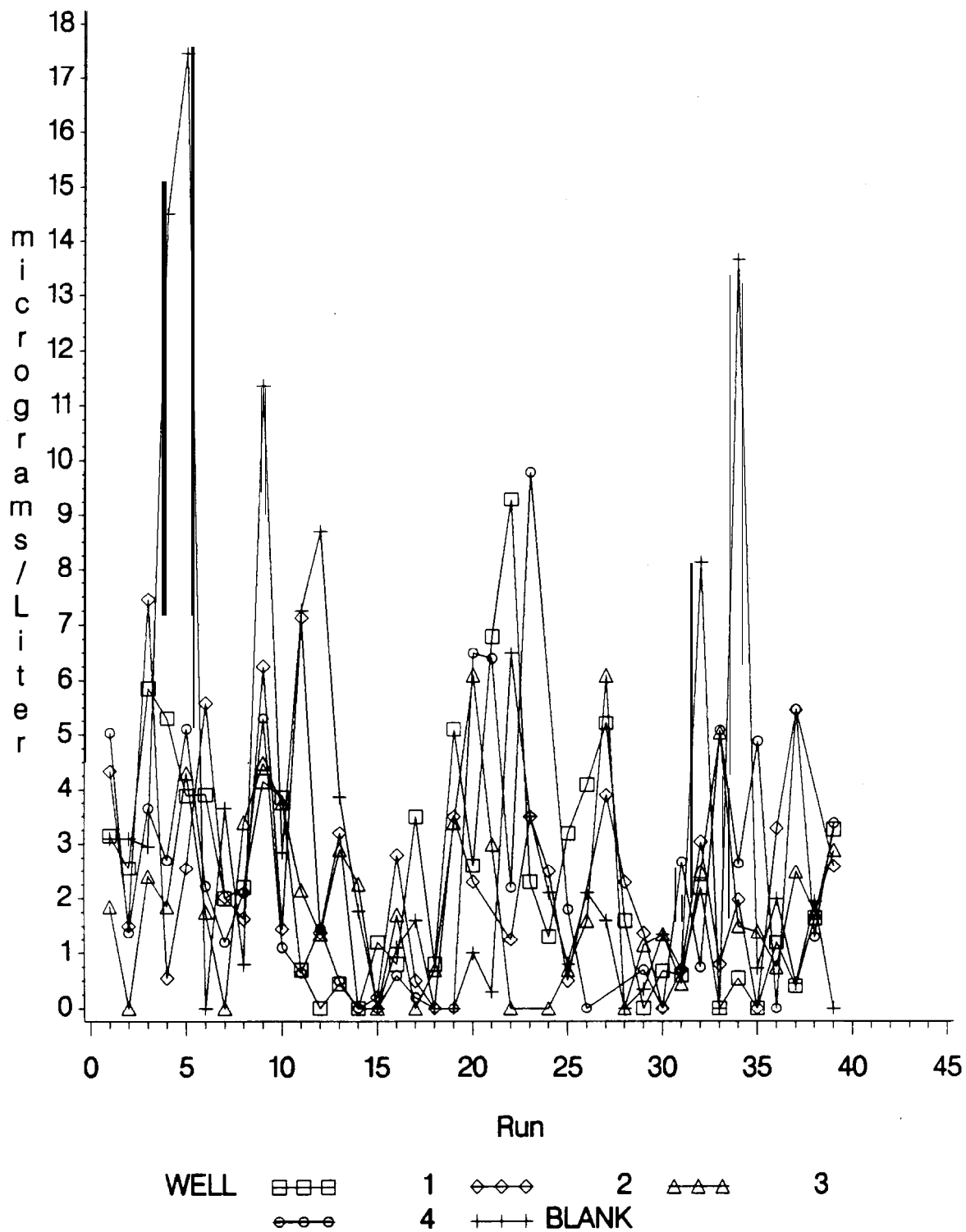


# Conductivity

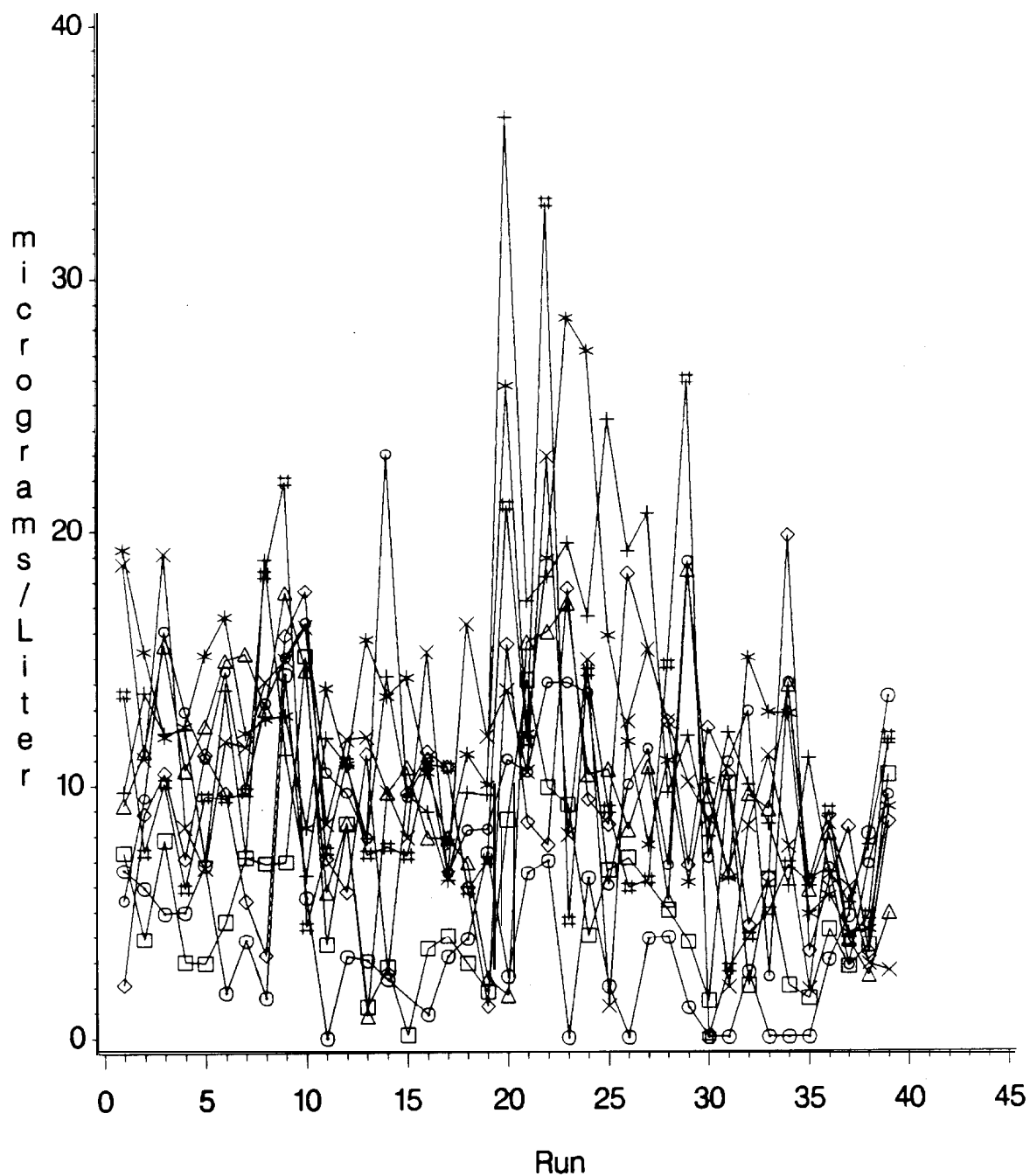


WELL	□□□	5	◇◇◇	6	△△△	8
	○—○	9	+—+	10	*—*	11
	*—*	12	#—#	13	○—○	BLANK

# Total Organic Halogen

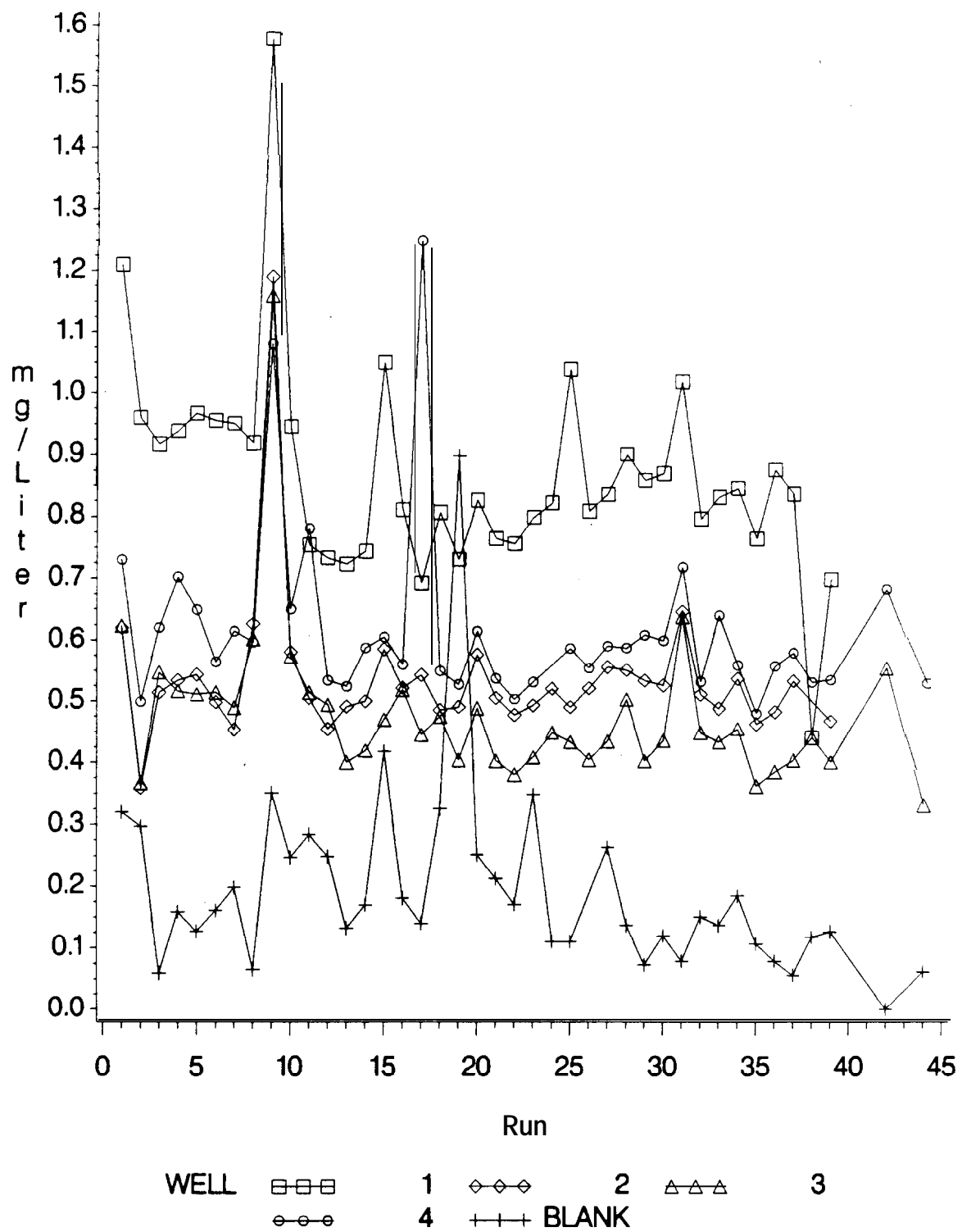


# Total Organic Halogen

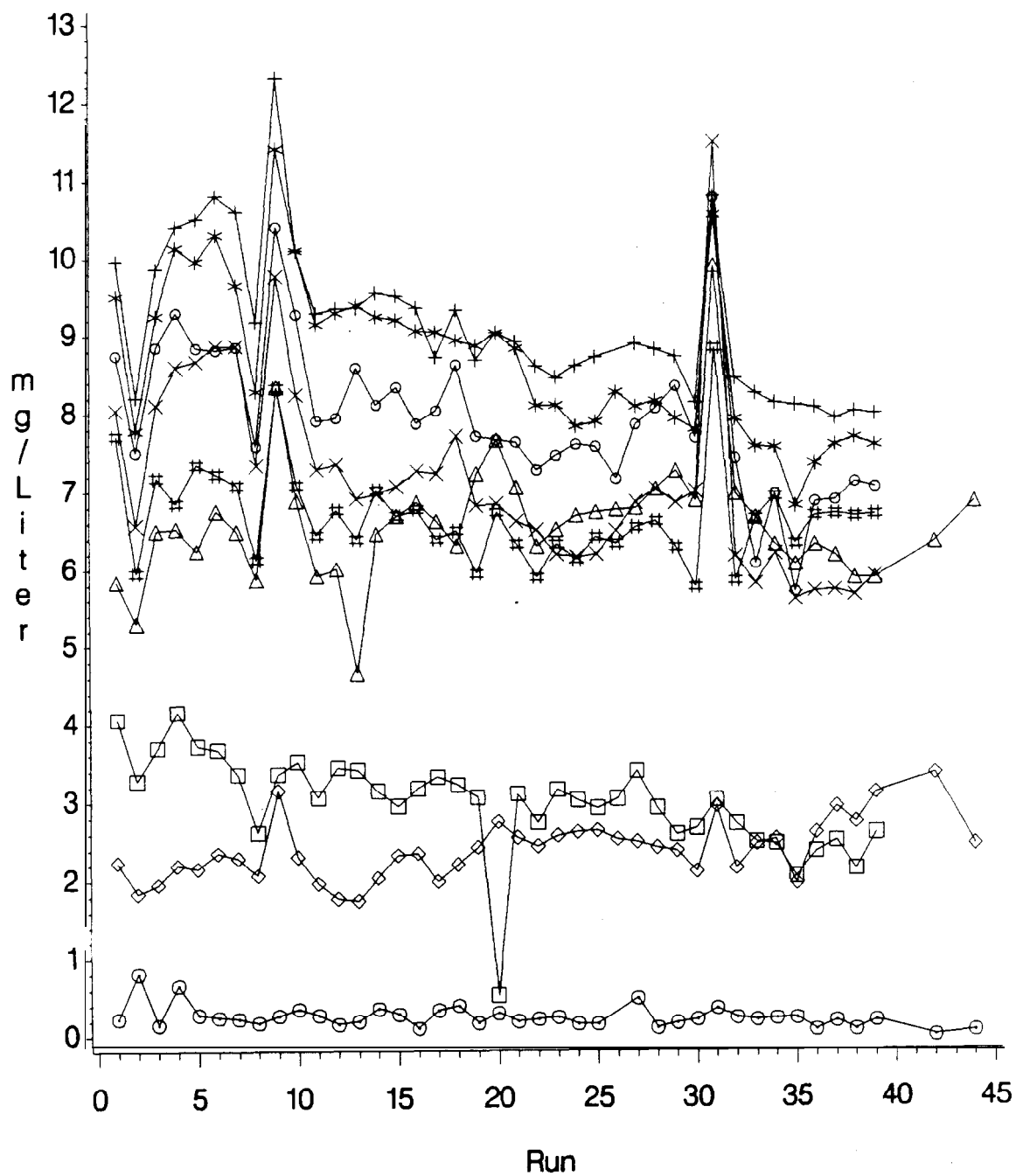


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
	○-○-○	9	+ - + - +	10	×-×-×	11
	*-*-*	12	#-#-#	13	⊖-⊖-⊖	BLANK

# Total Organic Carbon

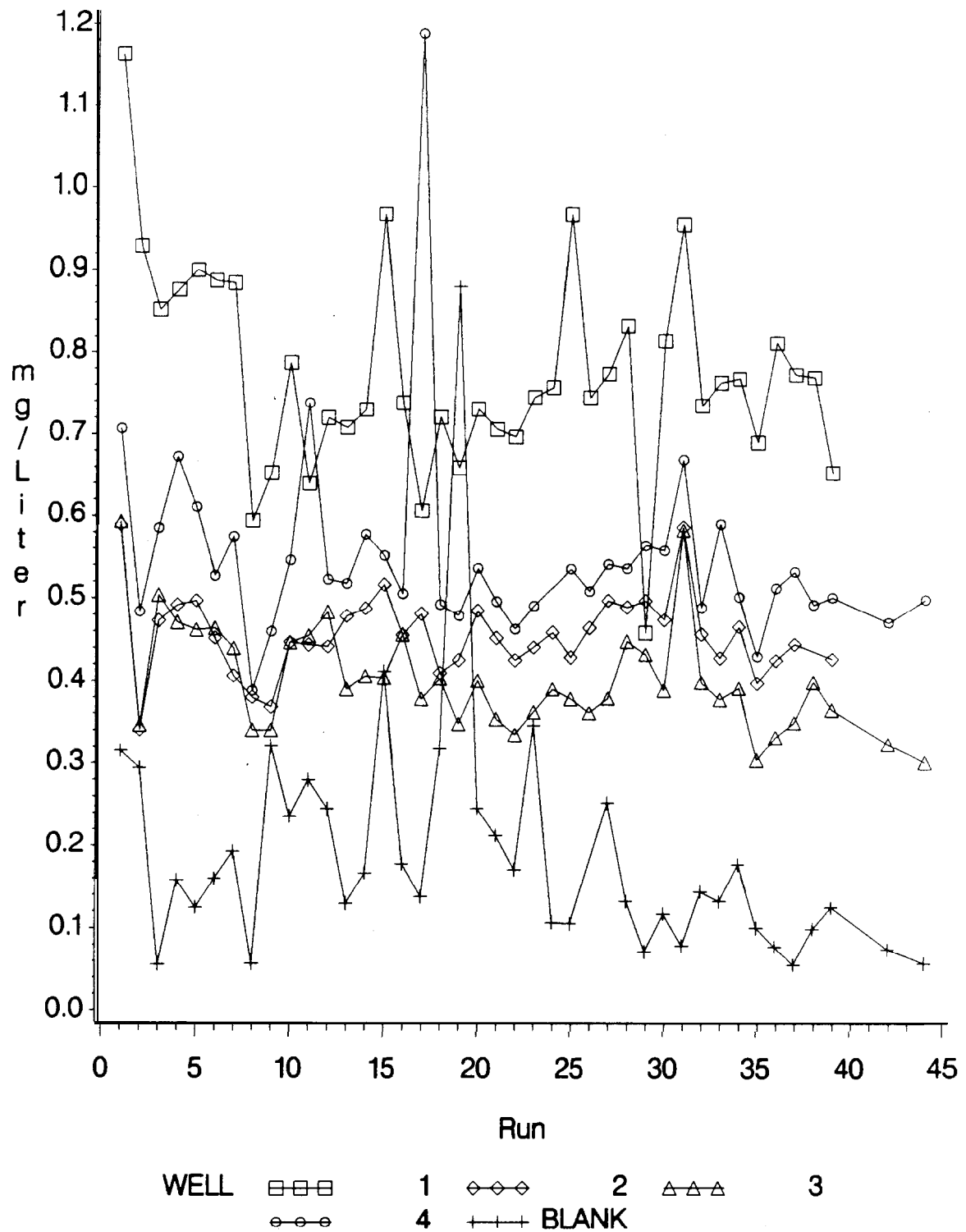


# Total Organic Carbon

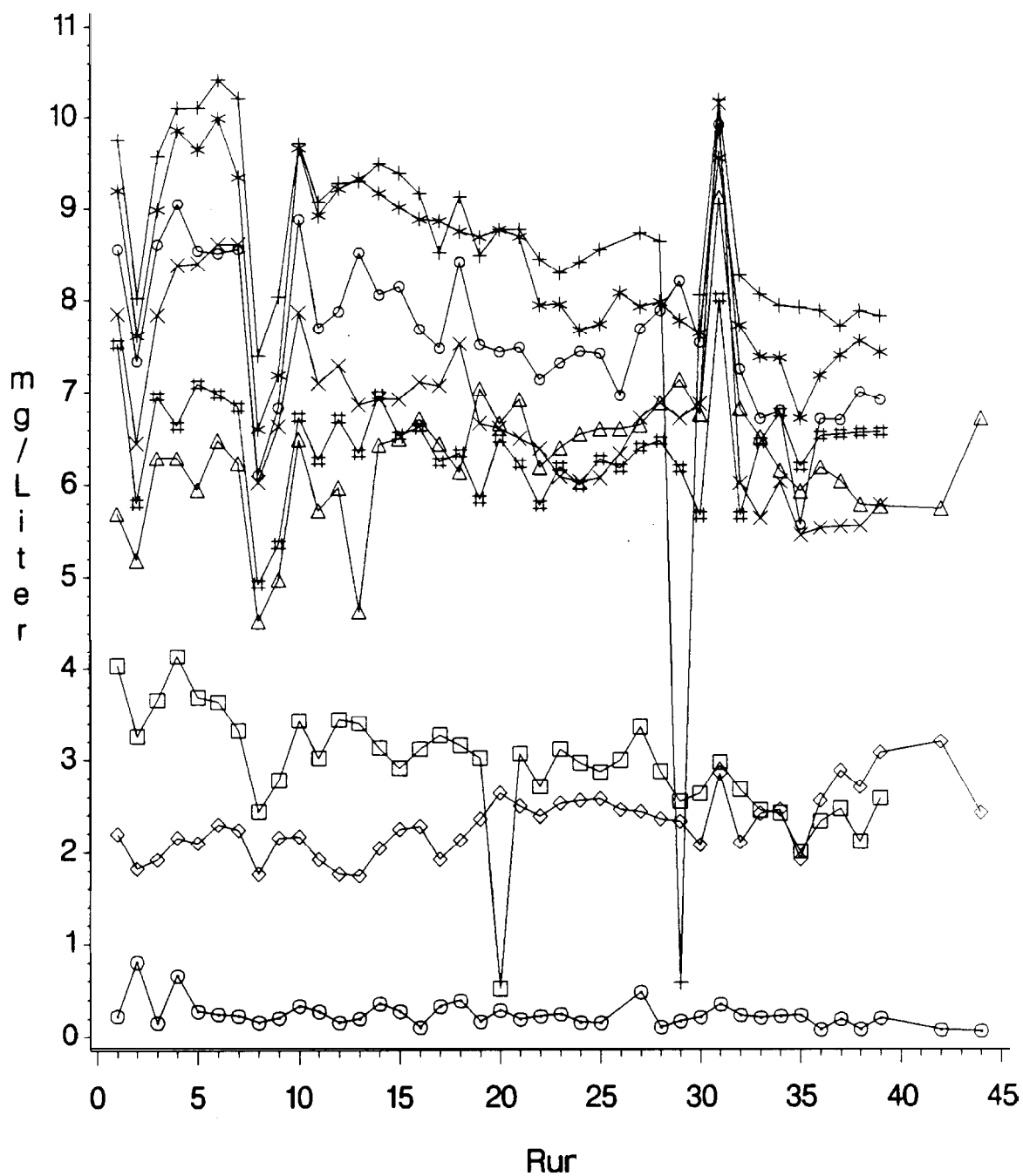


WELL	□ □ □	5	◇ ◇ ◇	6	△ △ △	8
	○ ○ ○	9	+ + +	10	* * *	11
	* * *	12	# # #	13	○ ○ ○	BLANK

# Non – Volatile Organic Carbon



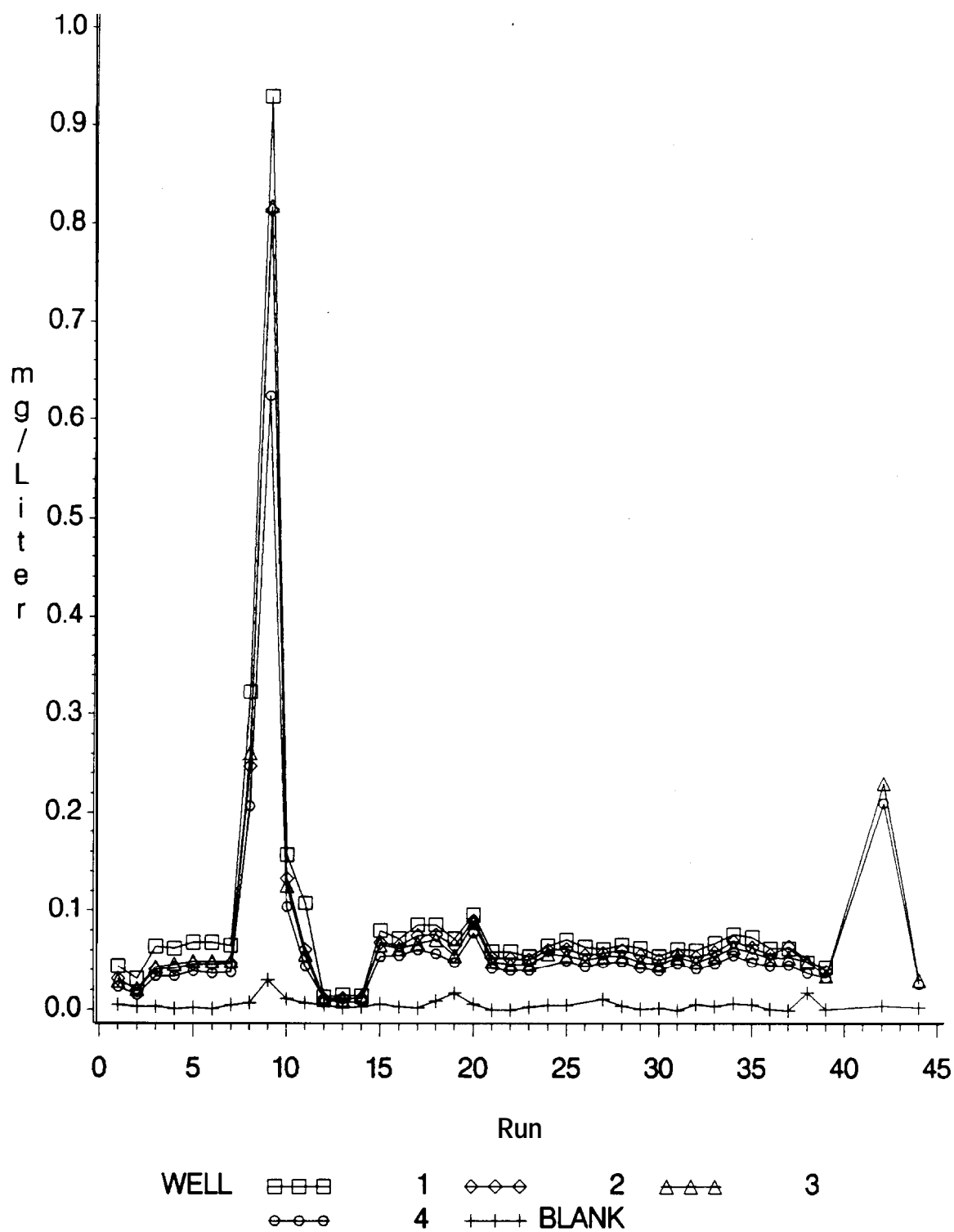
# Non – Volatile Organic Carbon



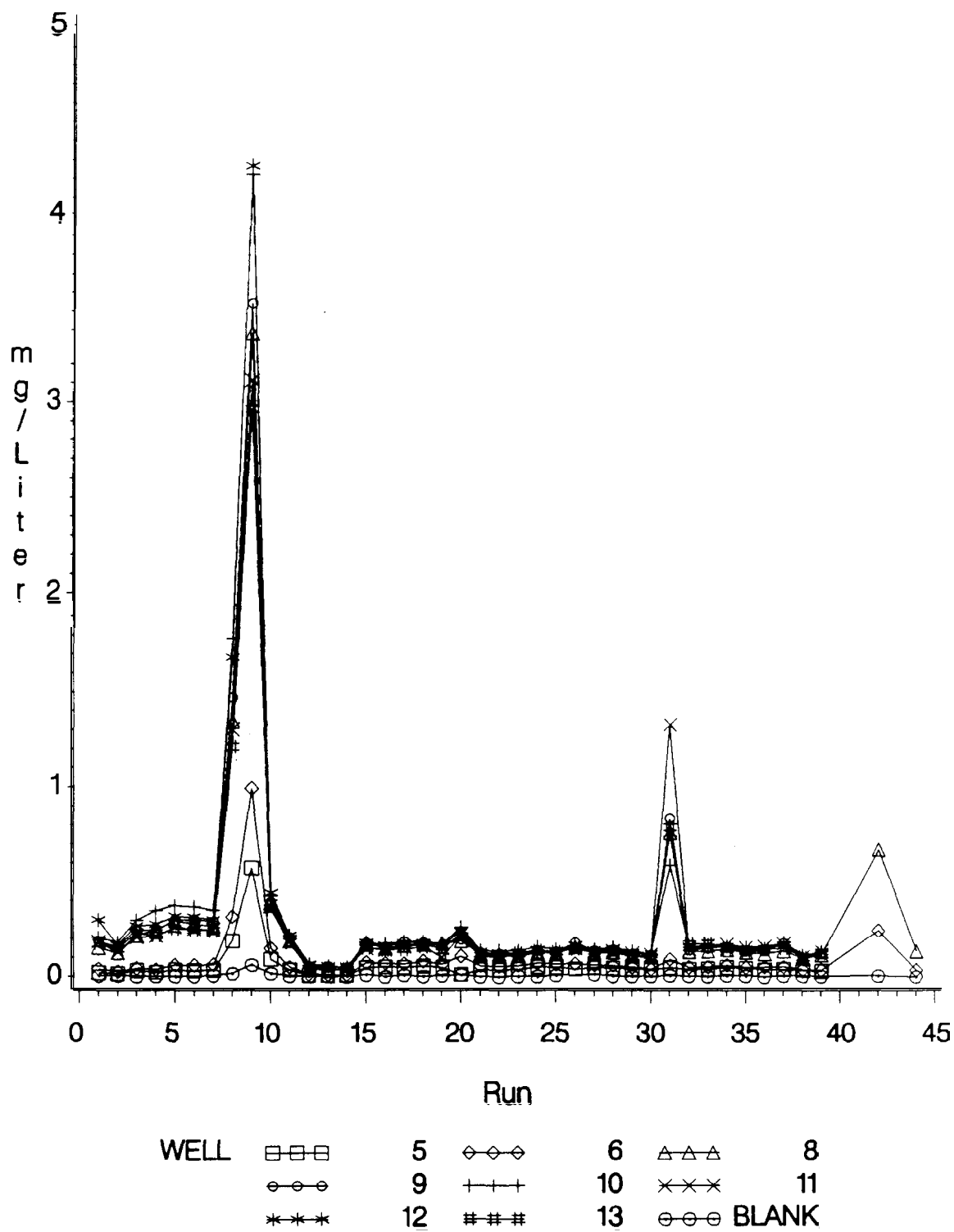
WELL	□□□	5	◇◇◇	6	△△△	8
	○●○	9	+ + +	10	×××	11
	* * *	12	# # #	13	○●○	BLANK



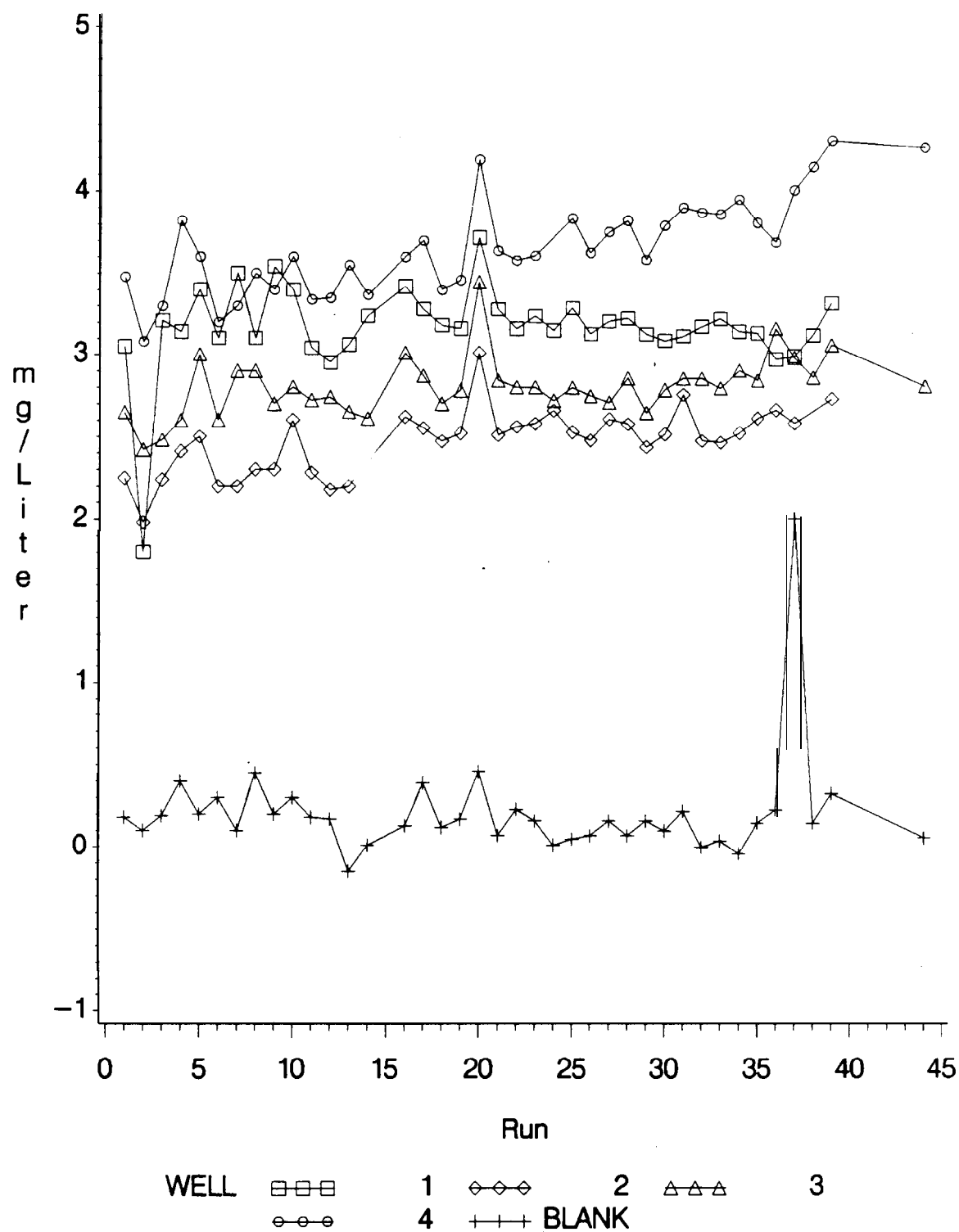
# Volatile Organic Carbon



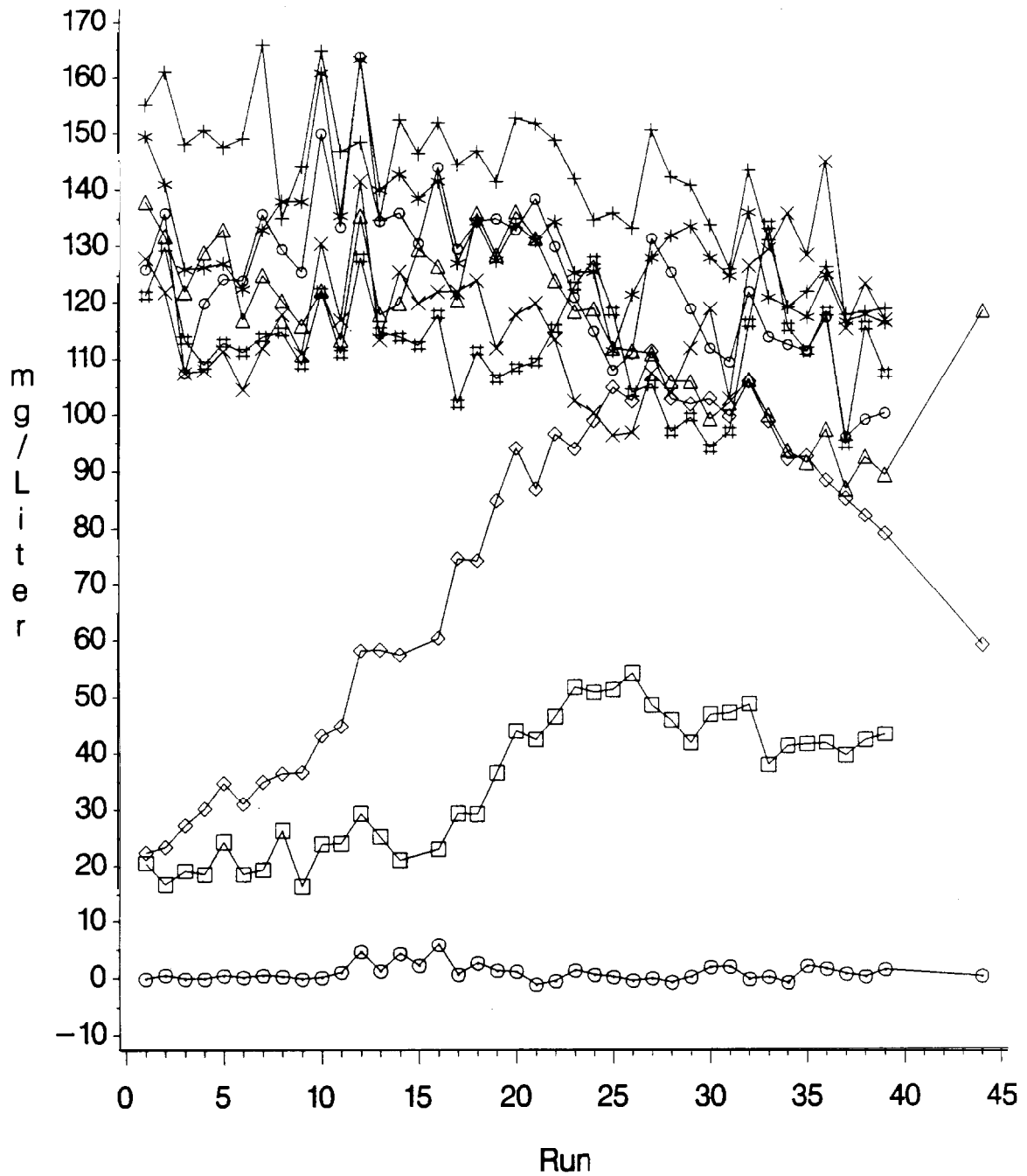
# Volatile Organic Carbon



# Sodium

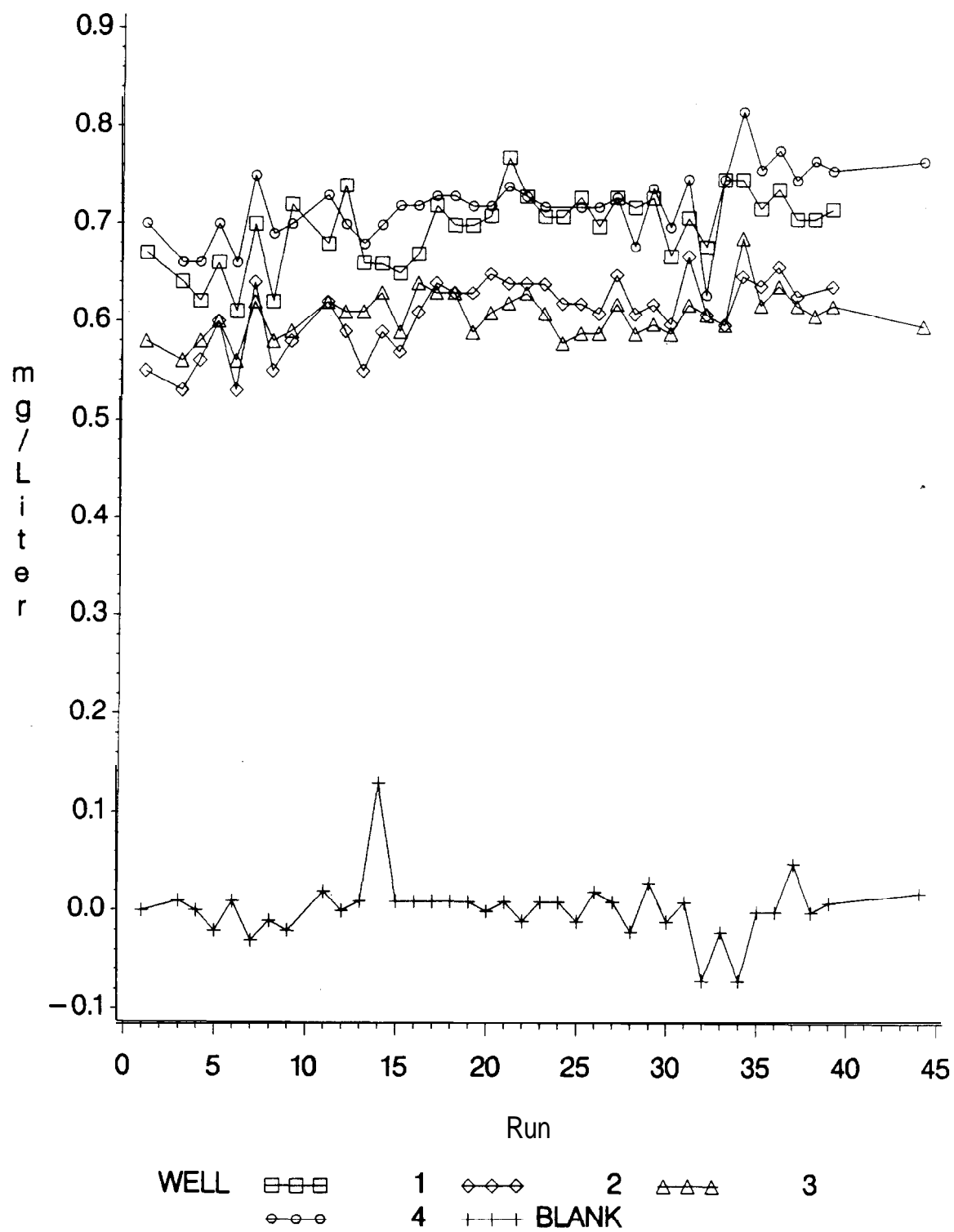


# Sodium

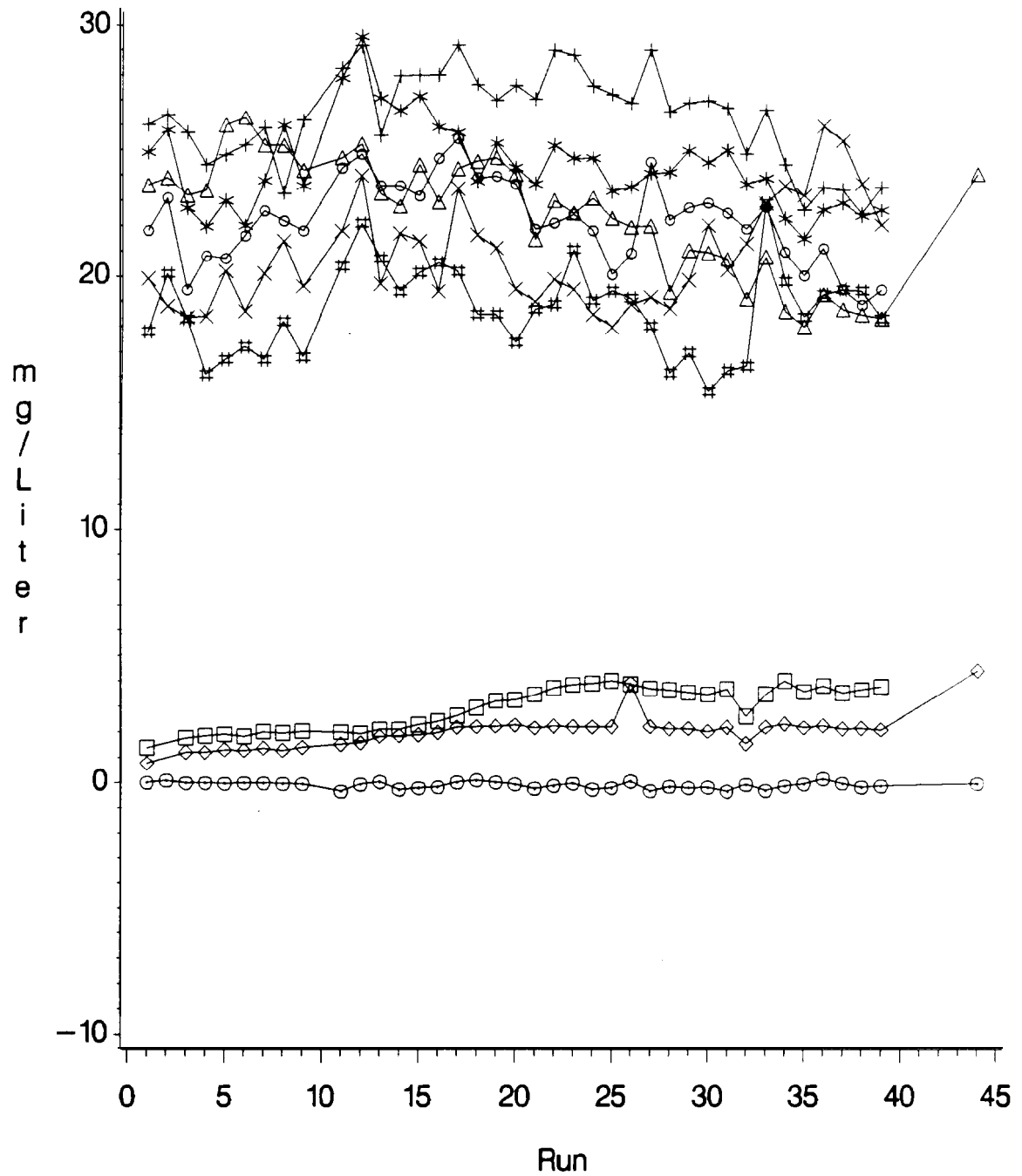


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
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	*-*-*	12	#-#-#	13	○-○-○	BLANK

# Potassium

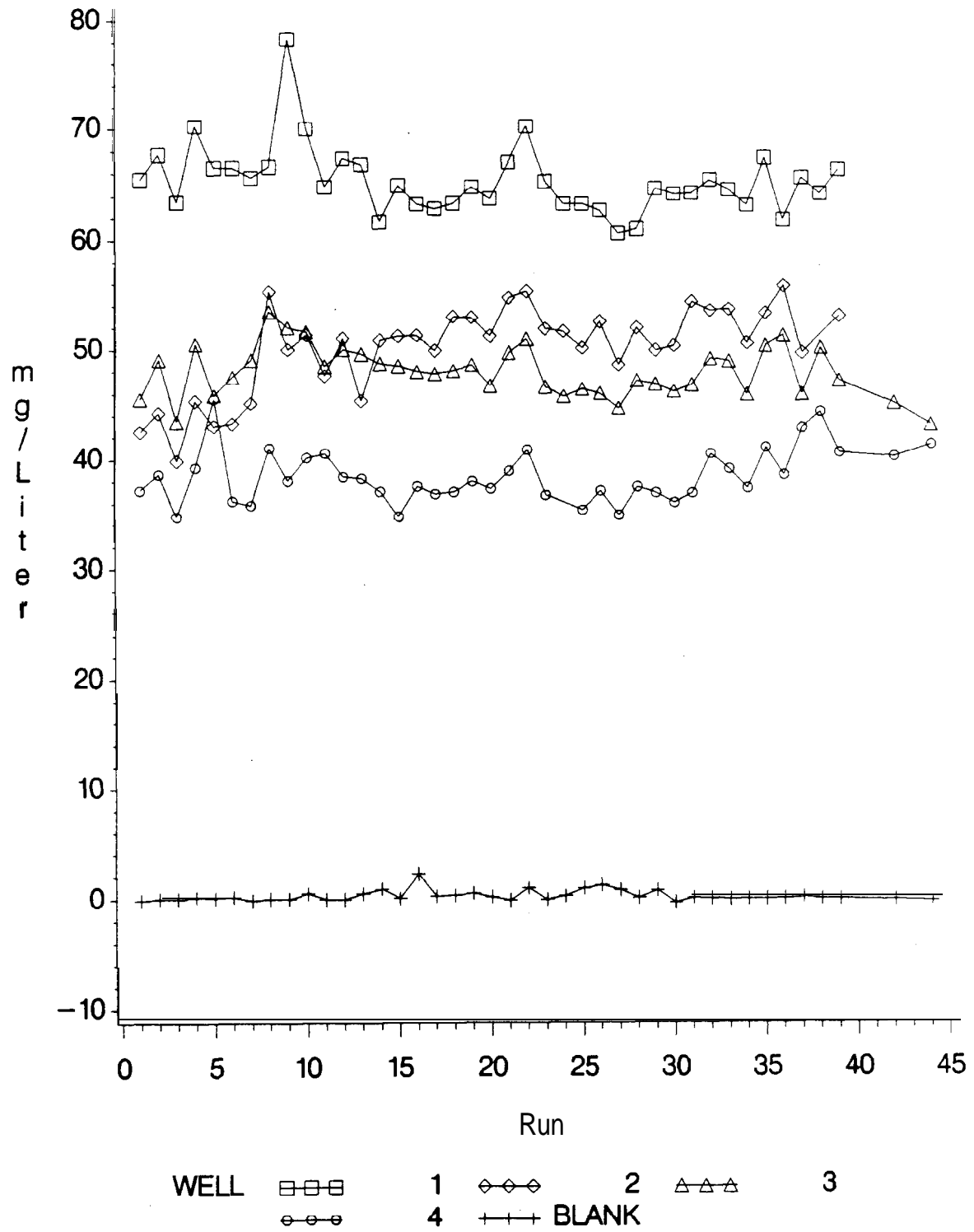


# Potassium

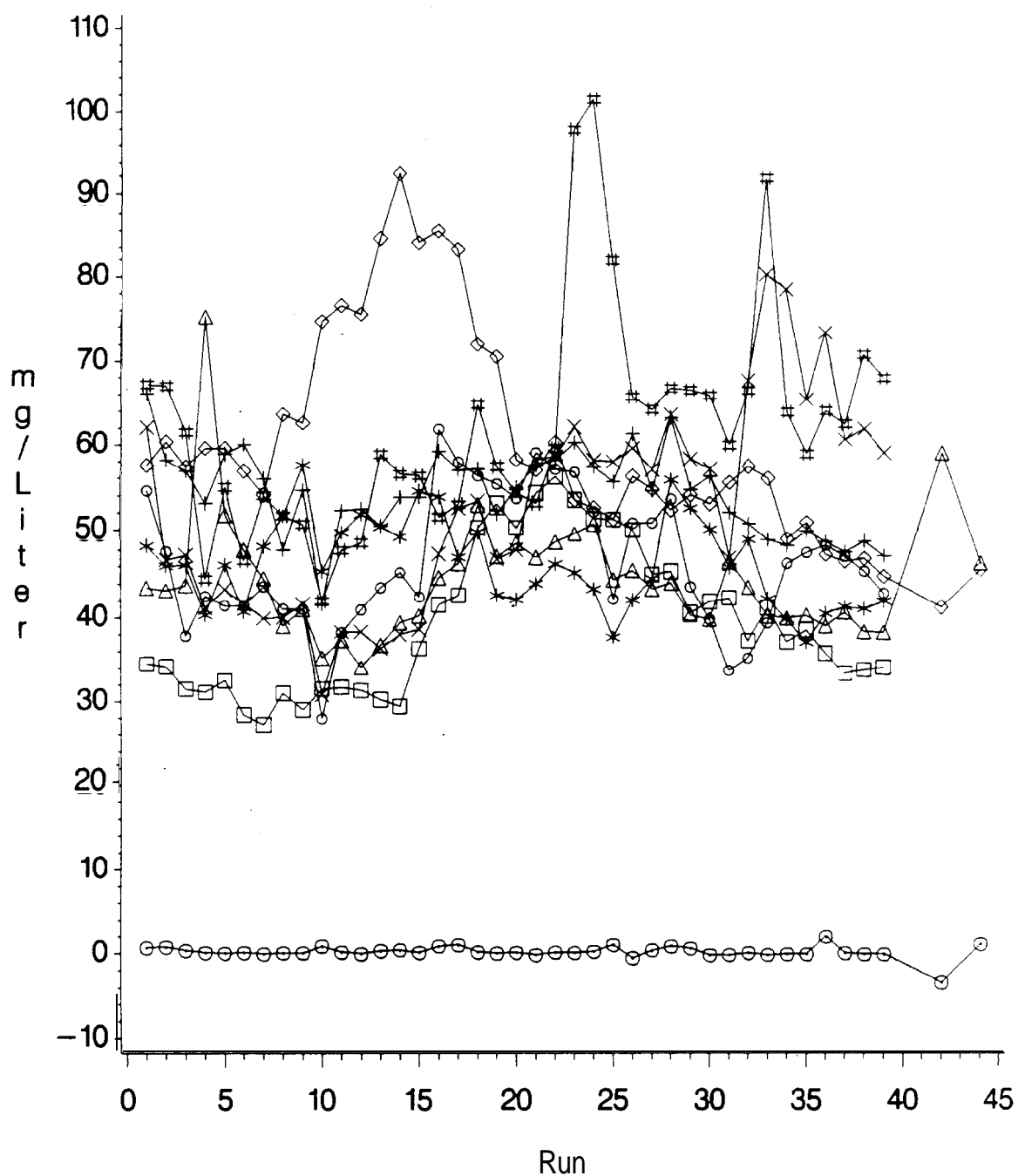


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	*-*-*	12	#-#-#	13	○-○-○	BLANK

# Calcium



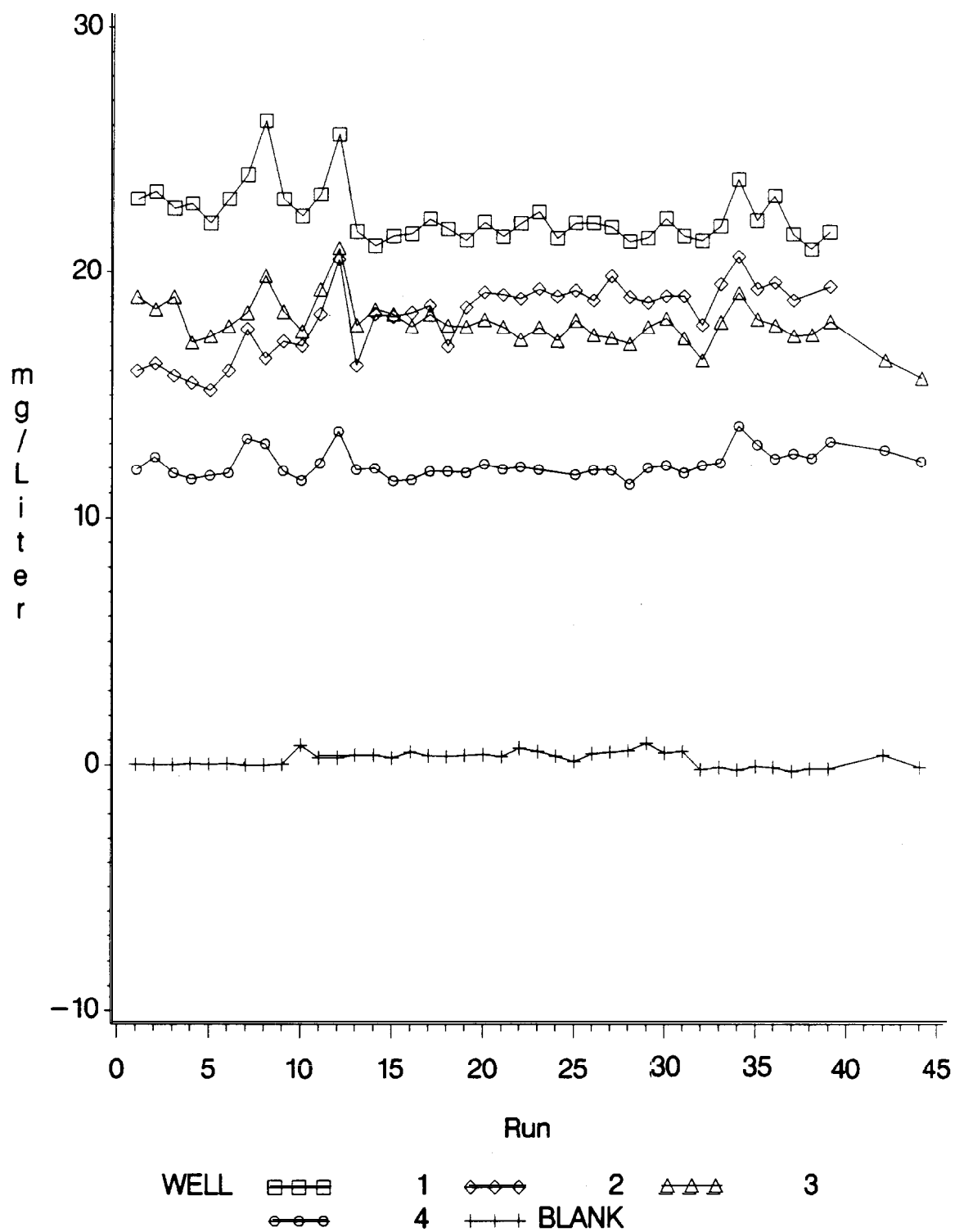
# Calcium



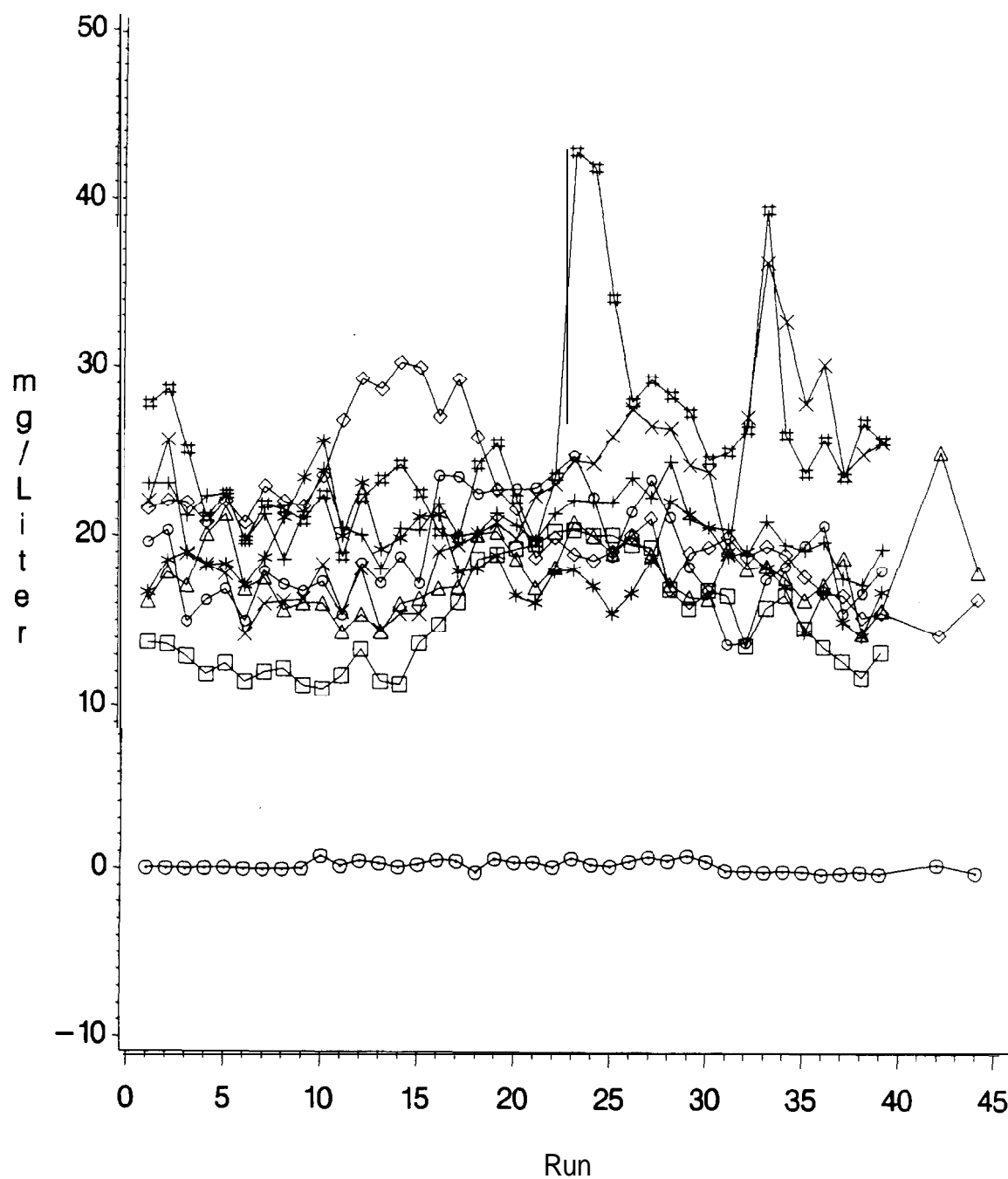
WELL	$\square-\square-\square$	5	$\diamond-\diamond-\diamond$	6	$\triangle-\triangle-\triangle$	8
	$\circ-\circ-\circ$	9	$+-+ -+$	10	$\times-\times-\times$	11
	$*-* -*$	12	$\#-\#-\#$	13	$\ominus-\ominus-\ominus$	BLANK



# Magnesium

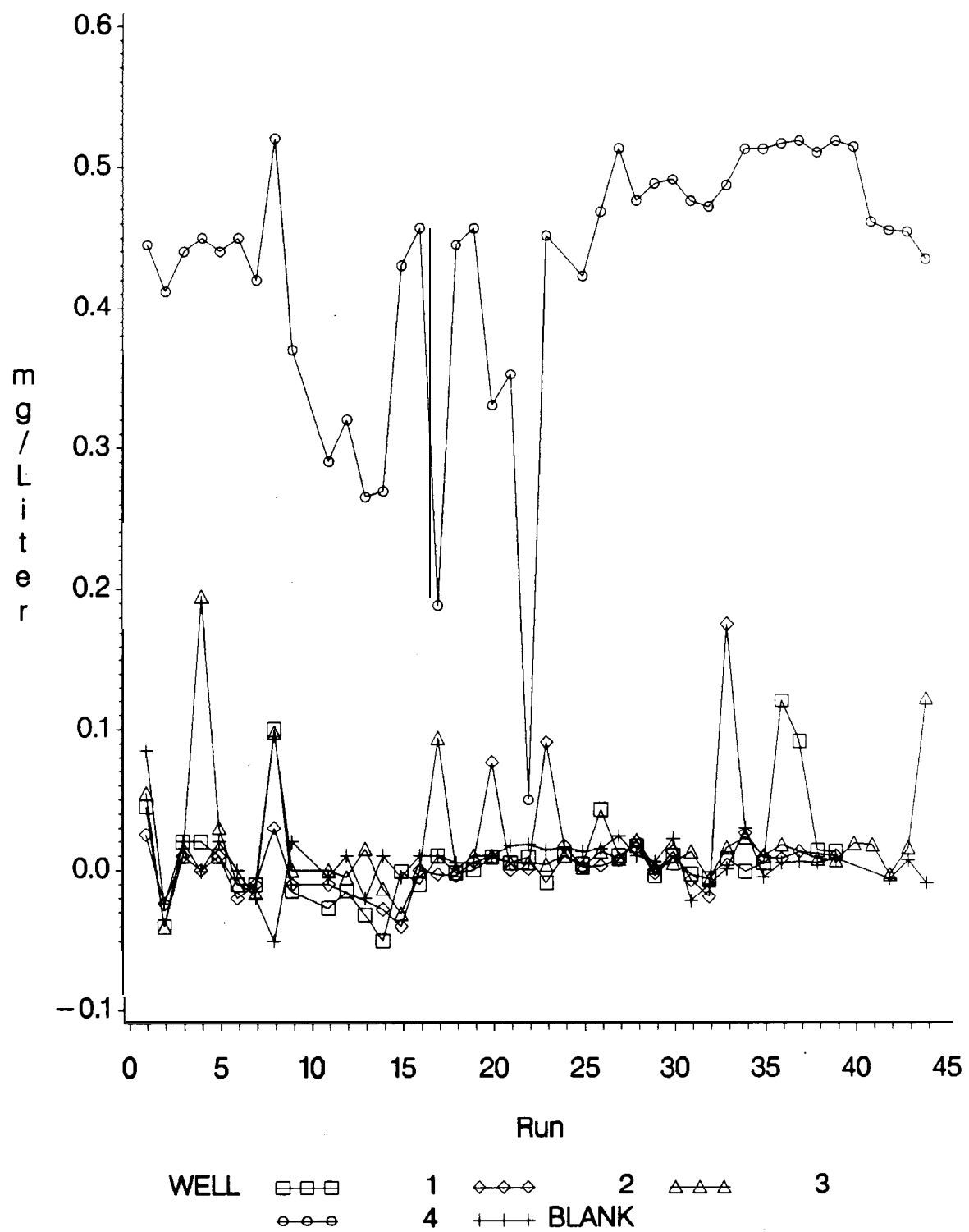


# Magnesium

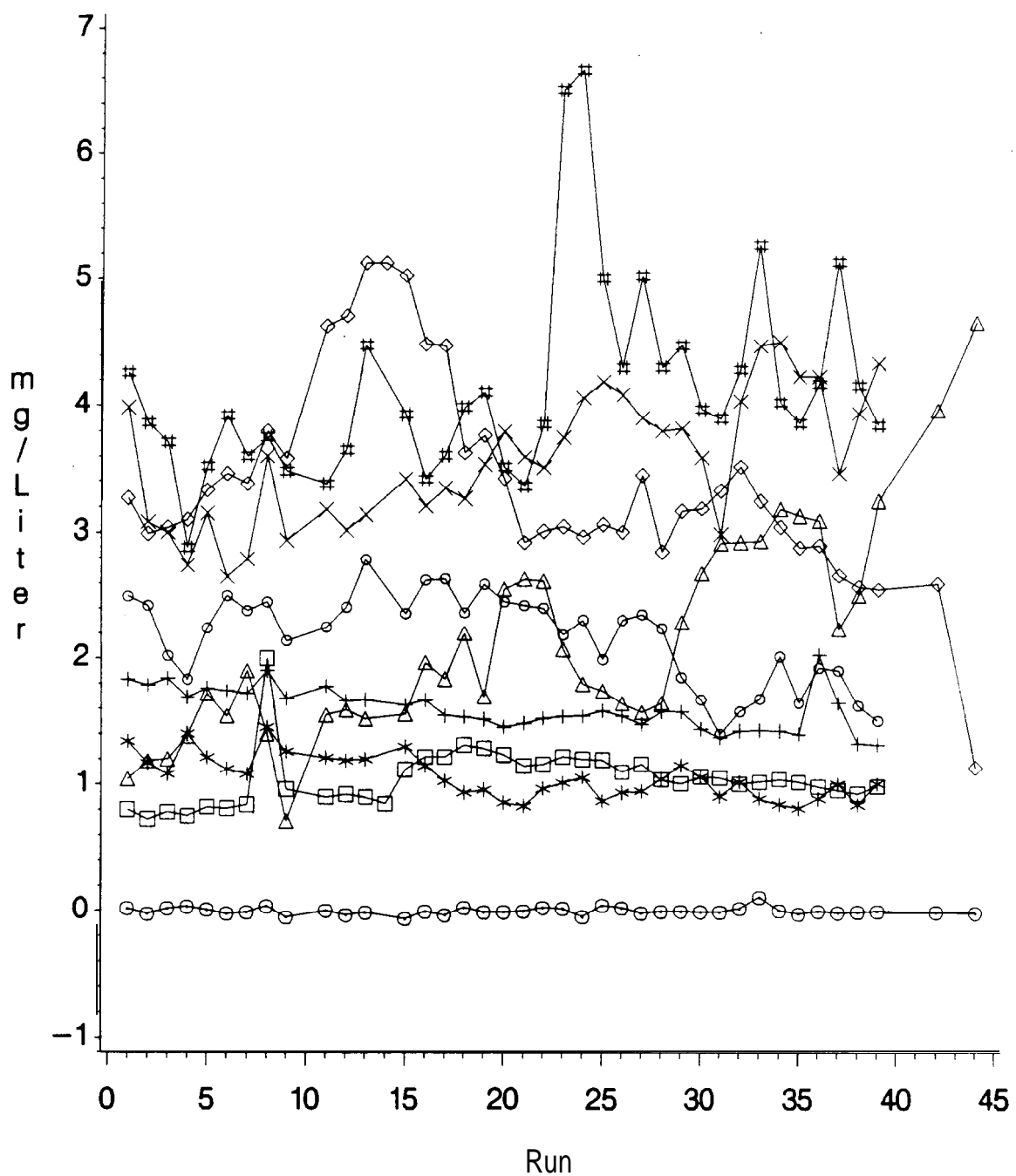


WELL	□ □ □	5	◇ ◇ ◇	6	△ △ △	8
	○ ○ ○	9	+ + +	10	× × ×	11
	* * *	12	# # #	13	○ ○ ○	BLANK

# Iron

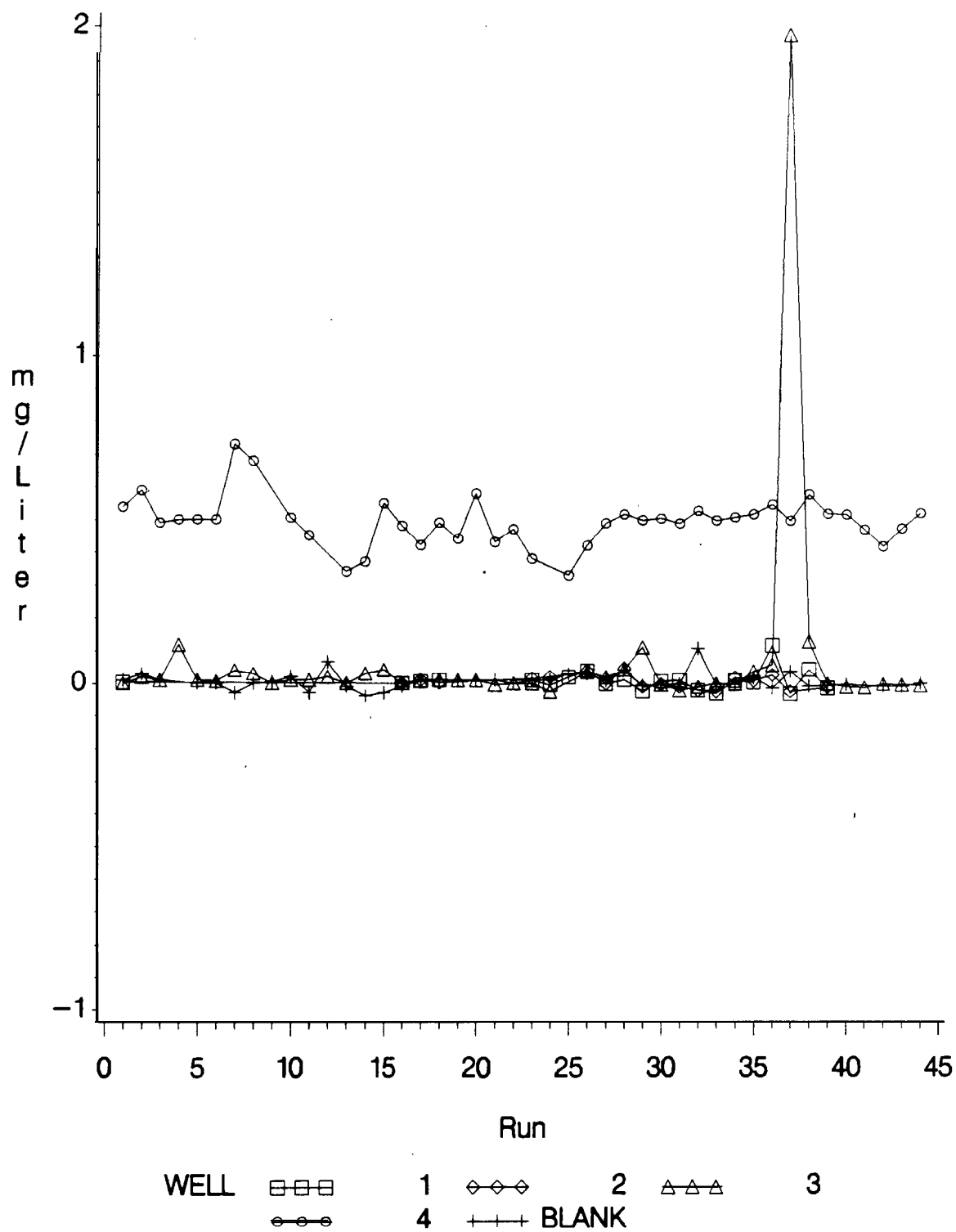


# Iron

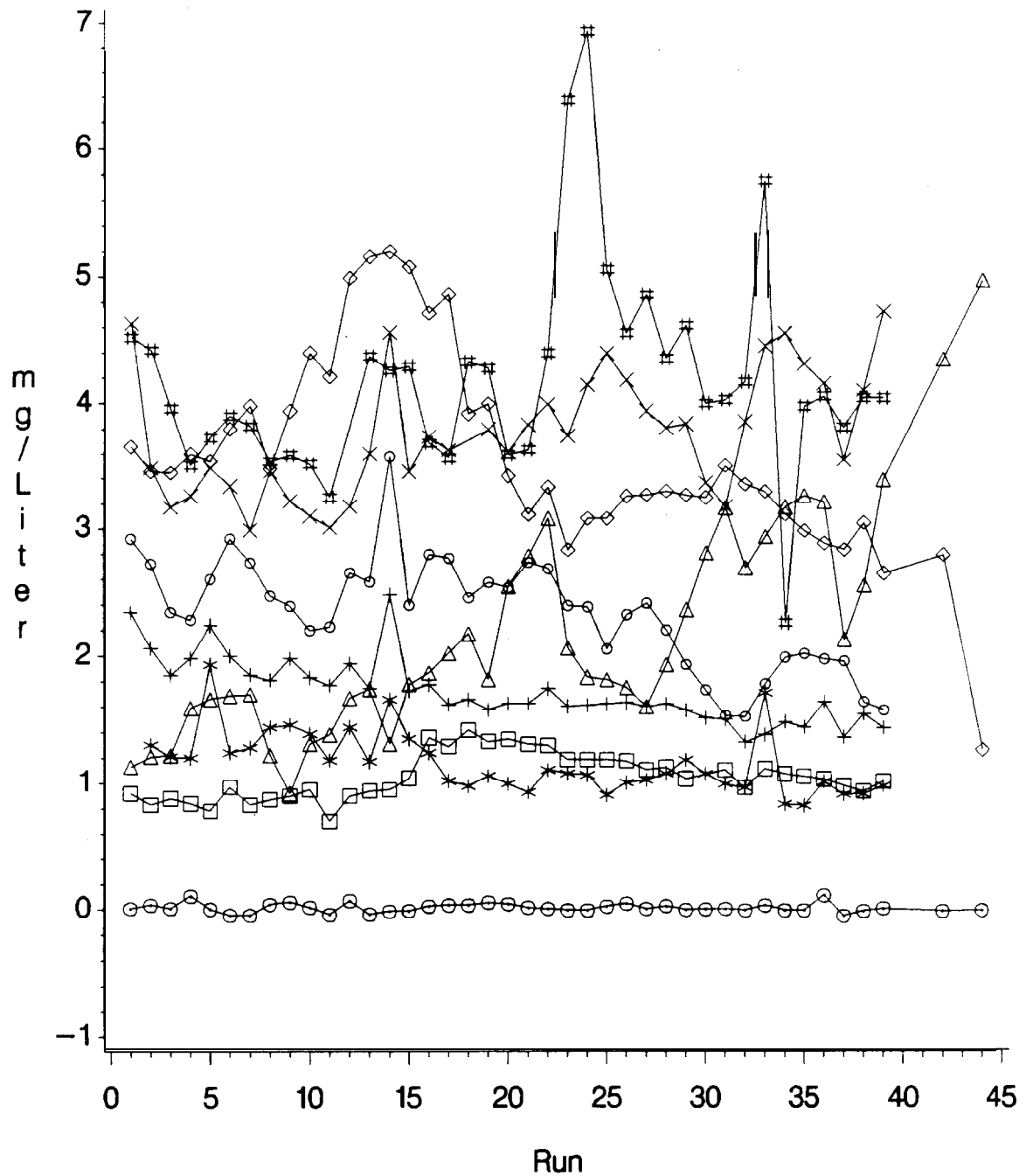


WELL	□□□	5	◇◇◇	6	△△△	8
	○-○-○	9	+ + +	10	×××	11
	* * *	12	# # #	13	○-○-○	BLANK

# Ferrous Iron

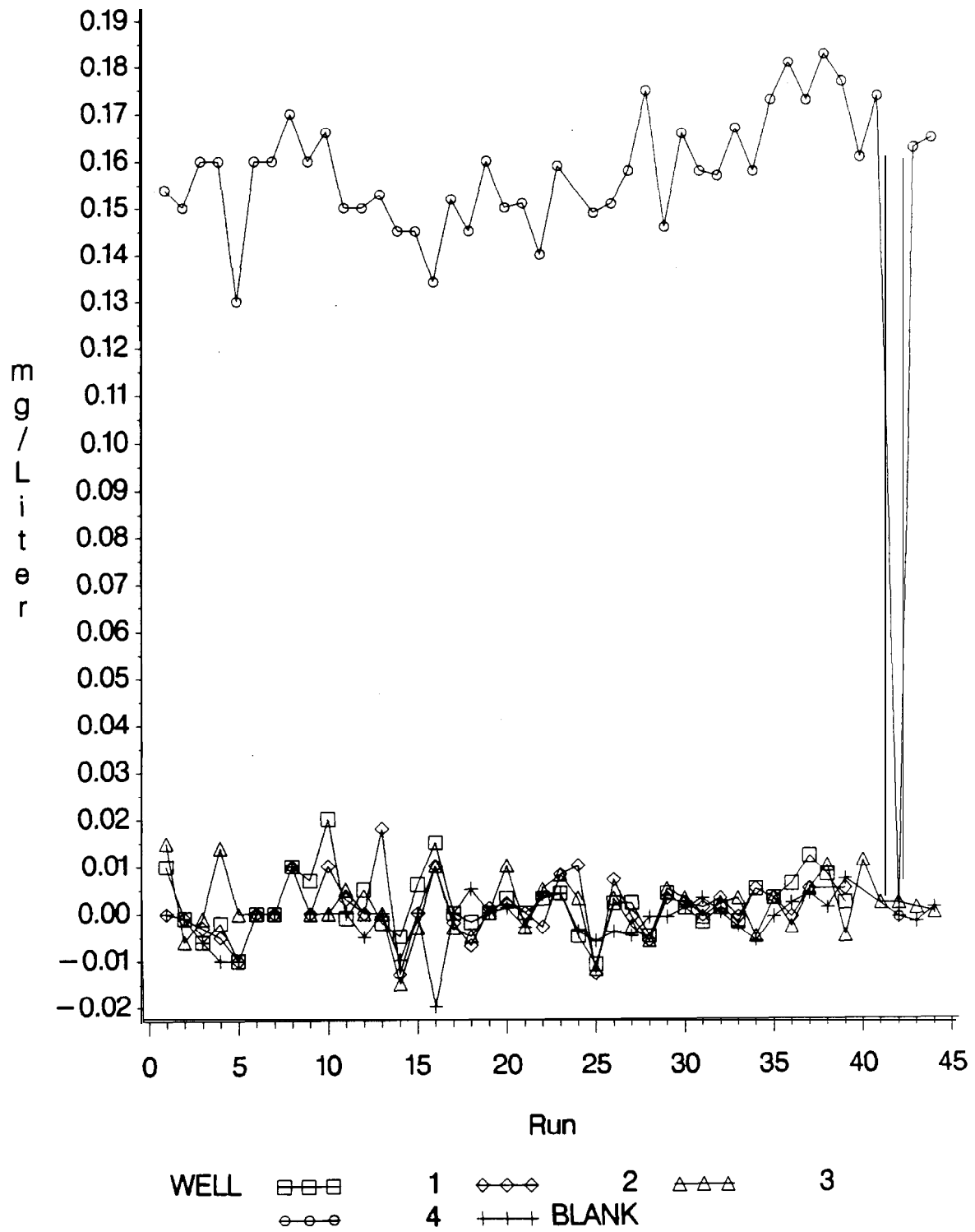


# Ferrous Iron

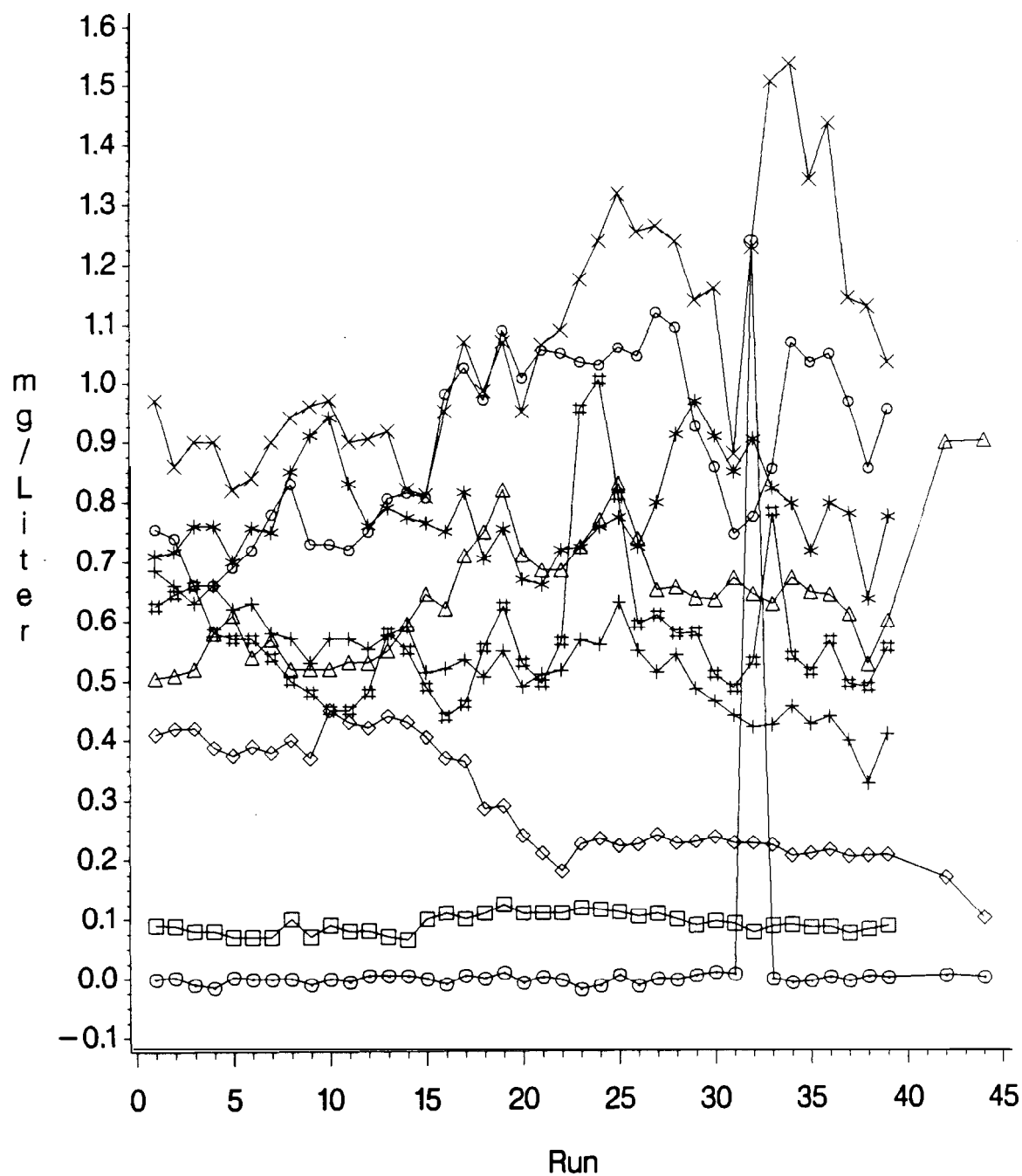


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
	○-○-○	9	+ + +	10	× × ×	11
	* * *	12	# # #	13	○-○-○	BLANK

# Manganese



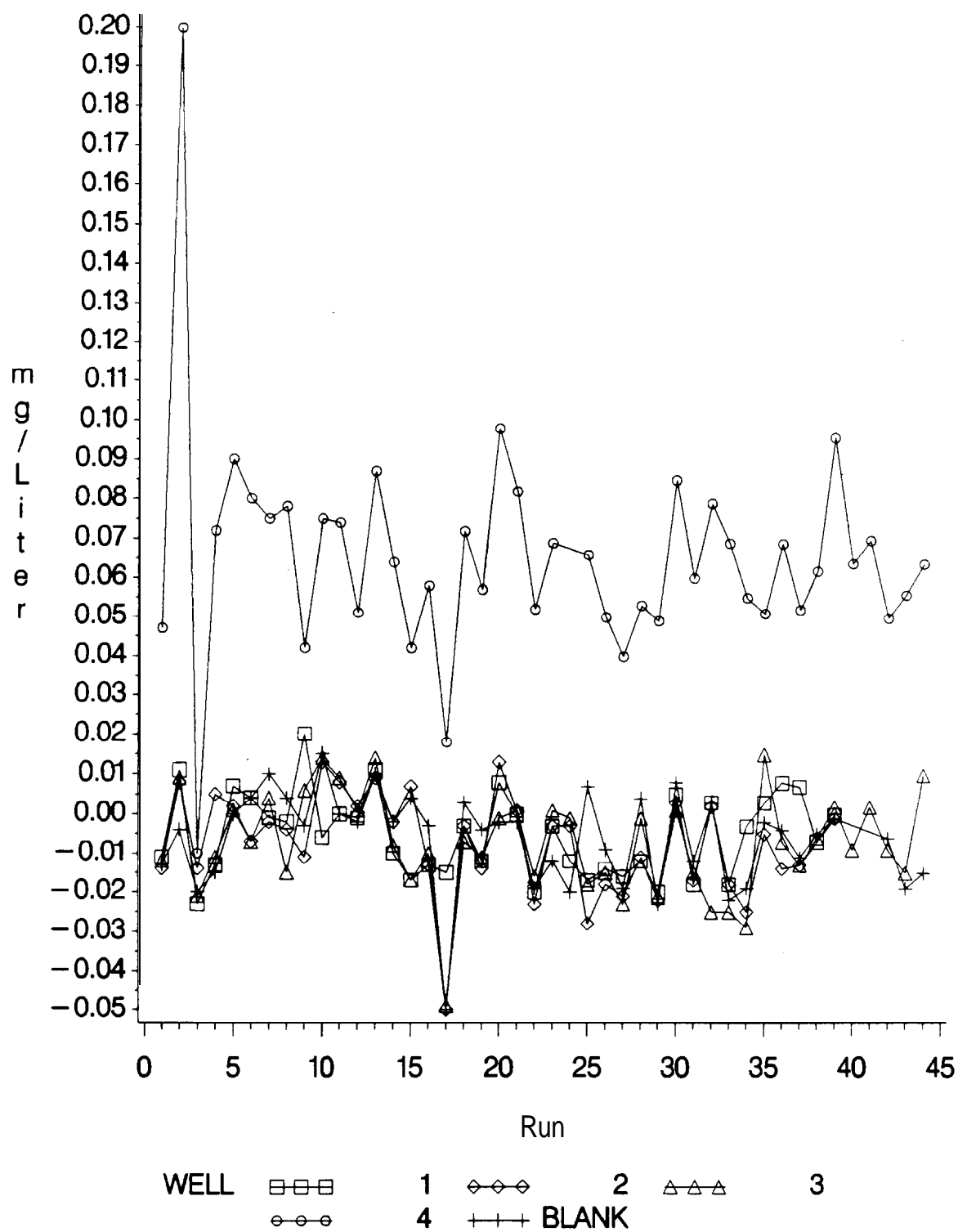
# Manganese



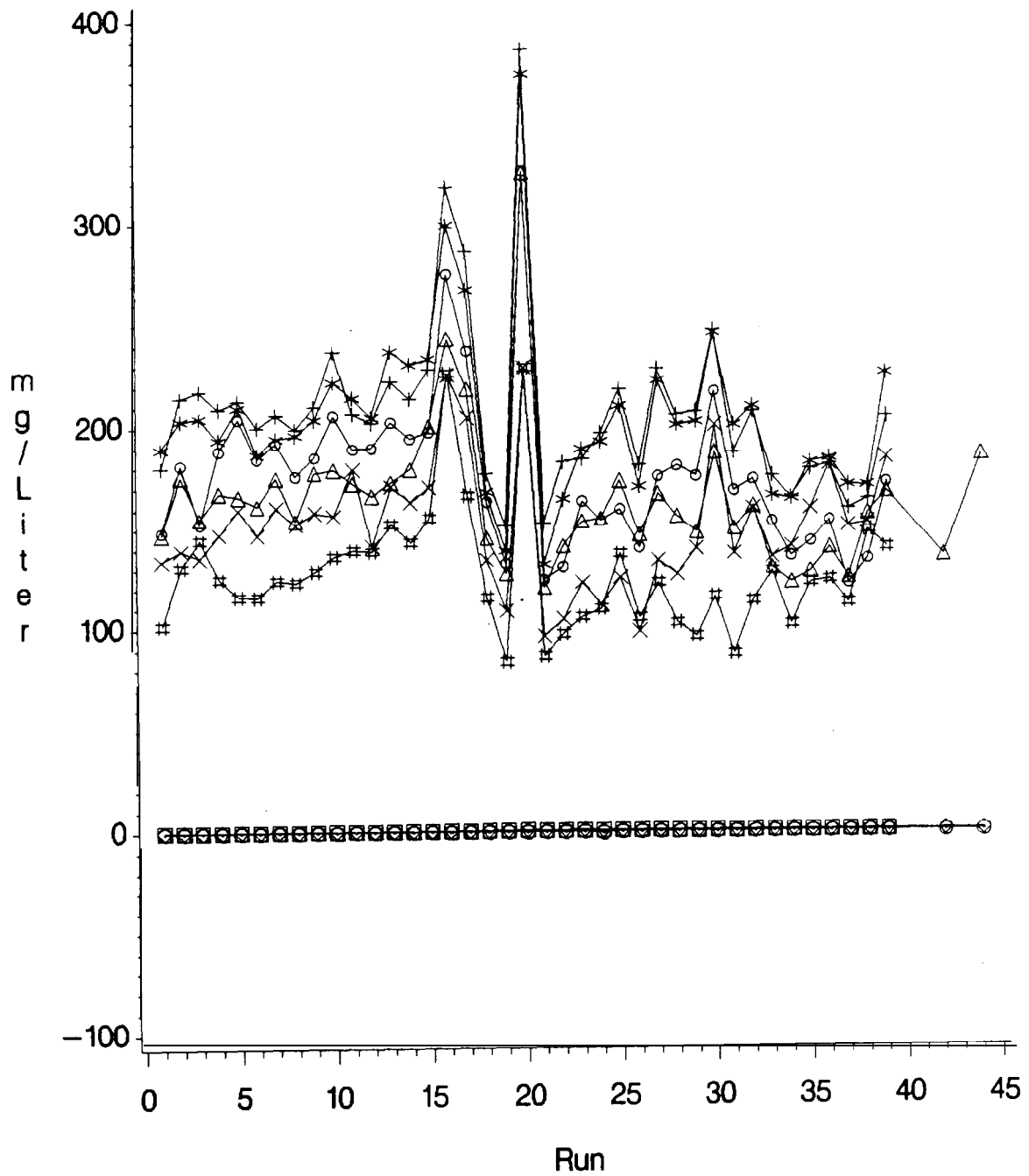
WELL	□□□	5	◇◇◇	6	△△△	8
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# Ammonia

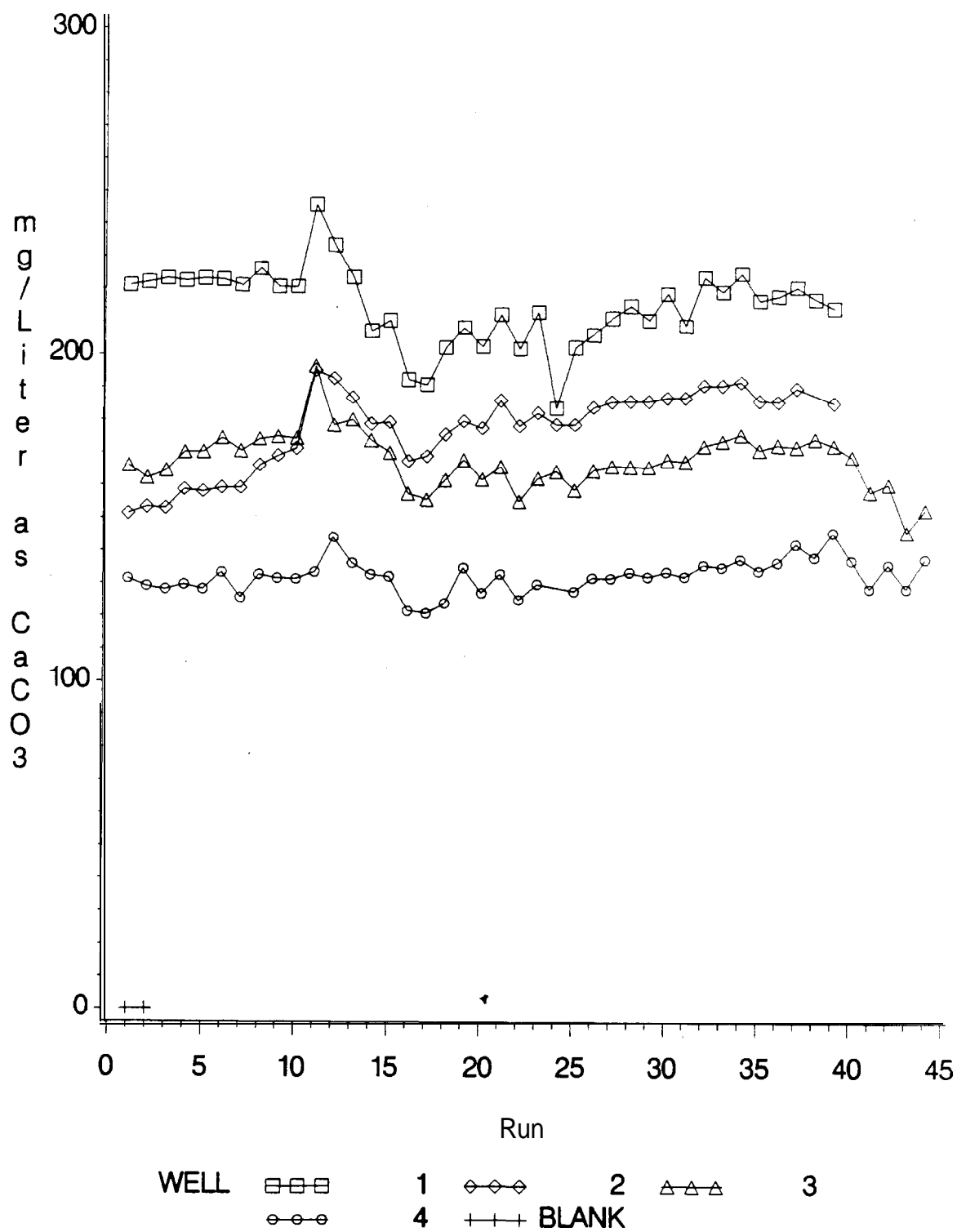


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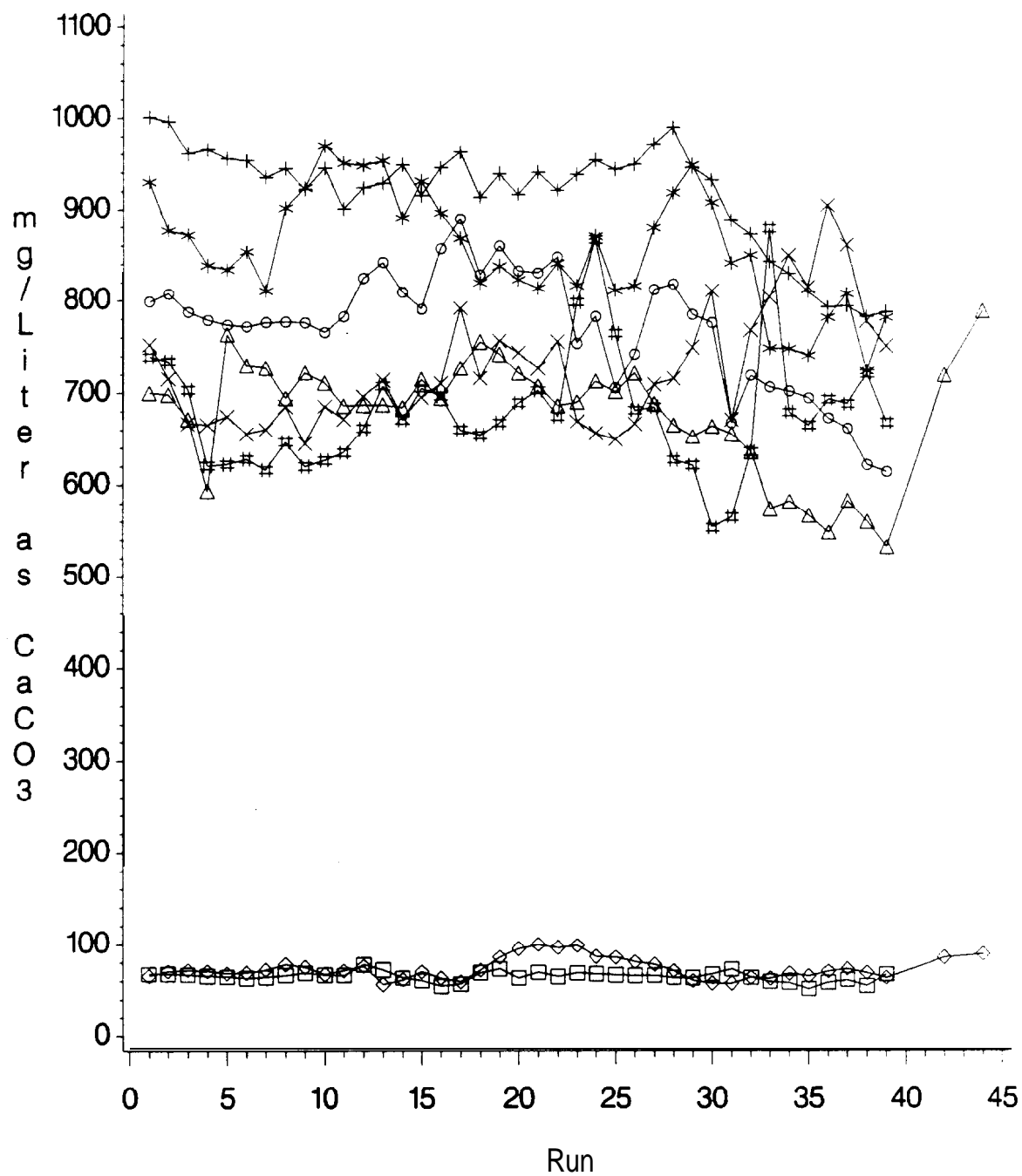


WELL	□ □ □	5	◇ ◇ ◇	6	△ △ △	8
	○ ○ ○	9	+ + +	10	× × ×	11
	* * *	12	# # #	13	○ ○ ○	BLANK

# Alkalinity

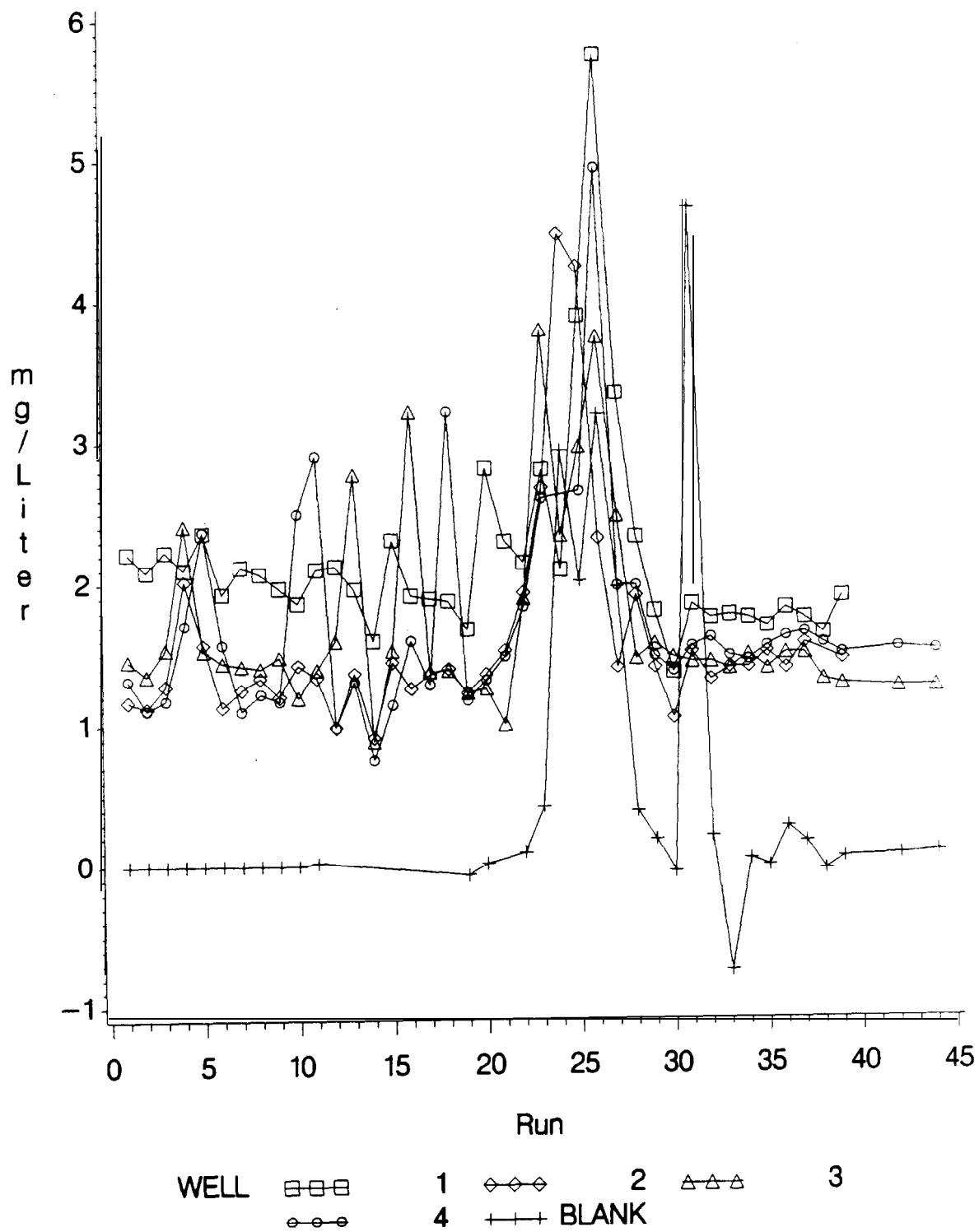


# Alkalinity

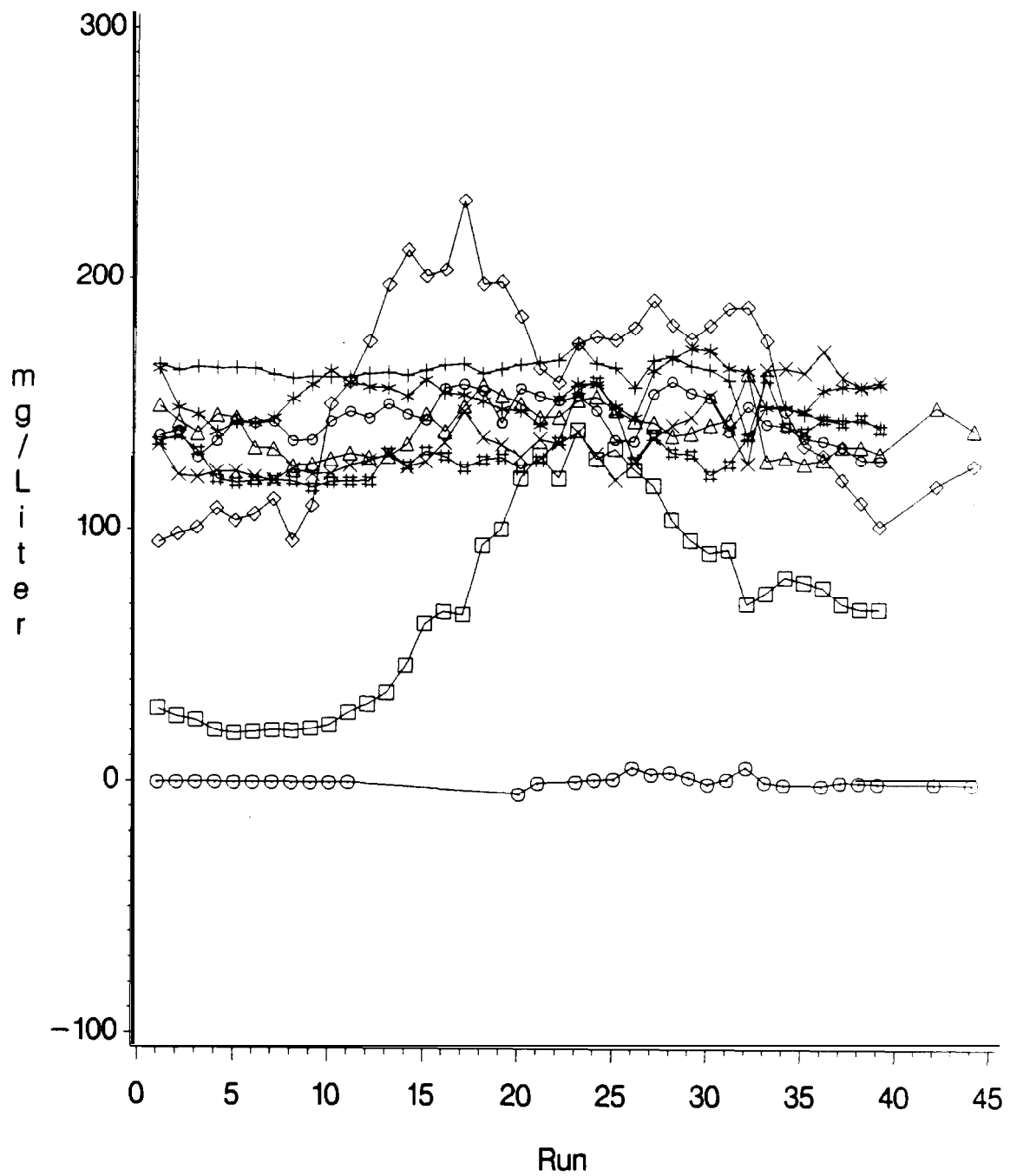


WELL	□ □ □	5	◇ ◇ ◇	6	△ △ △	8
	○ ○ ○	9	+ + +	10	× × ×	11
	* * *	12	# # #	13	○ ○ ○	BLANK

# Chloride

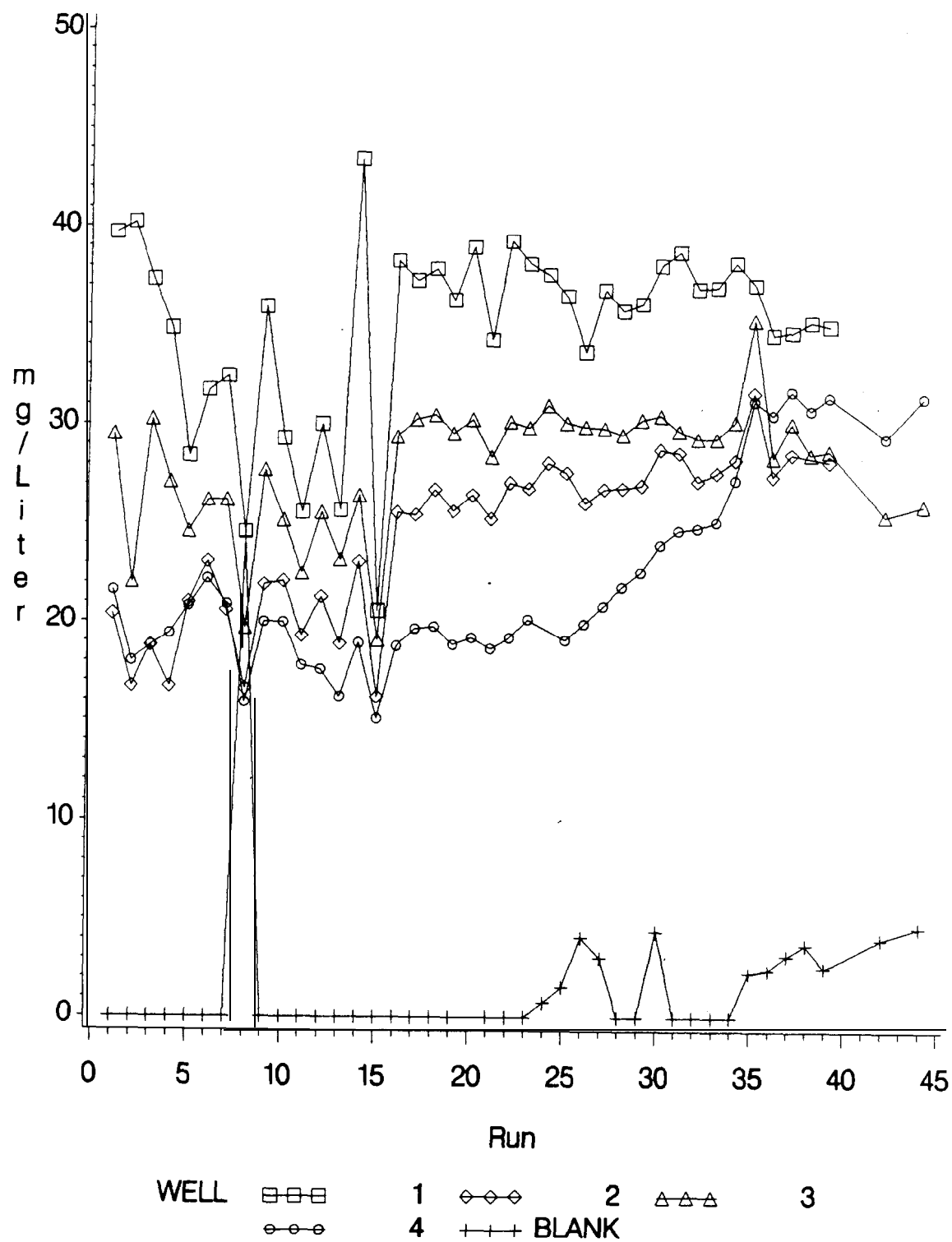


# Chloride

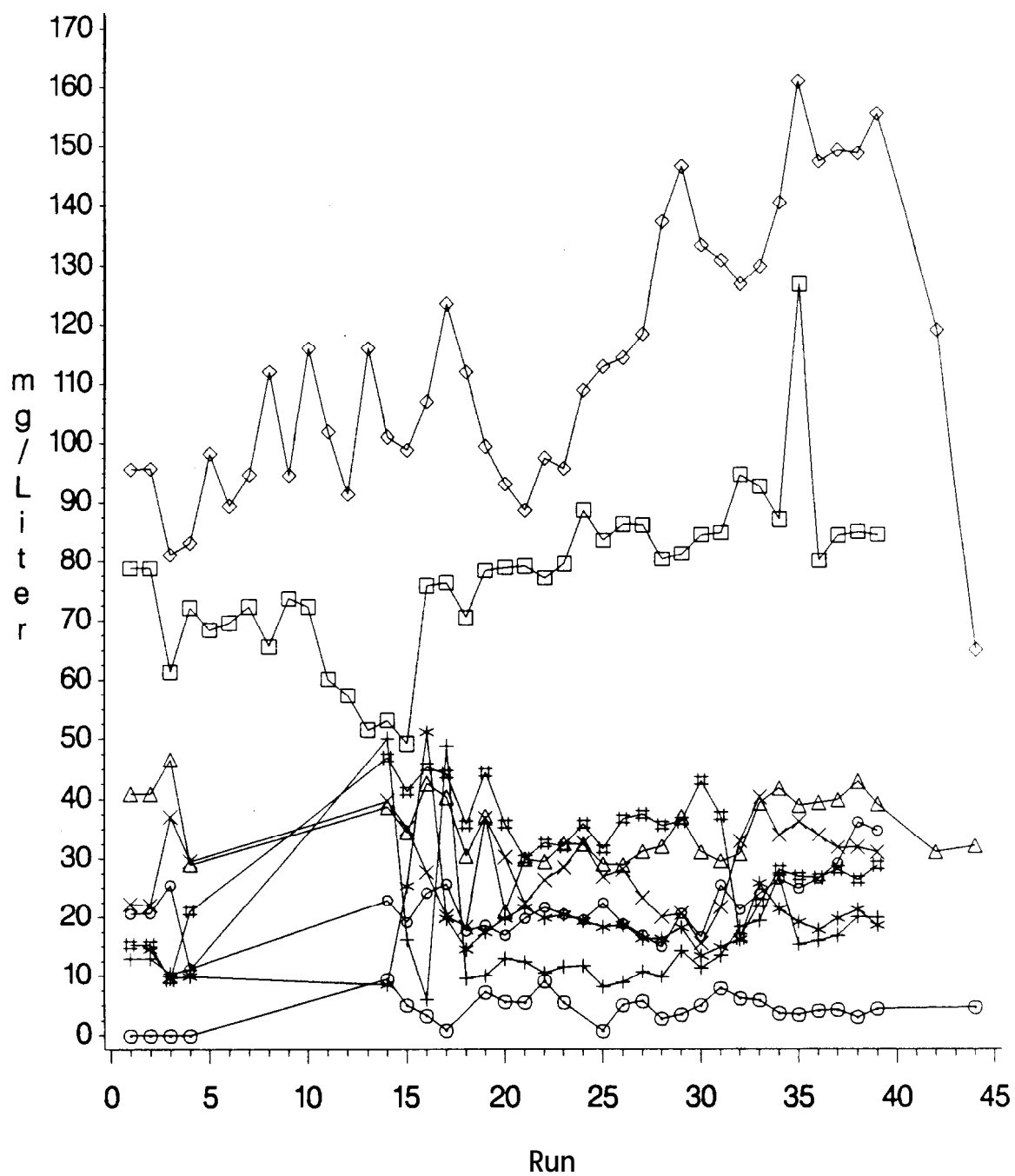


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	○-○-○	9	+ + +	10	* * *	11
	* * *	12	# # #	13	○-○-○	BLANK

# Sulfate



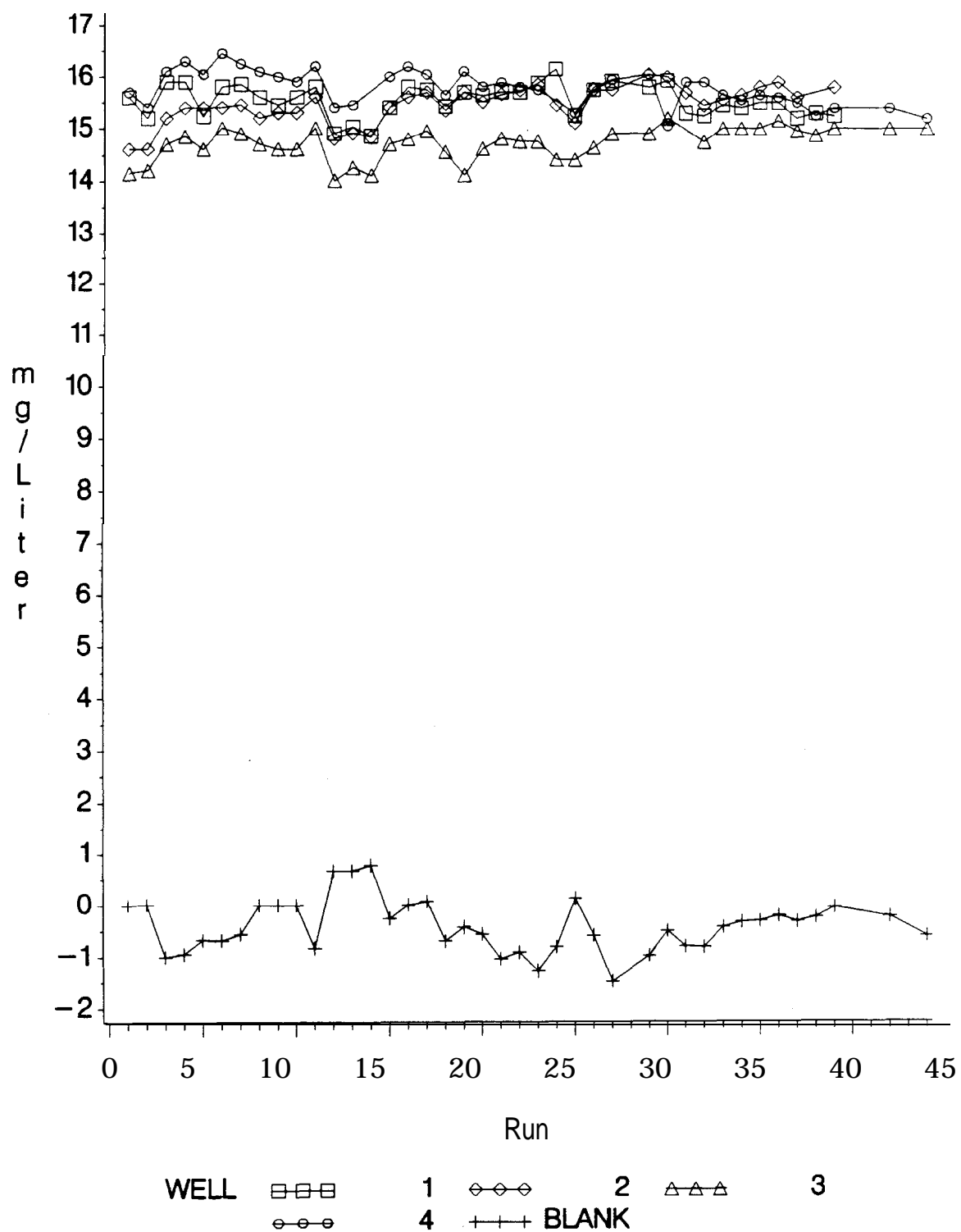
# Sulfate



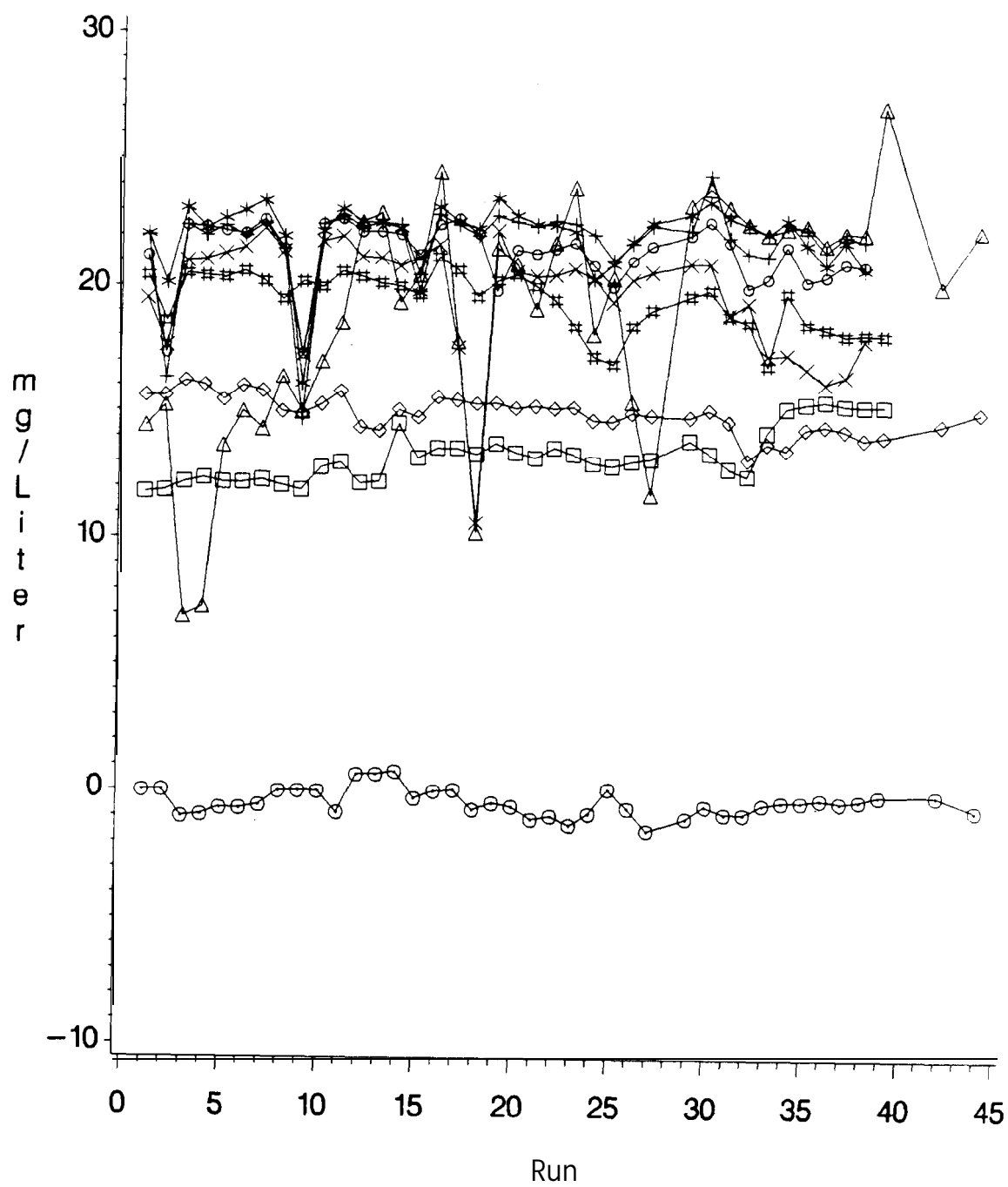
WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
	○-○-○	9	+ + +	10	× × ×	11
	* * *	12	# # #	13	○-○-○	BLANK



# Silica

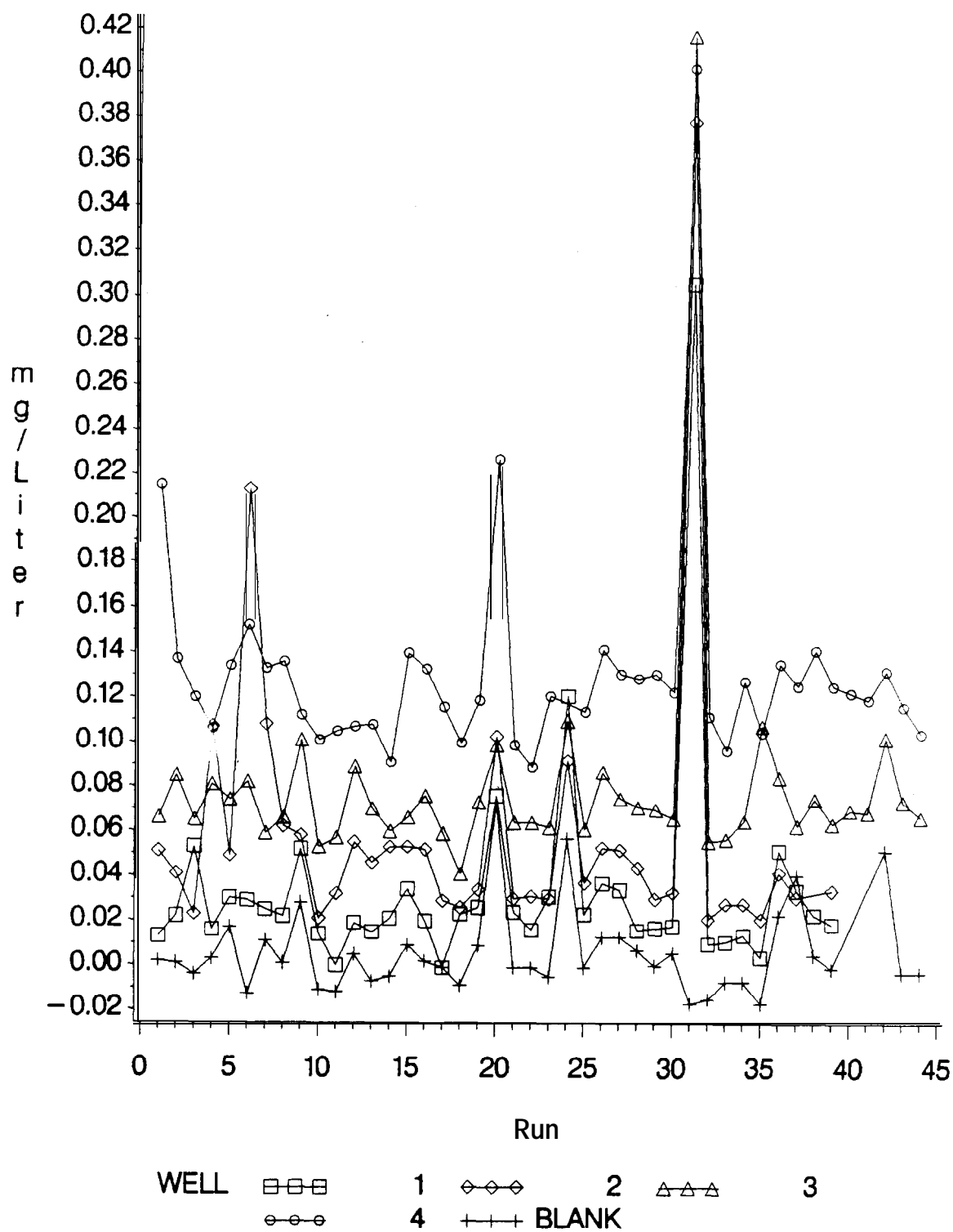


# Silica

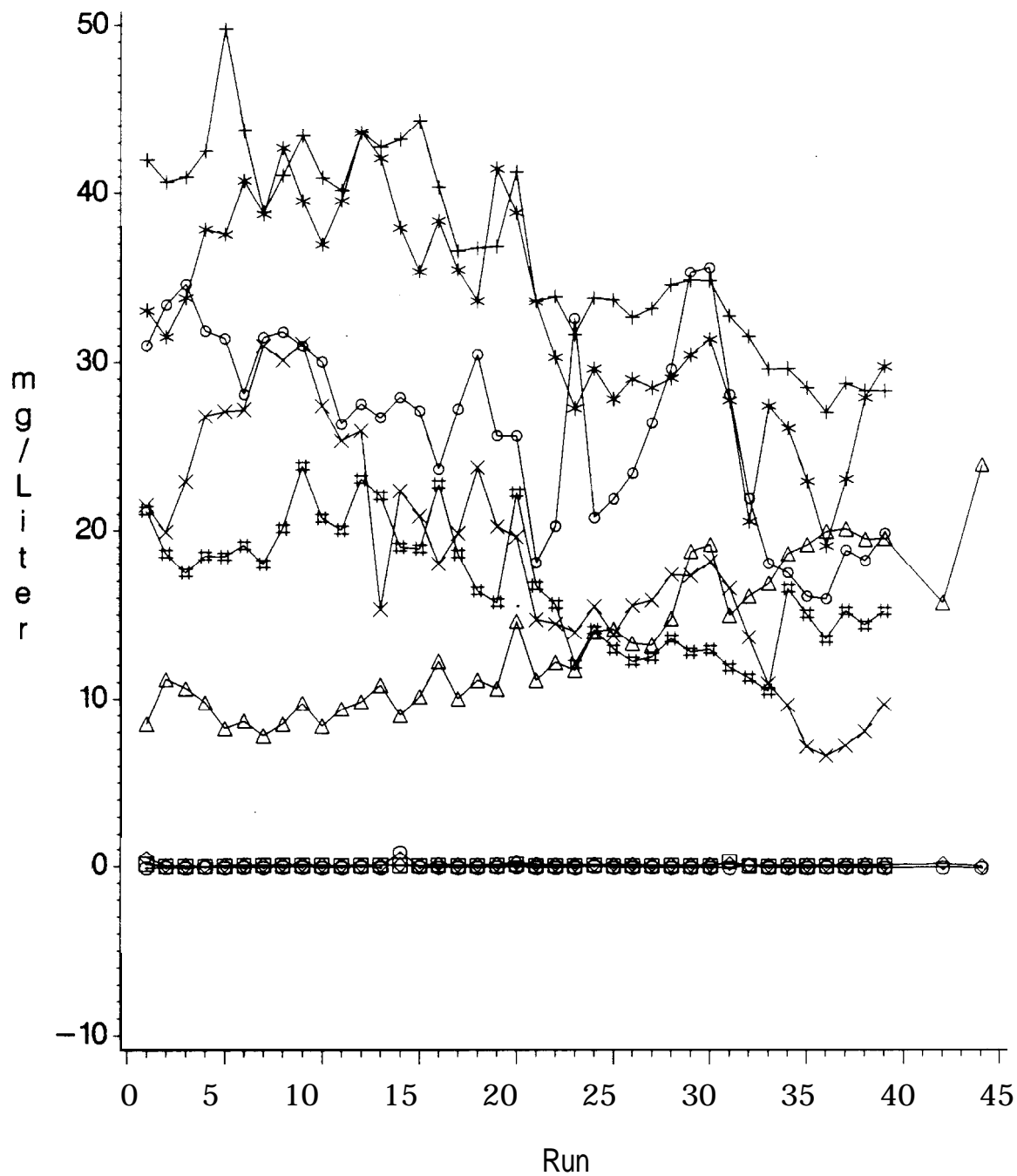


WELL	□□□	5	◇◇◇	6	△△△	8
	○-○-○	9	+ + +	10	×××	11
	*-*-*	12	###	13	○-○-○	BLANK

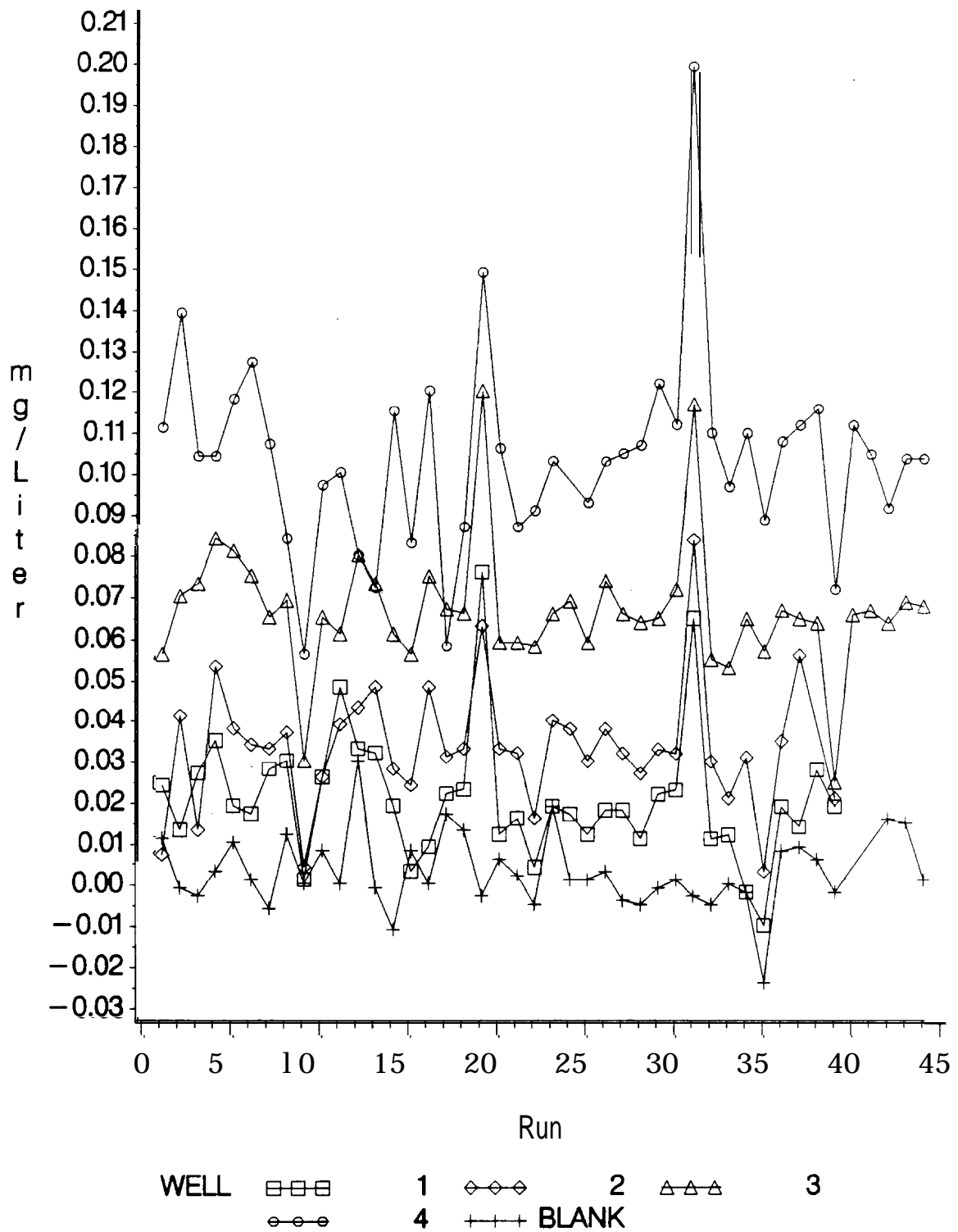
# Total Phosphate



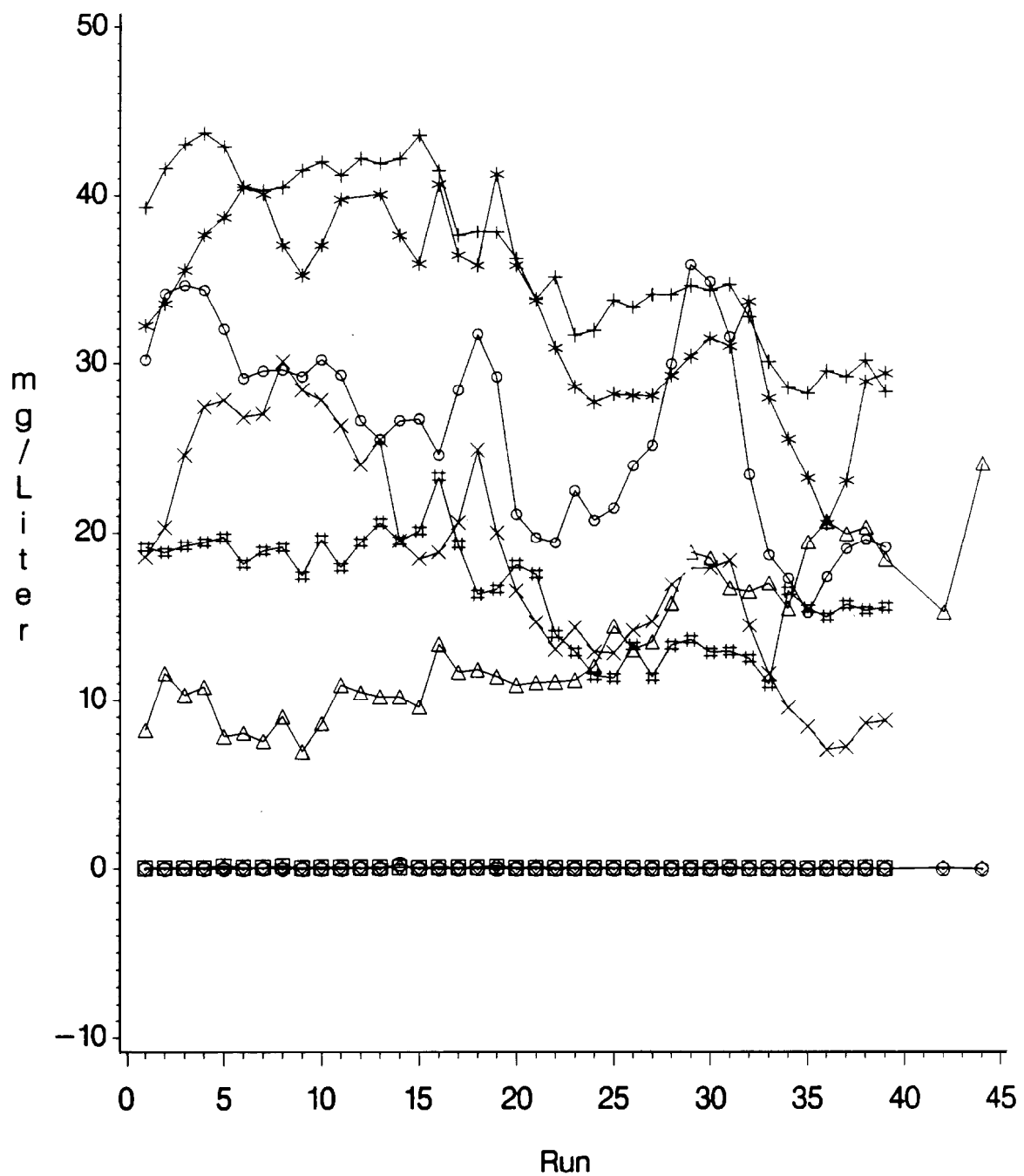
# Total Phosphate



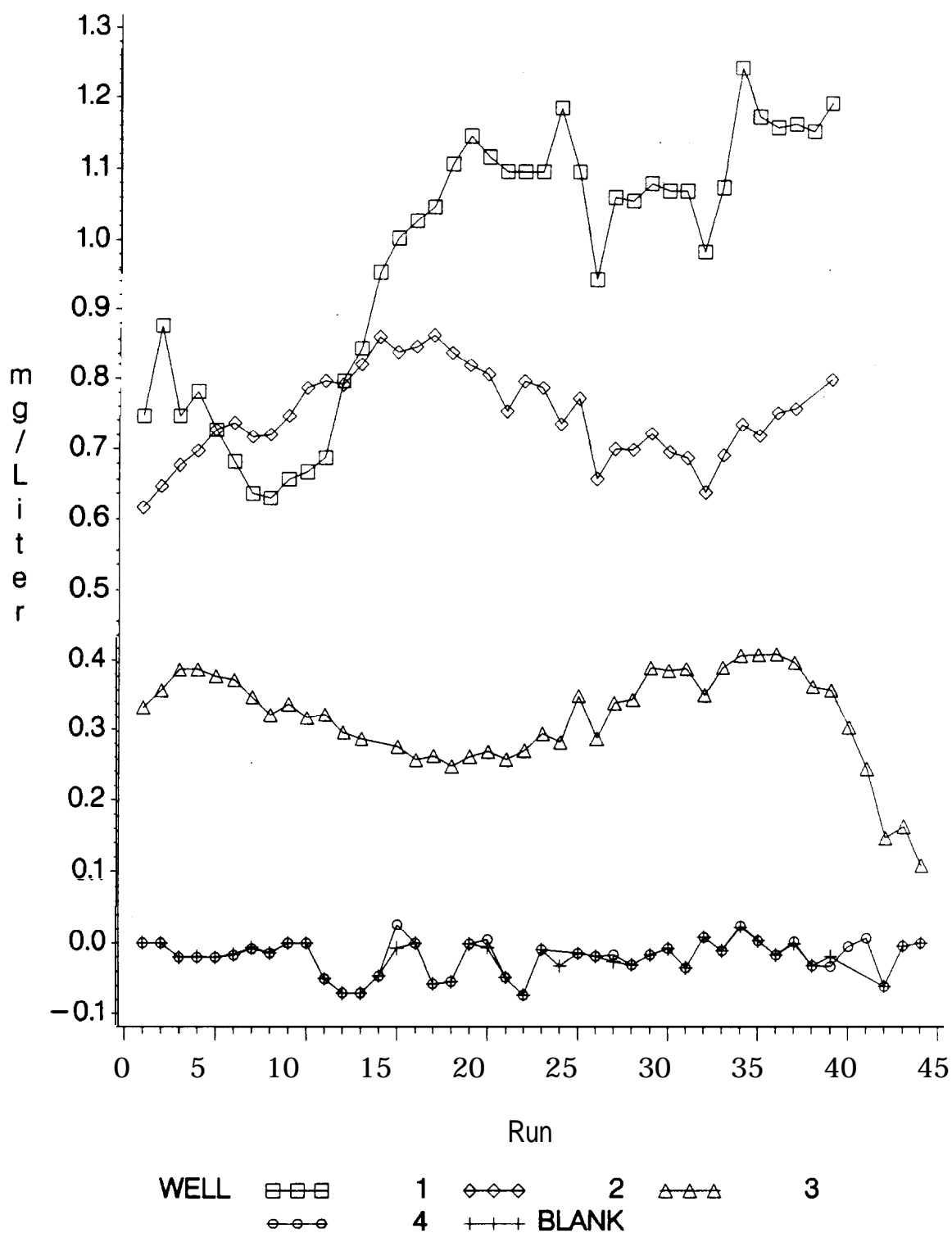
# ortho - Phosphate



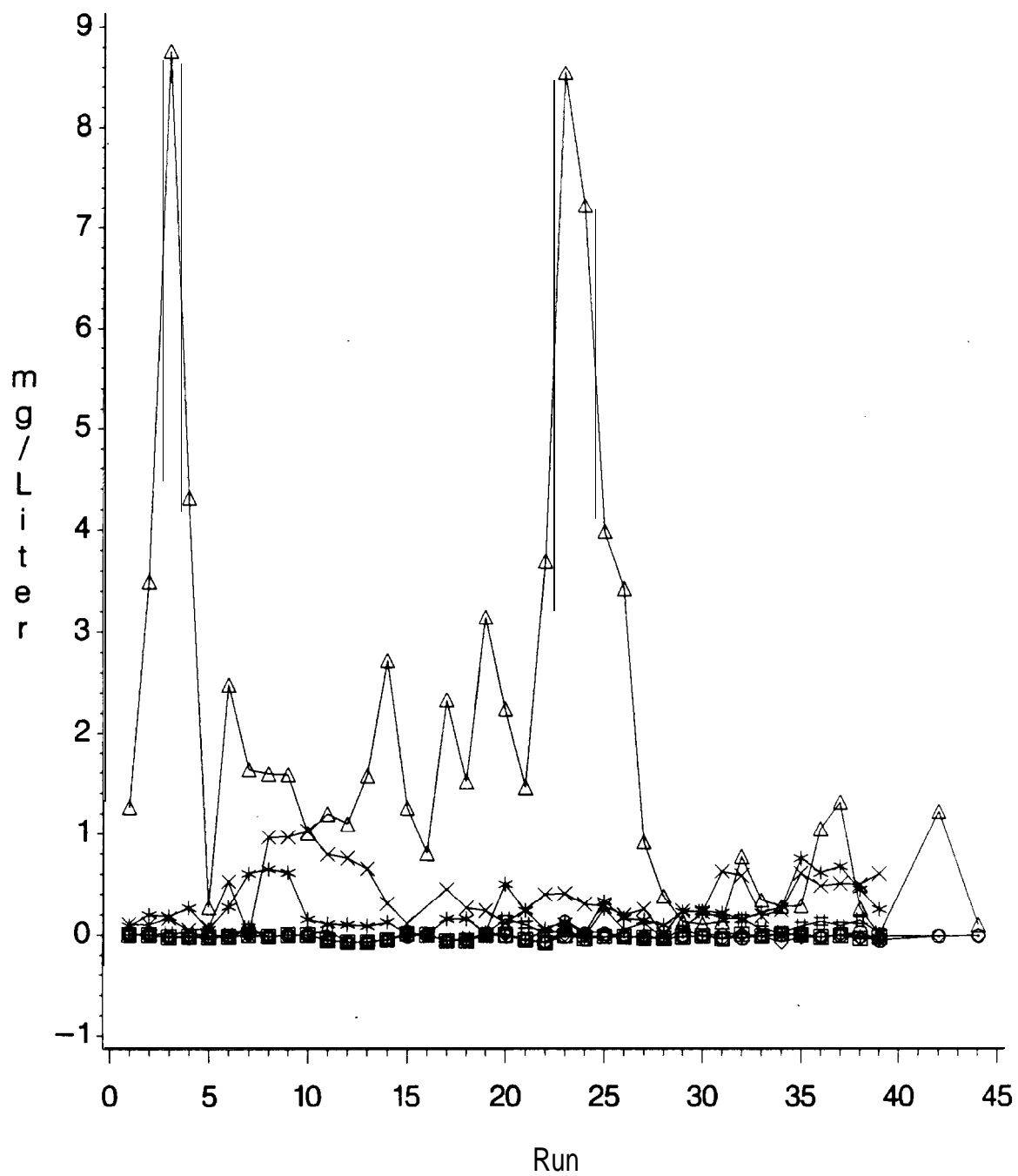
# ortho - Phosphate



# Nitrate + Nitrite Nitrogen



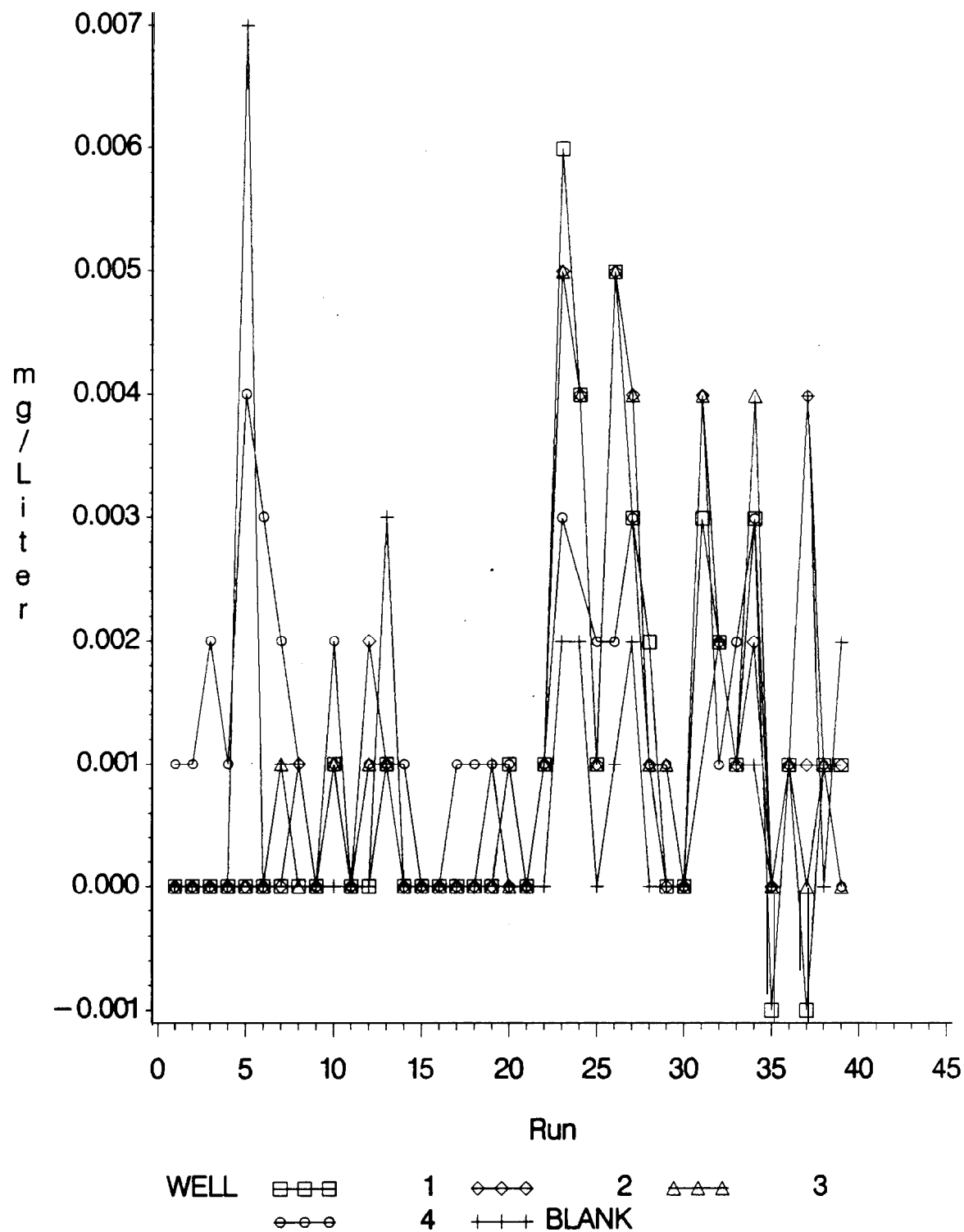
# Nitrate + Nitrite Nitrogen



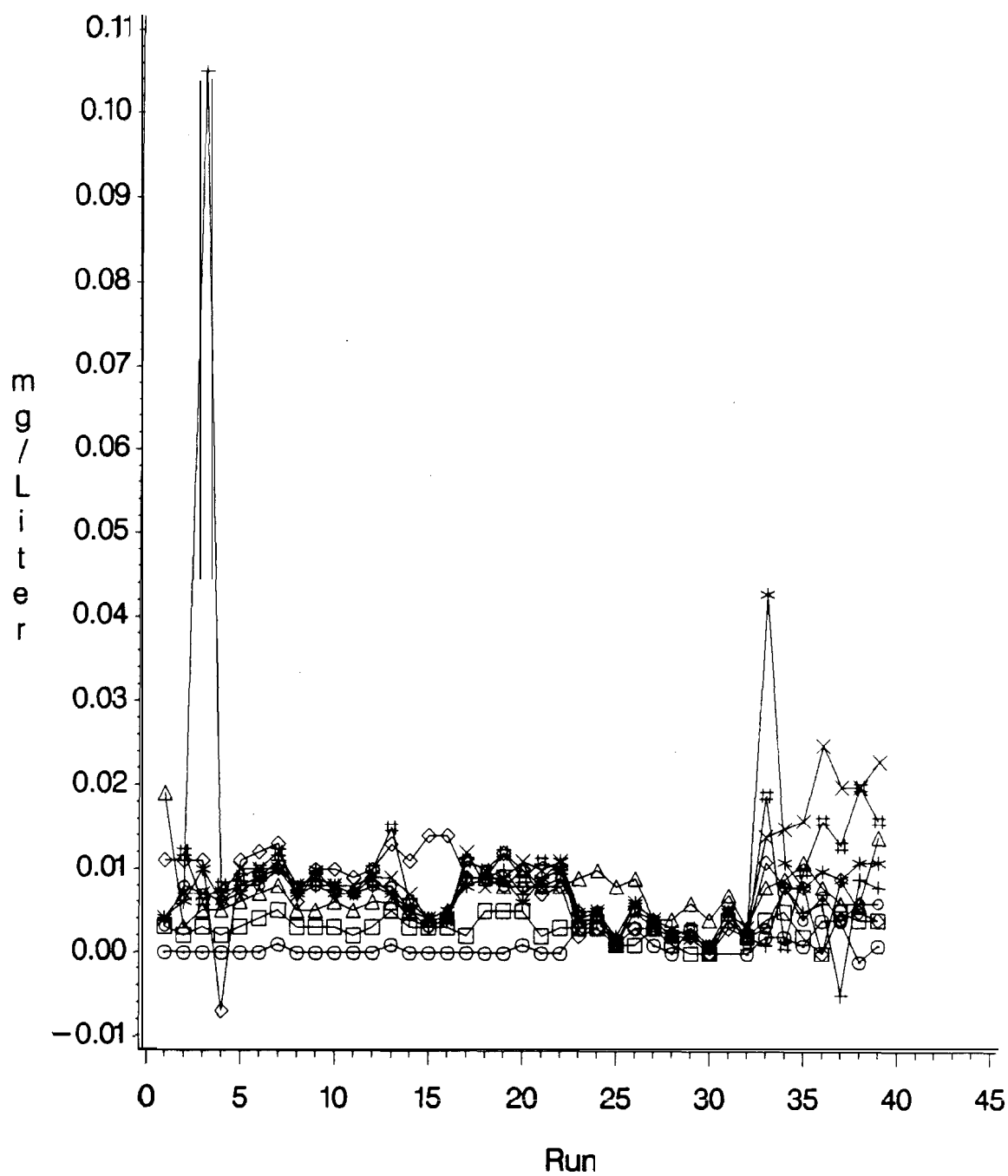
WELL	□□□	5	◇◇◇	6	△△△	8
	○-○-○	9	+ + +	10	×××	11
	* * *	12	##	13	○-○-○	BLANK



# Nitrite Nitrogen

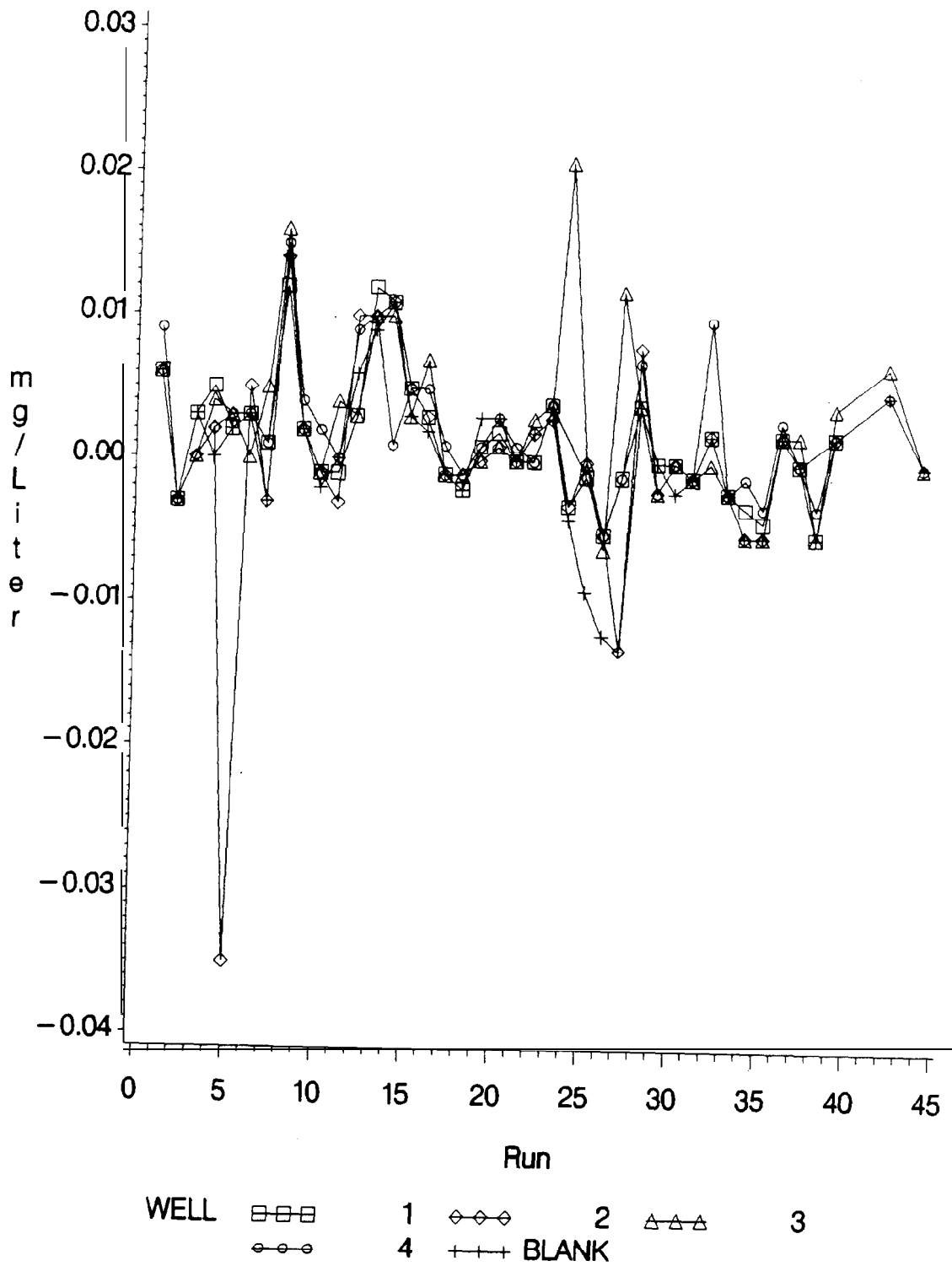


# Nitrite Nitrogen

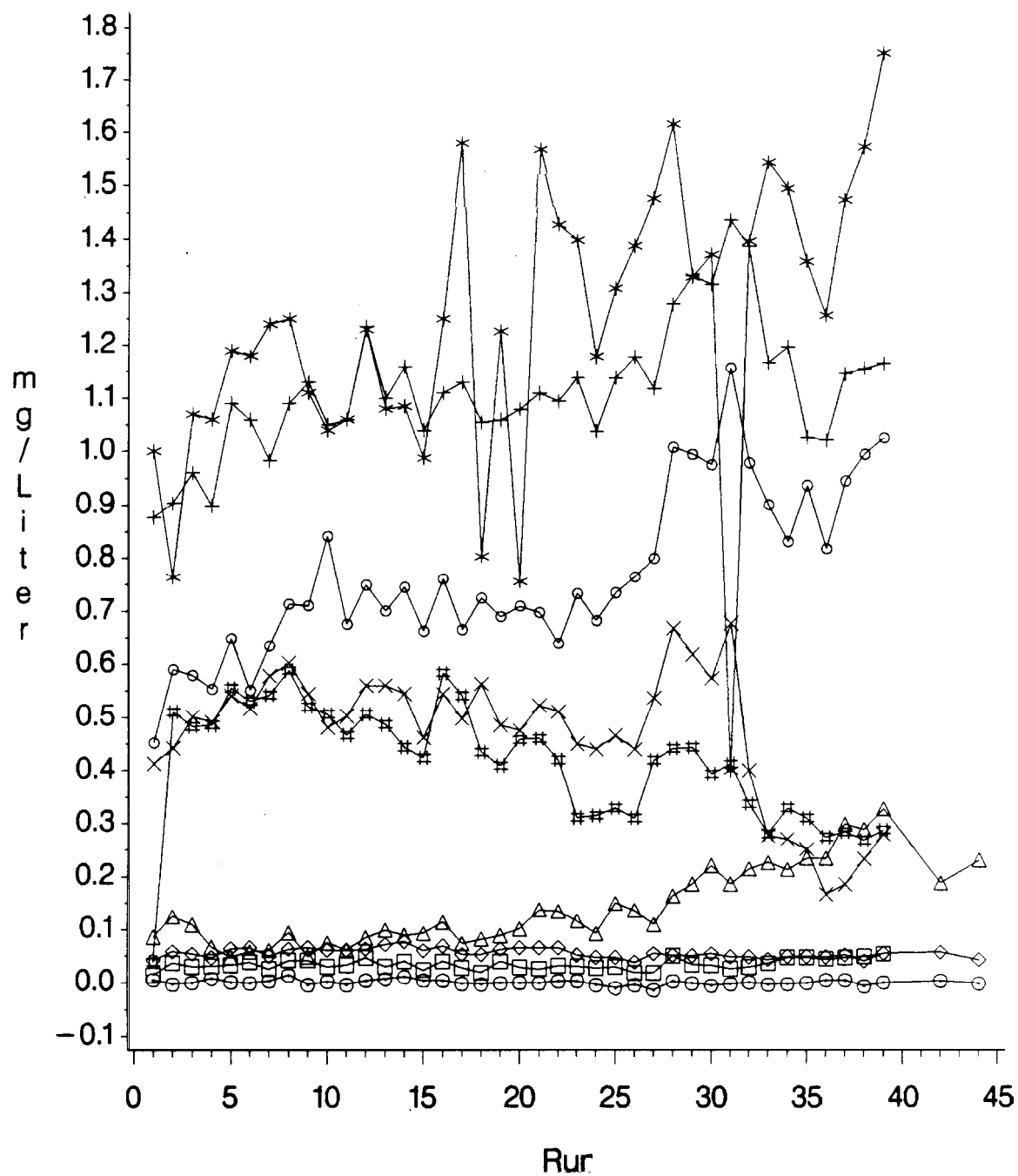


WELL	□□□	5	◇◇◇	6	△△△	8
	○—○	9	+—+	10	×××	11
	*—*	12	#—#	13	○—○	BLANK

# Sulfide

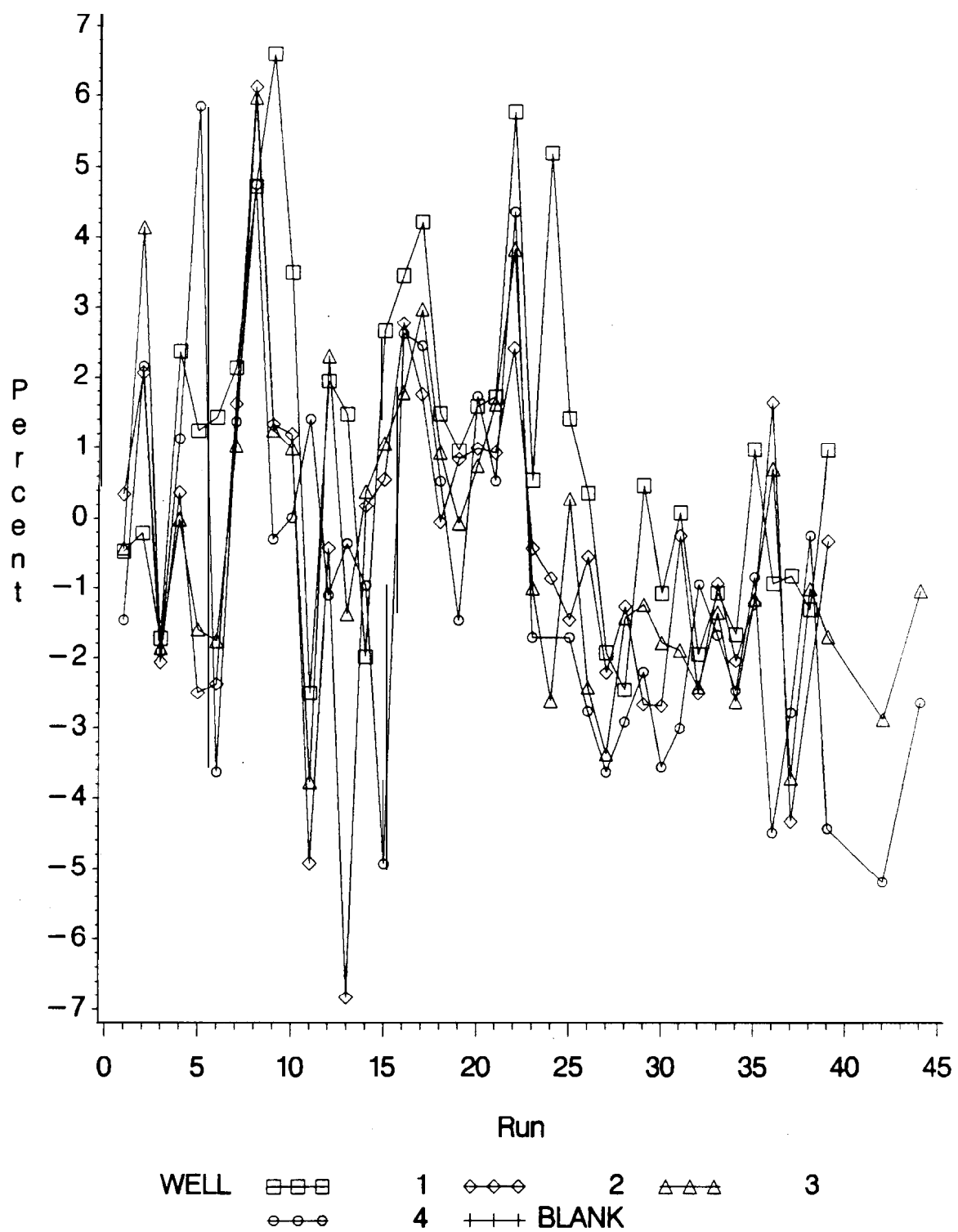


# Sulfide

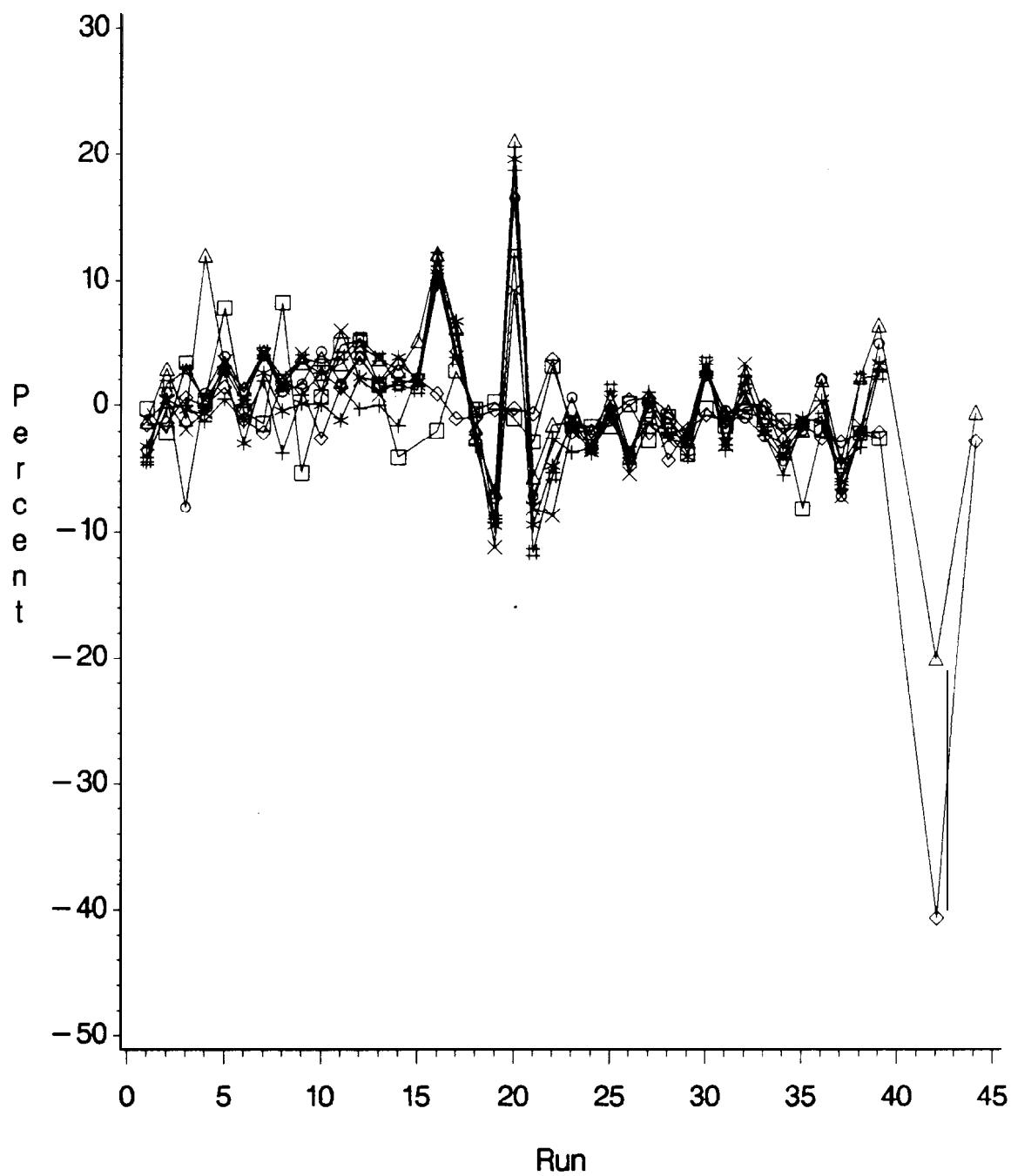


WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
	○-○-○	9	+--+	10	×-×-×	11
	*-*-*	12	#-#-#	13	○-○-○	BLANK

# Ion Balance Error

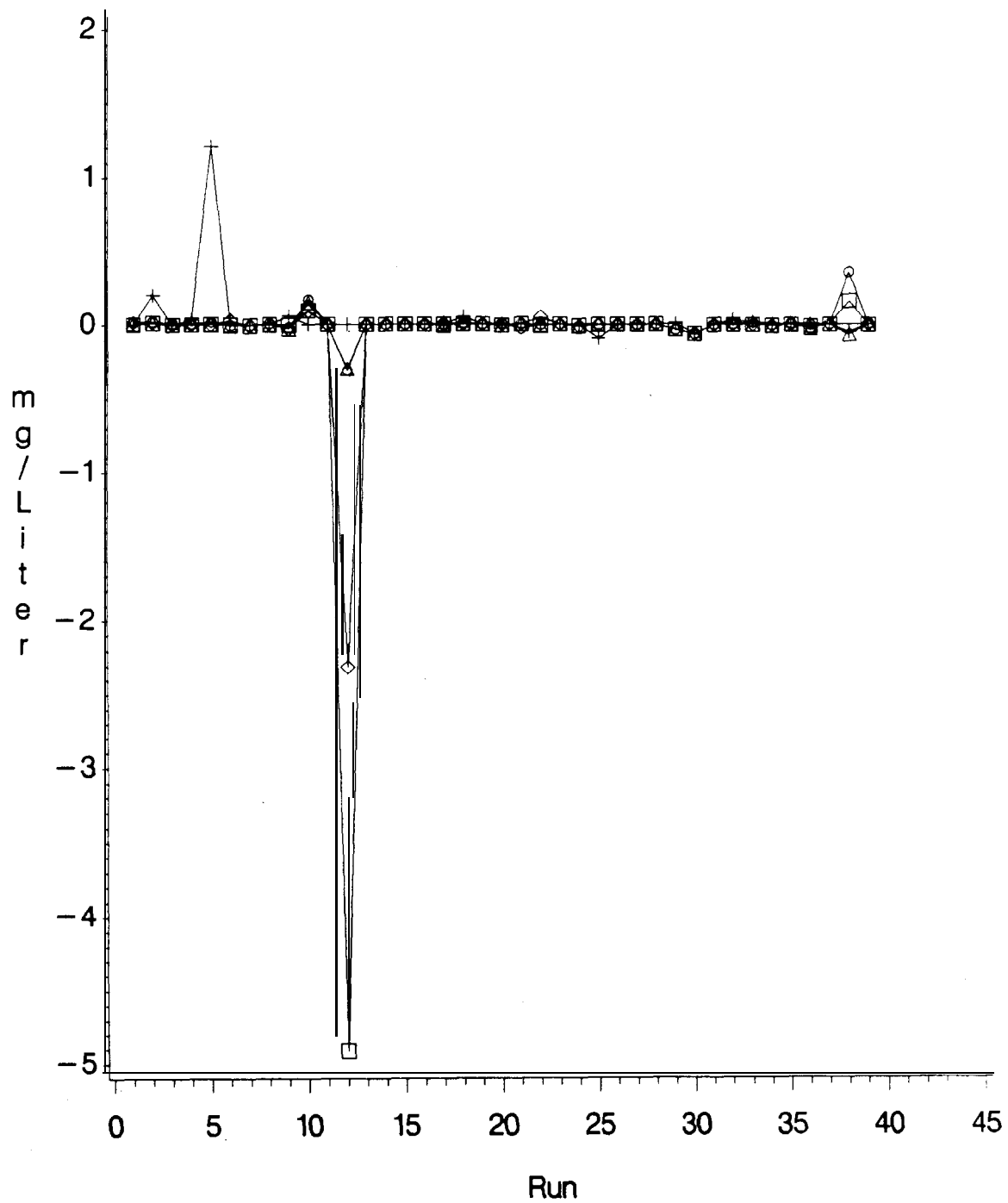


# Ion Balance Error



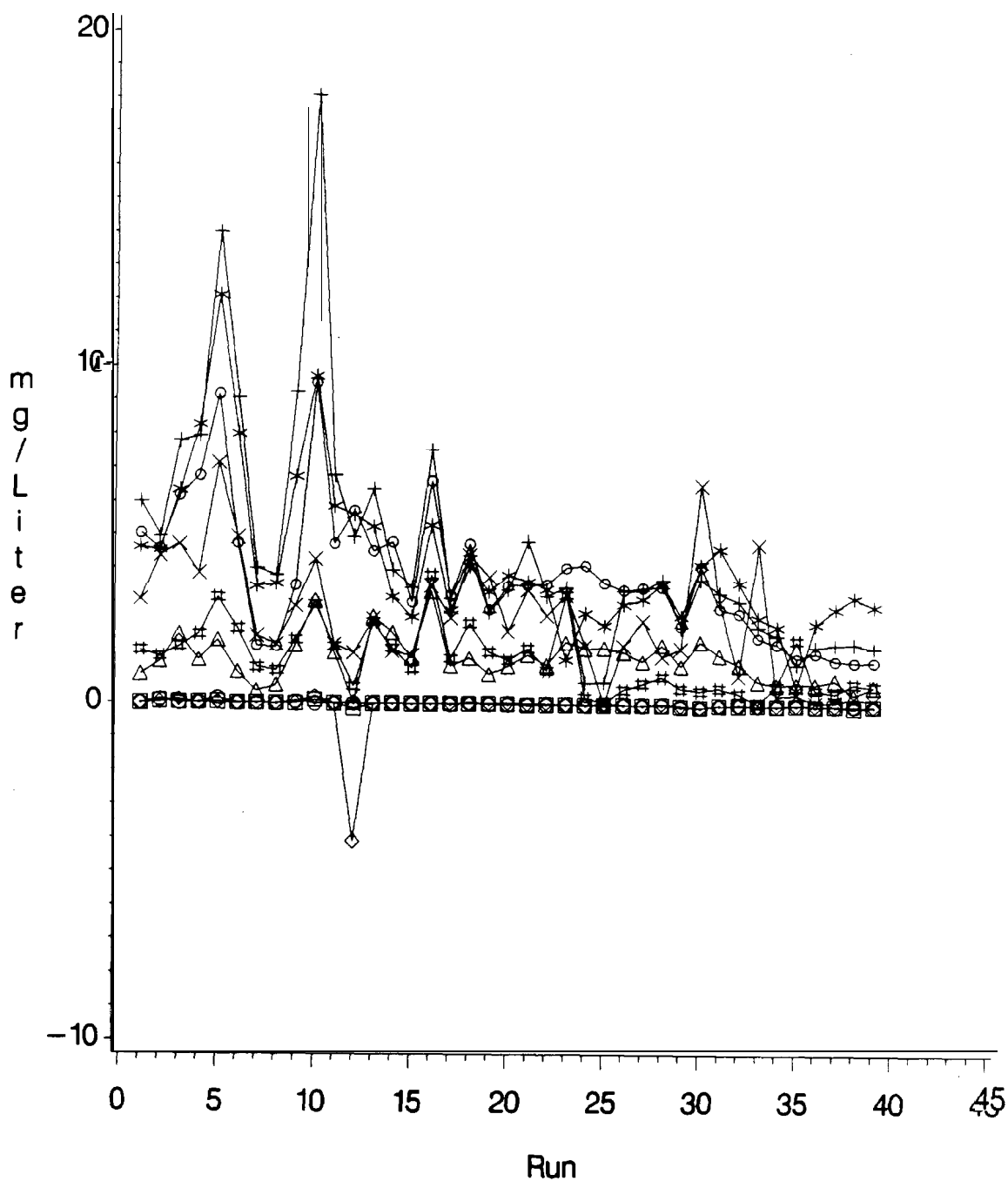
WELL	□ □ □	5	◇ ◇ ◇	6	△ △ △	8
	○ ○ ○	9	+ + +	10	× × ×	11
	* * *	12	# # #	13	⊖ ⊖ ⊖	BLANK

# Methane



WELL 1 2 3  
4 BLANK

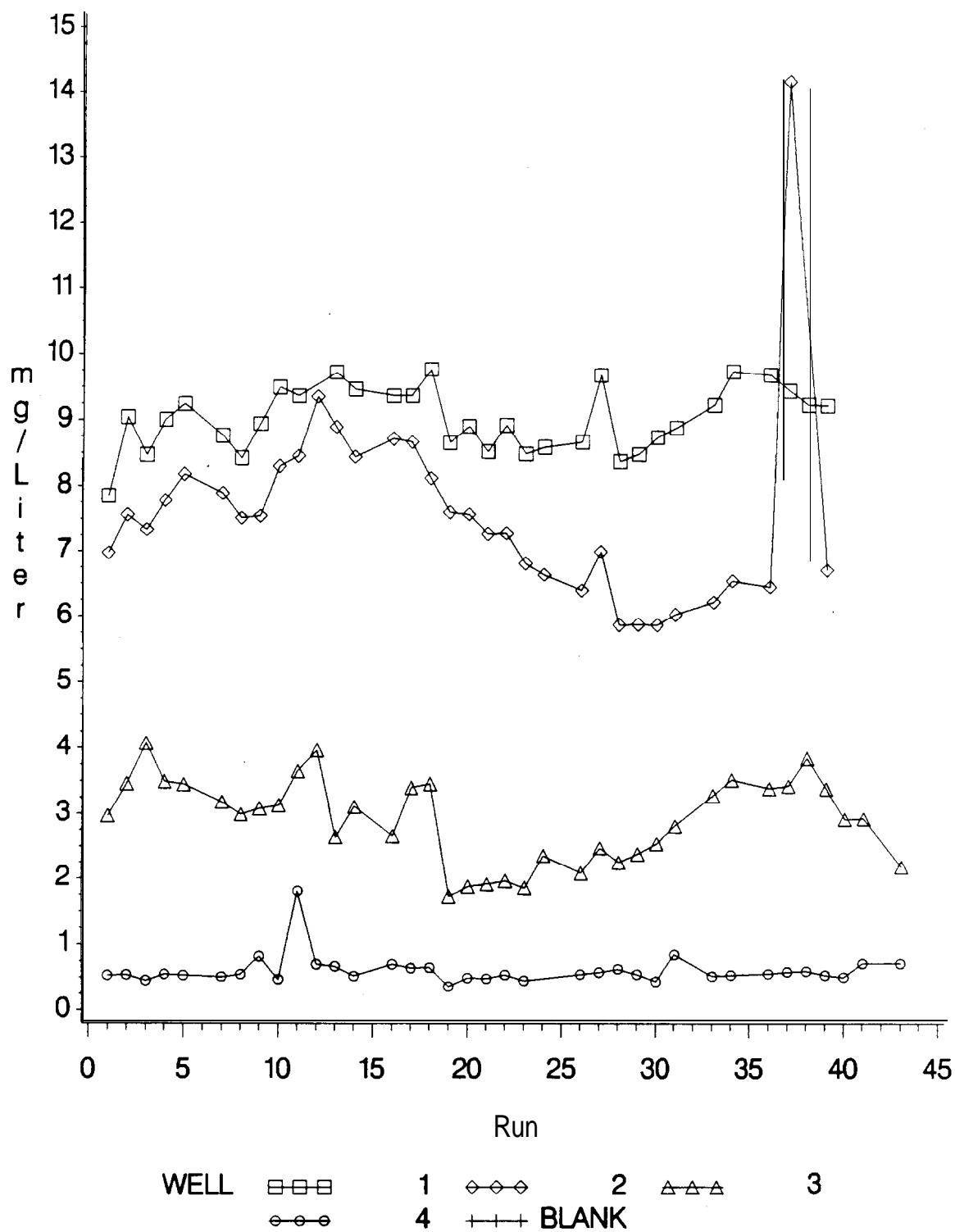
# Methane



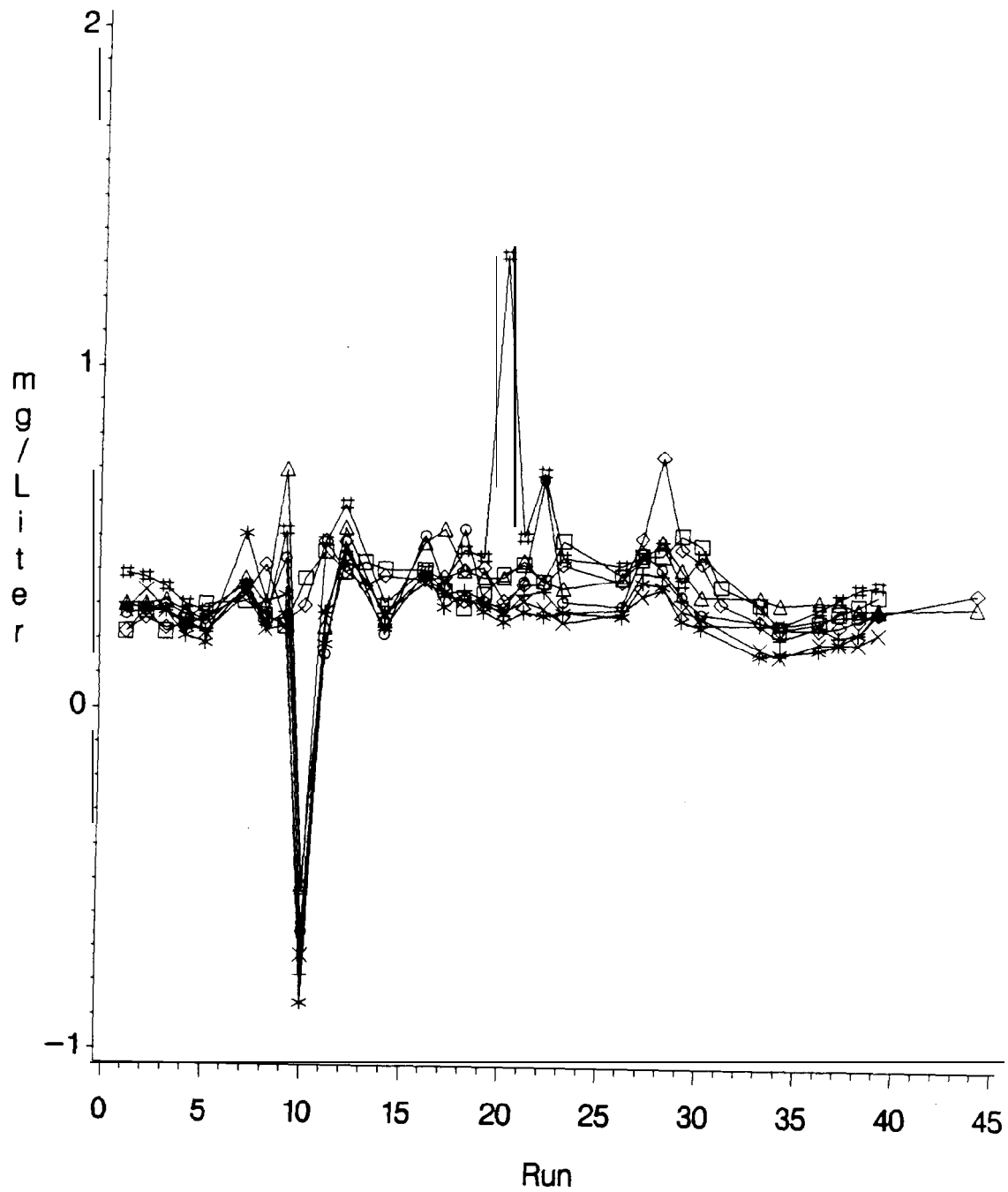
WELL		5		6		8
		9		10		11
		12		13		BLANK



# Probe Dissolved Oxygen

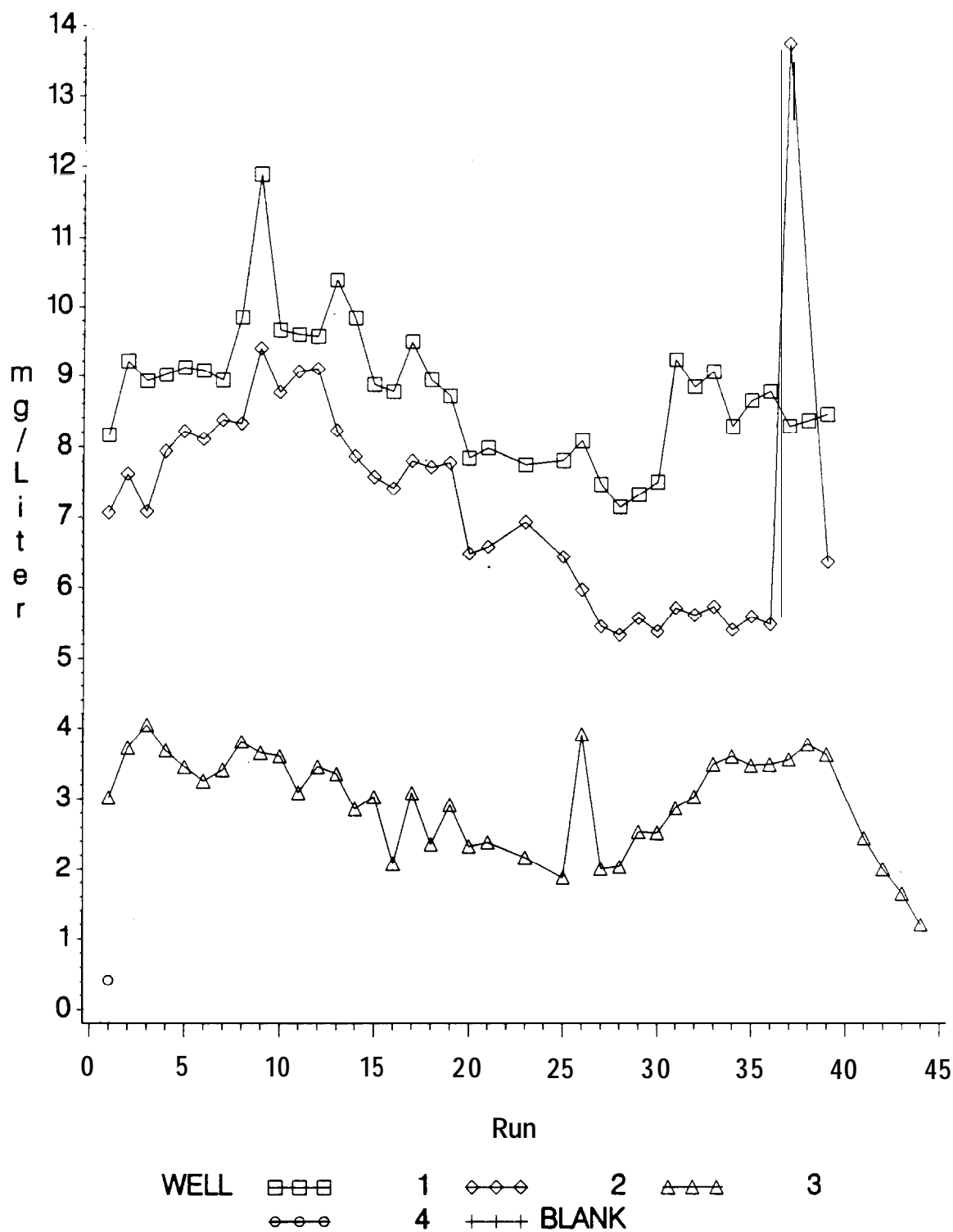


# Probe Dissolved Oxygen



WELL	□-□-□	5	◇-◇-◇	6	△-△-△	8
	○-○-○	9	+--+	10	×-×-×	11
	*-*-*	12	#-#-#	13	⊖-⊖-⊖	BLANK

# Winkler Dissolved Oxygen



## APPENDIX C

**GROUND WATER ELEVATIONS MEASURED DURING EACH BIWEEKLY SAMPLING RUN  
AT THE SAND RIDGE AND BEARDSTOWN SITES. (ELEVATIONS AT THE SAND RIDGE SITE  
ARE IN FEET RELATIVE TO AN ARBITRARY 1000 FOOT REFERENCE POINT.  
ELEVATIONS AT BEARDSTOWN ARE IN FEET RELATIVE TO MEAN SEA LEVEL.)**

**TABLE C-1. GROUND-WATER ELEVATIONS IN WELLS AND PIEZOMETERS AT SAND RIDGE**

SAMPLING DATE RUN		WELL NAME AND NUMBER						
NUMBER		D035 (#1)	D050 (#2)	D065 (#3)	D0105 (#6)	SRI	SR2	SR3
03/10/86	1	962.03	962.41	962.63	962.66	961.80	961.95	962.39
03/24/86	2	962.28	962.26	962.29	962.32	961.64	961.60	962.23
04/07/86	3	962.16	962.18	962.17	962.22	961.53	961.70	962.13
04/21/86	4	962.05	962.06	962.06	962.11	961.41	961.57	962.03
05/05/86	5	962.01	962.01	962.02	962.05	961.37	961.53	961.97
05/19/86	6	961.97	961.99	961.98	962.01	961.34	961.49	961.93
06/02/86	7	961.89	961.92	961.92	961.95	961.20	961.38	961.66
06/16/86	8	961.88	961.89	961.89	961.93	961.21	961.41	961.84
06/30/86	9	961.86	961.61	961.84	961.87	961.20	961.36	961.80
07/14/86	10	961.81	961.62	961.62	961.64	961.16	961.31	961.77
07/28/86	11	961.76	961.75	961.75	963.77	961.11	961.26	961.73
08/11/86	12	961.72	961.74	961.74	961.76	961.08	961.26	961.70
08/25/86	13	961.70	961.71	961.71	961.74	961.04	961.20	961.67
09/08/86	14	961.64	961.65	961.65	961.68	960.99	961.16	961.61
09/22/86	15	961.57	961.58	961.59	961.62	960.91	961.08	961.54
10/06/86	16	961.46	963.69	961.18	961.56	960.62	960.99	961.44
10/20/86	17	963.43	961.43	961.43	961.46	960.75	960.93	961.39
11/04/86	18	981.50	961.51	961.51	961.55	960.65	961.01	961.66
11/17/86	19	961.58	961.59	961.59	961.62	960.95	961.10	961.56
12/01/86	20	961.65	961.66	961.66	961.66	961.03	961.17	961.61
12/15/86	21	961.68	961.69	961.70	961.73	961.07	961.21	961.66
12/29/86	22	961.75	961.76	961.79	961.80	961.14	961.28	961.72
01/12/87	23	961.87	961.87	961.87	961.89	961.24	961.38	961.62
01/26/87	24	961.93	961.93	961.93	961.99	961.30	961.15	961.89
02/09/87	25	961.91	961.91	961.94	961.96	961.29	961.45	961.90
02/23/87	26	961.96	961.98	961.97		961.34	961.09	961.92
03/09/87	27	961.98	961.99	961.99	962.03	961.37	961.52	961.91
03/23/87	28	961.99	962.01	962.00	962.02	961.39	961.53	961.96
04/06/87	29	961.86	961.66	961.86	961.90	961.20	961.39	961.62
04/20/87	30	961.79	961.81	961.62	961.65	961.21	961.36	961.76
05/04/87	31	961.75	961.76	961.76	961.79	961.12	961.26	961.72
05/18/87	32	961.80	961.82	961.60	961.83	961.14	961.30	961.75
06/01/87	33	961.60	961.60	961.60	961.64	961.15	961.32	961.76
06/15/87	34	961.75	961.77	961.75	961.60	961.11	961.26	961.72
06/29/87	35	961.69	961.69	961.69	961.73	961.05	961.22	961.66
07/13/87	36	961.56	961.59	961.56	961.60	960.93	961.09	961.54
07/27/87	37	961.11	961.16	961.47	961.49	960.81	960.96	961.61
08/10/87	38	961.27	961.36	961.37	961.39	960.71	960.68	961.32
08/24/87	39	961.17	961.24	961.24	961.26	960.59	960.75	961.20

**TABLE C-2. GROUND-WATER ELEVATIONS IN BEARDSTOWN SAMPLING WELLS**

DATE	SAMPLING RUN NUMBER	SAMPLING WELL NAME AND NUMBER							
		BT18 (#5)	BT23 (#6)	BT25 (#8)	BT30 (#9)	BT35 (#10)	BS30 (#11)	BP30 (#12)	BT33 (#13)
03/11/86	1	444.45	444.41	443.39	443.38	443.35	443.37	443.39	443.50
03/25/86	2	444.16	444.12	443.26	443.23	443.20	443.24	443.26	443.34
04/08/86	3	443.93	443.90	443.06	443.04	443.00	443.05	443.06	443.15
04/22/86	4	443.84	443.80	442.97	442.95	442.91	442.95	442.97	443.05
05/06/86	5	443.66	443.62	442.80	442.78	442.75	442.78	442.79	442.90
05/20/86	6			442.59	442.56	442.54	442.58	442.59	442.69
06/03/86	7	443.55	443.49	442.54	442.58	442.54	442.60	442.59	442.71
06/17/86	8	443.94	443.87	442.84	442.82	442.79	442.82	442.83	442.93
07/01/86	9	443.51	443.46	442.59	442.58	442.57	442.57	442.59	442.70
07/15/86	10	444.71	444.66	443.53	443.50	443.47	443.50	443.50	443.62
07/29/86	11	445.16	445.10	443.80	443.78	443.77	443.79	443.80	443.92
08/12/86	12	444.42	444.38	443.47	443.45	443.41	443.46	443.48	443.59
08/26/86	13	443.74	443.69	442.94	442.91	442.88	442.91	442.93	443.00
09/09/86	14	443.29	443.25	442.48	442.45	442.44	442.46	442.48	442.55
09/23/86	15	443.68	443.61	442.65	442.62	442.61	442.64	442.66	442.74
10/07/86	16	445.45	445.41	444.37	444.34	444.30	444.35	444.36	444.45
10/21/86	17	445.24	445.20	444.27	444.26	444.23	444.26	444.27	444.37
11/05/86	18	445.74	445.67	444.65	444.63	444.58	444.62	444.64	444.72
11/18/86	19	445.08	445.03	444.18	444.16	444.11	444.16	444.17	444.25
12/02/86	20	445.34	445.28	444.28	444.24	444.23	444.26	444.28	444.37
12/16/86	21	444.86	444.81	444.03	444.01	443.98	444.02	444.04	444.11
12/30/86	22	444.69	444.65	443.91	443.88	443.87	443.89	443.91	443.97
01/13/87	23	444.41	444.28	443.54	443.62	443.60	443.63	443.64	443.71
01/27/87	24	444.36	444.31	443.57	443.54	443.53	443.56	443.58	443.66
02/10/87	25	444.72	444.67	443.78	443.75	443.73	443.76	443.77	443.86
02/24/87	26	444.27	444.20	443.40	443.39	443.36	443.40	443.41	443.49
03/10/87	27	443.97	443.94	443.16	443.12	443.10	443.12	443.14	443.23
03/24/87	28	444.07	444.04	443.19	443.16	443.15	443.18	443.19	443.27
04/07/87	29	444.19	444.17	443.37	443.34	443.32	443.35	443.37	443.45
04/21/87	30	444.43	444.40	443.57	443.54	443.52	443.54	443.56	443.65
05/05/87	31	444.27	444.23	443.40	443.37	443.34	443.38	443.39	443.49
05/19/87	32	444.14	444.06	443.23	443.20	443.17	443.21	443.22	443.31
06/02/87	33	443.95	443.90	443.04	443.02	442.98	443.01	443.03	443.14
06/16/87	34	443.70	443.66	442.81	442.78	442.76	442.80	442.81	442.90
06/30/87	35	443.29	443.24	442.41	442.39	442.36	442.39	442.41	442.56
07/14/87	36	442.94	442.90	442.05	442.04	442.01	442.03	442.04	442.14
07/28/87	37	442.41	442.37	441.48	441.46	441.44	441.46	441.48	441.57
08/11/87	38	442.03	442.00	441.05	441.03	441.00	441.03	441.05	441.18
08/25/87	39	441.76	441.73	440.78	440.76	440.72	440.75	440.78	440.89

TABLE C-3. GROUND-WATER ELEVATIONS IN BEARDSTOWN PIEZOMETERS

DATE	SAMPLING RUN NUMBER	PIEZOMETER NAME																	
		B1	B2.1	B2.2	B3.1	B3.2	B4	B5	B6.1	B6.2	B7	B8.1	B8.2	B8.3	WLR2.1	WLR2.2	W2	W9	W18
03/11/86	1	444.57	444.72	444.72	444.24	444.20	443.23	442.96	444.33	444.33	443.87	444.17	443.78		443.42	443.39	441.7	445.4	444.04
03/25/86	2	444.23	444.28	444.29	443.96	443.93	443.09	442.84	444.09	444.09	443.70	444.06	443.58		443.28	443.25	441.7	444.7	443.86
04/08/86	3	443.99	444.05	444.06	443.74	443.71	442.88	442.65	443.86	443.85	443.47	443.87	443.38		443.07	443.04	441.4	444.6	443.63
04/22/86	4	443.92	443.95	443.95	443.64	443.62	442.79	442.52	443.81	443.81	443.44	443.77	443.28		442.99	442.96	441.3	444.5	443.61
05/06/86	5	443.75	443.82	443.82	443.49	443.45	442.62	442.37	443.62	443.62	443.23	443.64	443.12		442.82	442.78	441.1	444.3	443.38
05/20/86	6	443.54	443.62	443.63	443.31	443.29	442.45	442.21	443.41	443.41	443.01	443.42	442.93		442.62	442.59	440.9	444.2	443.15
06/03/86	7	443.65	443.73	443.73	443.38	443.34	442.45	442.20	443.48	443.50	443.07	443.41	442.98		442.63	442.56	440.8	444.3	443.26
06/17/86	8	444.02	444.14	444.15	443.71	443.67	442.65	442.41	443.82	443.82	443.33	443.59	443.22		442.86	442.82	441.0	444.7	443.50
07/01/86	9	443.57	443.65	443.68	443.32	443.30	442.42	442.17	443.45	443.45	443.05	443.41	442.93		442.61	442.60	441.0	444.3	443.21
07/15/86	10	444.80	444.95	444.96	444.45	444.41	443.35	443.08	444.56	444.56	444.04	444.29	443.91		443.53	443.50	441.8	445.4	444.20
07/29/86	11	445.29	445.53	445.53	444.85	444.81	443.59	443.32	444.93	444.92	444.34	444.55	444.25		442.84	443.81	441.9	446.2	444.50
08/12/86	12	444.50	444.53	444.54	444.19	444.18	443.30	443.04	444.34	444.35	443.94	444.27	443.81		443.50	443.47	441.8	446.1	444.09
08/26/86	13	443.81	443.80	443.83	443.56	443.53	442.75	442.49	443.70	443.70	443.34	443.76	443.22		442.95	442.92	441.4	444.3	443.47
09/09/86	14	443.35	443.38	443.40	443.13	443.11	442.34	442.09	443.22	443.22	442.86	443.32	442.80		442.51	442.48	441.0	443.9	443.00
09/23/86	15	443.77	443.90	443.89	443.42	443.40	442.48	442.21	443.55	443.55	443.10	443.38	443.01		442.68	442.64	441.0	444.5	443.24
10/07/86	16	445.54	445.68	445.68	445.23	445.21	444.24	443.99	445.30	445.30	444.82	445.04	444.73		444.38	444.35	442.8	446.0	444.94
10/21/86	17	445.31	445.36	445.35	444.97	444.94	444.08	443.76	445.17	445.18	444.78	445.02	444.57		444.31	444.28	442.7	445.5	444.97
11/05/86	18	445.83	445.93	445.92	445.41	445.39	444.42	444.08	445.64	445.66	445.22	445.31	444.95		444.68	444.65	442.9	446.0	445.43
11/18/86	19	445.18	445.21	445.20	444.85	444.82	443.97	443.70	445.03	445.04	444.62	444.90	444.48		444.20	444.16	442.5	445.5	444.77
12/02/86	20	445.43	445.60	445.60	445.08	445.06	444.10	443.83	445.17	445.19	444.73	444.87	444.61		444.30	444.27	442.7	445.9	444.88
12/16/86	21	444.92	444.96	444.96	444.66	444.64	443.86	443.61	444.81	444.84	444.48	444.68	444.32		444.06	444.02	442.6	445.4	444.63
12/30/86	22	444.75	444.78	444.78	444.49	444.46	443.75	443.49	444.66	444.68	444.33	444.55	444.18		443.93	443.90	442.4	445.2	444.49
01/13/87	23	444.50	444.53	444.53	444.24	444.22	443.47	443.22	444.39	444.41	444.06	444.28	443.91		443.66	443.63	442.2	444.9	444.21
01/27/87	24	444.42	444.49	444.49	444.20	444.17	443.44	443.20	444.27	444.30	443.95	444.27	443.87		443.61	443.57	442.1	444.9	444.08
02/10/87	25	444.81	444.84	444.84	444.46	444.43	443.61	443.36	444.64	444.67	444.24	444.40	444.07		443.80	443.77	442.2	445.1	444.42
02/24/87	26	444.33	444.46	444.46	444.10	444.08	443.27	443.01	444.15	444.18	443.82	444.08	443.74		443.43	443.40	441.8	445.1	443.96
03/10/87	27	444.04	444.14	444.14	443.82	443.81	443.03	442.79	443.87	443.90	443.53	443.86	443.47		443.18	443.14	441.6	444.7	443.65
03/24/87	28	444.15	444.29	444.29	443.91	443.89	443.07	442.85	443.96	443.97	443.56	443.88	443.54		443.22	443.18	441.6	444.9	443.70
04/07/87	29	444.28	444.35	444.36	444.04	444.02	443.21	442.95	444.17	444.18	443.79	444.01	443.68	444.45	443.41	443.38	441.8	444.9	443.96
04/21/87	30	444.51	444.55	444.54	444.22	444.19	443.36	443.08	444.43	444.45	444.07	444.13	443.84	444.50	443.58	443.54	441.8	445.0	444.28
05/05/87	31	444.34	444.34	444.34	444.03	444.02	443.20	442.87	444.27	444.29	443.93	444.00	443.67	444.44	443.43	443.40	441.6	444.8	444.15
05/19/87	32	444.17	444.18	444.19	443.88	443.86	443.01	442.69	444.10	444.12	443.77	443.87	443.50	444.36	443.24	443.21	441.3	444.6	443.99
06/02/87	33	444.03	444.05	444.06	443.71	443.69	442.84	442.51	443.95	443.97	443.60	443.70	443.34	444.23	443.07	443.03	441.2	444.5	443.81
06/16/87	34	443.80	443.80	443.80	443.51	443.49	442.62	442.29	443.72	443.74	443.37	443.51	443.18	444.12	442.84	442.81	440.8	444.3	443.58
06/30/87	35	443.40	443.43	443.43	443.12	443.11	442.24	441.95	443.23	443.25	442.87	443.29	442.74	444.19	442.44	442.40	440.5	444.1	443.03
07/14/87	36	443.01	443.08	443.07	442.77	442.75	441.86	441.57	442.89	442.91	442.52	443.03	442.50	444.11	442.10	442.05	440.1		442.70
07/28/87	37	442.47	442.56	442.57	442.25	442.22	441.30	441.02	442.30	442.33	441.94	442.50	441.85	443.74	441.52	441.47	439.5		442.09
08/11/87	38	442.10	442.19	442.19	441.84	441.82	440.86	440.55	441.93	441.95	441.54	442.24	441.46	444.00	441.11	441.05	439.1	442.8	441.70
08/25/87	39	441.83	441.94	441.95	441.58	441.56	440.58	440.29	441.64	441.66	441.23	442.05	441.17	443.87	440.82	440.77	438.9	442.7	441.38

