

Chloroform Contamination in Part of the Alluvial Aquifer, Southwest Louisville, Kentucky

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Prepared in cooperation
with the
U.S. Environmental Protection Agency

U.S. GEOLOGICAL SURVEY WATER-SUPPLY PAPER 2202

UNITED STATES DEPARTMENT OF THE INTERIOR

JAMES G. WATT, Secretary

GEOLOGICAL SURVEY

Dallas L. Peck, Director



UNITED STATES GOVERNMENT PRINTING OFFICE 1983

Library of Congress Cataloging in Publication Data

Davis, R. W. (Robert W.), 1927-

Chloroform contamination in part of the alluvial aquifer,
southwest Louisville, Kentucky

(Geological Survey water-supply paper ; 2202)

Bibliography: p.

Supt. of Docs. no: I 19.13:2202

1. Water, Underground—Pollution—Kentucky—Louisville.
2. Chloroform. I. Matthews, Edward W. II. United States. Environmental Protection Agency. III. Title. IV. Series.

TD225.L8D38 628.1'6836

82-600106

AACR2

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Abstract

A well in the Ohio River alluvium at Louisville, Ky., has been yielding water with chloroform concentrations as high as 34.80 mg/L since July 1975. A spill of 5,000 gallons of chloroform in 1970, 120 feet from the well, is probably the source of the contamination. The chloroform is adsorbed in the unsaturated zone in the alluvium; the greatest concentrations are presently at and slightly above the water table. Lesser amounts of carbon tetrachloride are found with the chloroform. Its source is unknown.

The two contaminants were above the water table in the alluvium until a long-term trend of rising groundwater levels caused water to reach the contaminants and the water-chloroform mixture began moving downgradient to the well. High river stages cause a seasonal cycle of water-level rise, generally in late spring and midsummer; the ground water comes in contact with more chloroform, and the chloroform concentration of the well water increases. No carbon tetrachloride has been observed in the well water.

INTRODUCTION

Chloroform, CHCl_3 , is not a naturally occurring substance, and its presence in either surface or ground water is attributed to man-produced causes. On July 2, 1975, well 22 at the Louisville Works of E. I. duPont de Nemours and Company (henceforth shortened to DuPont) produced water containing 25 mg/L¹ (milligrams per liter) of chloroform from the sand and gravel alluvial aquifer in southwestern Louisville, Ky. (figs. 1 and 2). The well was pumping water for cooling at a rate of about 630 gal/min (gallons per minute). The analysis was made as part of a routine program of sampling of well water at the DuPont plant begun in January 1974 in compliance with the

company's National Pollutant Discharge Elimination System (NPDES) permit. The original determination was made from a scan for organic compounds, an indicator of pollution; the pollutant was later identified as chloroform.

Tests for chloroform in water from other wells in the area were negative, but well 22 continued to produce water containing chloroform. The apparent obvious source of the chloroform was about 120 feet south of well 22 at a storage facility of the Triangle Refineries, Inc., shown in figure 2. Triangle has one 420,000-gallon and two 20,000-gallon chloroform storage tanks. They unload barges and store and deliver chloroform to DuPont for use as a raw material in its plant. Transfer from barge to storage and from storage to DuPont is by pipeline, most of which is underground. The obvious source became less clear when inspection of pipes and tanks and bookkeeping records of chloroform shipments showed no recent losses of chloroform.

Objectives and Scope of Report

The objectives of this study are twofold: (1) to determine the source of contamination and the areal extent of ground water contaminated by chloroform, and (2) to investigate and evaluate the probable distribution of chloroform in the aquifer under various pumping and non-pumping conditions.

The scope of the study was to complete the objectives by either conventional or nonconventional techniques. When the main mass of the contaminant was found to be in the unsaturated zone instead of below the water table, the approach to the study changed, but the objectives and scope remained the same.

As unexpected relationships became apparent, additional data beyond the scope of the project were collected. These data are presented and discussed, but some conclusions are tentative as the project was not funded to study such items as the subsurface movement in response to precipitation of a volatile liquid adsorbed on silicates or the movement of a hydrophobic substance in response to pumping along a water surface-substance interface.

¹Results of DuPont's and U.S. Environmental Protection Agency's analyses are reported here in milligrams per liter; the original data are in parts per million. At the concentrations and densities involved in this study, both units of measure are equivalent.

Chronologic Summary

A chronologic summary of events before the start of this study follows:

- April 1970 —DuPont's well 22 begins production; yield, 818 gal/min; 24-inch casing; screened from 95 to 116 feet; depth of well, 116 feet.
- August 1970 —Triangle Refineries, Inc., reports a spill of 5,000 gallons of chloroform by overflowing a 20,000-gallon storage tank when an operator fell asleep. The spilled chloroform dissipated rapidly by evaporation and by percolating into the ground. None was salvaged.
- January 1974 —DuPont begins sampling and analyzing water from well 22, and other wells, to detect possible contamination. No organic compounds in samples.
- July 1975 —25 mg/L of chloroform analyzed in water from well 22 on July 2.
- July–September 1975 —Triangle and DuPont visually inspect above-ground chloroform pipelines and storage tanks. No visible leaks.
- November 1975 —DuPont management decides to pump well 22 continuously to prevent migration of chloroform away from area of well. Chloroform is first detected at outfall where cooling water from well 22 enters Ohio River.
- April 1976 —DuPont informs Kentucky State Department for Natural Resources and Environmental Protection of chloroform contamination.
- Spring 1976 —Triangle Refineries, Inc., pressure-tests all pipelines and "vacuum box"-tests the large chloroform storage tank. The two small storage tanks are visually inspected. No leaks.
- May 1976 —DuPont informs U.S. Environmental Protection Agency (EPA) of chloroform contamination. State personnel sample well 22 and other wells in vicinity outside of DuPont's property for presence of chloroform; water from well 22 contains 18.5 mg/L of chloroform. Water from two other wells has very low chloroform values: 0.0013 mg/L from well 5 of American Synthetic Rubber Corporation, 450 feet north of well 22 and 0.0015 mg/L from well 1 of Reynolds Metals Company, about 1 mile north of well 22. No detecta-

ble chloroform from domestic wells along Senn Road. The minimum detectable limit for chloroform is 0.001 mg/L.

- August 1977 —EPA representatives visit area.
- March 1978 —U.S. Geological Survey begins investigation.
- April 15–17, 1978 —Mechanical failure stops pumping of well 22.
- May 1978 —Well repair and screen rejuvenation by chemicals begins. Yield in April had decreased to 100 gal/min.
- May 26, 1978 —Well 22 resumes pumping; yields range from 530 to 885 gal/min.

Acknowledgments.—During the course of this study we had contact with numerous people. We want to thank H. R. Deutsch, Environmental Control Coordinator, and Sherman Kline, Engineer, of the DuPont Company for their cooperation and advice and for access to data collected by DuPont. We also want to thank S. C. Bauman, Chemist at DuPont, for assistance with procedures for analyzing for chloroform and Delmer Goodin, Terminal Superintendent at Triangle Refineries, Inc., for his cooperation and access to sites for drilling on Triangle's property.

DATA COLLECTION

To find the source of chloroform being pumped from DuPont's well 22, two 1 1/2-inch-diameter wells were drilled in June 1978 with a power auger for sampling water from the aquifer at suspected points of contamination. Water samples were obtained by a specially constructed noncontaminating submerged pump which used a gas-operated, expandable Teflon² bladder to force water through a food-grade Tygon hose to the surface at the rate of about 1/3 gal/min.

Water was pumped from each sampled interval at least 1 hour with the intake of the pump as close to the screened interval as was practical or possible. Water samples were collected in test tube glass bottles with threaded Teflon seals. The bottles were filled to overflow with a positive meniscus, sealed, and chilled by ice or refrigeration until analyzed.

Water Sampling and Data

One well (test hole 1 in fig. 1) was drilled along Camp Ground Road, about 1,500 feet east of well 22, across the road from an active sanitary landfill area that

²The use of brand names in this report is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

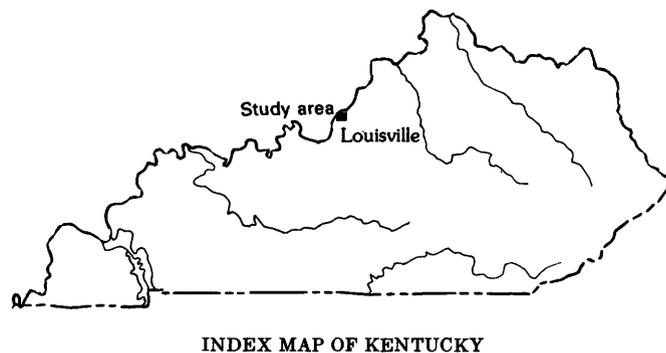
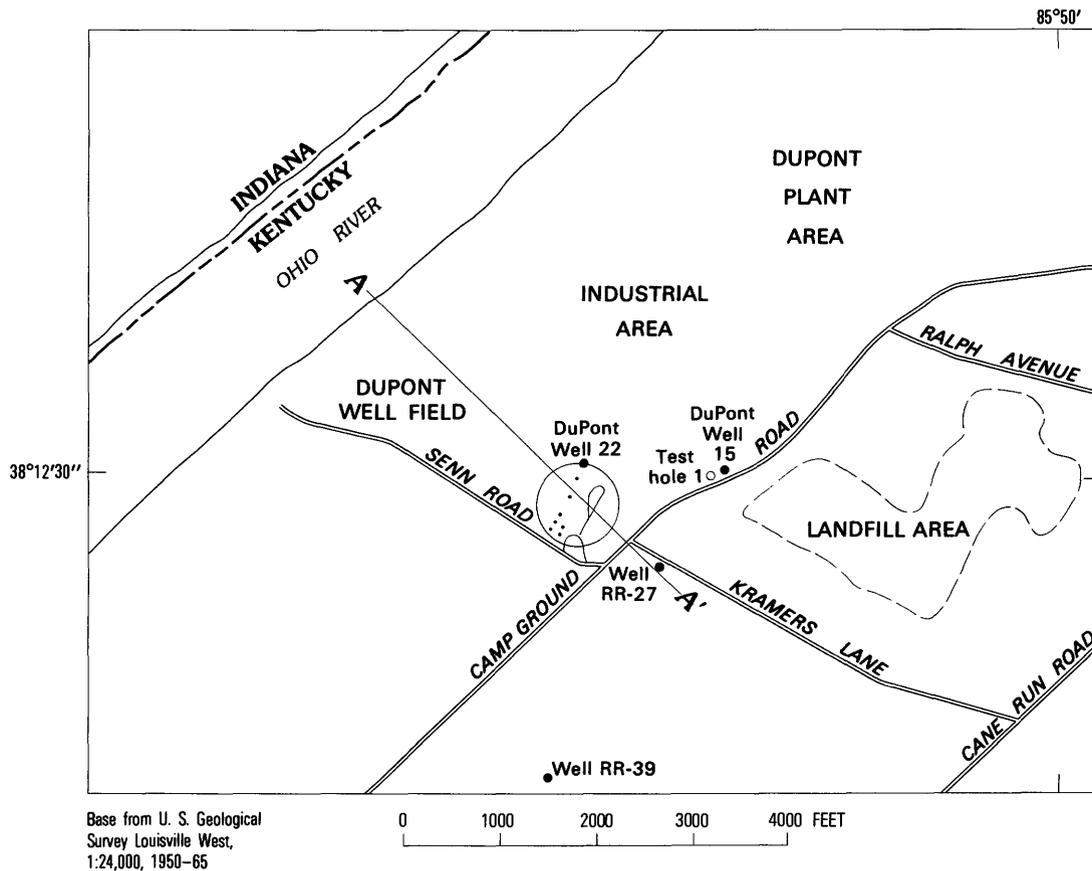


Figure 1. Location of the study area.

was known to generate methane gas. It was suspected that microbial action might, with the addition of chlorine from the refuse, convert some methane gas to chloroform. No chloroform was found in the water from six different levels ranging from 52 feet (altitude 398 feet) near the top of the water table to just above bedrock at 112.5 feet (altitude 338 feet). Water samples were pumped July 25, 1978. Earlier water samples were pumped from the 112.5-foot depth on June 14, 1978, and July 5, 1978; neither sample contained chloroform.

Concurrent with the drilling of the well near the landfill, a test well was drilled about 15 feet north of the northernmost small chloroform storage tank. Shale bedrock was found at 114 feet (altitude 338 feet). A sand point was installed from 112 to 114 feet, and water samples were collected from the well for chloroform determination. The amount of chloroform in the water was 1.10 mg/L on June 14, 1978, 0.38 mg/L on July 5, 1978, and none on July 18, 1978. About the same time, water from DuPont well 22 contained 24.6 mg/L of chloroform on

Table 1. Water levels and analyses of water from USGS well, 57.4 feet deep, and concentration of chloroform from DuPont's well 22

Date of sample	Water level below surface (ft)	Altitude of water level (ft)	Chloroform (mg/L)	Carbon tetra-chloride (mg/L)	Chloroform ¹ in DuPont's well 22 (mg/L)
Aug. 18, 1978	53.2	399	25.3	1.28	17.00
Sept. 6, 1978	54.0	398	16.3	.98	13.29
Sept. 6, 1978	54.0	398	16.9	1.02	

¹Analyses by DuPont.

June 6, 1978, and 23.1 mg/L on July 5, 1978. All five analyses were by the U.S. Geological Survey.

The 114-foot depth was sampled first because it was thought that the density of chloroform of 1.489 at 20°C (Sheflan and Jacobs, 1953, p. 209) would cause it to be more concentrated near the base of the aquifer than in the upper part. It was not. The presence and decreasing amounts of chloroform from the 114-foot well are thought to be contamination introduced by augering the well on June 12, 1978.

On July 18 and 19, 1978, temporary wells were made at depths of 105.5, 95, 84.5, and 74 feet by pulling the casing and screen of the "observation well" upward. The water table was at 52.8 feet below the land surface (altitude 399 feet). Because the pump was stuck in the casing 15 feet above the bottom of the well screen, water samples shallower than 74 feet (altitude 378 feet) could not be taken as had been planned. The pump had to be submerged to function. Water samples were collected at each depth and submitted for analysis. None contained chloroform when analyzed. On July 17 and 18, 1978, analyses of water from well 22 by DuPont showed 22.69 and 29.51 mg/L of chloroform, respectively.

After the last water sample was collected (at the 74-foot level), the casing and screen were pulled from the well, but the hole was not backfilled in case reentry with the auger became desirable. The uncased hole partially collapsed.

Several weeks later, a strong odor of chloroform was noted coming from the hole which was then open to only 29 feet. This indicated that the source of chloroform might not be in the ground water, but in the unsaturated zone above the water table. It also indicated that the uppermost part of the zone of saturation, the water table, might be in contact with chloroform-saturated sediments in the unsaturated zone. Therefore, another well was drilled a few feet from the previous test well to sample the uppermost part of the zone of saturation near the water table. The well was 57.4 feet deep (altitude 395 feet) with the water level at 53.2 feet on August 18, 1978. Water

from this well was sampled twice. The analyzed results are given in table 1.

These analyses showed that water in the uppermost part of the saturated zone contained a concentration of chloroform about equal to the greatest concentration that had been pumped from well 22 and that the concentration of chloroform in the water decreased as the water level declined. This was the beginning of an understanding of the mechanism of the chloroform contamination of well 22.

Soil Sampling and Data

Soil-sampling equipment was obtained that fitted inside a 6-inch hollow-stem auger and a test hole, labeled "USGS observation well" on figure 2, was drilled several feet from the previous hole. A split-spoon sampler with 6-inch-long cylinder inserts was used to collect 1-foot driven samples at various depths from 24 feet to the water table at 53 feet. A removable plug fastened to "A-rods" and functioning as part of the drill bit prevented sediments from entering the auger at the bit. At each sampled interval, the plug was removed from the auger by the "A-rods" and replaced by the split-spoon sampler which was lowered through the auger to the bottom and driven about 1 foot ahead of the auger.

The sampler was rapidly lifted from the hole through the hollow center of the auger after sampling at each depth. The middle part of each sample was put into a chilled glass bottle that contained 50 mL of isooctane (2,2,4-trimethylpentane) as a solvent. The bottle was swirled to dissolve the chloroform in the sample in the isooctane and was sealed with a lid having an impervious Teflon liner. The bottle and contents were chilled and sent in a refrigerated container to the U.S. Geological Survey's Central Laboratory in Doraville, Ga., for analysis by gas-liquid chromatography using an electron-capture detector. An additional 200 mL of isooctane were added to the samples several days before analysis at the laboratory.

Table 2. Analyses of soil samples from USGS observation well

Date of sample	Depth (ft)	Altitude (ft)	Chloroform (mg/kg)	Carbon tetra-chloride (mg/kg)	Chloride (mg/kg)
Aug. 31, 1978	24	428	24.7	0.80	88.5
Aug. 31, 1978	29	423	24.0	.52	49.5
Aug. 31, 1978	34	418	48.5	.97	105.5
Aug. 31, 1978	39	413	27.9	.51	69.2
Sept. 1, 1978	44	408	18.3	.43	93.2
Sept. 1, 1978	49	403	30.2	.51	78.0
Sept. 1, 1978	53	399	102	2.57	59.5

The volatile organic chloroform and carbon tetrachloride in the soil samples were dissolved in the solvent to prevent loss during storage. After calculating the amount of chloroform and carbon tetrachloride in the solvent, the soil samples (mostly sand, some small gravel, and a few clayey stringers) were dried and weighed. The results are expressed as milligrams (0.001 g) of compound per kilogram (1,000 g) of dry sample weight. For comparison, the same ratios could be expressed as grams per

million grams. The results of the analyses are given in table 2.

The core samples were not examined by a geologist, but the lithologic difference of the samples was noted by the analyst at the laboratory.

"It is interesting to note that the core samples taken at the 34- and 39-foot levels appeared to differ significantly from the other samples. The 34-foot sample contained a rather large amount of clay; the 39-foot sample

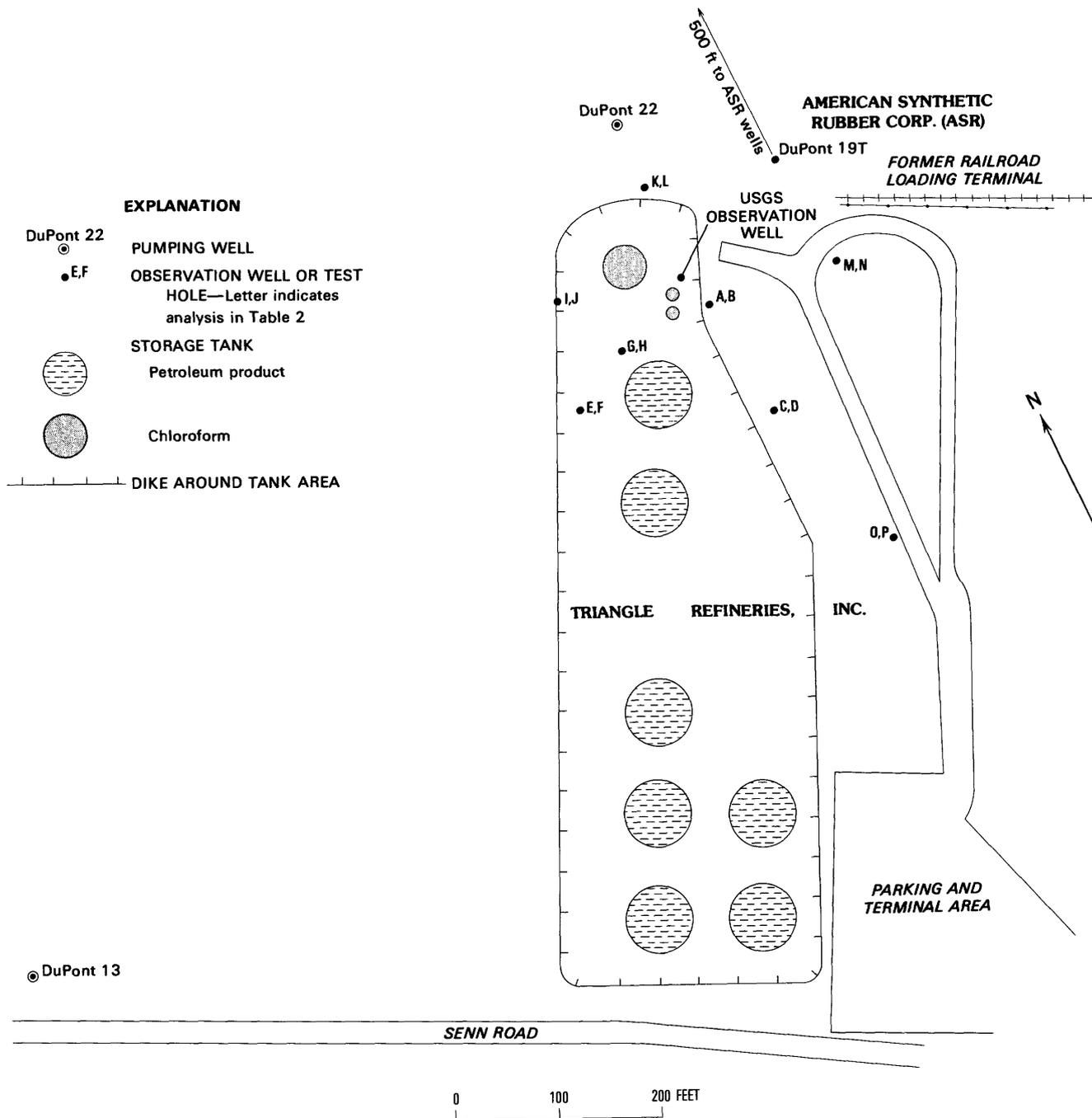


Figure 2. Location of features in the study area.

contained significantly less clay. The other samples were predominantly a broad range of sands."

To define the approximate extent of the contamination, additional core samples were taken. In the first soil samples, the samples from 34 feet (altitude 418 feet) and 53 feet (altitude 399 feet) contained the greatest chloroform and carbon tetrachloride concentration. Therefore, in October and November 1978, 16 additional samples (labeled A-P in table 3) were collected from 418-foot and 399-foot altitude from test holes drilled in the area of the chloroform storage tanks. Locations of sampled test holes are shown on figure 2. The results are given in table 3.

Unfortunately, it was impossible to make geologic logs of the auger holes, except to log all material below surficial material as "sand and gravel." Resistance to the drill, except for the sandy soil near the surface and thin gravel beds, was the same from near the surface to bedrock. Drill-cuttings returned by the auger after a short penetration were a heterogeneous mixture of sand and gravel that could not be ascribed to any particular depth.

A strong odor of chloroform was present in almost all test holes from the opening at the center of the hollow-stem auger after the soil samples were removed and the auger was being pulled from the holes. At some holes the vapor was strong enough to distort rays of light as the vapors from an open gasoline can do on a hot day.

Table 3. Analyses of soil samples from Triangle Refineries, Inc., area.

[Tr. = trace; Np. = None present]

Sample	Date (1978)	Altitude (ft)	Chloroform (mg/kg)	Carbon tetrachloride (mg/kg)
A ¹	Oct. 10	418	43.8	1.0
C	Oct. 10	418	27.2	1.1
E	Oct. 11	418	7.8	Tr.
G	Oct. 11	418	35.1	.8
I	Oct. 12	418	6.1	Tr.
K	Oct. 12	418	33.4	.4
M	Nov. 13	418	2.2	Np.
O	Nov. 14	418	.8	Np.
B	Oct. 10	399	43.8	1.0
D	Oct. 10	399	39.3	1.5
F	Oct. 11	399	24.1	Tr.
H ¹	Oct. 11	399	25.0	1.0
J	Oct. 12	399	24.2	Tr.
L	Oct. 12	399	56.5	1.6
N	Nov. 13	399	52.8	8.2
P	Nov. 14	399	Np.	Np.

¹Data may not be reliable; some solvent may have been lost in shipment because of faulty sealing.

Despite the strong odor of chloroform from the open center of the hollow-stem auger, none of the soil samples from the unsaturated zone were wet or looked or felt damp, and only one had a slight odor of chloroform.

DISCUSSION OF DATA

The amounts of chloroform and carbon tetrachloride in the soil samples "should be considered as semiquantitative since the methods used are not standardized. They are, however, based on sound analytical principles" (D. K. Leifeste, written communication, 1978).

The method of collection of the soil samples was standard for soil sampling of sediments containing nonvolatile constituents. Some volatile constituents probably were lost by vaporization while the sampler was being pulled from the hole and while the sediments were being prepared to be sealed. However, because all samples were treated the same way, the results, though semiquantitative, are comparable.

To outline the contaminant, soil samples were taken at altitudes of 418 and 399 feet in different parts of the storage-tank area. In this area the composition of the alluvium changes markedly in short distances (Price, 1964), as is shown on figure 3, and the composition of the alluvium is not consistent at identical elevations. However, sampling at the two elevations was expeditious and gave results that appear consistent.

The lower, 399-foot altitude, samples were from near the water table and may have been slightly below it during previous rises of ground water. Therefore these samples probably have been subjected to capillary and other forces, which, along with the hydrophobic (tending not to combine with water) characteristics of the two contaminants may have concentrated the contaminants at this level so that they are not characteristic of the original concentration of contaminants at this level.

Lines of equal concentration of chloroform and carbon tetrachloride at altitudes of 418 and 399 feet are illustrated later in this section. Also shown are graphs of chloroform or carbon tetrachloride concentration plotted against the distance from the chloroform storage tanks. In all of the graphs there appear to be two lines of different slope that best fit the data. One is in an approximately north-south direction through the storage tanks; the other is east-west, also through the tanks.

The lines of equal concentration are strongly biased to fit these graphs; therefore, the position of the lines of equal concentration may be greater or less than the values at some of the data points. The shape of the chloroform and carbon tetrachloride in the unsaturated zone is that of an ellipse. An alternate shape of the carbon tetrachloride concentration at 399-foot altitude is also shown.

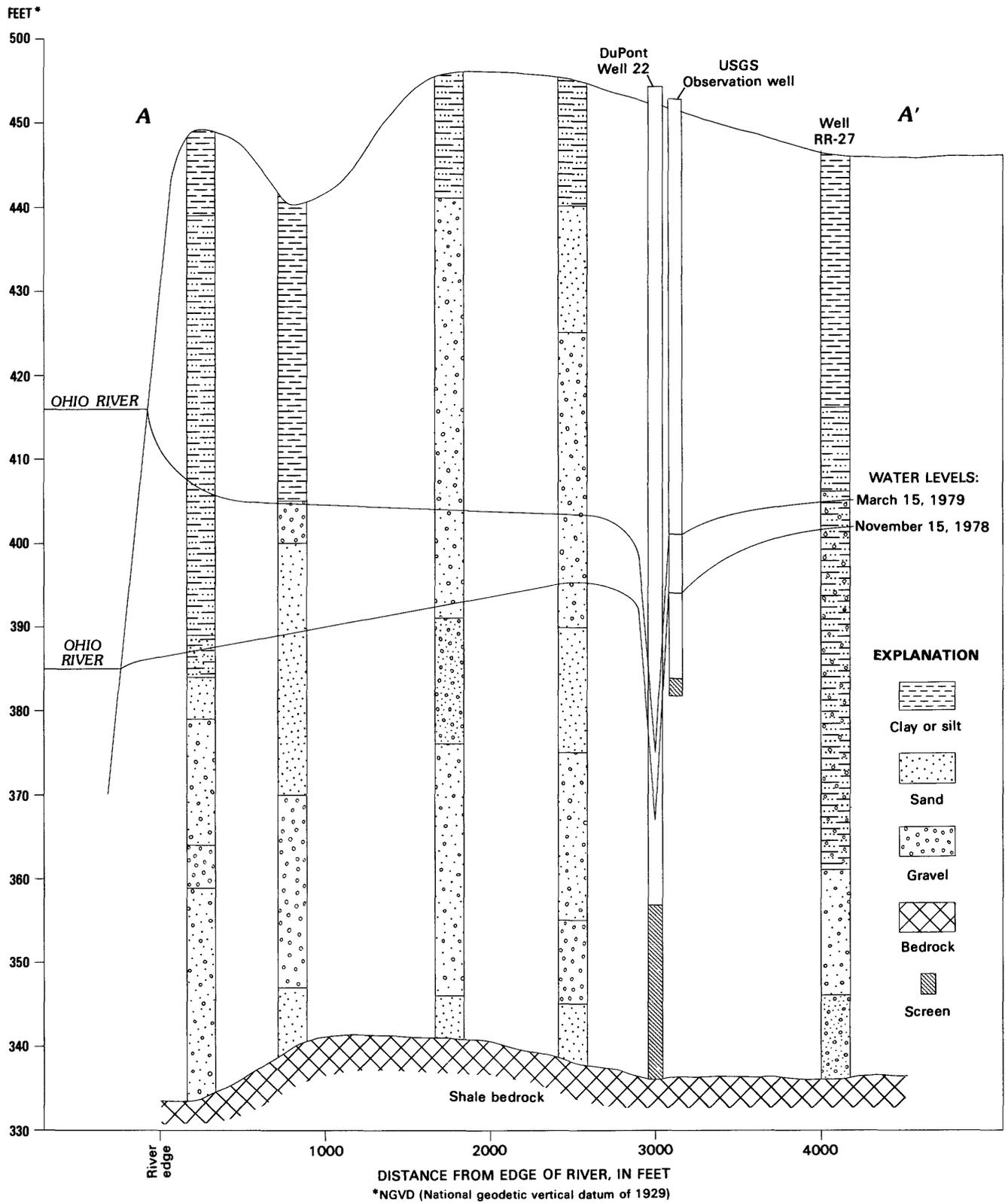


Figure 3. Types of sediments in the alluvium and water level changes. Location of section shown in figure 1. Geology modified from Price (1964) (western part of his section H-H').

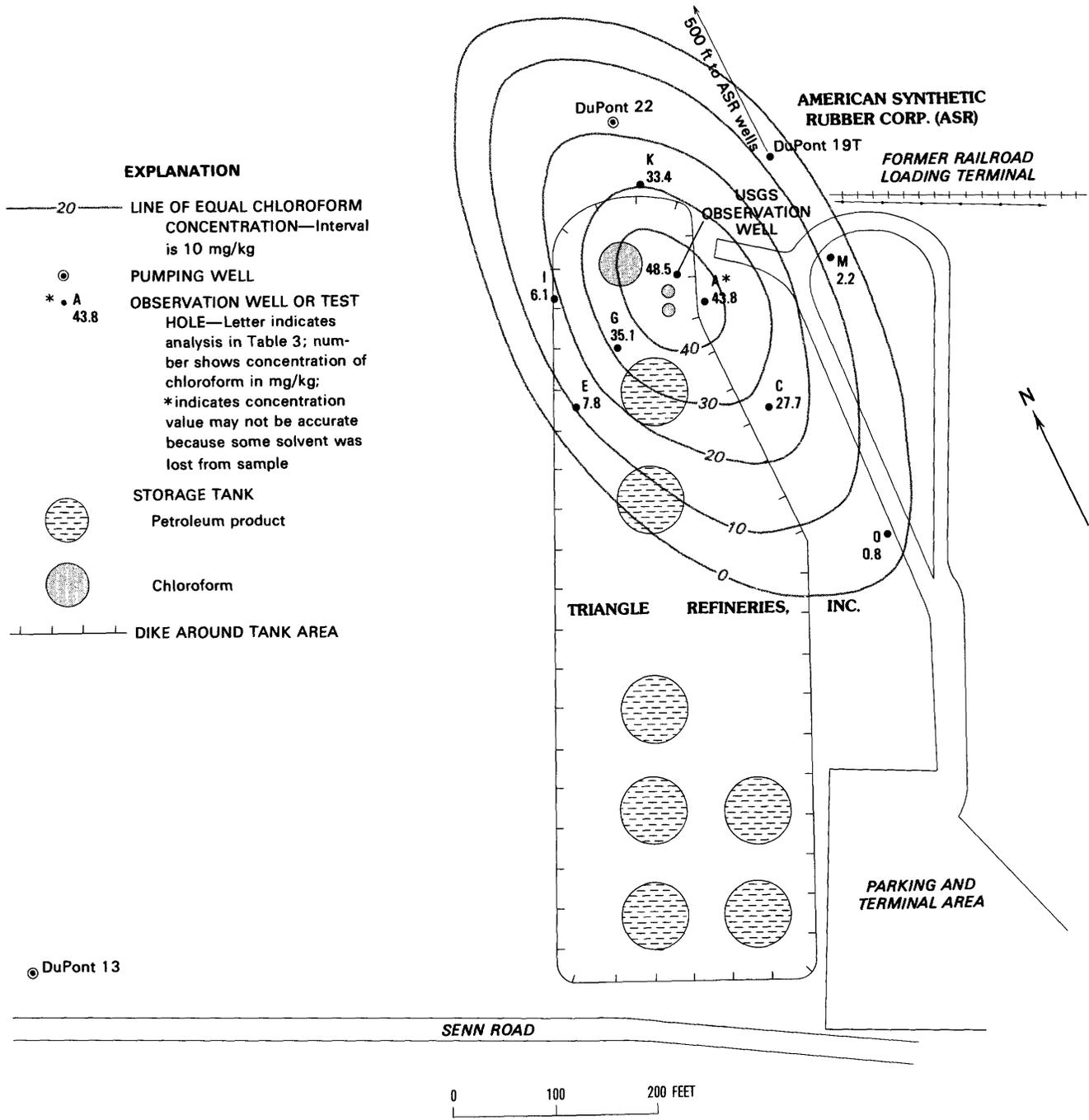


Figure 4. Concentration of chloroform in soil samples from the 418-foot altitude.

The reason for this elliptical configuration is not known; a speculative theory is that horizontal permeability is greater in a north-south direction, the generalized direction of movement of the stream that deposited the alluvial sediments, and the two volatile compounds moved more easily in these directions, possible in a gaseous phase. The normal shape of a contaminant is a plume from the point of contamination toward an area of discharge.

Chloroform Data

418-foot Altitude

Chloroform concentration at the 418-foot altitude was highest around the chloroform-tank area. Figure 4 shows lines of equal concentration of chloroform at the 418-foot altitude. The shape of the chloroform-contami-

nated area is elongated north-south and centered around the smallest tanks.

Figure 5 shows chloroform concentration plotted against distance from the northernmost small chloroform storage tank—the tank that overflowed in 1970. Six of the nine samples plot along the north-south correlation line, the others plot near an east-west correlation line, indicating that in most directions the decrease in chloroform content is probably linear, with distance from the tank, but at different rates of decrease.

399-foot Altitude

Chloroform concentration at the 399-foot altitude was highest around the chloroform tank area. Figure 6 shows chloroform concentrations at the 399-foot altitude. The shape of the chloroform-contaminated area is more radial than at the 418-foot altitude and extends farther eastward.

Figure 7 shows chloroform concentration plotted against distance from the northernmost small chloroform storage tank. Four of the nine samples plot on, or nearly on, the north-south correlation line; the others plot near the east-west correlation line except for sample P, which is outside the contaminated area, and sample N which is anomalously high.

Carbon Tetrachloride Data

418-foot Altitude

Carbon tetrachloride was an unexpected organic constituent found in the soil samples and in one water

sample taken from the uppermost part of the water table as previously described. Analyses of water from DuPont's well 22 by the U.S. Geological Survey and by DuPont's have never shown any organic contaminant other than chloroform. The method of analysis would have shown other volatile organic contaminants if they were present.

The carbon tetrachloride concentration at the 418-foot altitude was highest in sample C, southeast of the chloroform storage tank area. Figure 8 shows lines of equal concentrations of carbon tetrachloride at the 418-foot altitude as interpreted from the graph in figure 9. Sample C is considered anomalous. The area of carbon tetrachloride contamination appears elliptical as did the chloroform at this altitude.

Figure 9 shows carbon tetrachloride concentration plotted against distance from the northernmost small chloroform storage tank. Five of the nine samples plot near both the north-south and the east-west correlation lines; samples M and O are beyond the area of carbon tetrachloride contamination, and sample C is anomalously high.

399-foot Altitude

Carbon tetrachloride concentration at the 399-foot altitude is almost four times greater at test hole N, 165 feet from the northernmost small chloroform storage tank, than it is near the tank at the observation well or test hole B. Figures 10 and 11 show the concentration of carbon tetrachloride.

In figure 10, test hole N is not considered in the contouring. The greatest carbon tetrachloride concentrations are near the storage tank in an elliptical shape.

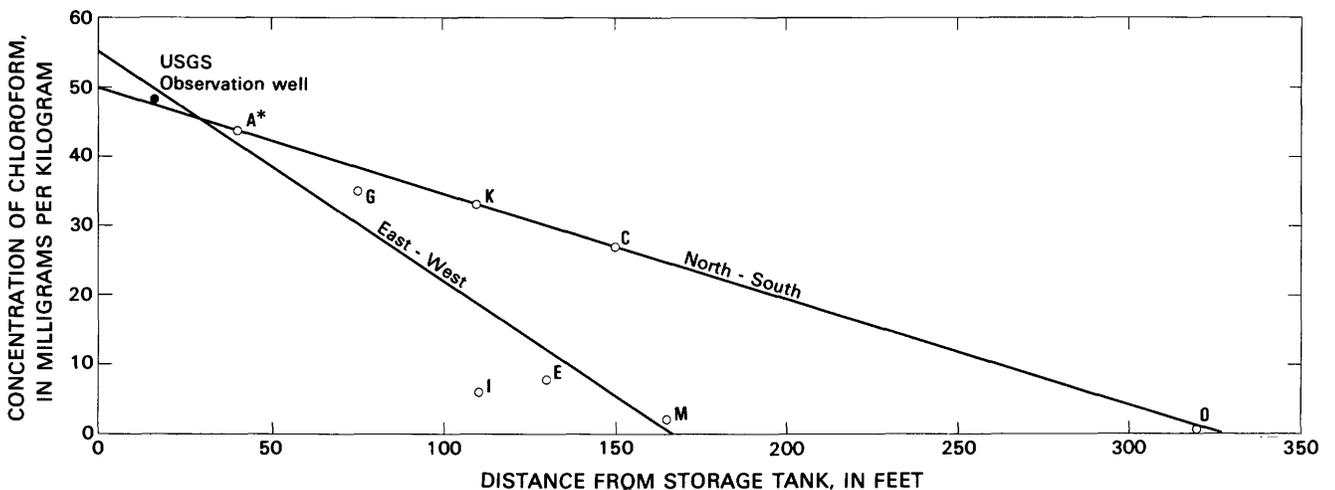


Figure 5. Concentration of chloroform from the 418-foot altitude in comparison with the distance from the northernmost small chloroform storage tank. An asterisk indicates that a concentration value may not be accurate because some solvent was lost from the sample.

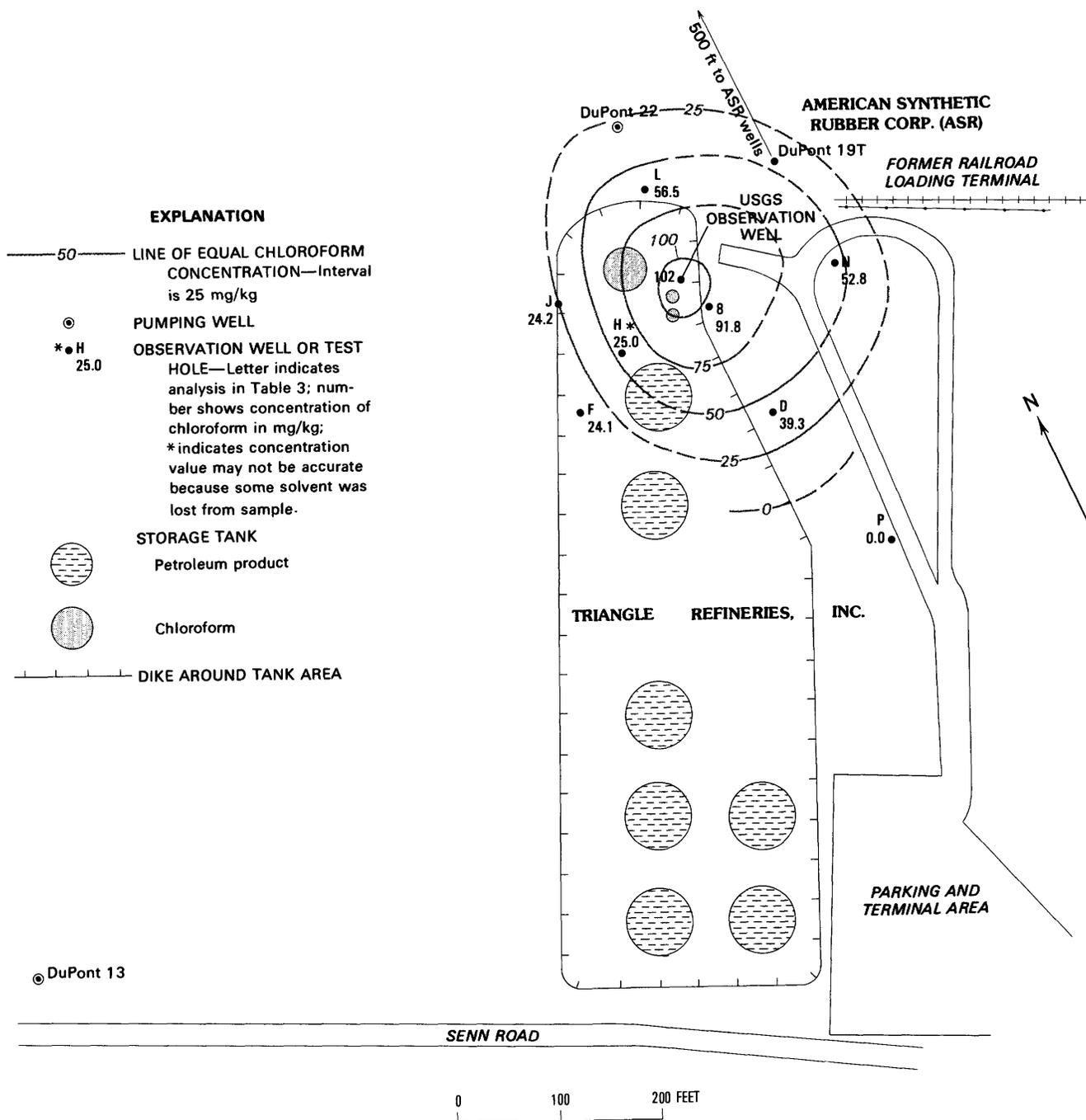


Figure 6. Concentration of chloroform in soil samples from the 399-foot altitude.

A different version of carbon tetrachloride concentration is shown in figure 11, which includes test hole N. In this figure the greatest concentration of carbon tetrachloride is about 200 feet east of the storage tanks. If this version is correct, it may be possible that the carbon tetrachloride and the chloroform in the soil samples could come from separate sources.

Figure 12 shows carbon tetrachloride concentration plotted against distance from the northernmost small chloroform storage tank. Four of the nine samples plot near the north-south correlation line; the other samples plot near the east-west correlation line except for sample P, which is beyond the area of carbon tetrachloride contamination and N, which is very anomalous.

Because concentrations of chloroform and carbon tetrachloride have produced logical maps of equal concentrations, there should be some area from which the carbon tetrachloride concentration diminishes with distance in a logical manner, either linearly or exponentially. Therefore, since samples D and L have almost equal concentrations and sample B and the sample taken at the "USGS observation well" similarly have almost equal concentrations, two circles having the same center and each passing through two points of equal concentration should be centered at the place from which concentrations decrease. This point is point X on figure 11.

Figure 13 shows the concentration of carbon tetrachloride plotted against distance from point X. Eight points, including the "trace and not present" amounts fall near the line and sample N is closer to the line than it is in figure 12. The correlation appears to be logical.

Point X is probably not a point but rather an area. The area is the former railroad loading terminal where, prior to about 1967, when the present pipeline was built, tank cars were loaded with chloroform for delivery to DuPont and where the empty tank cars were steam-cleaned upon return (Delmer Goodin, oral communication, 1979). Some drippage and spillage probably occurred. The

chloroform concentration from the 399-foot altitude in this area, sample N, is considered to be anomalously high in figure 7.

Carbon tetrachloride is a contaminant in chloroform formed in the process of making chloroform from methane. The DuPont Company will not accept more than 500 mg/L of carbon tetrachloride in chloroform. The carbon tetrachloride in their purchased chloroform is generally 0 to 100 mg/L (H. R. Deutsch, oral communication, 1979).

RELATION OF CHLOROFORM AND CHLORIDE CONCENTRATION TO WATER-LEVEL CHANGES

The maps of chloroform concentration in the alluvium, figures 4 and 6, show that there is a mass of chloroform in the unsaturated alluvial material beneath the area of the chloroform storage tanks. The first report of chloroform in water from DuPont's well 22 was on July 2, 1975. This is probably the first occurrence of chloroform in the water because duPont began analyzing for organic

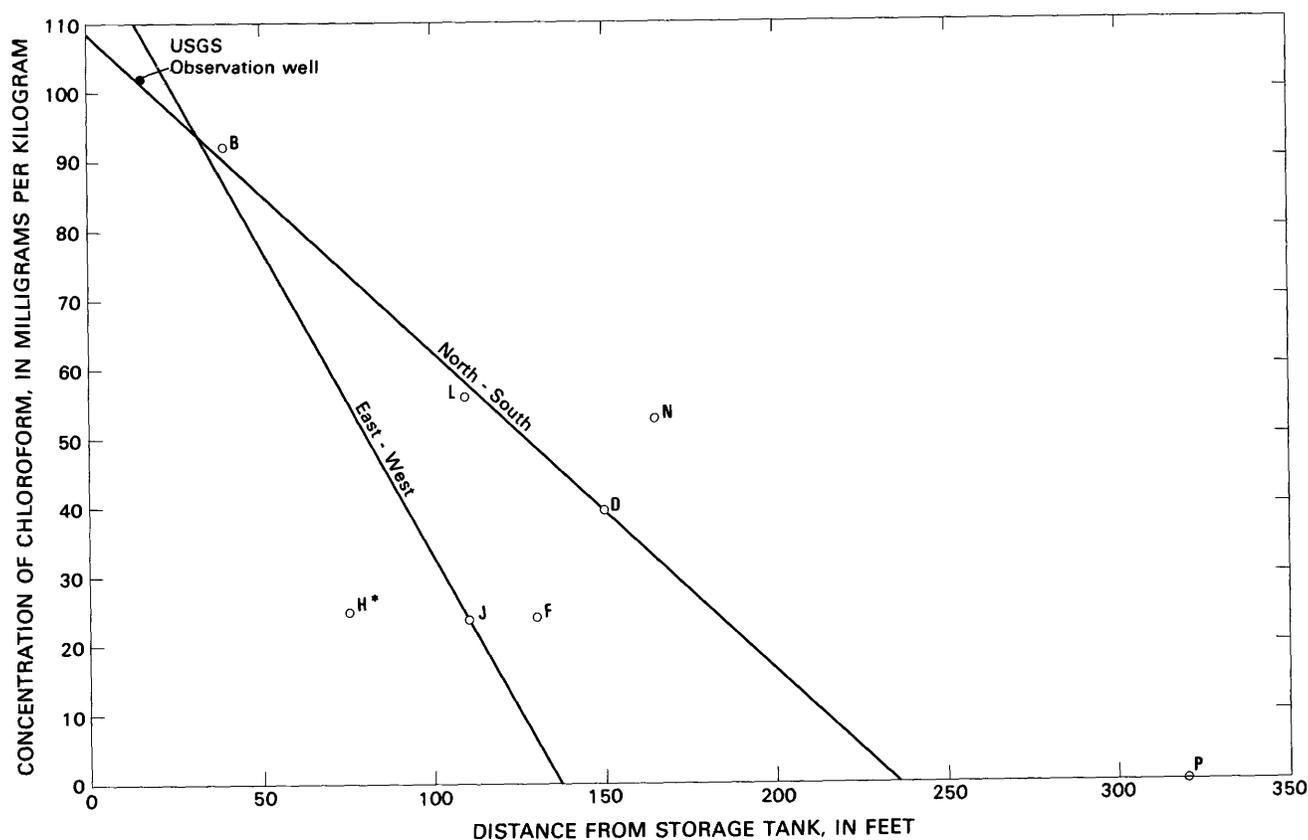


Figure 7. Concentration of chloroform from the 399-foot altitude in comparison with the distance from the northernmost small chloroform storage tank. An asterisk indicates that a concentration value may not be accurate because some solvent was lost from the sample.

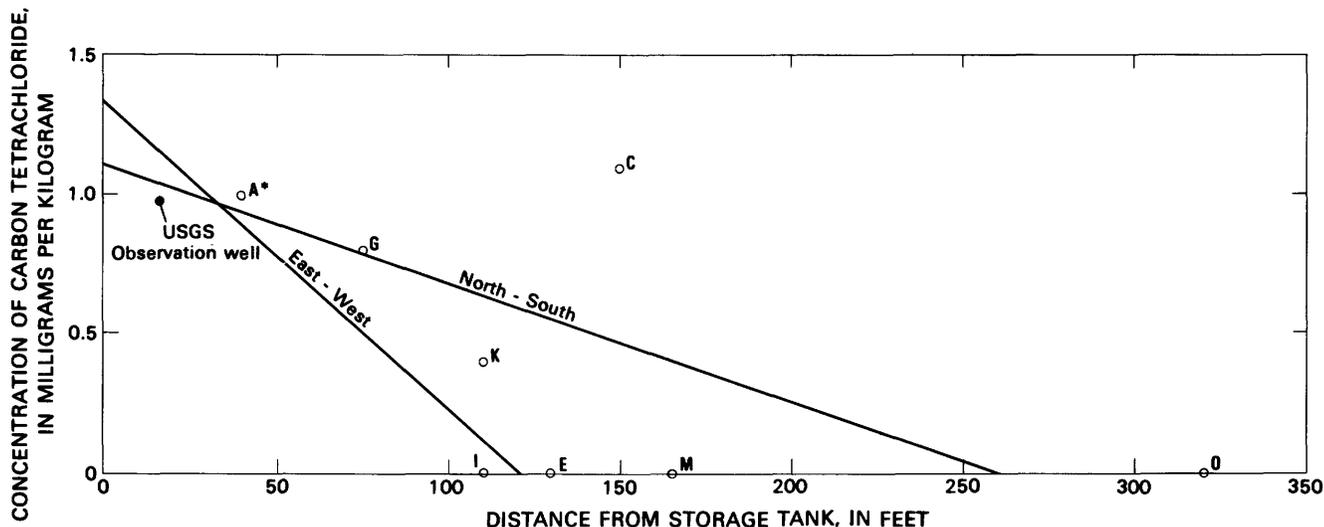


Figure 9. Concentration of carbon tetrachloride from the 418-foot altitude in comparison with the distance from the northernmost small chloroform storage tank. An asterisk indicates that a concentration value may not be accurate because some solvent was lost from the sample.

Observation well 19T, about 150 feet south of well 22, is measured weekly by DuPont by lowering a weight on the end of a steel tape until the observer touches or believes he has touched water. Water levels are converted to altitude and are reported to the nearest foot. The hydrograph from this well shows a water-level rise of about 20 feet since 1970 (fig. 15). Figure 15 also shows the chloroform concentration in water from well 22 as analyzed by DuPont. The fluctuation in chloroform concentration with the fluctuation in water level is clearly shown each year since 1975. The yearly rise of water level is caused by recharge to the aquifer from the Ohio River during the yearly spring rise or flood of the river and by a retardation of the natural movement of ground water toward the river through the alluvium.³

Changes of chloride concentration in water from well 22 are of unknown significance in relation to the chloroform production. Figure 15 shows chloride concentration in water from well 22 from 1970–1978. In 1975 the water level rose, followed by the appearance of high concentrations of chloroform and a rapid increase in chloride concentration. But note that in 1974 the chloride concentration rose similarly after a water level rise, but no chloroform was reported.

Of interest is the continued elevated chloride concentration until August 1976, when the chloride concen-

tration lowered to about 40–50 mg/L and remained near that level until June 1978 when after well rejuvenation both the chloroform and chloride concentration rose similarly and then decreased as the water level declined. The high chloride concentrations in late June were caused by residual hydrochloric acid used in the rejuvenation process.

For comparison, DuPont's well 13, outside of the chloroform contaminated area, has been sampled for chloride concentration randomly from April 1976 to May 1979. The average concentration of the 60 samples was 32 mg/L with a spread of from 21 to 67 mg/L; most chloride concentrations were about the average of 32 mg/L. From a hydrologic viewpoint, the rise in chloride concentration in well 22 appears to be the result of the ground-water table intercepting a decomposition product of chloroform. Chemically, such a reaction is considered impossible. Chloride content of the soil samples at the USGS observation well are listed in table 2; however, there are insufficient data from other areas to compare and analyze the data.

An unanswered question about the water level-chloroform response is the following: As the ground-water table in the alluvium rose to the base of the chloroform, had the chloroform been slowly moving downward to the water table, either in response to gravity from precipitation moving downward through the alluvium to the water table or from other forces, or had the chloroform been stationary after its initial movement and been adsorbed on the silicate alluvial matter? A literature search was made to determine adsorption and desorption properties of chloroform on silica and silicate minerals, but no data were found.

³See Addendum to this report for effects of the early December 1978 flood on the Ohio River and the chloroform concentration from well 22.

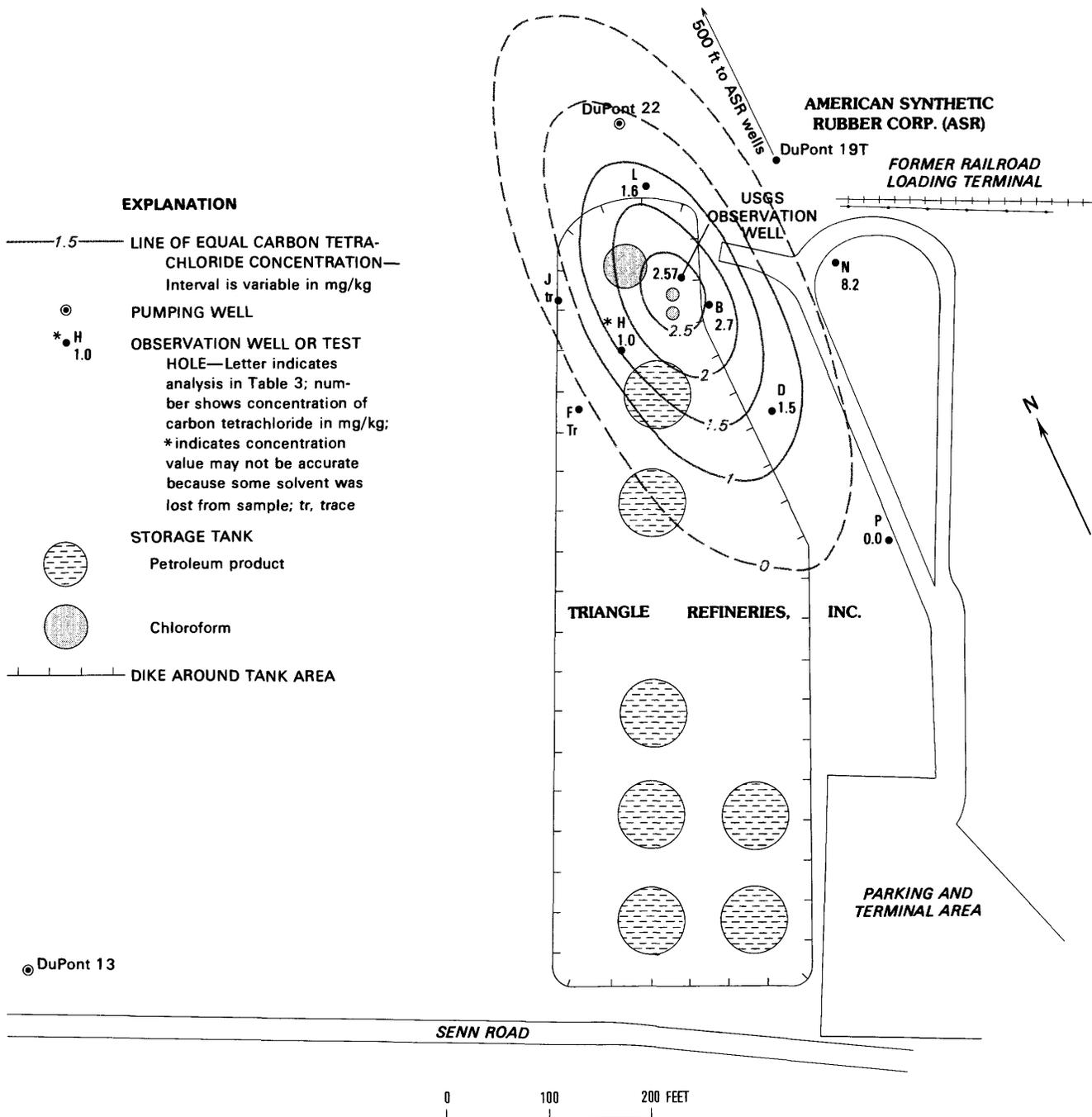


Figure 10. Concentration of carbon tetrachloride in soil samples from the 399-foot altitude. Sample N is not considered in the contouring.

SOURCE OF CHLOROFORM AND CARBON TETRACHLORIDE CONTAMINATION IN THE UNSATURATED ZONE

The source of the chloroform contaminating DuPont well 22 is the chloroform in the unsaturated alluvium around the chloroform storage tanks at Triangle Re-

fineries, Inc. The chloroform in the alluvium is probably from the reported spill of 5,000 gallons in 1970. Other sources may have been waste from the steam-cleaning of chloroform-carrying tank cars, minor leakage, drippings, and unreported spills of chloroform since 1957 when storage and shipping of chloroform began in this area. Data on the amount of chloroform that has been pumped by well 22 and the amount of chloroform remaining in the

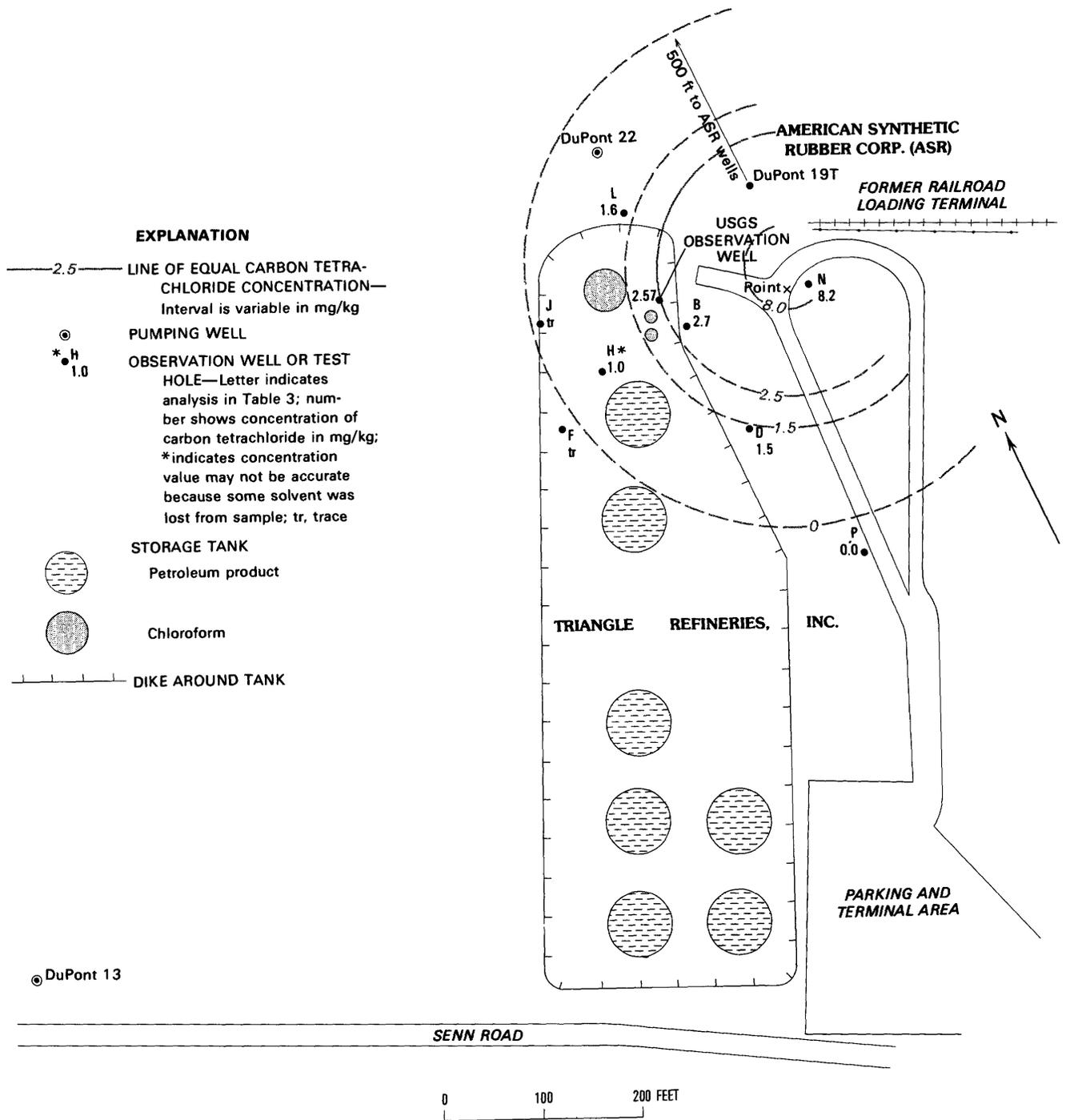


Figure 11. Concentration of carbon tetrachloride in soil samples from the 399-foot altitude. All samples are considered in the contouring.

unsaturated zone would be helpful in determining the source of the contaminant and the method of controlling the contaminant in the future.

In 1977, H. R. Deutsch (written communication, Dec. 9, 1977) reported to EPA that:

In response to your request for the total quantity of chloroform pumped from the No. 22 well, I must caution you that any number quoted is at the best

an estimate. The flow from our wells is read only once per week using an installed orifice and manometer. Changes in demand for well water causes the flow to change periodically without our having a record of it. With this knowledge we have re-estimated the amount of chloroform pumped from this well from July 1975 through November 1977 at approximately 35,000 pounds (about 2,800 gallons). This is a lower estimate than we have quoted from

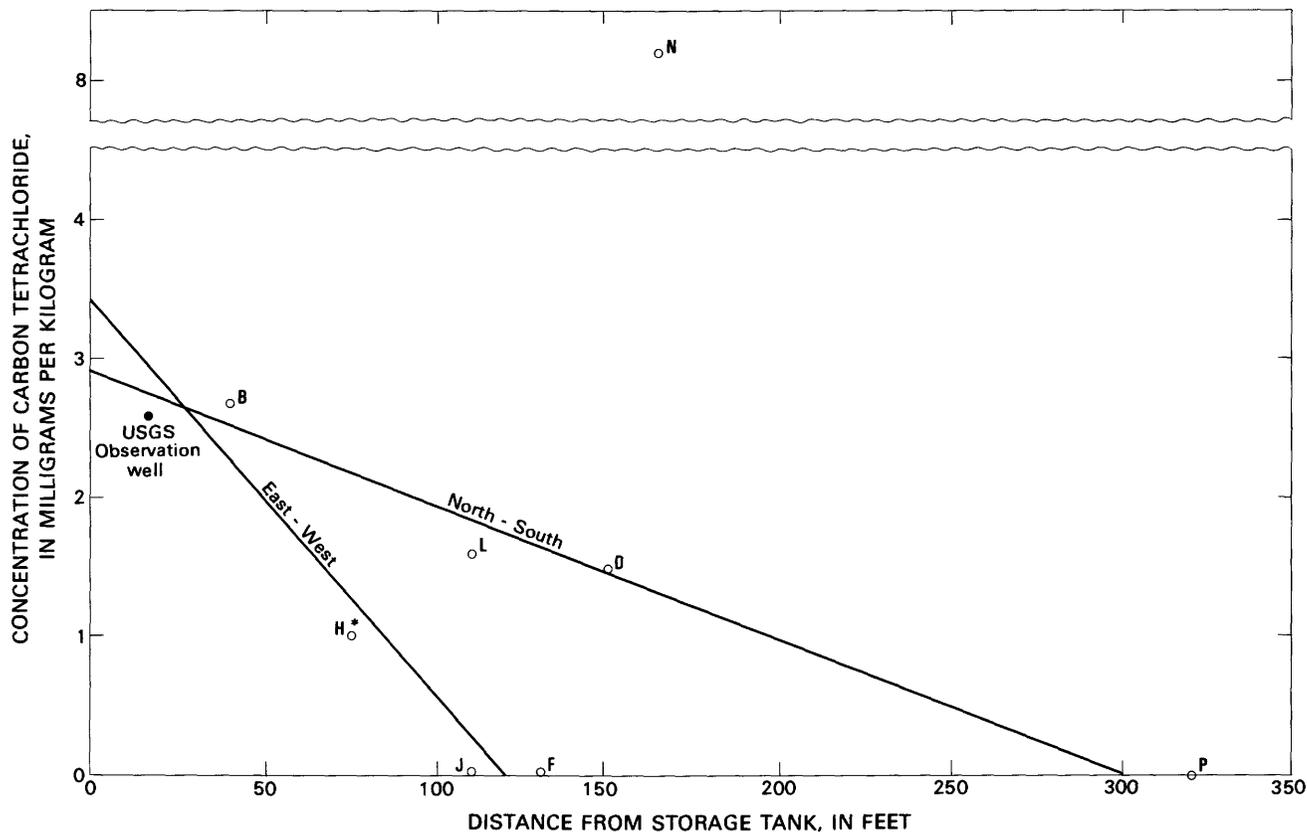


Figure 12. Concentration of carbon tetrachloride in soil samples from the 399-foot altitude in comparison with the distance from the northernmost small chloroform storage tank. An asterisk indicates that a concentration value may not be accurate because some solvent was lost from the sample.

past estimates, since in this most recent estimate weekly flow readings were used along with weekly average chloroform concentrations.

We have recalculated the amount of chloroform produced for the July 1971 through November 1977 period using weekly average chloroform concentrations and DuPont's weekly pumping rate (according to H. R. Deutsch, oral communication, 1979, in more detail than his 1977 estimate) and conclude that 40,741⁴ pounds (3,315 gallons) of chloroform were produced through November 1977. This is about 15 percent greater than Deutsch estimated but is subject to the same approximations or errors of measurement.

From December 1977 through April 1978, when the well failure occurred, our calculated pumpage of chloroform was 1,617 pounds (131 gallons).

After well rejuvenation in late May 1978 through February 1979, the well produced 51,000 pounds (4,149 gallons) of chloroform, or more chloroform in 9 months

than it had produced in the previous period of about 30 months.

Total chloroform produced from July 1975 through February 1979 is 93,358 pounds (7,596 gallons), which rounds to an estimate of 93,000 pounds (7,500 gallons), of chloroform, or 2,500 gallons more than Triangle's reported spill in 1970.

The data to calculate the amount of chloroform in the unsaturated zone are much less precise than pumpage data and chloroform concentration data and are at best considered an educated guess.

The average chloroform concentration of seven analyses from 29 feet of unsaturated sand, gravel, and clay stringers at a test hole by the storage tanks was 40 mg/kg (see table 2). Considering the chloroform storage tanks as the center of a chloroform-contaminated circle, the greatest radius of analyzed chloroform-bearing sediments is about 320 feet at the altitude of 418 feet and 240 feet at the altitude of 399 feet.

For convenience of calculating, consider the chloroform-bearing alluvium to be within a circle of 300-foot radius from the storage tanks, a thickness of 30 feet, an average concentration of 40 mg/kg (40 pounds/

⁴In this discussion, calculated values are presented and rounded in summation.

1,000,000 pounds), and an average weight for the alluvium of 100 pounds per cubic foot (the weight used for inventory by a local sand and gravel company). The volume of alluvium considered chloroform-bearing is 8,482,320 cubic feet and has a weight of 848,232,000 pounds; the chloroform contained therein is 33,929 pounds or 2,760 gallons.

The data on chloroform production and chloroform in the unsaturated zone indicate that a total of about 10,000 gallons of chloroform may have been in the ground at a previous time.

The source of the carbon tetrachloride in the unsaturated alluvium is not known but its greatest concentration is near the area of the chloroform storage tanks. However,

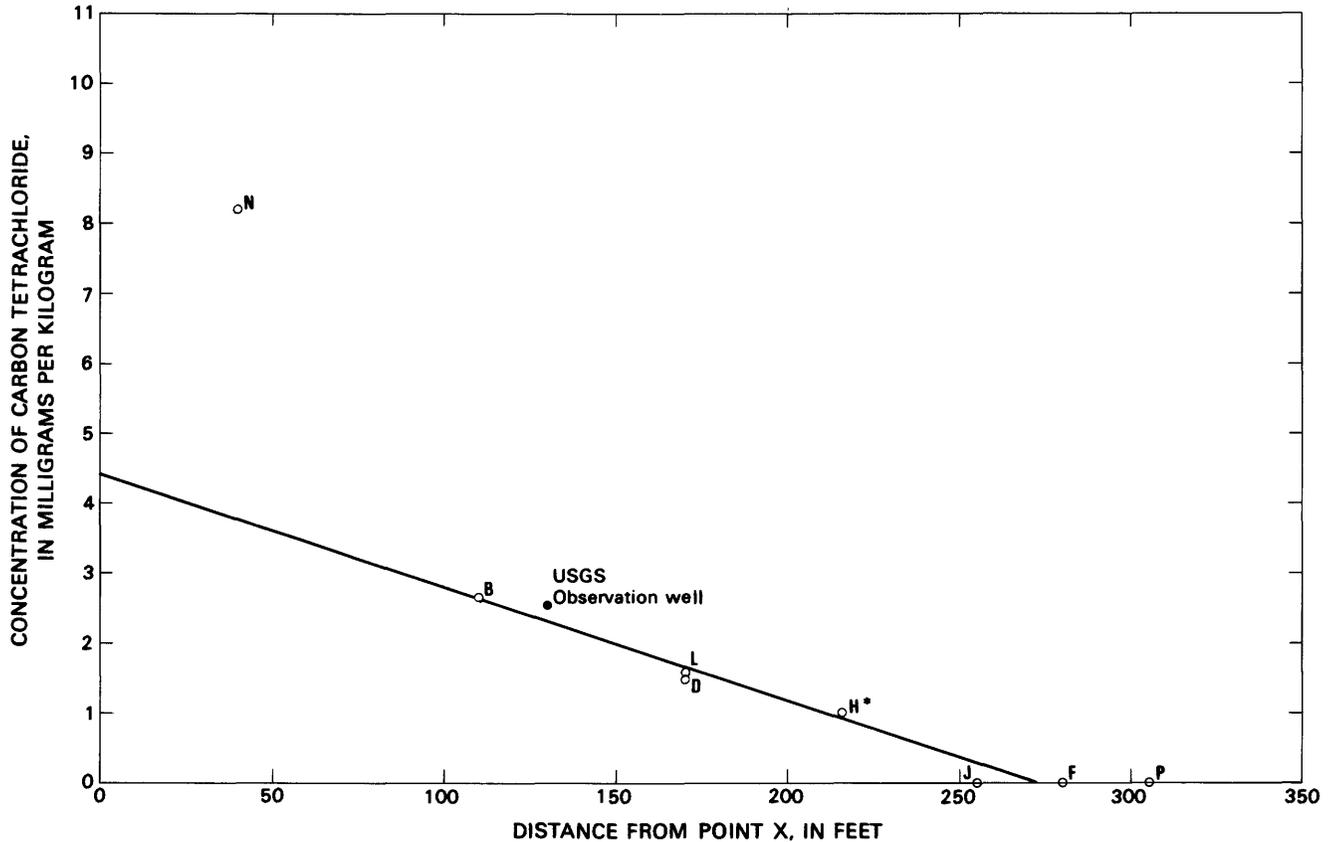


Figure 13. Concentration of carbon tetrachloride in soil samples from the 399-foot altitude in comparison with the distance from point X.

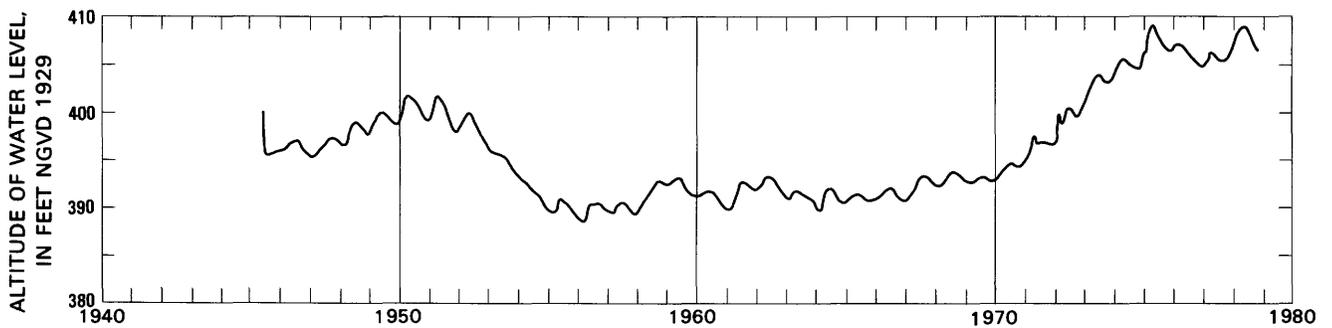


Figure 14. Ground-water levels in a well 0.6 mile south of well 22. The well, located in a livestock feedlot on Shanks Lane 0.5 mile west of Cane Run Road, is an observation well drilled in alluvial sand and gravel. It is 6 inches in diameter and 112 feet deep. Land surface is 446.27 feet NGVD of 1929. (Data from Whitesides, 1978, p. 38.) Data for July 1977 through December 1978 added by R. W. Davis, 1979.

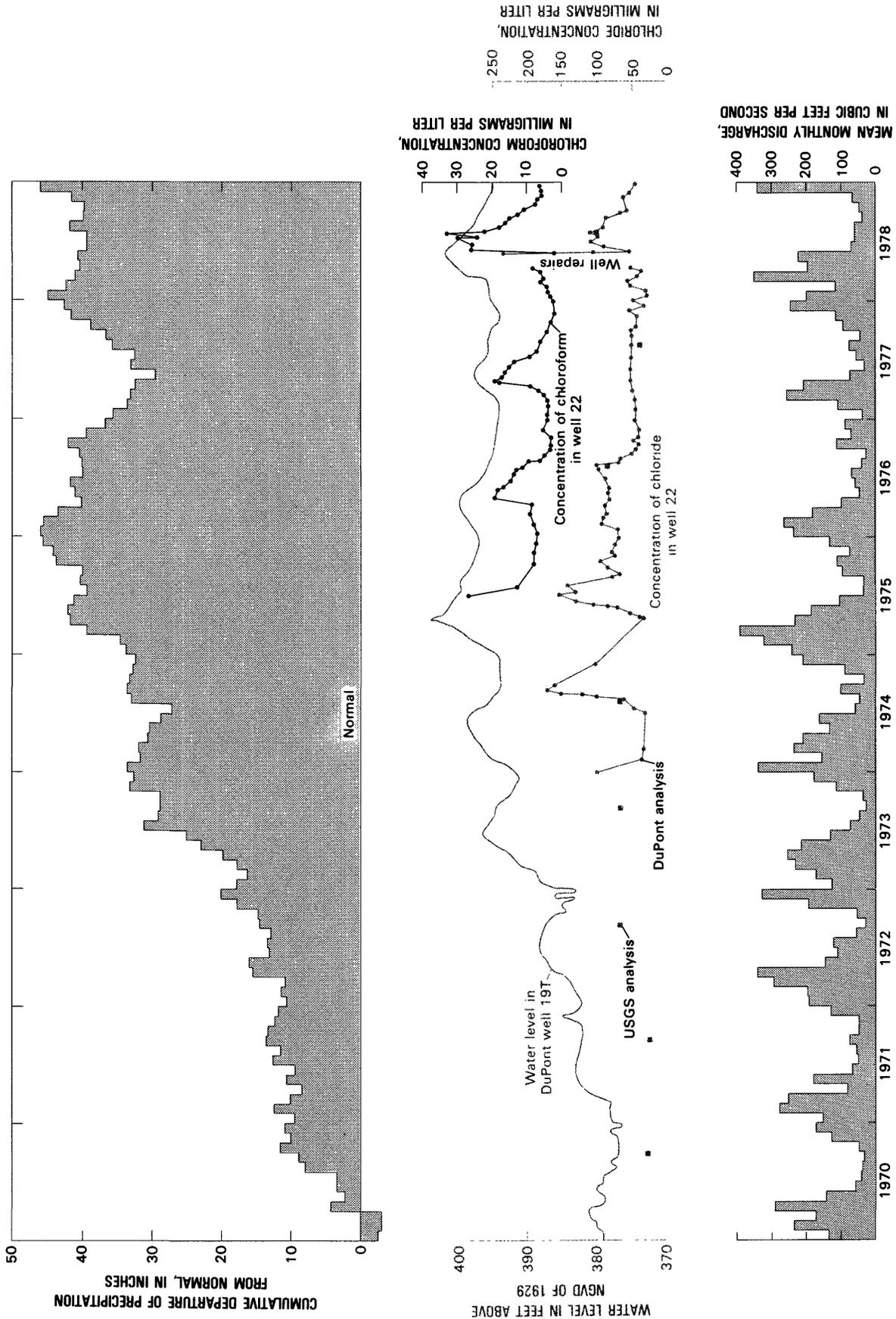
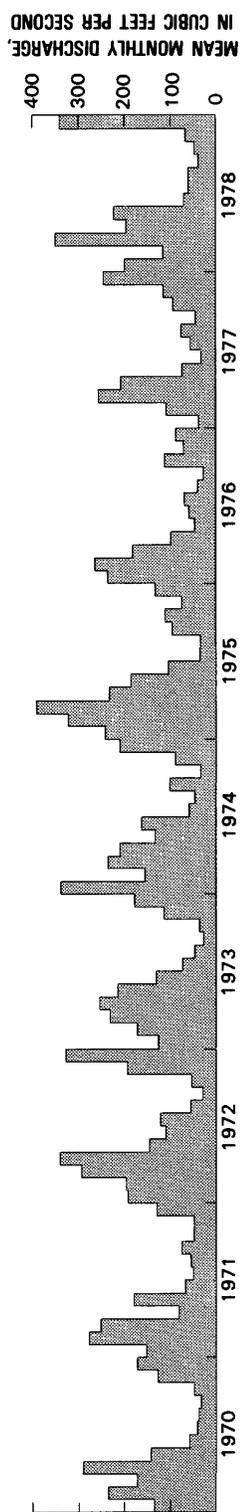


Figure 15. Ground-water levels in DuPont's observation well 19T and the concentration of chloroform and chloride in well 22. All data are from DuPont.



because the greatest concentration of 8.2 mg/kg was in sample N, shown in figure 11, the source, in part, may be from the tank-car loading area. There is a possibility that some unknown agent may have concentrated carbon tetrachloride at the sampled horizon and the sample may not be representative of the alluvium at that depth. Error of analysis is possible but not probable.

The only known or reported carbon tetrachloride in the area is the small amount, generally less than 100 mg/L, occurring as a contaminant in chloroform.

MECHANISM OF CHLOROFORM CONTAMINATION OF WELL 22

In discussing the mechanism of the chloroform contamination of water from well 22, two assumptions were made. One is that carbon tetrachloride, the lesser contaminant in the unsaturated zone, is dissolved in part of the chloroform but has not migrated as far as well 22 in concentrations large enough to be detected. The other assumption is that the contamination came from only one chloroform spill. Other sources of chloroform are considered minor and would move similarly to the one spill described. This discussion will mention only chloroform because the carbon tetrachloride is assumed to act in a similar manner.

On August 15, 1970, Triangle's northernmost 20,000-gallon chloroform storage tank overflowed a reported 5,000 gallons of chloroform. The chloroform is reported to have spread over a wide area and evaporated or percolated into the ground. The land surface in the diked area of the storage tanks is flat and sandy. Evidently, a large amount of the spill entered the soil as a liquid and moved downward. As the volatile liquid moved downward in the alluvium, it may have volatilized and moved laterally and preferentially in a north-south direction as a gas. The chloroform may have been adsorbed on silicates and other fine-grained minerals in the alluvium, and based on limited data from soil sampling (see Soil Sampling and Data), was preferentially adsorbed at clayey layers.

The chloroform that entered the ground moved until it was all adsorbed in the alluvial material and did not reach the water table. Had there been a larger or continuing source of chloroform, or had the spill been in a small area, the chloroform probably would have continued to move downward to the water table—at that time about 70 feet below the surface. Percolation of precipitation within the diked area may have flushed some of the chloroform from shallow to deeper positions, but data on such movement are unavailable.

In the summer of 1975 the ground-water level beneath the storage tanks rose and the chloroform and the water came in contact; some chloroform was dissolved in the water and began moving down the local hydraulic gra-

dient toward well 22. Between June 25 and July 2, 1975, the chloroform-contaminated water reached well 22; on July 2, 1975, the concentration was 25 mg/L. Fluctuations after July 2, 1975, are shown in figure 15.

Chloroform and water are slightly miscible; as the water level rose much of the chloroform at the water table-chloroform interface must have moved upward with the water. Some chloroform was dissolved in the ground water and was available to move with it toward well 22. As the water level declined, less chloroform was in contact with ground water and the amount retained in solution moved to well 22 as a residual amount.

The mechanism by which the chloroform enters the well screen and is pumped from well 22 is inferred. The pumping water level in well 22, when pumped at the increased 1978 discharge, is about 25 feet lower than the water level at the chloroform storage tanks. The chloroform is inferred to move down this gradient with or ahead of the ground-water movement toward the well, with the chloroform at or just below the water table. Since the top of the well screen is below the water table at the well, the chloroform probably moves down the outside of the well casing to the top of the screen and enters the well.

THE FUTURE

The second objective of this investigation was to evaluate the probable distribution of chloroform in the aquifer under various pumping and nonpumping conditions. As discussed previously, although the aquifer is contaminated, it is the unsaturated zone of the alluvium above the water table that contains the greater part of the contaminant. The ground water in the aquifer reacts with and moves part of the chloroform when the ground water comes in contact with it.

Considering the mechanism of the chloroform and carbon tetrachloride contamination, the problem is of small areal extent and there appear to be only two alternative methods to consider in evaluating the future. The possible alternatives for well 22 are to continue pumping or to stop pumping. A constraint on these two alternatives is the long-term trend of the water table. There has been a long-term rise of water level since 1970 (see fig. 14) and a late spring or midsummer seasonal rise.

Stop Pumping Well 22

The immediate reaction to not pumping well 22 when the water table is rising would be a rise of the water table around the well. This immediate and long-term rise would cause the water to contact more chloroform and in-

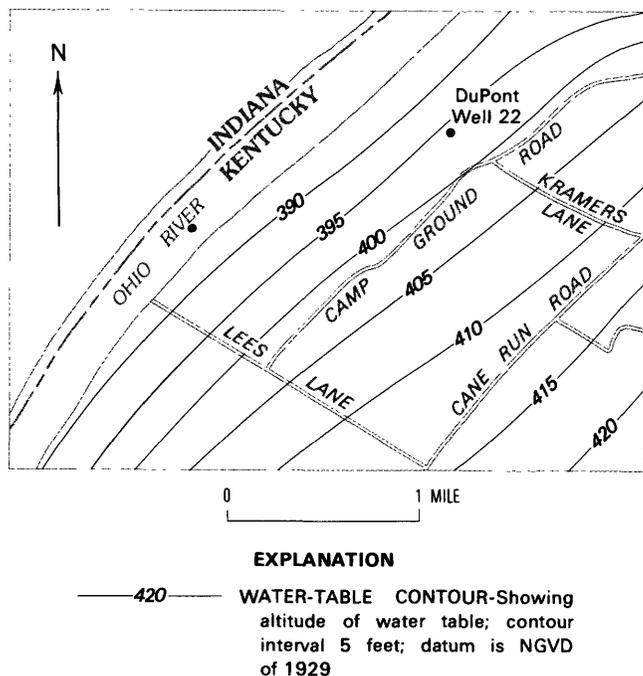


Figure 16. Configuration of water levels in the alluvium near well 22 on October 30 and 31 and November 1, 1978.

crease the chloroform concentration in the ground water close to the well.

A new equilibrium would be established and the contaminated water would move down the hydraulic gradient which naturally is westward toward the Ohio River as shown in figure 16. However, the effect of pumpage of about 1 million gallons of water per day from wells at American Synthetic Rubber Corporation is probably great enough locally to alter the gradient so that movement would be toward these wells, and the location of contamination would change. The nearest well, well 5, is about 450 feet from DuPont's well 22 and pumps 500 gal/min. Whether the wetted chloroform and carbon tetrachloride would be adsorbed by alluvial minerals in transit is unknown.

If the pumping of well 22 is stopped when the water table is declining, the immediate reaction would be a rise in the water table around well 22 and more chloroform would be in contact with ground water. However, as the water level declined, less chloroform would be in contact with the water, but any residual chloroform in the ground water would probably move toward the American Synthetic Rubber Corporation's wells.

After the water level declines below the chloroform, most of the adsorbed chloroform may remain in its present position until the next rise of the ground-water level, or it may be equally possible that water from precipitation moving downward through the contaminated alluvium

would desorb some chloroform and move it to the water table where it would move down the local hydraulic gradient, probably to the nearby wells of the American Synthetic Rubber Corporation.

Continue Pumping Well 22

If pumping of well 22 is continued, the chloroform concentration will be dependent on seasonal and long-term fluctuations of the ground-water table and possibly upon local recharge through the surficial materials as it has been since 1975.

If well 22 continues to be pumped and the water table rises, more chloroform will be in contact with the water and the chloroform concentration in water from well 22 will increase as it has every summer since 1975. The summer increase is seasonal. However, the continual pumping of chloroform is caused by the long-term rise of water level and will continue as long as the ground water is in contact with the chloroform until the chloroform supply is exhausted.

If the pumping of well 22 continues and the long-term water level declines, the chloroform concentration in water from the well will decline, and as the ground water loses contact with the base of the chloroform, only residual chloroform will be produced. The well would probably produce chloroform when the seasonal high water level contacts the base of the chloroform. With a further decline of the water level, even the seasonal high water level will not reach the base of the chloroform and only residual and perhaps no chloroform will be produced from well 22. However, the flushing effect of water from precipitation moving downward through the chloroform-laden alluvium is not known. Some chloroform may be desorbed and move downward to the water table.

If the long-term trend of water-level movement becomes downward, it appears, at first glance, that the contamination problem would be solved. It would not be. The chloroform evidently will either remain adsorbed on the alluvial material and remain relatively stationary until (1) a rising water level comes in contact with it and the chloroform again moves with the ground water or (2) local recharge is sufficient to move the chloroform to the water table.

SUMMARY

Well 22 at the DuPont chemical plant in Louisville continues to yield water containing variable amounts of chloroform. The concentration of chloroform increases as the water table rises and decreases as the water table declines. Test drilling shows that the contaminants, chloroform and lesser amounts of carbon tetrachloride, are in the unsaturated zone above the water table. They enter

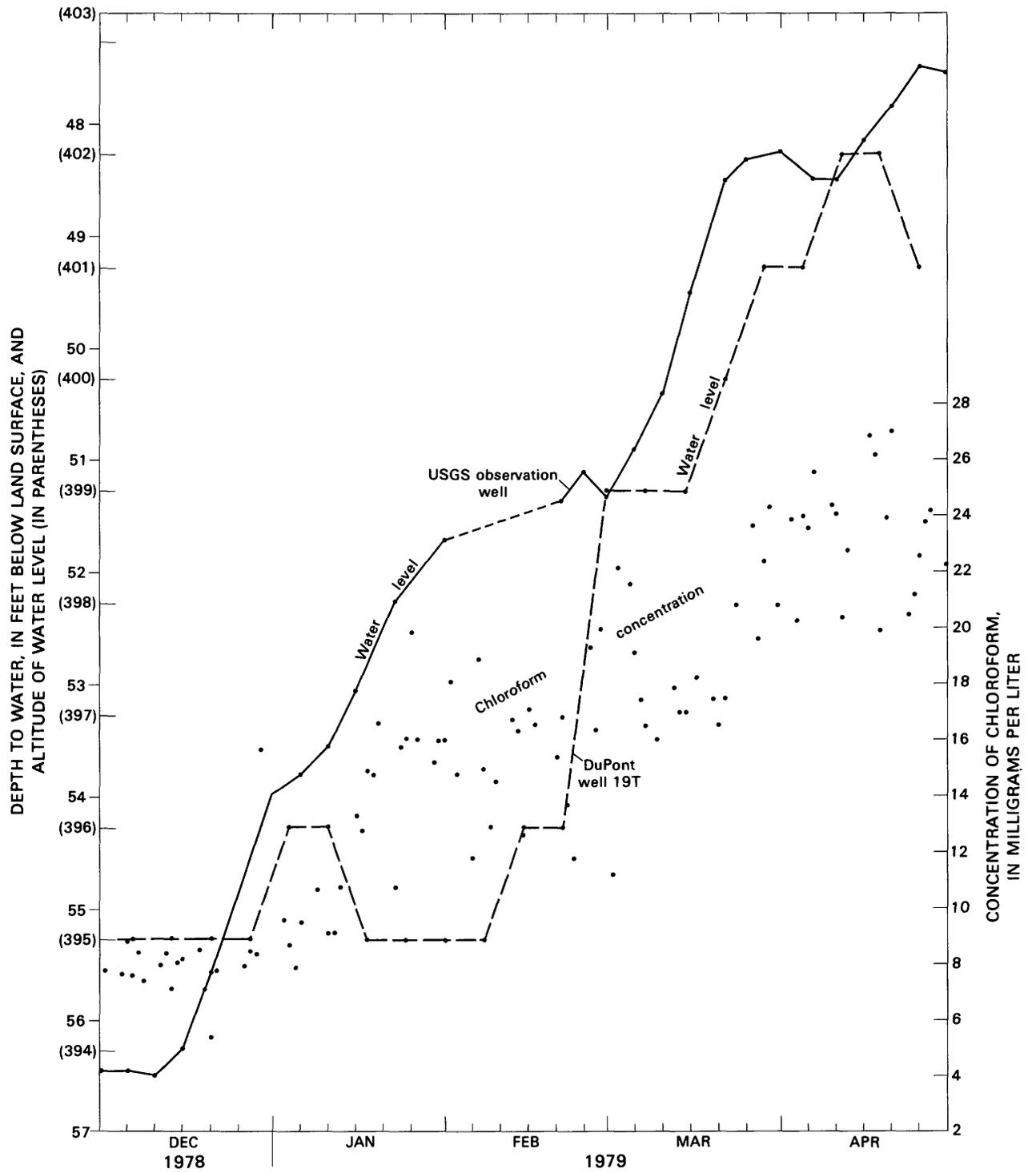


Figure 17. Water level at the USGS observation well at Triangle Refineries, Inc., and at DuPont's observation well 19T, and the chloroform concentration in DuPont's well 22.

the ground water when the water level rises above the base of the contaminated zone. No carbon tetrachloride has been analyzed in water from well 22.

The effect of precipitation in leaching the contaminants from the unsaturated zone to the zone of saturation is unknown. If well 22 continues pumping, the chloroform contamination will probably continue until the source is

exhausted or until the ground-water level declines below the contaminated zone. If well 22 stops pumping, the contaminant will probably migrate northward to the well field of the American Synthetic Rubber Corporation.

The source of the chloroform is probably a reported spill of 5,000 gallons at the Triangle Refineries, Inc., in 1970.

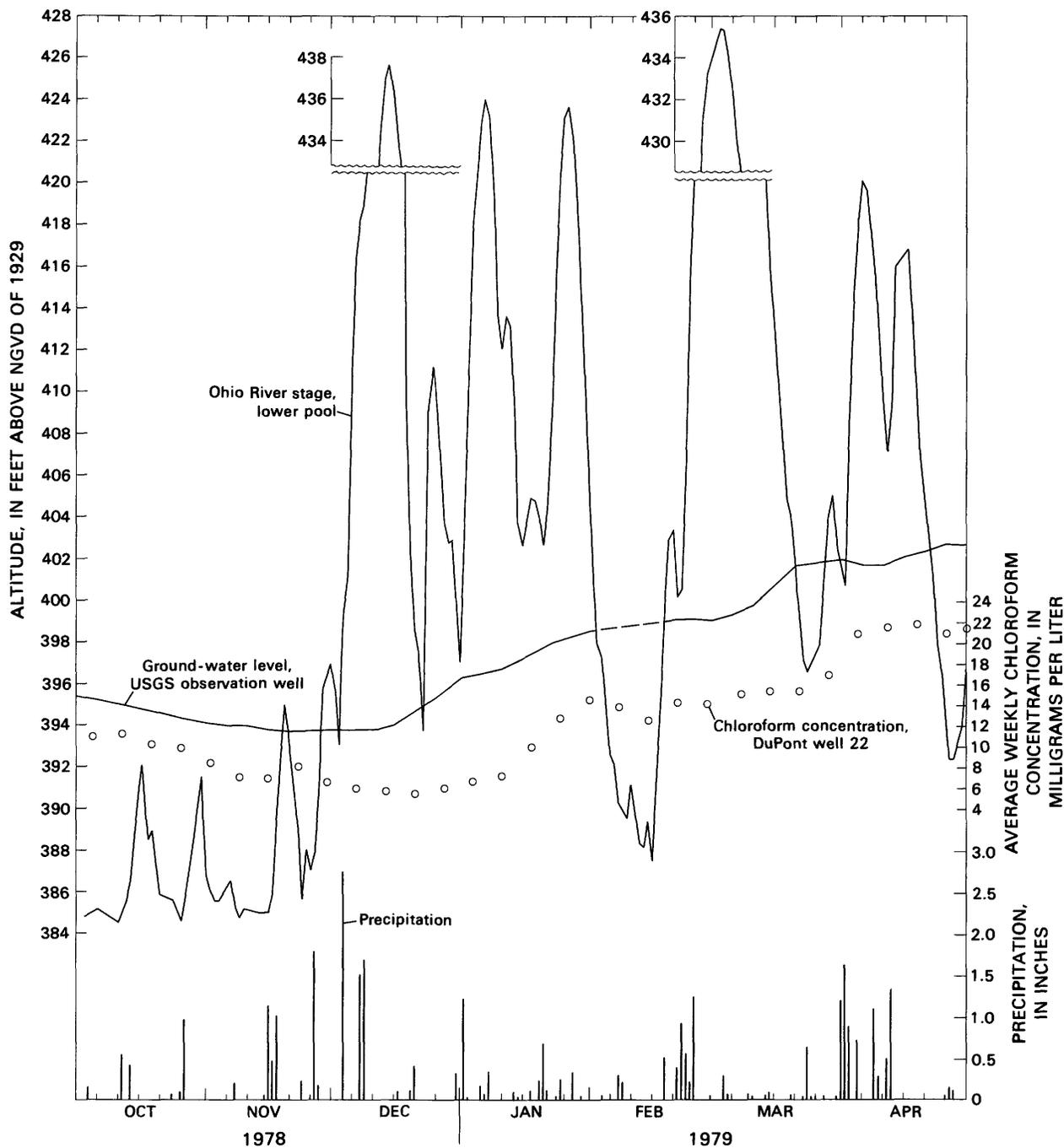


Figure 18. Water level at the USGS observation well at Triangle Refineries, Inc., the chloroform concentration in DuPont's well 22, the Ohio River stage, and precipitation at Louisville, Ky., from October 1978 through April 1979.

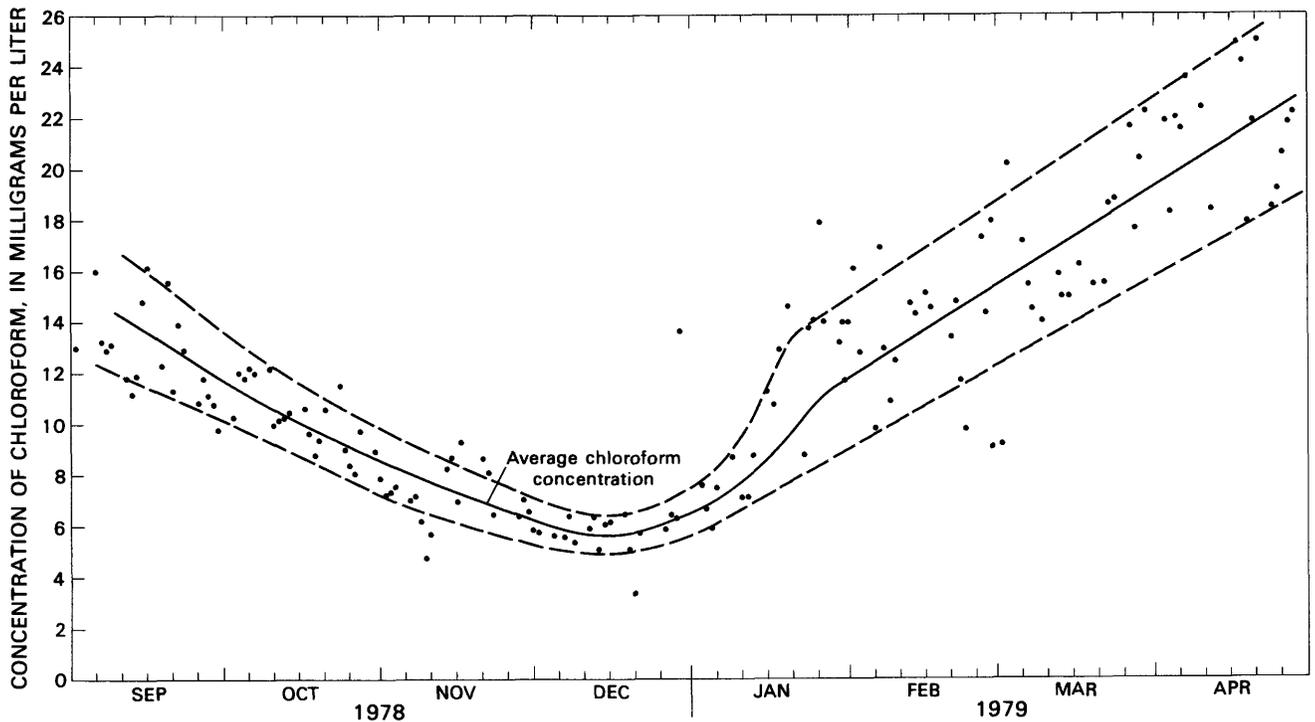


Figure 19. Reported concentration of chloroform in water from DuPont's well 22 and the calculated average value from September 1978 through April 1979.

ADDENDUM

After this report was written and while it was being reviewed, the Ohio River flooded at Louisville in December 1978. This was the first early flood of the river since the chloroform contamination was discovered in well 22. An automatic water-level recorder in a new observation well, 68.8 feet deep (altitude 381.5 feet), recorded the rising water levels in the alluvium at the chloroform storage area of the Triangle Refineries, Inc. Water from well 22 was analyzed by DuPont for chloroform concentration almost daily.

This rise of ground-water level in response to the flooding was an earlier-than-anticipated chance to monitor accurately the relation between ground-water levels at the site of the contamination and the concentration of chloroform in water from well 22.

These new data are presented in four illustrations that show the relation between the chloroform concentration in water from well 22 with ground-water levels, river stages, and precipitation.

Figure 17 shows water levels in the USGS observation well (equipped with automatic water-level recorder), reported water levels in well 19T, and reported chloroform concentration from well 22.

The long-term trend of water levels in the two wells is very similar, although some discrepancies exist in short-

term trends. This long-term trend agreement strengthens the use of DuPont's water-level data in figure 15 in establishing a mechanism of contamination.

Figure 18 shows an increase in chloroform in water from well 22 from October 1978 through April 1979. Also shown are water levels in the USGS observation well at the chloroform tanks, the Ohio River stage in the lower pool, and precipitation in Louisville as measured by the National Weather Service at Standiford Field.

Heavy rainfall in late November and early December in the Ohio River basin caused a rise in the stage and flooding of the Ohio River and a rise in ground-water levels. The increase in chloroform concentration in water from well 22 lagged the rise in ground-water levels by several weeks.

The stage of the Ohio River remained above normal the remainder of the winter, ground-water levels continued rising, and precipitation was evenly spaced during the winter until March when rainfall was 2.34 inches below normal. During this time the chloroform concentration in water from well 22 continued to rise.

To show the effect of rising ground-water levels on the concentration of chloroform in water from well 22, the chloroform concentration must be averaged because of the large daily fluctuation, as reported by DuPont. Figure 19 shows the reported chloroform concentrations from September 1978 through April 1979. The upper and lower

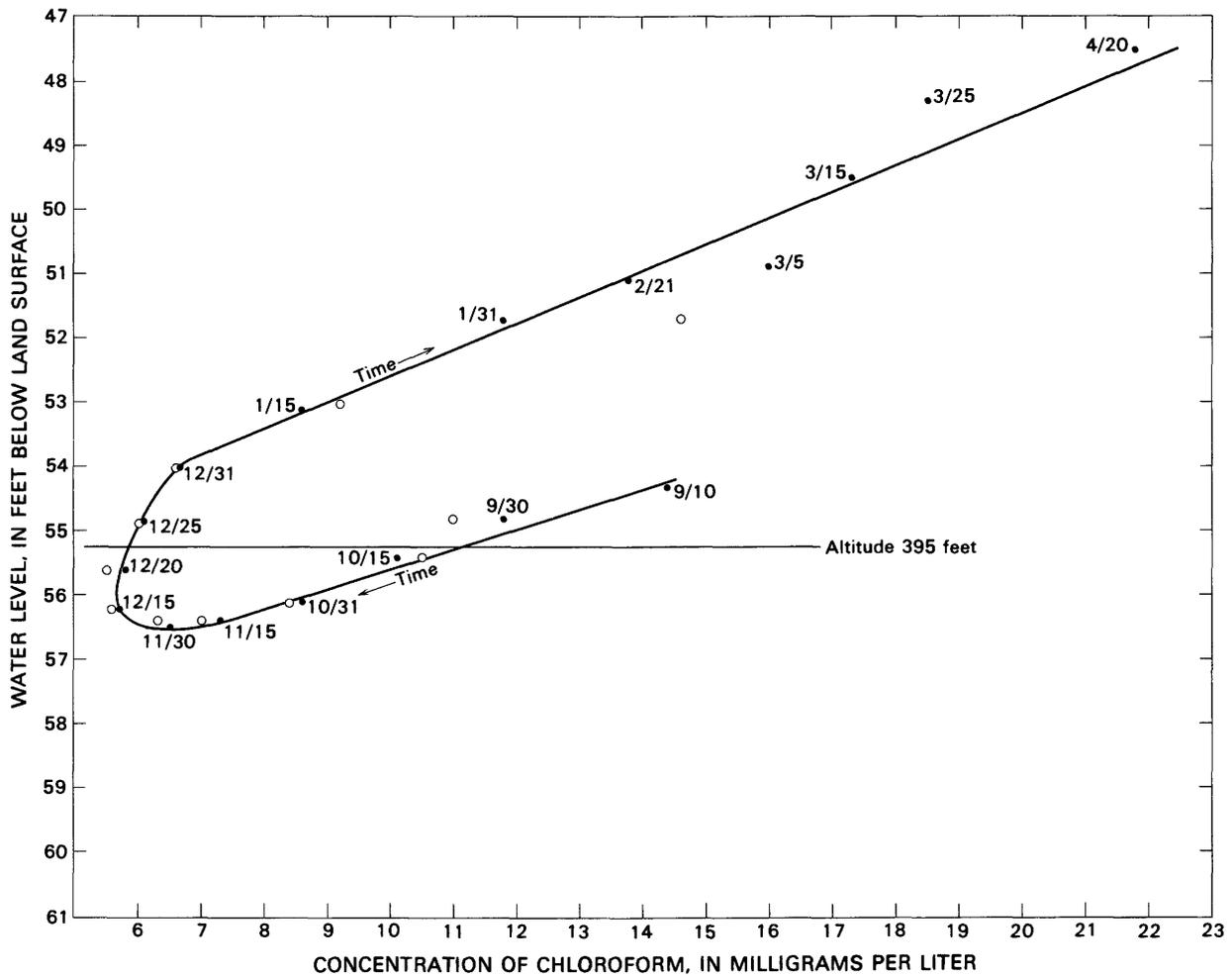


Figure 20. Chloroform concentration in water from DuPont's well 22 as a function of the water level in the USGS observation well. The dotted circles indicate average weekly chloroform concentrations (fig. 18) plotted against water level (for the week of September 30, 1978, through the week of January 31, 1979, only).

dashed lines enclosed most of the data. The solid line is drawn midway between the dashed lines and is considered to represent the average chloroform concentration for the period of time.

Figure 20 shows the average chloroform concentration as a function of water level in the USGS observation well. As the ground-water level dropped to about 394-foot altitude the chloroform concentration decreased. The chloroform concentration decreased in early December even though the water level had risen slightly. After the water level had risen above the 395-foot altitude, the chloroform concentration rose rapidly. Except for the transition period from falling to rising water levels, the relation between water level and chloroform concentration is linear.

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Conversion of Inch-Pound Units to Metric International System of Units (S.I.) and Glossary

Data in this report are given in inch-pound units. To convert inch-pound units to International System of Units (S.I.), the following conversion factors are used:

<i>Multiply inch-pound</i>	<i>By</i>	<i>To obtain metric units</i>
in (inch)	25.4	mm (millimeter)
ft (foot)	.3048	m (meter)
mi (mile)	1.609	km (kilometer)
gal (gallon)	3.785	L (liter)
gal/min (gallon per minute)	6.309×10^2	L/s (liter per second)
ft ³ /s (cubic foot per second)	.02832	m ³ /s (cubic meter per second)

National Geodetic Vertical Datum of 1929 (NGVD) is a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada. It was formerly called "Sea Level Datum of 1929" or "mean sea level."