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Wisconsin Groundwater Management Practice Monitoring Project

No. 40

GROUNDWATER
Wisconsin's
buried treasure

Wisconsin Department of Natural Resources

CHARACTERIZATION OF GROUNDWATER IMPACTS AT AN ABOVE GROUND PETROLEUM STORAGE TERMINAL

BY:

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A Report Submitted to the Wisconsin Department of Natural Resources
and The Cenex Petroleum Company.

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INTRODUCTION

The objective of this study is to evaluate the groundwater impacts from condensate discharges at a petroleum storage facility. Condensate is waste water from petroleum storage tanks that is normally discharged either to a diked area adjacent to the storage tanks or to an oil/water separator. Oil/water separators typically discharge to drainage ditches or other surface waters, but at some facilities they discharge into diked areas. This paper addresses condensate discharges which go to diked areas either directly or indirectly via an oil/water separator.

Oil/water separators are installed at these facilities to provide treatment of routine runoff from the loading area and provide on-site treatment in the case of a spill. Separators are occasionally used to treat the small amounts of condensate produced from normal plant operation for lack of a better on-site method.

Oil/water separator discharges are currently regulated under the Wisconsin pollution discharge elimination system (WPDES, or wastewater discharge permit program). The State of Wisconsin Department of Natural Resources (WDNR) is concerned with the impacts that condensate discharges may have on groundwater quality. This study was proposed in January of 1986 to investigate these concerns by measuring groundwater volatile organics and some nonvolatile organics at such a storage facility in Wisconsin. Results will be used by the WDNR to identify process, treatment or equipment changes that could later be incorporated into the statewide permitting system.

DNR WPDES records were reviewed to determine petroleum storage facilities in Wisconsin. Eight facilities were identified and asked for permission to conduct the study. Cenex Petroleum agreed to a study at their petroleum storage facility near McFarland, Wisconsin.

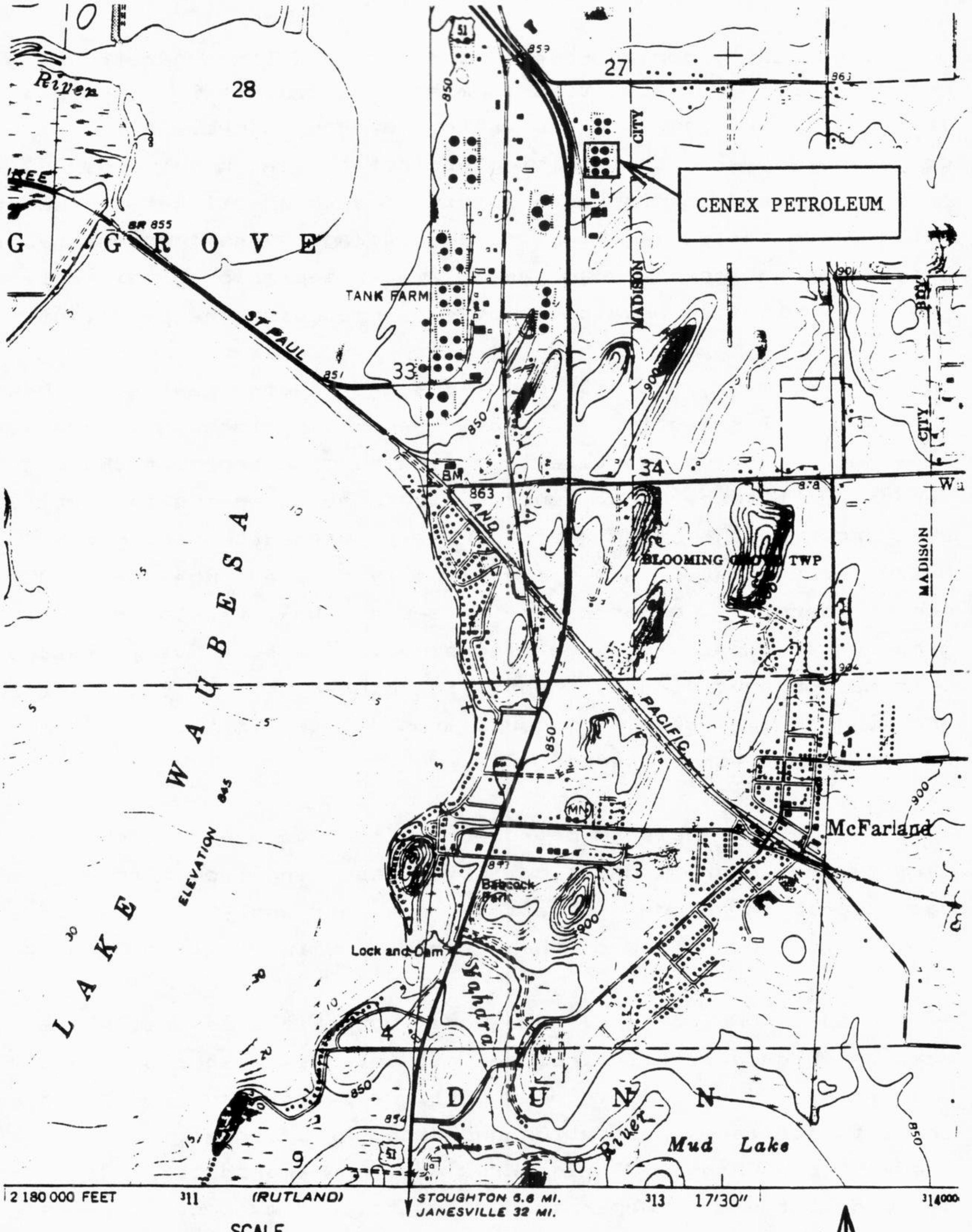
The site is located in lowlands near other similar storage facilities in the SE1/4, NE1/4, SW1/4, Section 27, T7N, R10E, Dane county (Figure 1). There are no known public water supplies between the study area and Lake Waubesa. The study began in July of 1986 and was planned to last one year.

Lake Waubesa lies to the west of the property and appears, for the majority of the time, to be a groundwater discharge area. On occasion, heavy rains cause local surface flooding and appear to cause groundwater gradient reversal. During these periods, Lake Waubesa may recharge to the groundwater. Plant operators indicated that the whole property was susceptible to flooding until fill and drainage were provided about 10 years ago.

Existing information on groundwater petroleum contamination at tank farms is mainly from spill response activities. There has been very little research into contamination resulting from permitted daily operations. A computerized literature search of Chemical Abstracts and Selected Water Resources Abstracts yielded no pertinent reports on groundwater impacts from normal operations of above ground petroleum storage facilities or oil/water separators.

This study determined the constituents of the wastewater streams and characterized groundwater pollution from the tank farm. Final recommendations to the State of Wisconsin and regulated facilities are based on groundwater impacts.

Figure 1 - Site Location Map



BACKGROUND

Organically contaminated water is typically generated at petroleum storage facilities from spillage in the loading area and from water that enters the petroleum storage tanks. All contaminated water that originates from the catchment drains surrounding the loading area is diverted to an oil/water separator. Water accumulating in the petroleum storage tanks (condensate) is discharged periodically to the oil/water separator or directly to the ground inside containment dikes surrounding the petroleum tanks.

These small intermittent discharges of condensate were unknown to WDNR until recently. Oil/water separator discharges have been previously allowed by state laws because discharges at these sites were thought to be mainly surface drainage. Condensate that is discharged to the diked areas directly, without entering the oil/water separator is not specifically covered under the WPDES general permit. Concerns were raised by WDNR over the possible groundwater impacts of such discharges. There was very limited information specifically identifying condensate VOC concentrations and discharge amounts from tank farms. This limited WDNRs' ability to evaluate these systems.

State laws apply to petroleum storage terminal discharge permits and to groundwater pollution resulting from plant operation. Three administrative codes that apply are Chapters NR 205, NR 214 and NR 140 of the Wisconsin Administrative Code.

Chapter NR 205, Wis. Adm. Code, authorizes general WPDES permits which currently includes oil/water separator discharges. Chapter NR 214 Wis. Adm. Code, outlines permitting procedures and criteria for land application and disposal of industrial wastewater. Chapter NR 214, Wis. Adm. Code, prohibits "discharge of toxic pollutants or hazardous wastes to land disposal systems, unless the applicant can demonstrate and the department determines that the discharge of such pollutants will be in such small quantities that no environmental pollution will result".

Concentrations of organics in tank farm discharges were previously believed to be so small that environmental pollution was negligible. Most oil/water separator discharges have been to surface waters where most VOCs readily volatilize to the atmosphere.

DNR is also concerned that unregulated discharges may cause possible conflicts with recently created groundwater standards in Chapter NR 140 Wis. Adm. Code. Chapter NR 140 Wis. Adm. Code, establishes groundwater quality standards , establishes points of standards application and establishes responses the department may require if a groundwater standard is approached or exceeded. This code also specifies a preventive action limit (PAL) for substances with established groundwater standards. For substances that have carcinogenic, mutagenic or teratogenic properties or interactive effects, the PAL is 10% of the enforcement standard. For all other substances, the PAL is 20% of the enforcement standard. The major petroleum constituents which have PALs are listed in Table 1.

Table 1

Substance	Enforcement Standard (ppb)	PAL (ppb)	Detection Limit(ppb)
Benzene	.67	.067 (10%)	1.0
Toluene	343	68.6 (20%)	1.0
Xylene	620	124 (20%)	2.0

Note: The detection limit for benzene is higher than the PAL and enforcement standard.

PALs establish a contaminant level, below the enforcement standard, at which the WDNR must assess cause, significance and appropriate response for the contamination. Remedial action responses are decided at the discretion of WDNR and are usually more rigorous for PALs exceeded at the property boundary.

Major volatile petroleum constituents of concern in this study include ethylbenzene, benzene, toluene and xylene. All of these VOCs are lighter than water, but their water solubilities and vapor pressures vary. Some properties of these compounds are listed in Table 2. Despite variability in solubility, all compounds in Table 2 show solubilities greater than any concentrations measured in this study.

Table 2

PROPERTIES OF SELECTED ORGANIC COMPOUNDS

Name	Density	Solubility H_2O(mg/L)	Henry's Law C Dimensionless	Log O/W Part.Coef.	Vap.P. mmHg
Benzene	0.88	1,780-1,800	.22 @20°C	2.13	95.2
Toluene	0.87	535-627	.27 @25°C	2.69	28.0
Ethyl-benzene	0.87	150-152	.27 @20°C	3.15	7.0
Xylenes	0.86-0.88	170-200	.24*@25°C*	2.8-3.2	6.6-8.7*

* Calculated in Appendix F

Data from: EPA, 1982; CRC, 1976; Stephen, H, 1979; Dean,.1985; Lyman 1985; Leo and Hansch, 1971.

The Cenex petroleum storage terminal (tank farm) stores leaded gasoline, unleaded gasoline, #1 fuel oil and #2 fuel oil. These products are supplied by a 12" underground pipeline from the Chicago area and stored in six tanks with a combined capacity of 7.14 million gallons. Petroleum products are metered into tanker trucks and hauled to various bulk plants and gas stations around the state. Other similar petroleum distribution points are located in

Milwaukee, Green Bay, Chippewa Falls, Junction City, Cadott, Wausau, LaCrosse and Superior.

Separator discharges from the adjacent petroleum storage facility to the north go to a filter field on that property. These discharges do not appear to have an impact on the Cenex property. This is due to the fact that the Cenex facility is located in an area normally upgradient from any other petroleum storage tanks (Figure 1). Dike drainage is discharged to a drainage ditch which runs straight south through the east side of the Cenex property (Figure 2). This drainage could have potentially caused background contamination, but no such contamination attributable to this source was detected during this study.

The site (Figure 2) consists of the tank and catchment area, the loading area and an an office/garage facility. The site is kept very clean and no significant spillage was observed in the loading area during the course of this study.

The loading area is one of two areas that generates contaminated water. This area is totally paved. The amount of contaminated runoff is minimized by covering the loading area to help keep out precipitation. Rain that is not intercepted by the roof may contact organics left on the loading area and wash into the drain and into the 2500 gallon oil/water separator. If enough precipitation and surface runoff enter the oil/water separator, it discharges into the dike.

Wastewater is also generated from water intrusion and condensation in petroleum storage tanks. Water accumulates on the bottom of the tanks until it is drawn off through a bottom valve. In effect, this means that organic contaminants have from 6 months to a year to saturate the water fraction.

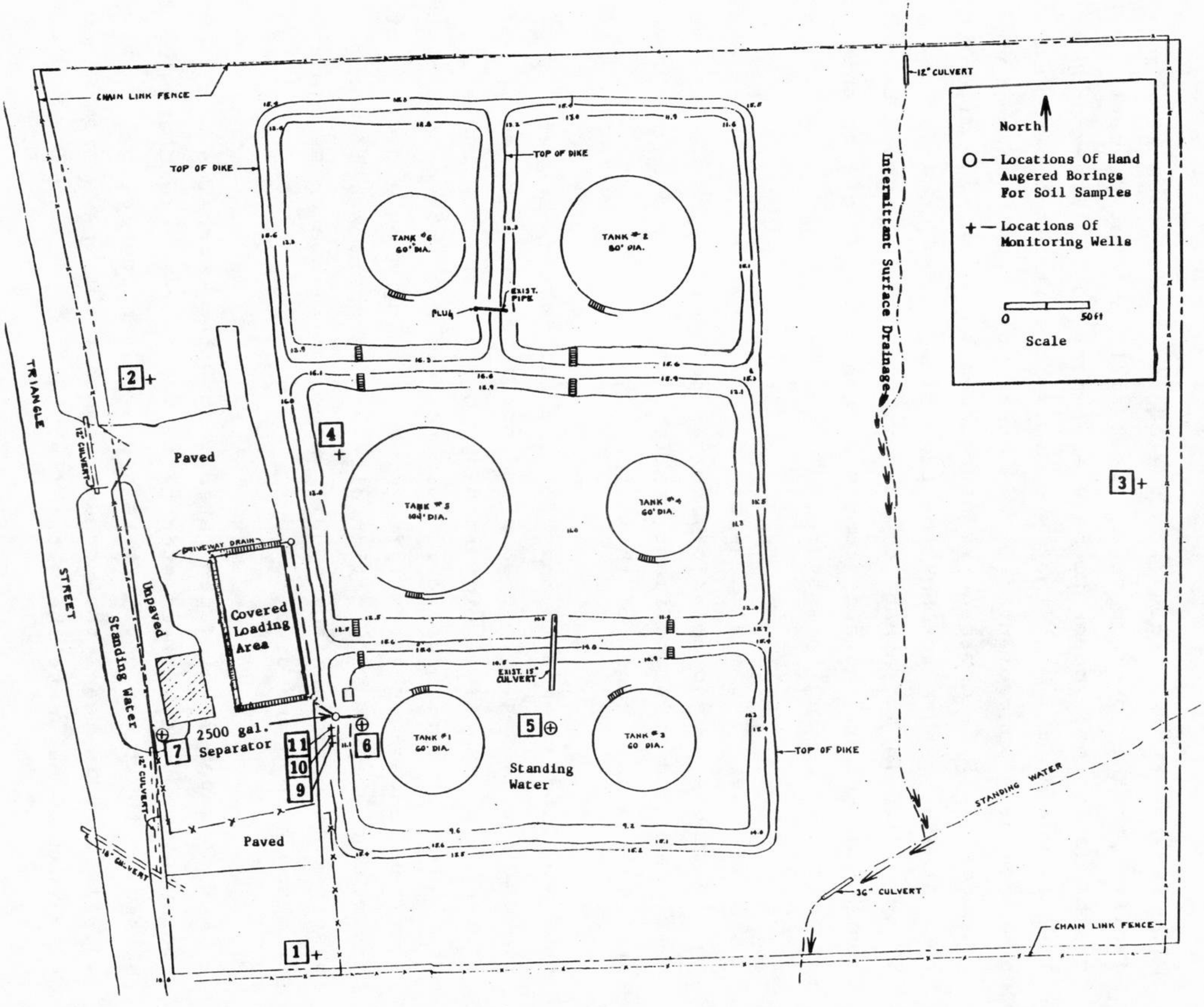


Figure 2 - Cenex Facility

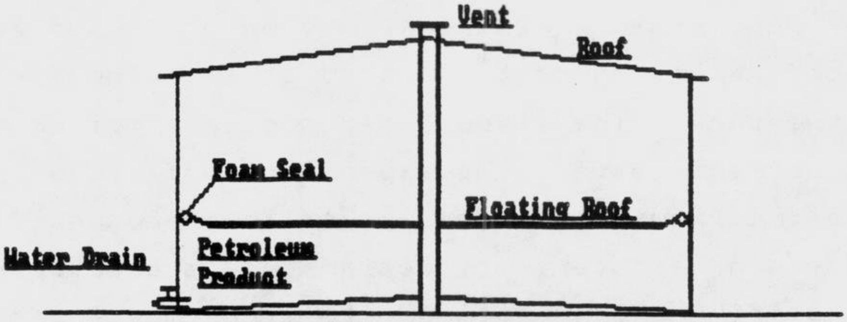
The three basic storage tank designs used at this facility are shown in Figures 3, 4 and 5 (Sutton, 1967 and Hubbert, 1951). The single outer roof design (Figure 4) may have a fixed roof or an expansion roof depending on the method of allowing for gas volume changes in the tank. The fixed outer roof accomplishes this with a pressure adjustment valve. The expansion roof rides on top of gasses above the liquid and rises or falls to adjust for pressure changes. The single outer roof designs are susceptible to water accumulations from condensation due to air temperature changes inside the tank. Condensate is also produced in the double roof design in this way.

Water may also enter any of the tank designs from the underground terminal supply pipeline. Condensate from single outer roofed and double roofed tanks requires draining approximately once per year.

Water accumulates in the single floating roof tank because of direct exposure to precipitation. Most of this water is drained off the roof periodically. Wastewater is produced from seepage along the seals on the edge of the floating roof. This wastewater will also be referred to as condensate. Because of the additional water produced, single floating roof tanks must be drained at least twice per year.

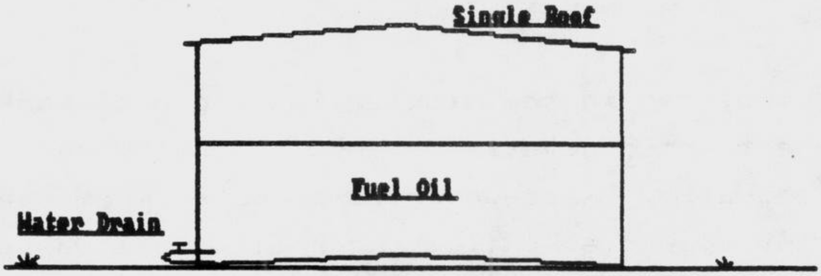
The five tanks on site that produce smaller amounts of condensate, approximately 500 gallons each per year, are drained directly to the soil inside the containment berm. Condensate from the single floating roof tank (#1) is discharged through a hose to the oil/water separator (Figure 6) about two times per year. The amount of condensate produced is proportional to the amount of rain and snow accumulation on the roof of the tank. In the fall of 1986, the floating roof tank had to be cleaned as part of regular

Figure 3



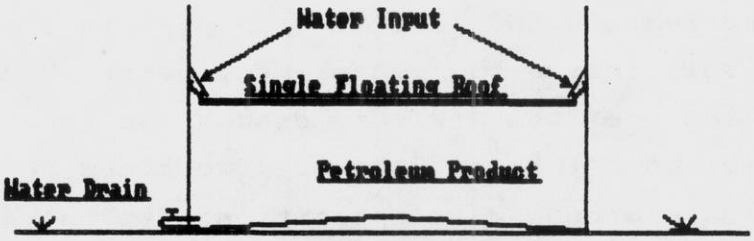
FLOATING DOUBLE ROOF TANK DESIGN

Figure 4



SINGLE OUTER ROOF TANK DESIGN

Figure 5



SINGLE FLOATING ROOF TANK DESIGN

maintenance so the tank was totally emptied of condensate. Amounts of condensate reported during 1986 were larger because of this and should be considered worst case for this site.

Cenex provided access to their records for information on quantities of condensate draw off. Tank farm operators record the amount of condensate removed from a tank so that it will not be mistaken for petroleum losses due to normal processes such as evaporation and volume/temperature changes. Records were reviewed back to 1984. Before 1986, condensate pumping losses were lumped in with actual petroleum losses. In 1986, Cenex changed their record keeping method and began recording condensate losses. Because of this, condensate production amounts are based on 1986 records only. The total condensate amount in Table 3 should be considered a reasonable total for all tank drainage per year.

Table 3

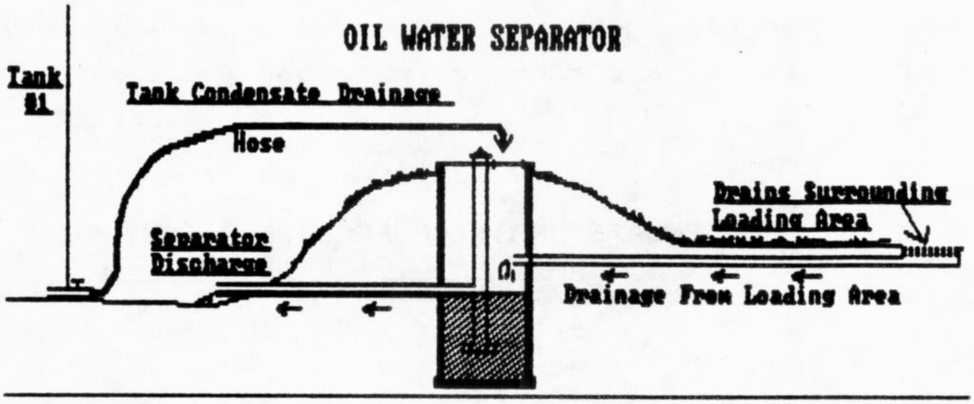
CONDENSATE DRAINAGE RECORDED FOR 1986

	DATE	GALLONS DRAINED
Tank #1	9/11/86	1320
	9/12/86	6169
	9/15/86	220
	9/17/86	200
	9/18/86	2423
	9/22/86	4188
	Subtotal	14520
Other 5 tanks (estimate)		2500
	Total	17020

A schematic of the oil/water separator is shown in Figure 6. When the wastewater rises above the discharge pipe, wastewater from the bottom of the separator is discharged inside the berm. When there is no loading, the separator remains filled to the bottom of the discharge pipe. The separator is designed to separate petroleum contaminated wastewater into two phases. If two phases were present, the less dense petroleum product could be pumped off the top while the aqueous wastes are discharged through the separator outlet. Because most of the waste at this site is organic matter dissolved in water, the separator acts primarily as a holding tank providing waste dilution and some evaporation before discharge into the dike.

The oil/water separator had historically been pumped and cleaned on a yearly basis, but recent plant operations do not include this. This is primarily due to the expense of treating the 2500 gallons of waste generated from this procedure.

Figure 6



METHODOLOGY AND INITIAL FINDINGS

WELL INSTALLATION

The wells were not all installed at the same time because there was no background groundwater information for the site and some wells were to be installed after initial results were analyzed. Five wells were initially installed to characterize groundwater quality and flow patterns. Water table wells were used because they yielded water level information and they could be used to indicate the presence of free product on the water table surface. The organics in question are lighter than water so both floating and dissolved VOCs at the water table could be detected by water table wells.

Three of the five wells initially installed for this study were located to the west or down gradient of the tanks. With Lake Waubesa, a discharge area lying to the west ,regional groundwater flow was estimated to be westerly. Two background wells (1 and 2) were installed down gradient (SW and NW of the separator discharge area respectively) and one well (3) was installed up gradient at the property boundary, (Figure 2). Well #4 is located inside the containment berms centered downgradient of the storage tanks. Well 5 is located inside the containment berm that received separator discharge.

Wells 6 and 7 were installed after initial results from the first five wells were analyzed. Well 6 was located at the separator discharge and well 7 was located downgradient from well 6. These two locations were thought to be the most likely to show any groundwater contamination. A piezometer nest, (wells 9, 10 and 11) was also installed later to detect any vertical movement of a contaminant plume. Well 8 was a potable water supply well on the site which did not yield useful data.

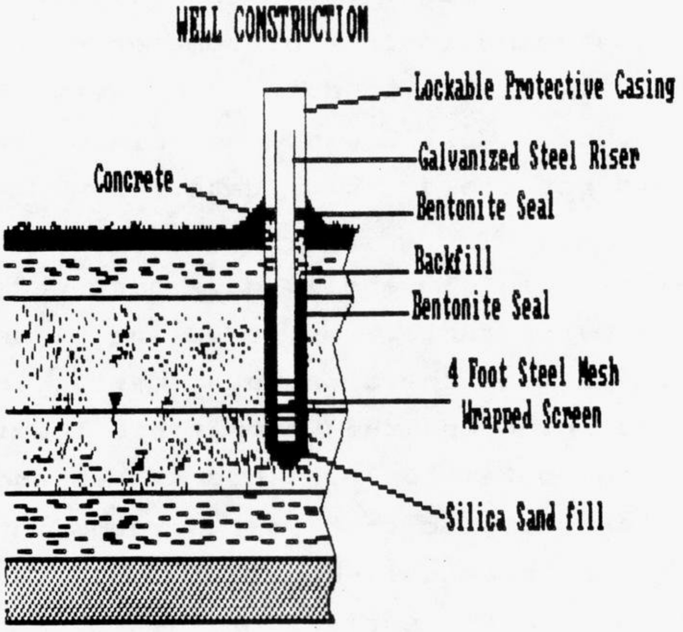
All wells except 10 and 11 have screened intervals which intercept the water table. Wells 10 and 11 were screened at deeper elevations as part of the piezometer nest. The four foot screens were placed to intercept the water table leaving 0.5 to 2 feet of screen above the water table. This leaves enough distance above and below the water table so that well screens intercept the water table even if there are seasonal changes in its elevation. In this way, floating product on the surface of the water table can enter the well. Well installation is illustrated in Figure 7. Relative well screen elevations are listed in Table 4. Average water table elevations are shown in Appendix B-53.

Table 4

Well	Elevation To The Bottom Of Screen	Average Water Table Elevation	**Ave.** Depth Of Water in Well
1	847.03	852.89	5.86
2	849.82	852.82	1.99
3	848.76	853.07	4.31
4	849.20	852.84	3.64
5	849.06	853.00	3.94
6	849.51	852.92	3.41
7	**849.33**	**853.62**	**4.29**
9	838.38	853.47	15.09
10	844.43	853.46	9.03
11	849.75	853.44	3.69

Note: All well screens are 4 feet long except for wells 10 and 11 which had 2 foot screens. Wells 9, 10 and 11 are a piezometer nest (Data is in Appendix B-53).

Figure 7



Well screens are standard 2" steel wrapped with 60 gauze (.010 slot) steel mesh. Galvanized steel risers were used. A boring rig with a solid stem auger was used for installing all wells except 6 and 7. Wells 6 and 7 were installed by hand with a post hole auger.

Due to the shallow water table, wells 3 and 5 could not be sealed with bentonite. The top of the screen is so close to the land surface that bentonite could contaminate the water samples. A surface seal was provided by filling the remaining foot of open hole above the silica sand with clayey drillings. The protective casing was pushed down to the top of the screen and concreted in. Adequate seal from surface contamination is provided by concrete around the protective casing.

SOILS

Because the drilling rig with solid stem auger mixes soil layers and because boreholes were very shallow, all soil samples were taken from hand augered boreholes after the wells were drilled. No drilling log was made nor soil samples taken of rig augered borings in favor of the more accurate hand augered borings. Samples taken from the solid stem auger were identified in the field while drilling was taking place, but more accurate identification of soil layers came from hand augered samples taken at 0.5 to 1 foot increments. Since all three hand augered holes showed similar soil strata, no further soil investigation was conducted.

Soil samples were taken for particle size analysis and VOC analysis at three boring locations using a hand auger. These locations can be seen on Figure 2. The hand augered borings for wells 6 and 7 were used both for sampling and well construction. A separate borehole was hand augered near well 5 for soil sampling purposes only. Borings are located so that soil samples could be correlated with groundwater samples at monitoring wells 5, 6 and 7.

Petroleum odors were detected in the wet fine sand samples that came from below the clay silt layers near wells 5 and 6. The results of particle size analyses for these samples are listed in Appendix C.

Soil stratigraphy is shown in Figure 8. Shallow borings indicated that shallow clay and silt layers covered a homogeneous fine sand layer. Later deeper drilling showed that this fine sand layer was underlain by a thick silty clay layer. The driller on site indicated that he had encountered this type of deposit on the west side of Lake Waubesa and he estimated that this layer extended to sandstone at about 50 feet.

Potable well logs for the adjacent tank farm to the north indicate this clay layer as "hardpan" from 35 to 60 feet where sandstone begins. Well logs for the two potable wells drilled previously on the Cenex property did not delineate separate drift layers, but indicated that sandstone was encountered at 50 feet.

Figure 8

SOIL PROFILE, CENEX PETROLEUM TERMINAL

The unsaturated zone soils were sampled for VOCs above, within and below the upper clayey layer near wells 5, 6 and 7. Soil VOC analysis could indicate the amount of VOC adsorption onto soils. A significant part of any organic contamination may be bound in this way. Clay and silt soil layers, which have more absorption capacity and less permeability than sands, could be acting as a barrier to organic movement.

Each soil VOC grab sample was taken in two 40 ml vials each of which was provided with a teflon septum. All samples were removed directly from the borehole wall and immediately iced. VOC loss in sample collection was minimized by using the vials to collect the soil sample from the borehole wall. About 10 mls of the 40 ml vials were to be filled with soil so that extraction fluid (methanol) could be added in the lab without removing the cap and losing VOCs. This insitu extraction procedure was developed and is felt acceptable by the State Lab of Hygiene (SLH) to minimize loss of VOCs. As part of the SLH standard quality assurance program, recovery tests were previously conducted in developing this procedure. Samples were analyzed by the GC purge and trap method for four VOCs (benzene, ethylbenzene, toluene and xylene) detected in groundwater samples.

Vials for soil VOCs were mistakenly filled to capacity, capped and iced in the field. After the SLH indicated that too much sample was taken, vials were emptied of about 30 mls of sample in a 35°F cold room and resealed. This process was completed in 30 to 60 seconds to minimize VOC loss.

Loss of VOCs from soil samples may have occurred during the removal of sample from the borehole or during sample reduction. Loss also occurs from sample vials if any soil comes between the septum seal and glass vial. Possible methods of reducing losses from soil VOC samples include infield dry icing or infield extraction.

Volatilization during sample collection was suspected to have reduced soil VOC levels. For this reason, VOC sample results were inconclusive with regard to soil VOC adsorption.

GROUNDWATER MEASUREMENTS

A wetted chalked tape was used to measure water table elevations. Error for this measurement is + or - .02 feet resulting from uneven water lines on the chalked surface. This does not significantly change the projected water tables.

Water table maps were constructed using a computerized plotting program. Gradient or contour lines were extrapolated from water level measurements entered into the program. Parameters used in the program included 50 grid divisions, a search radius of 50 and a smoothing factor of .5. It should be noted that this program projects contour lines beyond areas with water level data. Water table gradient lines are less reliable for outlying areas away from monitoring wells.

Water level measurements from water table wells indicate local groundwater flows are westerly with some variation apparently from local recharge. Water table maps constructed at different times during the study are shown in Appendix A.

Appendix A-48 was generated to show the effect of well 7 on groundwater contours. Water levels from well 7 were higher by about one foot than adjacent areas. These high water level measurements could be due to localized recharge or perched water table. Analysis of survey results showed that the error of closure was 0.01 feet, so surveying error does not explain the high water elevations. A perched water table is unlikely considering that well 7 terminates at an elevation close to wells 2, 4, 5 and 6. Groundwater mounding near well 7 may be from localized recharge nearby. This recharge is likely coming from localized ponding of surface water in a roadside ditch located about 10 feet west of well 7. Water accumulates in the ditch because the culvert invert elevation is above the bottom of the ditch. Surface drainage has recently been redirected to the south along drainage ditches close to the east side of the Cenex property. This ditch receives this drainage and highway runoff from the north which contribute to the water ponded below the drainage culvert. To show normal area wide groundwater flow patterns, data from well 7 was excluded from all water table maps except for A-48.

Because well 7 was in a mounded groundwater area, contaminants from the oil/water separator would not be detected. Three initial samplings yielded nondetects at this well and therefore sampling was discontinued.

Slug/recovery tests for hydraulic conductivity utilized a pressure transducer and bailer. The slug test involves recording head increase with time after an instantaneous drawdown. The pressure transducer used in this study was calibrated at 2.63 units per foot change in the laboratory. Changes in head were recorded at 10 second intervals for 4 to 7 minutes. The water level in feet was plotted against time for recovery tests (Appendix D-55). These plots generally became nonlinear after 40 seconds.

Hydraulic conductivities for the fine sand layer in which the monitoring wells terminated were estimated to be $10^{-2.92}$ to $10^{-4.26}$cm/s. Calculations for hydraulic conductivity were performed according to methods established in Bouer and Rice, 1976 and are shown in Appendix D. Average linear velocities were calculated from these conductivities to show only that groundwater movement had the potential to move contaminants to the monitoring wells from the separator discharge.

Velocities were calculated using Darcy's Law, $V = -K/n * dh/dL$, where V is the average linear velocity, K is the hydraulic conductivity, n is the effective porosity (assumed to be .3) and dh/dL is the head gradient. Water level measurements in Appendix B show that gradients range from $2.8*10^{-4}$ft/ft to $8.5*10^{-4}$ft/ft. Hydraulic conductivities in Appendix D-57 were converted to ft/s obtaining a K range of $1.8*10^{-6}$ft/s to $3.94*10^{-5}$ft/s. Velocities calculated using Darcys Law ranged from $1.68*10^{-9}$ft/s to $1.12*10^{-7}$ ft/s.

Average linear velocity represents an overall estimate of the macroscopic change in location per unit time of groundwater moving through porous media. This velocity estimation method averages velocity deviations caused by soil spacial heterogeneities. This produces a single velocity term in the direction of groundwater flow. This is normally lower than microscopic velocities which are higher due to the longer tortuous paths that individual water molecules actually follow in pore spaces. This calculation was performed only to show that there is an existing groundwater velocity on site capable of producing contaminant transport from the separator to the monitoring wells. This information should not be used to estimate contaminant transport velocities because no consideration was given to dispersion, chemical reactions, biological reactions or retardation factors which effect contaminant velocity.

Wells were prepared for sampling by purging completely 3 times with a diaphragm pump. A minimum of six well volumes were removed from wells 9 and 10. Larger volumes were removed from wells 9 and 10 because the wells could not be completely purged of standing water. According to acceptable methods established by the WDNR, six well volumes should assure that samples taken from the wells were representative of groundwater quality. Samples were taken with a teflon bailer immediately after well recovery to minimize VOC volatilization. Estimated time from bailer filling to vial filling was usually less than 1 minute, but always less than two minutes.

Groundwater grab samples were taken from wells using standard procedures after the wells were bailed. Four 40 ml zero headspace samples were taken for each VOC grab sample and immediately iced in a prefabricated mailer supplied by the SLH. VOC mailers were always delivered to the SLH less than 7 hours after the first sample was taken. The SLH analyzed these samples using Gas Chromatography with a mass spectrometer detector (GC-Mass-spec.). Some of the compounds analyzed using this technique are listed in Table 5 and again on the sample sheet in Appendix E. This analysis has the capability of detecting hundreds more organics which were indicated, if present, but are not quantified. Those volatile organics listed in Appendix E and the upper part of Table 5 were quantified, if detected, using proven purge and trap GC techniques. Additional organic compounds detected but not quantified are also shown in Table 5.

In addition to the normal groundwater samples, "bailer blanks" were used to indicate cross contamination between sample points. After the standard rinsing procedure, the bailer was filled with distilled water which was then used to fill the 40 ml vials. Only one bailer blank could be taken for each sampling because funds were insufficient to pay for the analysis of bailer blanks for each well. To minimize the effect of cross contamination, wells were sampled in order from least to greatest expected contamination. The bailer blank was taken just before sampling wells with known contamination which were sampled last. All bailer blanks taken during the study showed no presence of organic cross contamination between wells.

VOC loss from samples is assumed to occur at any point where samples are exposed to air. Care was taken to minimize exposure time and temperature during sample taking. VOC loss may also occur during preparation of the well for sampling (purging). Aeration of incoming water may occur if groundwater cascades down the screen while flowing into the well. In water table wells, the unsaturated zone around the screen becomes aerated during each purging.

Table 5

VOCs Tested For In Each Analysis
(see also Appendix E)

Acrolein
Acrylonitrile
Benzene *
Bromobenzene
Bromodichloromethane
Bromoform
Bromomethane
n-Butylacetate
Carbon Disulfide
Carbon Tetrachloride
Chlorobenzene
Chloroethane
2-Chloroethylvinyl Ether
Chloroform
o-Chlorotoluene
p-Chlorotoluene
Dibromochloromethane
1,2-Dibromo-3-Chloropropane
o-Dichlorobenzene
m-Dichlorobenzene
p-Dichlorobenzene
1,1-Dichloroethane *
1,2-Dichloroethane
1,1-Dichloroethylene
1,2-Dichloroethylene
Dichloroiodomethane
1,2-Dichloropropane
cis-1,3-Dichloropropene
trans-1,3-Dichloropropene
Ethylbenzene *
Fluorotrichloromethane
Isopropylbenzene
Methylethylketone
Styrene
1,1,1,2-Tetrachloroethane
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Tetrahydrofuran
Toluene *
1,1,1-Trichloroethane
1,1,2-Trichloroethane
Trichloroethylene *
Trichlorotrifluoroethane
Vinyl Chloride
Xylenes *

** Compounds detected during this study. None of the remaining compounds were detected in any samples taken.

Other organics that were detected but not quantified during this study are:

Alkylated benzene
Napthalene
Methyl napthalene
Dimethyl napthalene
Acetone
1,2 Dichloroethane
Trichloroethylene

Field pH and specific conductivity measurements were obtained on all groundwater samples. This data is given in the next section in Table 6. Generally, pH and conductivities remained stable, but some variation can be attributed to changes in battery output at cold temperatures.

SEPARATOR SAMPLING

Condensate drainage and separator discharge were each sampled on two occasions. Sample collection, preservation and analyses were performed according to procedures listed in the previous section on groundwater measurements (p.21). Separator discharge was sampled during a rain storm on August 26, 1986 when constituents entering the tank were from the loading area runoff only. The separator discharge was sampled again on November 5, 1986 when contaminants entering the separator were from petroleum tank condensate drainage only. During the November 5th sampling, wastewater levels in the separator were measured and time intervals were recorded to estimate condensate inflow rates. Condensate was discharged to the separator for 48.5 minutes before the separator filled enough to flow.

On two occasions, condensate grab samples were taken during condensate drainage into the separator. On the first occasion, (September 9, 1986), test results were erroneous because the discharge from the petroleum storage tank contained pure product. This occurred because a leak developed in the bottom draw line which goes through pure product before it exits the petroleum storage tank. Pure product was forced through this line along with condensate from the bottom of the petroleum storage tank. The second condensate drainage grab sample was taken on November 5, 1986.

The November 5 separator discharge grab sample was taken 4.5 minutes after the separator began discharging. This was less than an optimum length of time because of the unknown and uncontrolled amount of dilution which occurred from the previously accumulated water in the separator. Given a longer flushing period, the separator discharge organic concentrations should have been more representative of long term conditions. Condensate discharge had to be discontinued prematurely because there was not enough condensate left in the petroleum storage tank and a sample had to be taken before pure gasoline began discharging to the separator.

Due to lack of funds for analysis, wastewater from the separator was not sampled before this testing to indicate existing concentrations of VOCs. Funding was also too limited to take composite samples.

On the November 5, sampling date, the initial water level of the oil/water separator was found to be one foot below the invert elevation of the discharge pipe. This could be due to evaporation or leakage from the concrete tank. Leakage from the tank is suspected because the tank was covered and water evaporation was minimized.

RESULTS

The data from water level measurements are given in Appendix B. The computed groundwater contours are given in Appendix A. These contours indicate that groundwater movement is in a westerly direction. Horizontal gradients are very low, ranging from .028 feet per 100 feet to .085 feet per 100 feet and the water table is 5 to 10 feet below the ground surface. No vertical gradients could be measured at the piezometer nest (wells 9, 10 and 11). This may be from insufficient vertical separation distance between the nested wells to allow measurement or vertical gradients may be very low..

Using Darcy's Law an estimate of average linear velocity of the groundwater in the area was made (Appendix D). Velocities estimated for the sand layer were low, ranging from $1.68*10^{-9}$ft/s to $1.12*10^{-7}$ ft/s. These calculated groundwater velocities indicate that there is an existing groundwater velocity on site capable of producing contaminant transport from the separator to the monitoring wells. Because hydraulic conductivities are relatively high in the sand layer, it appears that low gradients in this area are important in limiting groundwater velocity. It is important to recognize that this is an estimate of average groundwater velocity and is not applicable to contaminant transport velocity because it does not consider the effects of contaminant transport processes which cause velocity deviations.

Deviations in water table maps appear to be from recharge influences. Because of the low gradients in the area, the water table elevations can be affected by localized recharges and discharges. During heavy rains, area groundwater flow appears to be reversed due to recharge from Lake Waubesa (Appendix A-45). This is supported by the tendency for flooding from Lake Waubesa in past years before surface water control. Reversed gradients may also be responsible for part of the contamination at well 5.

Field results for pH and specific conductance or conductivity are given in Table 6. No clear trends or indications of contamination are observable in these data. pH levels basically remained between 6 and 7, showing no extremes. pH values within this range should be considered similar because groundwater sample pH change was rapid and could account for the variations in Table 6. This rapid change in pH was mainly due to carbon dioxide from the atmosphere dissolving in the sample.

Although the VOCs analyzed in this study could not be detected by the conductivity meter, VOC groundwater contamination could indirectly affect a change in ionic species and conductivity levels. Higher groundwater conductivities could be from inorganic impurities which may be part of the separator discharge or from chemical and biological reactions of organic contaminants in the soil which may also liberate ionic species. Generally, conductivities which are orders of magnitude higher than background levels indicate a high probability of groundwater contamination. This is not the case in this study, as shown in Table 6. Conductivity values show no major extremes or trends. Values measured during this study are well within the conductivity range of potable waters in the U.S. (50 to 1,500 umhos/cm), (APHA,1975). Well 4 shows somewhat lower conductivities than other wells, but this down gradient well would normally be higher than well 3 (up gradient) if inorganic contamination were occurring. Equipment variation from temperature extremes and battery failure may account for some of the changes in conductivity from one well to another.

Table 6(pH/Conductivity(umhos/cm))

Well#	9/3/86	10/1/86	11/5/86	11/19/86	1/14/87	Average
1	7.0/598	6.0/609	6.6/-	6.6/723	7.0/450	6.6/595
2	6.6/384	6.0/262	6.5/-	6.2/555	7.0/400	6.5/400
3	6.7/425	6.1/498	6.6/-	6.8/572	7.0/400	6.6/473
4	6.4/319	6.0/220	6.4/-	6.3/300	7.2/300+	6.5/285
5	- /416	6.4/565	6.6/-	6.4/600	6.8/410	6.6/498
6			6.0/-	6.0/670	6.6/500	6.2/585
7			6.2/-	6.2/940	6.9/550	6.4/745
9						
10						
Average	6.7/428	6.1/430	6.4/-	6.4/623	6.9/430	

\+ General equipment failure (meter failed to red line)

The results of VOC testing of condensate, separator discharge and groundwater samples are given in Tables 7,8 and 9. VOCs were present in all three types of samples. Mixtures of other hydrocarbon groups were also present. The term "hydrocarbons" is given to mixtures of organics that cannot be matched to a specific pattern of peaks upon analysis (e.g.#1 or #2 fuel oil). This term can also be applied to groups of long chain alkanes for which the SLH has no standards. Their presence is detected by GC-Mass spec., but separate extractions must be conducted to quantify these organic species. Longer straight chain components of these fractions may be less volatile and persist longer than benzene, toluene, xylene and ethylbenzene.

The napthalene derivatives present in the samples are typical additives to motor fuels, (Windholtz, et al., 1983). The SLH did not quantify this mixture of organics, but did detect their presence. Detection is indicated by a * in Tables 7,8 and 9.

Table 7 shows the analytical results for condensate samples taken directly from waste condensate being fed to the oil/water separator. Results show high concentrations of VOCs for both sampling dates.

Table 8 gives the results for samples taken directly from the separator discharge on two separate occasions. On 8/26/87, the input to the separator was from loading area runoff only. On 11/5/86, the input to the separator was from waste condensate feed only. VOC levels appear to be higher in the case where input to the separator was from condensate feed only.

Concentrations of benzene, ethylbenzene, toluene and xylenes were estimated to show the theoretical well mixed concentration in the separator from dilution alone. These are the theoretical highest (upper bound) concentrations of VOCs in the separator just before separator discharge begins. The difference between the theoretical and measured values indicates the magnitude of the VOC losses that occurred. The calculated well mixed concentrations (Appendix G) for benzene, ethylbenzene, toluene, and xylenes were 7468 ppb, 170 ppb, 4061 ppb and 642 ppb respectively. This estimation assumes that no losses of VOCs occurred from the separator, that separator contents are well mixed, that this concentration occurs just before the separator discharges and that negligible VOC concentrations exist in the separator before condensate feed begins.

Maximum concentrations could not be predicted during the loading area runoff sampling because the separator was already discharging and no time intervals could be recorded (see Appendix G)

The results indicate that the actual measured VOC concentrations from the separator discharge were lower than can be explained by dilution alone. Possible reasons for this are:

(1) The separator was not well mixed and the separator contents were not at steady state concentrations..
(2) VOC losses occurred from the separator
(3) VOC losses occurred from the samples during sample collection

Because there was no special mixing device in the separator, it follows that the chamber was not well mixed. Mixing properties of the separator were not addressed in this study, so actual mixing deficiencies could not be proven. Separator VOC concentrations should stabilize at some "steady state" level equal to the raw condensate concentration if the condensate is fed for a long enough time to completely flush the separator. Results from separator discharge sampling are believed to be low because condensate was not fed to the separator long enough for the separator discharge concentrations to reach steady state.

Table 7

Tank 1 Condensate VOC Grab Sample Concentrations (ppb)

Parameter	Date and Concentration	
	9/3/86	11/5/86
Benzene	41,000	57,000
Ethylbenzene	4,900	1,300
Toluene	53,000	31,000
Xylene	2,900	4,900
Hydrocarbons	*	*
Alkylated benzene	*	*
Naphthalene	*	*
Methyl napthalene	*	*
Dimethyl naphthalene	*	*

* - Detected but not quantified.

Note: (1) Pure product was accidentally allowed in the 9/3/86 condensate sample.
(2) All compounds listed in Table 5 were tested for but not detected unless listed above.

Table 8

VOC Grab Sample Concentrations From Separator Discharge (ppb)

8/26/86 Input To Separator From Loading Area Runoff Only

Parameter	Concentration
Xylenes	32.0
Hydrocarbons	*
Alkylated benzenes	*

11/5/86 Input To Separator From Condensate Discharge Only

Parameter	Concentration
Benzene	180.
Ethylbenzene	9.6
Toluene	61.0
Xylenes	720.0
Hydrocarbons	*
Alkylated benzene	*
Naphthalene	*
Methyl napthalene	*
Dimethyl naphthalene	*

* - Detected but not quantified

Note: (1) The 11/5/86 results do not represent equilibrium or well mixed separator conditions.

(2) All compounds listed in Table 5 were tested for but not detected unless listed above.

It is known that volatilization may be a mechanism in VOC loss during the sampling process . Volatilization during condensate residence time in the separator and during sample taking may account for major VOC losses. Residence time in the separator was estimated to be 6.2 hours. Residence time calculations were based on a separator holding capacity at discharge or "active capacity" which was calculated to be 1533 gallons (Appendix G-61). Condensate was fed to the tank at about 4.1 gpm. The total depth of the tank was calculated to be 11.8ft, based on a 3 foot radius and a 2500 gallon design volume. It was assumed in residence time calculations that a discharge rate of 4.1 gpm is the normal feed rate, that steady state VOC concentrations were reached for the four detected organics before the 6.2 hours and that the air in the separator is at an equilibrium concentration with the water. A residence time of 6.2 hours is long enough for significant VOC volatilization to occur.

Table 9

Results of VOC Analysis of Groundwater Grab Samples (ppb)

Well	Parameter	Sept.3	Oct.1	Nov.5	Nov.19	Jan.14	April.15
#1		ND	ND	ND	ND	ND	+
	Xylenes	ND	ND	5.9	ND	ND	+
#2		ND	ND	@	ND	ND	+
#3		ND	ND	ND	ND	ND	+
#4		ND	ND	ND	ND	ND	+
#5	Benzene	ND	ND	ND	2.4	ND	+
	Xylenes	ND	ND	4.0	23	2.4	+
	Ethylbenzene	ND	1.6	ND	1.8	1.9	+
	Toluene	ND	ND	ND	1.6	ND	+
	Alkylated benzenes	ND	*	*	*	*	+
	Hydrocarbons	ND	*	*	*	*	+
#6	Benzene	-	-	380.	80.	99.	290
	Xylenes	-	-	8100.	3200.	1700	850
	Ethylbenzene	-	-	42.	18.	38.	32
	Toluene	-	-	1900.	89.	110.	250
	Alkylated benzenes	-	-	*	*	*	*
	Hydrocarbons	-	-	*	*	*	*
	Napthalene	-	-	*	*	*	*
	Methyl napthalene	-	-	*	*	*	ND
	Dimethyl napthalene	-	-	*	*	*	ND
	Acetone	-	-	ND	*	ND	ND
	1,2 Dichloroethane	-	-	ND	ND	ND	6.1
	Tetrachloroethylene	-	-	ND	ND	ND	1.8
#7	Alkylated benzenes	-	-	ND	*	ND	-
#9	Benzene	-	-	-	-	-	280
	Xylenes	-	-	-	-	-	4.1
	Ethylbenzene	-	-	-	-	-	13
	Alkylated benzenes	-	-	-	-	-	*
	Hydrocarbons	-	-	-	-	-	*
	Napthalene	-	-	-	-	-	*
	Methyl napthalene	-	-	-	-	-	*
#10	Benzene	-	-	-	-	-	630
	Xylenes	-	-	-	-	-	5900
	Ethylbenzene	-	-	-	-	-	1000
	Toluene	-	-	-	-	-	230
	1,2 Dichloroethane	-	-	-	-	-	17
	Alkylated benzenes	-	-	-	-	-	*
	Hydrocarbons	-	-	-	-	-	*
	Napthalene	-	-	-	-	-	*
	Methyl napthalene	-	-	-	-	-	*
	Benzothiopene	-	-	-	-	-	*

\+ = no sample taken   * = presence detected but not quantified - no well installed. ND = not detected. @ = GC/MS failure & vial breakage, no sample results. All compounds listed in Table 5 were tested for but were not detected unless specified.

This time is also longer than the time period that condensate drained to the separator which indicates that the separator may not have been flushed completely.

Results from VOC analysis on well samples are shown in Table 9. Except for a benzene detect on November 19 at well 5, detects at wells 1 and 5 are close to the detection limits for VOCs listed in Table 1, so trends in specific compounds through time should not be assumed. Results from the piezometer nest (wells 9, 10 and 11) indicate possible downward movement of contaminants. Note that the piezometer nest was not installed until April of 1987. Downward movement could be from drawdown pulling contaminants from the water table surface because the top of the screen in the deepest well (#9) was only 11.6 feet below the water table. Well 11 intercepts the water table and was not sampled for VOCs during this study due to limited funding. Well 6 (another water table well 15 feet from well 11) was sampled instead. Condensate discharges from tank #1 were in the month of September 1986 only. This was approximately two months before sampling began at well 6 and seven months before wells 9, 10 and 11 were sampled.

Tetrachloroethylene, acetone and 1,2 dichloroethane were present in samples taken from well 6. A deeper well (#10) yielded samples which also contained 1,2 dichloroethane. These are common solvents used in many products including cleaning agents and degreasers. They are constituents of many products used in connection with the diesel trucks filled at the facility each day. A possible source of these compounds is the loading area outside and inside the catchment drains. Trucks are frequently parked in the outer driveway area while waiting to be filled. Some of the precipitation runoff from the driveway occasionally flowed off the pavement and puddled at the base of the containment berm about 10 feet from the peizometer nest. Separator discharge originating from loading area inside drains and deposited at well 6 would have contained the same contaminants. The probability that these organics came from off site is low because there were no evident sources upgradient from the piezometer nest.

Soil VOC test results are given in Table 10. Petroleum products were expected to be detected in the soils because of the petroleum odor of sand samples from borings near well 5 and in construction of well 6. Despite this, no VOCs were detected by SLH analysis except in well #6 where ethylbenzene was found at low levels.

According to SLH written advice included with sample results, reported low levels (in ug/g) should be interpreted only as a qualitative indication of the presence of a specific organic. SLH stated,

> "...Concentrations were assigned relative to aqueous standards (known amounts of VOCs added to organic free deionized distilled water). Since the association of volatiles in soil matrices can be complex and can result in low recoveries of VOCs, the accuracy of the quantitation is uncertain. The degree of uncertainty will vary depending on the makeup of the soil matrix, including the homogeneity of the sample. However, the results more likely underestimate, rather than overestimate, the free concentrations of VOCs in the solid matrix...."

Table 10

RESULTS OF SOIL TESTS FOR VOCs October, 1986

Location	Sample	Result of VOC Tests For Benzene, (All results in ug/g).			
	Depth/Soil	Benzene/	E.benzene/	Toluene/	Xylenes
Boring Near Well # 5	.5ft. Clay Silt	ND/	ND/	ND/	ND
	3.0ft Clay Silt	ND/	ND/	ND/	ND
	3.7ft Sand	ND/	ND/	ND/	ND
Borehole of Well # 6	1.5ft. Clay Silt	ND/	ND/	ND/	ND
	2.5ft. Clay Silt	ND/	ND/	ND/	ND
	3.5ft. Sand	ND/	0.8/	ND/	ND
Borehole of Well # 7	3.0ft. Clay Silt	ND/	ND/	ND/	ND
	4.0ft. Clay Silt	ND/	ND/	ND/	ND
	5.0ft. Clay Silt Sand	ND/	ND/	ND/	ND
	6.0ft. Sand	ND/	ND/	ND/	ND

ND = Not Detected

DISCUSSION

There was no separate petroleum phase or layer observed at the top of the water table. Because screens spanned the area above and below the water table, water table wells 1 through 6 would have shown the presence of a floating petroleum layer which would have been detected in the VOC analysis. Bailed samples did not contain any separate gasoline fractions and there was no visual evidence of a floating petroleum layer on the surface of the well water. This suggests that there were no major leaks on site which would leave product accumulated on the surface of the water table.

Most of the VOC detects and all of the higher sample concentrations occurred very near the point of separator discharge. These VOCs correspond to the components of gasoline. The results indicate that VOCs are entering groundwater below the separator discharge point (well 6). This contamination appears to be from dissolved gasoline in the condensate discharged from Tank #1 near the oil/water separator. This tank contained unleaded gasoline and was the only tank discharged to the oil/water separator according to Cenex personnel. The contaminants were assumed to be dissolved because there was never any separate phase evident in groundwater samples. The amount of dissolved VOC in solution appears to be well within the saturation concentrations for the major VOCs quantified (Table 2).

Although VOC contaminants are present in groundwater below the point of discharge, there is no indication that contamination has spread to the property boundaries. No VOCs were detected at wells 1 through 4 during the course of this study except for an isolated detect of xylenes at well 1.

It was observed that there was a reduction in most organic constituents from the separator discharge to the groundwater below that point (well 6). Benzene, ethylbenzene and toluene levels in well 6 were lower than their condensate concentrations. Xylene concentrations, however, were not significantly lower than the condensate concentration. Data is insufficient to show whether there is an actual trend in xylene concentrations. This study did not attempt to quantify losses of organics from volatilization, soil adsorption, dilution, or bacterial degradation at the ground surface near the discharge point. These processes may play an important part in the relative amounts of organics left in groundwater.

VOC detects at well #6 show a gradual decline as time elapsed after a major condensate discharge in November of 1986. Condensate discharges occurred in September only, so levels of VOCs may have been higher if sampled before November. There is not sufficient information from this study to determine whether subsequent declines were from contaminant movement, bacteriological degradation, dilution, evaporation or other processes.

VOCs were detected on separate occasions in wells 5, 6 and 1 (Table 9). The detect at well 1 indicates the presence of xylene only at a low level. This well could on occasion be within a plume downgradient to the southwest of the separator. The amount of contaminant being transported from the point of discharge to the point of groundwater sampling can be reduced by adsorption onto subsurface clays, subsurface bacteriological degradation, dispersion and subsurface chemical reactions. More information is needed to quantify subsurface VOC concentration changes caused by any of these mechanisms. This information is necessary for accurate predictions using contaminate transport models.

Sampling of groundwater at lower elevations near the separator discharge detected VOCs 10 feet below the water table. Contamination at well 9 indicates that either the plume has moved downward at least to the 838 foot elevation or contaminants were drawn down to this elevation during well preparation. There is insufficient information to establish contaminant distribution beyond this depth.

Water level measurements from the piezometer nest (wells 9, 10 and 11 Appendix B), do not indicate that strong downward gradients are present. The vertical distance between upper and lower screens in the well nest may have been too small to detect vertical gradient differences. A clay layer encountered at about 30 feet prevented screen placement below this point.

The clay layer above the sandstone should retard contaminant transport in the vertical direction. The degree of retardation depends on actual clay layer thickness and continuity. Based on information obtained during this study, the clay layer in this area should act as an aquitard to downward contaminant movement. Horizontal movement should be in a westerly direction.

The hydraulic conductivities of the fine sand aquifer are estimated in Appendix D-57 for rough comparison purposes. The values lie within the normal range for clean sand to silty sand (Freeze, 1979). Upper bound velocity estimates using the highest hydraulic conductivity and hydraulic gradient indicate that the horizontal travel time from the separator to well 11 (16 feet) was 4.5 years (Appendix D-58). Conversely, lower bound velocity estimates indicate a travel time of 302 years for the same distance. These calculations assume that the contaminants are perfect tracers moving at the speed of the groundwater and that Darcy's Law holds. Calculated velocities were highly variable and were only used to show the possibility of contaminants being transported to monitoring wells under perfect conditions. Contaminants originating from the separator discharge could have potentially been transported to some of the monitoring wells in the time since discharges began.

Accurate contaminant transport predictions cannot be made from the information gathered in this study without considering the effects of retardation, dispersion, complexation or any other contaminant transport processes which may cause contaminant velocity variations.

Storage tanks which are discharged directly to the ground appear to be having no noticeable effects on groundwater quality. Tanks 2 through 6 are discharged in this manner with no measurable impacts at wells 2 or 4.

Contamination from the oil/water separator discharge may be enhanced by discharging to a local low or depressed surface areas. Discharge from the separator is not spread out over the soil surface which would increase the amount of evaporation. Water ponds at the discharge point to a depth of about 1 foot, which then increases infiltration rates. Separator discharge flows overland inside the berm towards well #5 which is installed at the lowest part of the area. It appears that this process may be responsible for the detects at well #5.

The major source of VOC loading to the separator appears to be from condensate drainage and not the loading area drainage (Table 8). Because drainage from the loading area is exposed to air, VOCs have a chance to volatilize by the time loading area drainage enters the separator.

An estimate of the amounts of four major species potentially entering the groundwater can be made assuming that yearly discharges of condensate total 17,020 gallons. This yields 8.1 pounds of benzene, 0.185 lbs of ethylbenzene, 4.4 lbs of toluene and 0.70 lbs of xylene. The calculations for determining these amounts can be found in Appendix G-64.

Estimation of initial separator VOC concentrations in Appendix G-62 shows that measured VOC concentrations were lower than the values predicted from dilution alone in the separator. It is assumed for these calculations that there is no loss due to volatilization; that the water in the separator initially contained no VOCs; that the tank is well mixed and that the system is at steady state; . In actuality, volatilization reduces VOC concentrations when condensate is discharged into the separator and during the condensate residence time of 6.2 hours in the separator (Appendix G). Because there was little mixing in the tank and condensate was fed to the tank for only 48.5 minutes, optimum steady state VOC concentrations were not reached in the separator discharge.

The results show lower concentrations of VOCs in separator discharge while condensate was being fed to the separator than in groundwater from well 6. The lower separator discharge VOC concentrations may be from the grab sample not being representative of well mixed separator discharge over the entire discharge period. Given enough time for flushing, separator VOC concentrations would normally stabilize at some level approaching feed condensate concentrations which are well above groundwater VOC levels.

Oil/water separators do not provide conditions which optimize dissolved VOC removal. Separators of this type are normally used to separate water and organic phases for separate treatment. Since the organics in condensate waste streams are dissolved, physical separation by density difference does not occur. This would not be the case if pure petroleum product is accidentally fed to the separator which would occur if condensate drainage is continued too long.

To minimize the VOCs available to enter the groundwater, wastewater should be processed in a way that maximizes VOC volatilization and reduces the rapid infiltration caused in part by surface ponding. Splash pads can aid in diverting water horizontally over the soil surface. Regrading may help to divert water away from the discharge area to prevent ponding. Volatilization may also be greatly increased by spraying the waste instead of discharging it directly to the ground.

Conditions for VOC removal could be improved with increased air circulation in the separator chamber. Loss due to volatilization is directly proportional to the amount of air flowing through the separator. Ventilation occurs through a manhole that is removed during condensate discharge with unknown air exchange properties. It is assumed that, without forced circulation, the air in the separator eventually stagnates to some degree and loss of volatiles is reduced.

An estimate of the amount of forced air in the separator that would be needed to achieve removal of detected organics to groundwater standard levels is given in Appendix G. This estimate shows that to achieve desired removal efficiencies, small amounts of air would be needed. This result may be partially due to the fact that this estimate assumes system gas/liquid phase equilibrium causing an underestimate of the actual air requirement. Gas/liquid phase equilibrium occurs when concentrations of dissolved compounds reach steady state in a liquid and the gas in contact with the liquid. In actuality, there are interferences which inhibit the amount of VOC moving from the liquid to the gas phase. To reach equilibrium, a high degree of contact between wastewater and air must be achieved. This varies with the type of treatment used (e.g. spraying, tank aeration or air stripping). It should be noted that other removal factors such as biological degradation, evaporation and soil surface volatilization may aid in reducing VOC levels. Bench scale tests should be performed on separator waste to better estimate possible removal efficiencies and treatment techniques.

A common practice in the industry is to discharge separator waste to surface waters. This practice may serve to reduce groundwater contamination at the expense of surface water quality near the outfall. The majority of VOCs may be removed from surface water by evaporation alone if given sufficient time. Because of continuous exposure to air, surface waters may be more appropriate for receiving VOC contaminated wastes.

If leakage occurs from the separator itself, surface reduction of VOCs is circumvented and waste condensate may enter groundwater directly at higher concentrations. For this reason, separators should be inspected regularly for leaks and repaired if necessary.

CONCLUSIONS

Condensate from the petroleum storage tanks at the Cenex tank farm near McFarland WI contains high concentrations of VOCs. The organics dissolve into the water phase after long periods of contact with petroleum products in storage tanks. The major volatile constituents detected were benzene, xylene, ethylbenzene and toluene. Other organics were detected, but were not quantified. Surface drainage from the truck loading area had lower levels of VOCs.

Condensate production from a floating single roof storage tanks is about 30 times that of an outer roofed storage tanks. Areas with a high proportion of this type of tank may have a higher potential for pollution of ground or surface water. More research is needed on other tank farms to better estimate groundwater impacts on an industry-wide basis.

Certain hydrogeological conditions reduced potential groundwater impacts to the lower sandstone aquifer in the study area. Clayey silts at the surface and clays below the sand layer should retard vertical migration of an organic plume. Horizontal movement of groundwater is in a westerly direction towards the Lake Waubesa discharge area.

Volatile organics from the oil/water separator are reaching the groundwater below the point of discharge, but there is no indication that significant contamination extends to the property boundary. Further study is needed to determine the exact extent of the contaminant plume.

The oil/water separator used at this facility provides some dilution and aeration of waste water containing dissolved gasoline fractions. Because VOC constituents of gasoline are dissolved in condensate, a liquid/liquid phase separator such as the one used at this site does not appear to be an appropriate treatment device for VOC removal. This assumes that environmental impacts are great enough to require improved removal.

Contamination may also be coming from a leak in the separator itself. Any subsurface leakage of condensate would not be subject to surface volatilization and would result in direct transfer of contaminants to groundwater. Subsurface leakage or discharge of condensate should not be allowed due to the potential for direct groundwater contamination.

Groundwater VOC levels immediately below the separator outfall are above the standards set by NR 140 , but appear to fall below detection limits at the property boundary. Immediate response to reduce the perceived impacts involves maximizing aeration and minimizing infiltration below the point of discharge.

RECOMMENDATIONS

Periodic separator cleaning and inspection at this facility should resolve any question about oil/water separator leakage. The use of existing equipment should be investigated for improving VOC removal. In any case, discharges should be exposed to air wherever possible to volatilize VOCs before infiltration. This is an advantage for surface water discharges.

Initially, aeration can be increased by installing a splash pad below the point of discharge and raising the point of discharge if possible. The splash pad should extend far enough to divert separator water away from the depressed area inside the berm to prevent ponding. Minor regrading may also help in diverting separator discharge from the low areas.

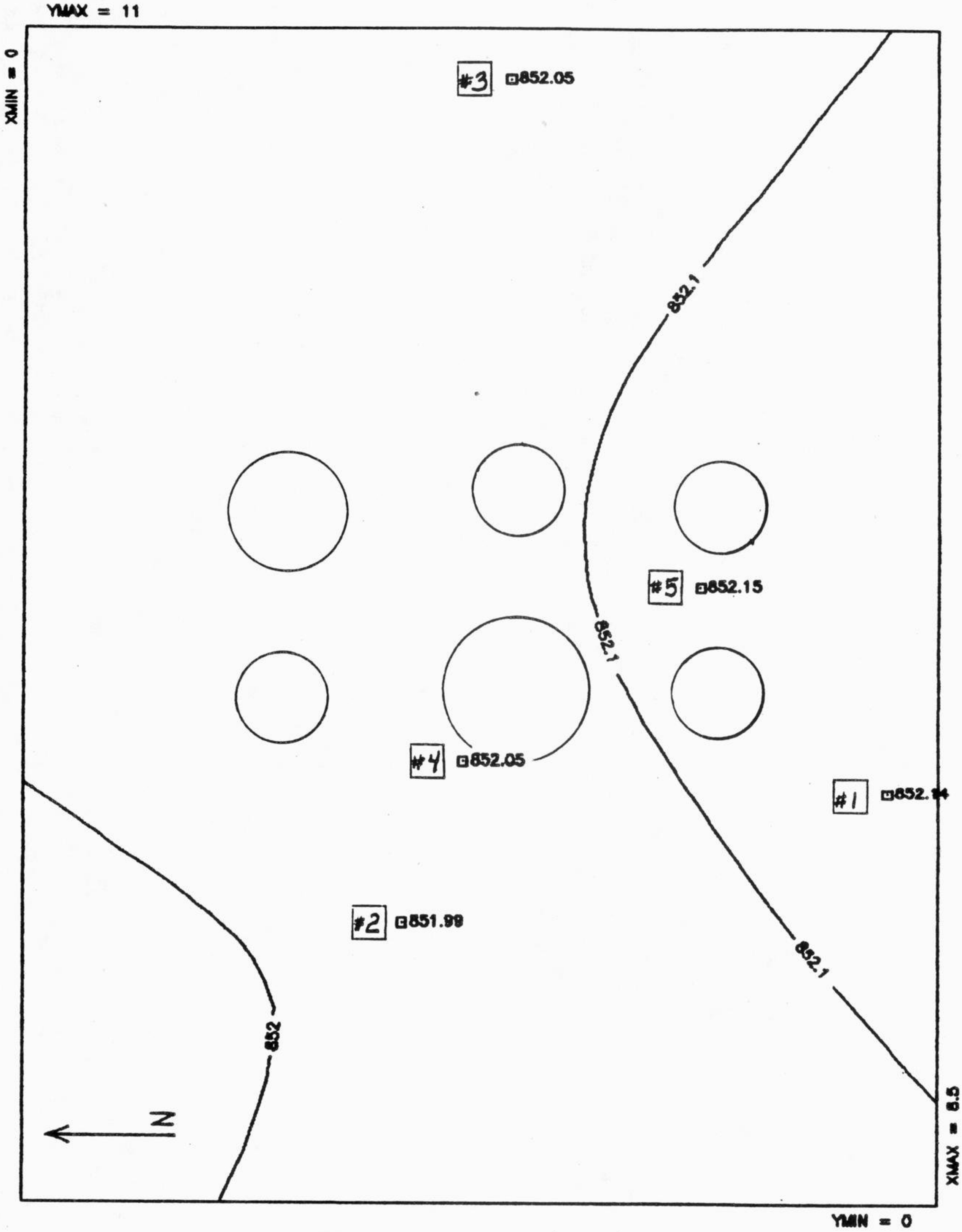
Volatilization should also be maximized during drainage of condensate from storage tanks which are normally drained to the ground. Condensate may be drained through a hose and pressure nozzle to spray condensate into the air before infiltration. The nozzle can be fixed in one position on the ground by mounting it on an improvised moveable stand. Spraying can be applied at any convenient stage of waste disposal.

Continued monitoring of this site is needed to see if condensate handling changes produce noticeable results. The amount of VOC reduction from biological degradation, soil evaporation and surface evaporation should also be evaluated to determine practical levels for surfaces discharges. Other process or equipment changes pending future investigation may include dike lining or air stripper usage.

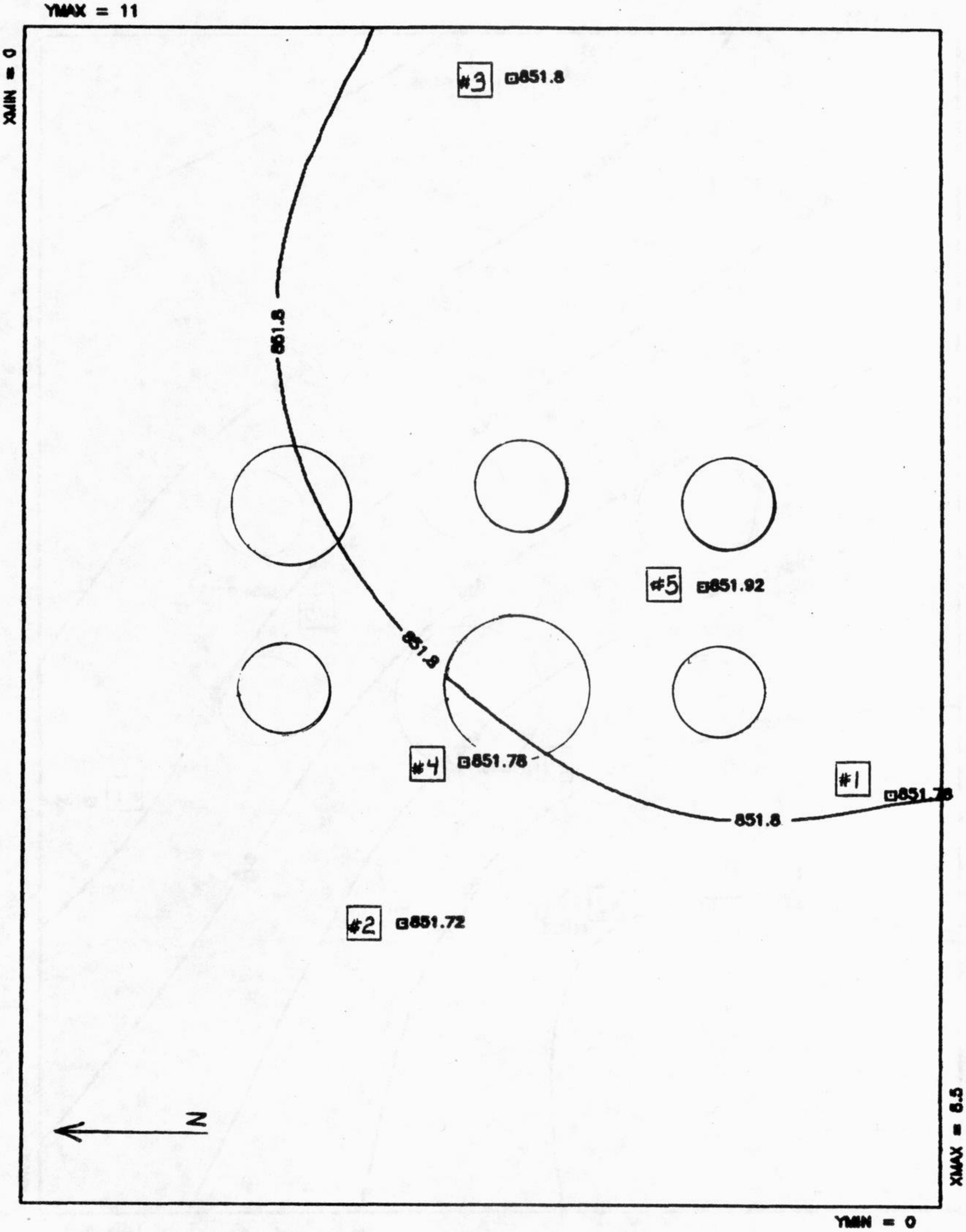
More information should be gathered through similar studies on a statewide or nationwide basis to determine if these results are typical of all tank farms and if the impacts of condensate discharges from above ground storage terminals are great enough to cause concern. Based on these findings, further study may be initiated to determine whether oil/water separators are appropriate for treatment of condensate discharges. More study is needed to determine cost effective, practical methods to prevent VOCs from entering the groundwater.

Because of its relative isolation from other contaminate sources, the Cenex study site appears to be well suited for further study. Further study will benefit both the regulatory agency and the petroleum industry by finding practical, cost effective methods to minimize groundwater impacts from petroleum storage facilities.

APPENDICES



WATER TABLE 8/15/86



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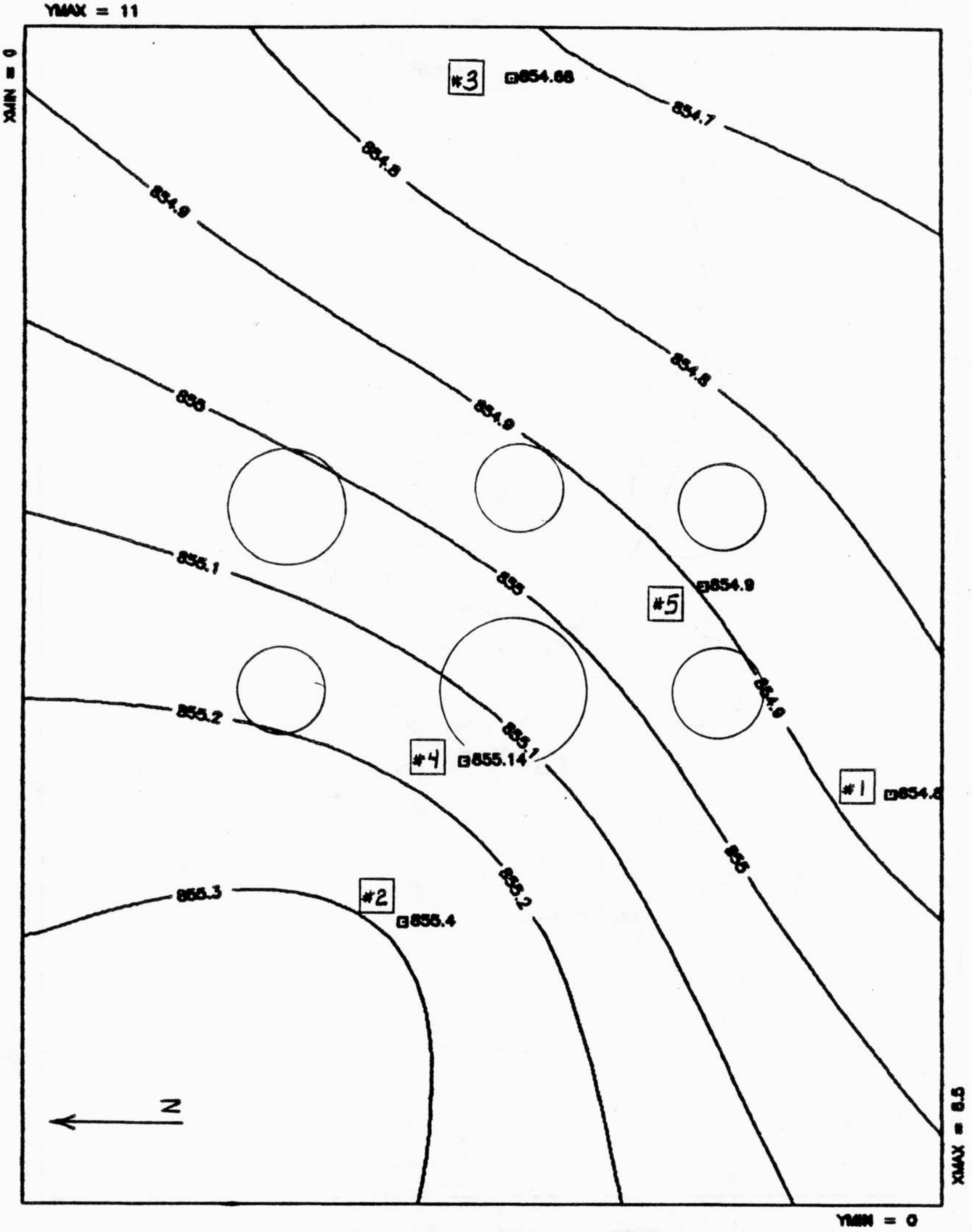
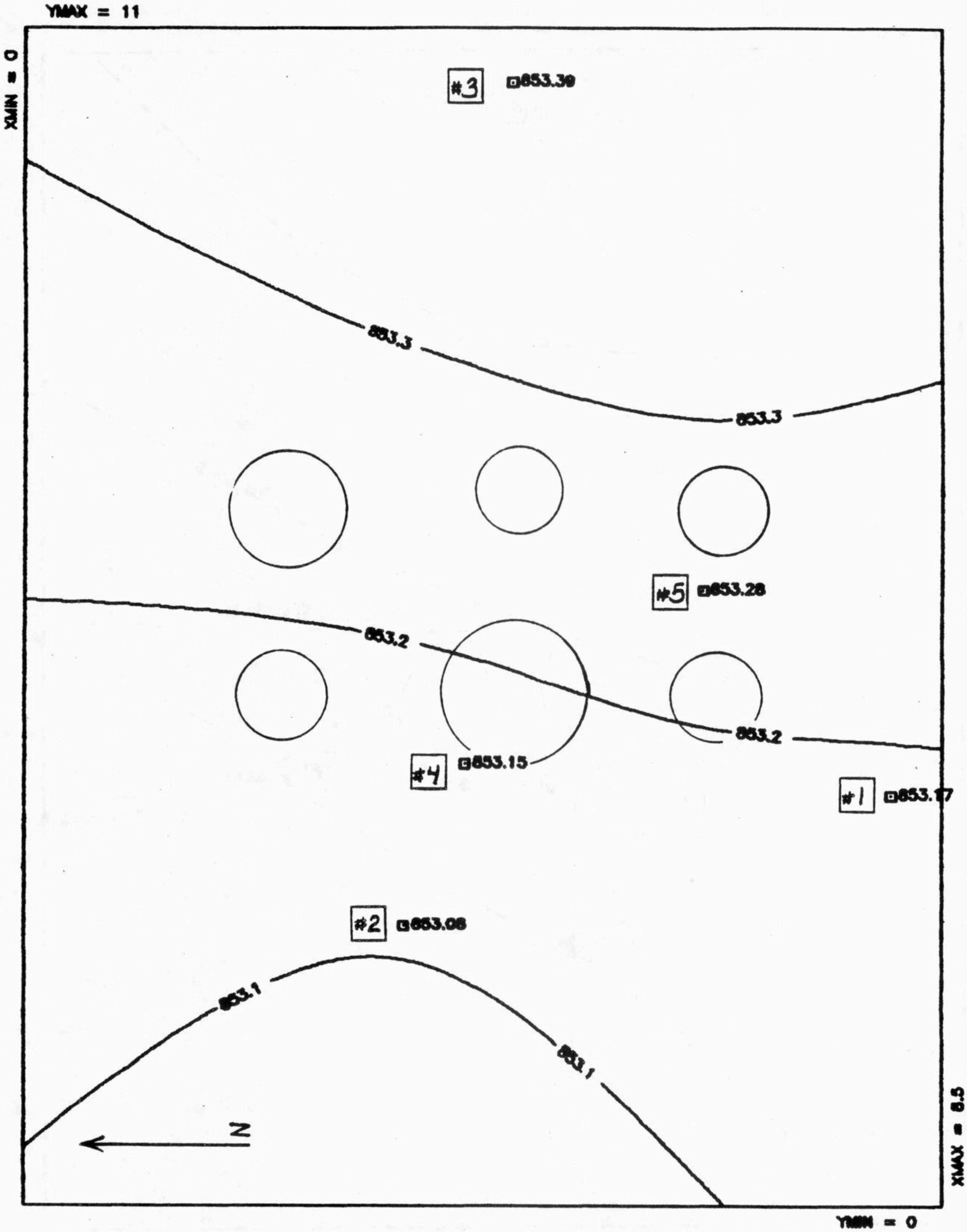


WATER TABLE 10/1/86



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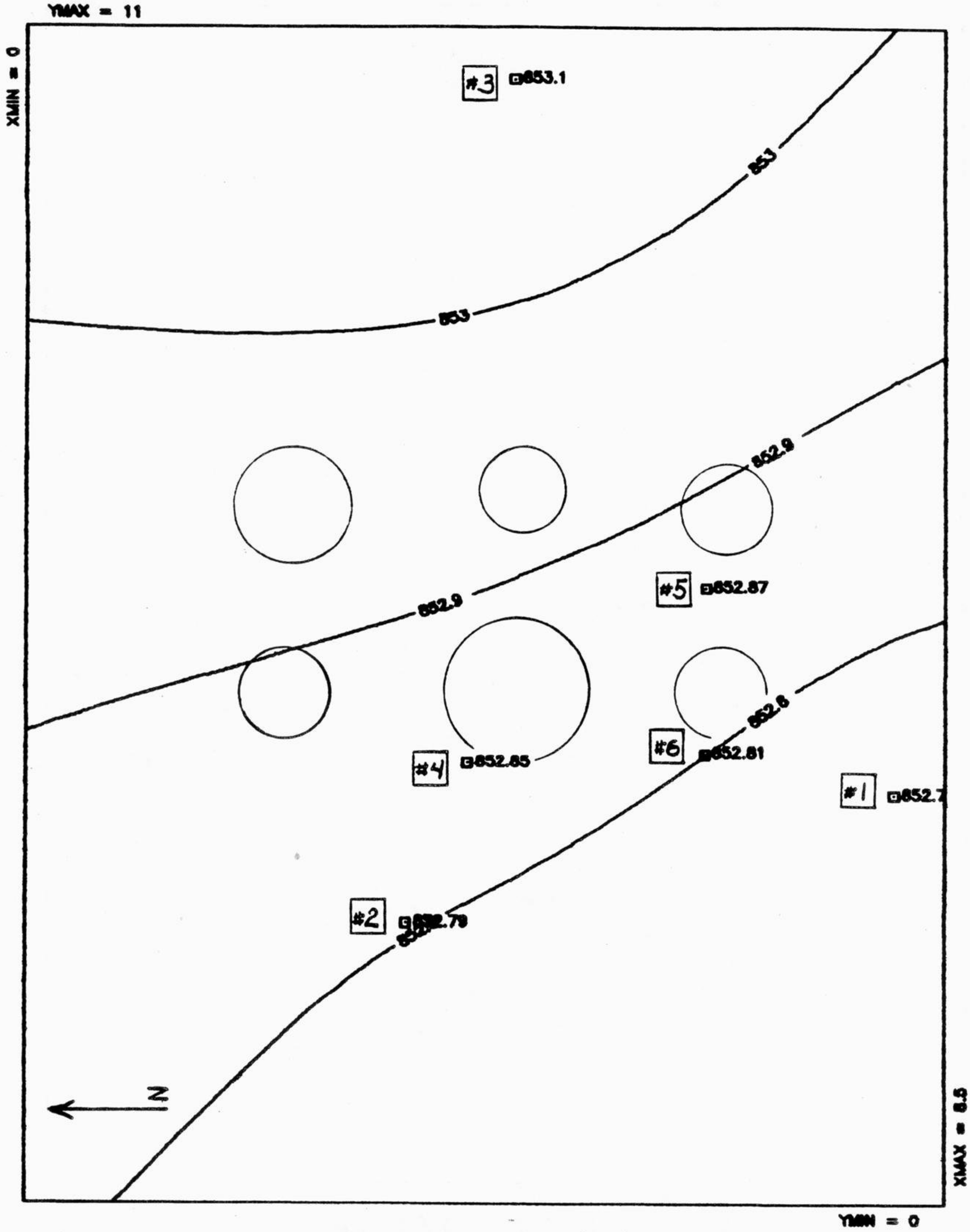
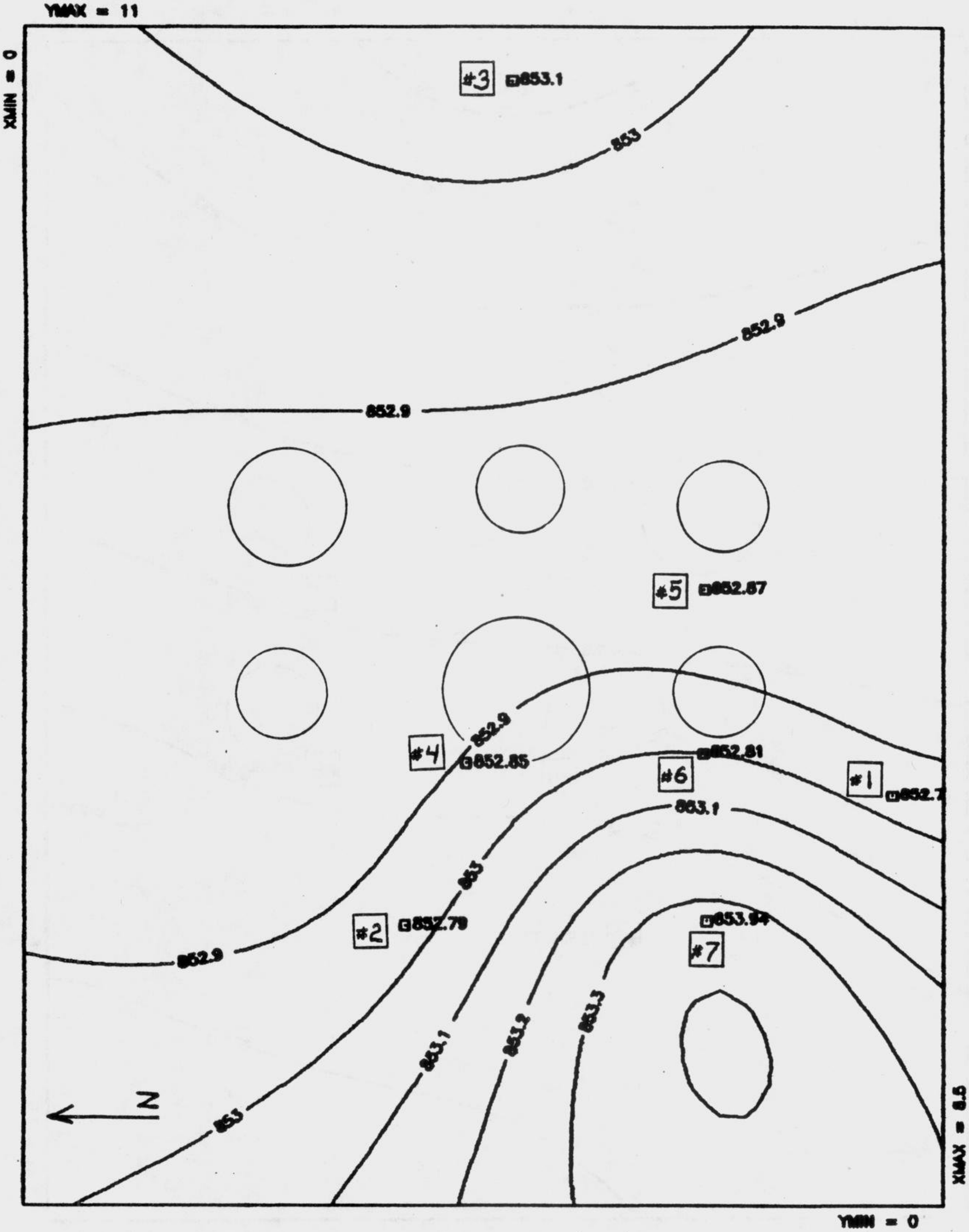
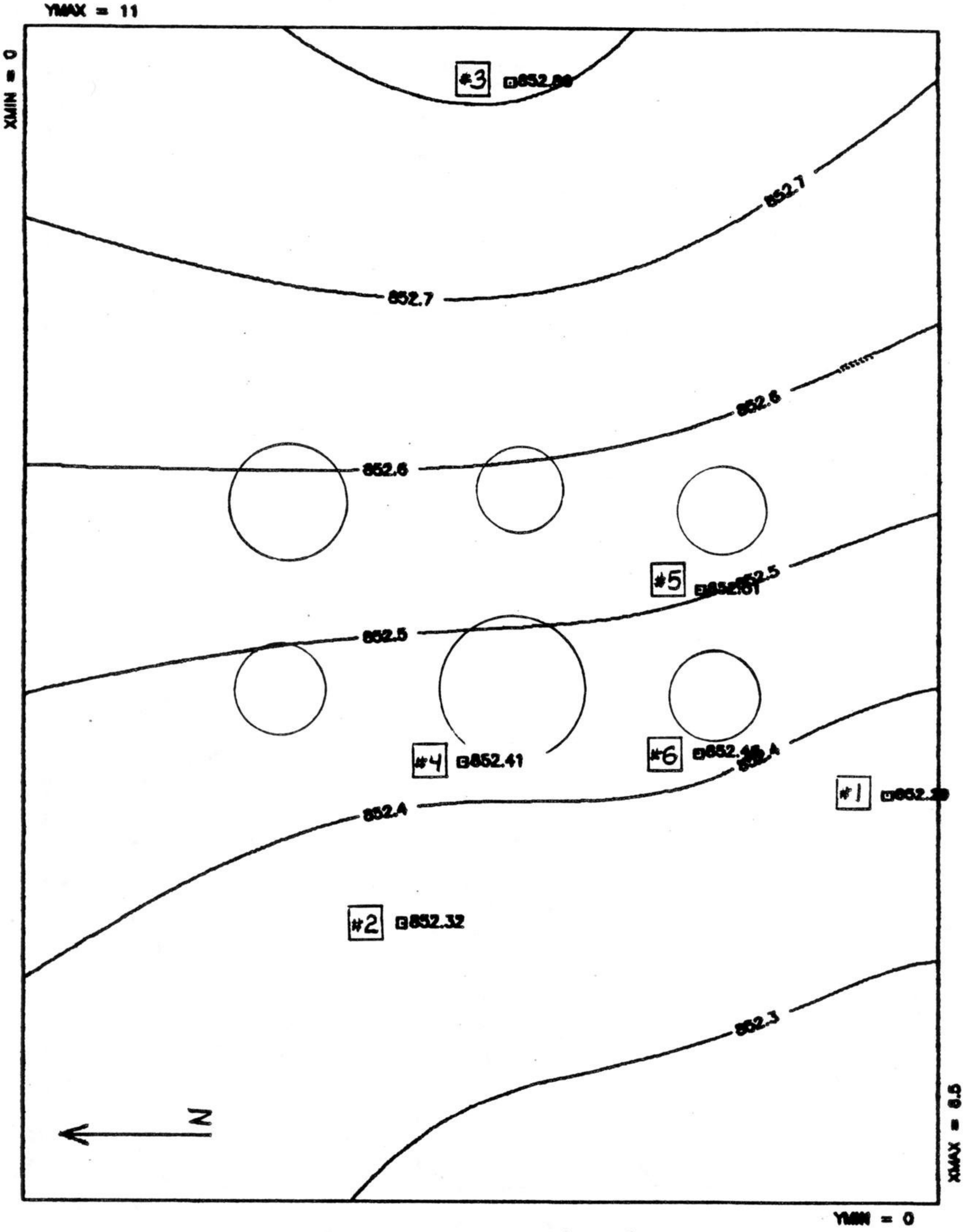


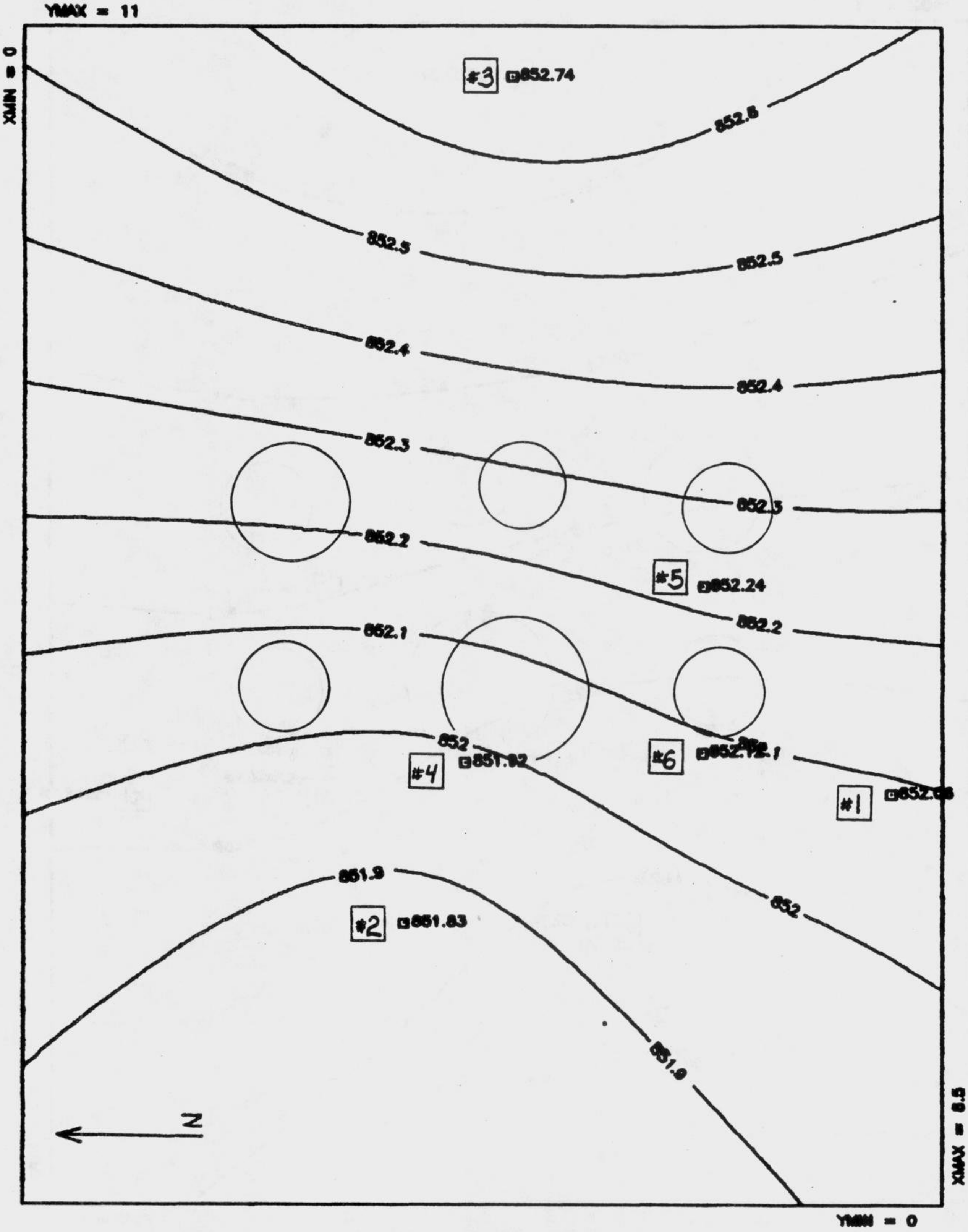
WATER TABLE 11/5/86



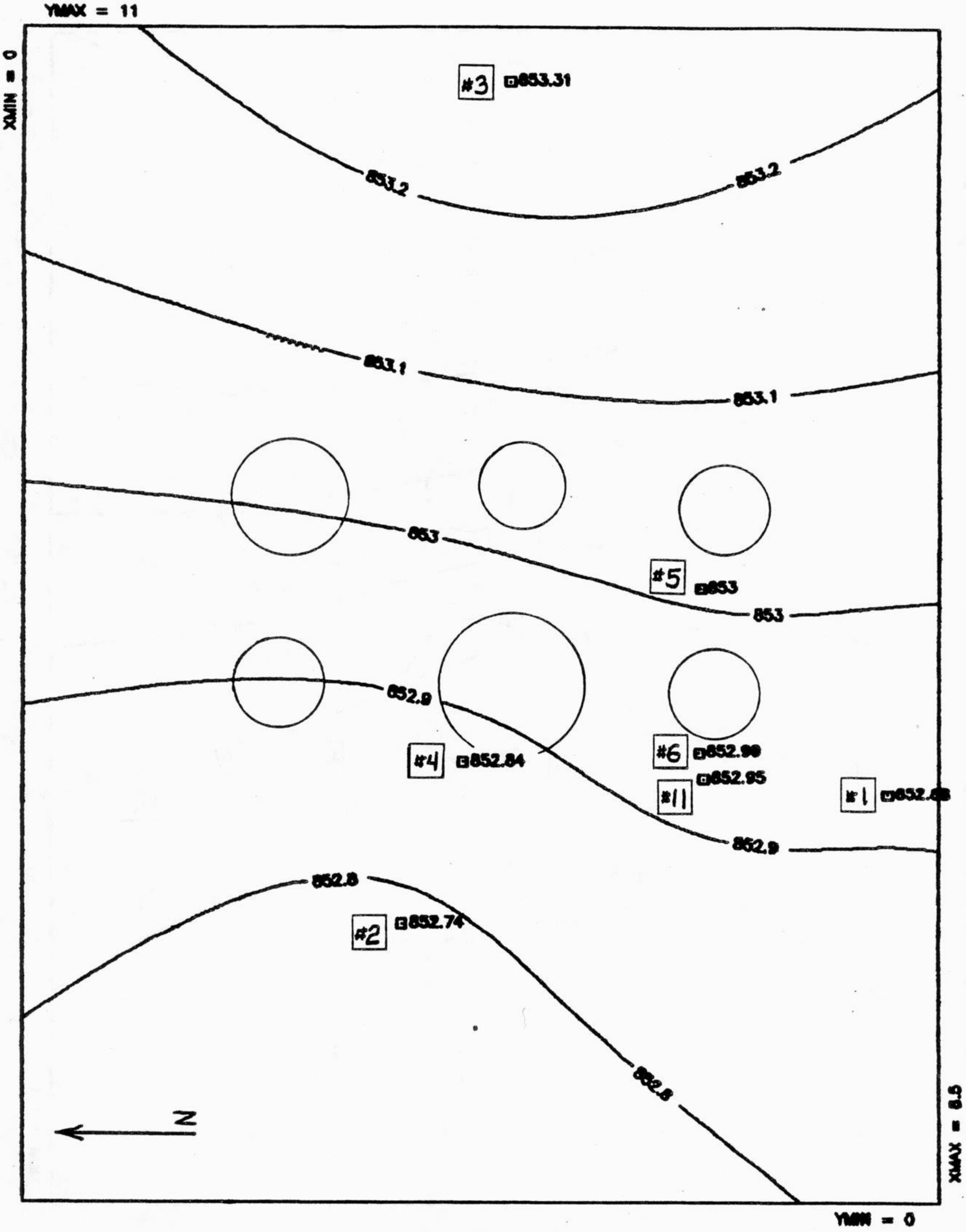
WATER TABLE 11/5/86



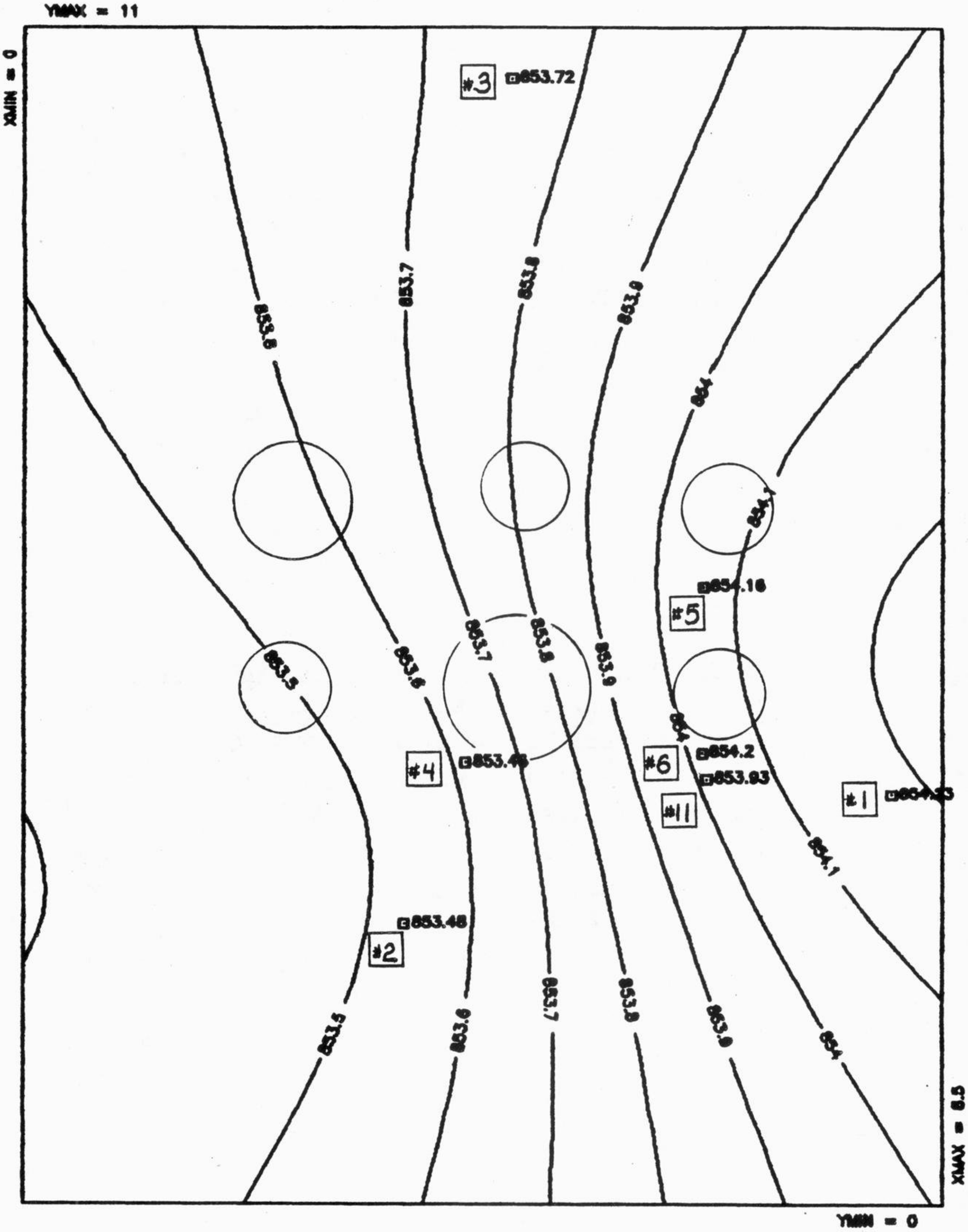
WATER TABLE 11/19/86



WATER TABLE 1/14/87



WATER TABLE 3/24/87



WATER TABLE 4/15/87

WATER TABLE ELEVATIONS

	Coordinates inches						
Well	**X**	**Y**	**8/15/86**	**9/3/86**	**10/1/86**	**10/27/86**	**11/5/86**
1	8.03,	3.82,	852.14	851.78	854.80	853.17	852.70
2	3.52,	2.61,	851.99	851.72	855.40	853.08	852.79
3	4.52,	10.49,	852.05	851.80	854.68	853.39	853.10
4	4.08,	4.12,	852.05	851.78	855.14	853.15	852.85
5	6.29,	5.75,	852.15	851.92	854.90	853.28	852.87
6	6.28,	4.21,				No Data	852.81
7	6.31,	2.65,				854.15	853.94
9	6.45,	3.99,					
10	6.38,	3.98,					
11	6.32,	3.97,					

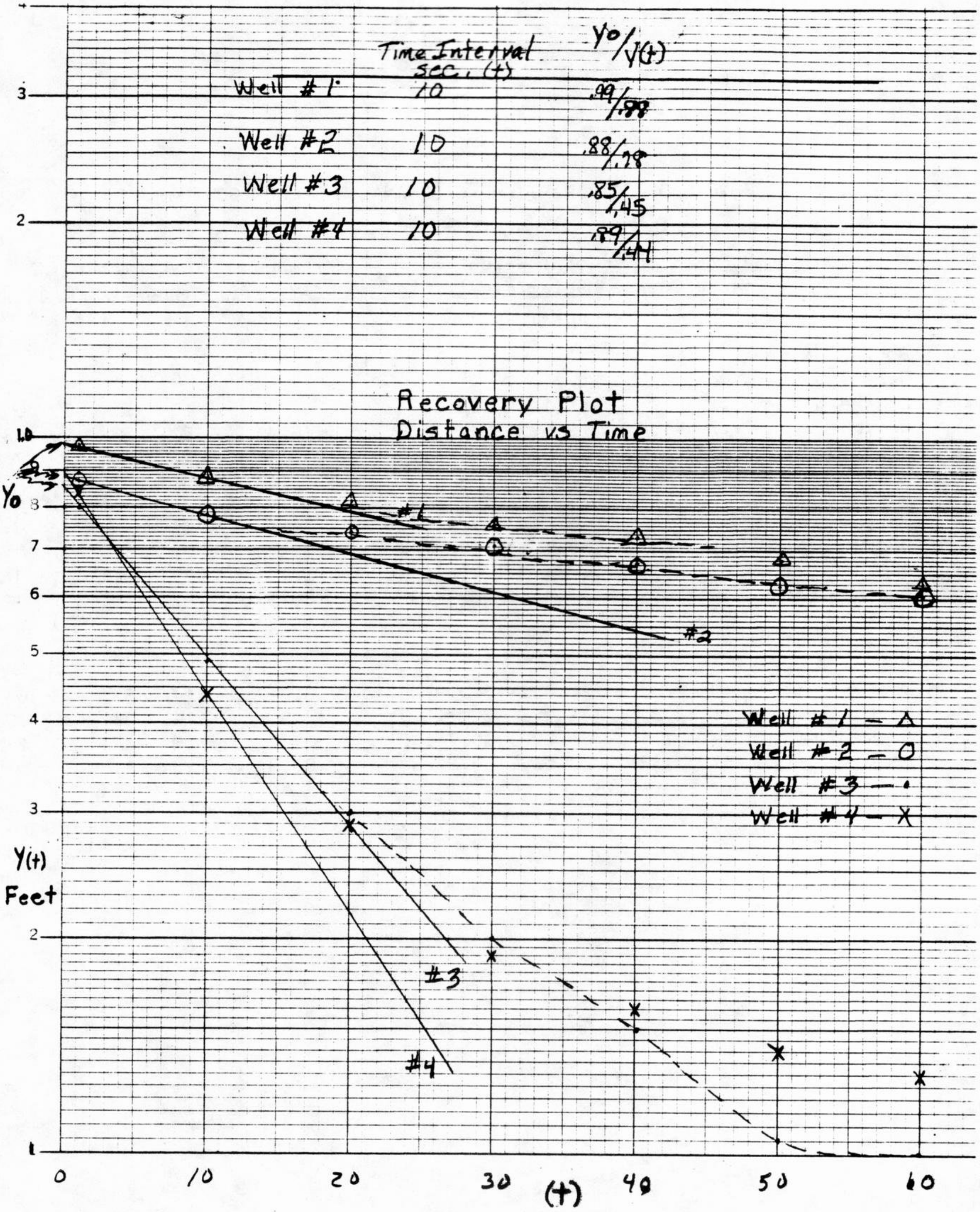
Well	11/19/86	1/14/87	3/24/87	4/15/87	Average
1	852.26	852.06	852.88	854.23	852.99
2	852.32	851.83	852.74	853.48	852.82
3	852.86	852.74	853.31	853.72	853.07
4	852.41	851.92	852.84	853.46	852.84
5	852.51	852.24	853.00	854.16	853.00
6	852.46	852.12	852.99	854.20	852.92
7	853.43	852.99	No Data	No Data	853.62
9			852.95	853.99	853.47
10			852.95	853.96	853.46
11			852.95	853.93	853.44

PARTICLE SIZE ANALYSIS

RESULTS OF SOIL PARTICAL SIZE ANALYSIS FROM BORINGS

Location	Sand Fraction % Total Weight					Total Sand	Hydrometer (%)			
	V.Coarse	Coarse	Medium	Fine	V.Fine	& Gravel(%)	Sand	Silt	Clay	Gvl
Boring Near Well # 5										
Depth=.5ft.	.1	.2	1.1	1.3	1.1	3.8	10	52	38	0
Depth= 3ft.	.7	1.4	6.5	6.7	2.8	16.4	22	59	19	.3
Depth=3.7ft.	1.7	6.6	35	23.7	1.4	70.6	72	20	8	2.2
Borehole of Well # 6										
Depth=1.5ft.	.1	.4	1.8	1.7	1.4	5.4	22	51	27	0
Depth=2.5ft.	.1	.3	1.9	2.1	1.3	5.7	7	61	32	0
Depth=3.5ft.	.6	4.9	45.1	28.3	.8	80.5	82	7	11	.8
Borehole of Well # 7										
Depth=3.0ft.	.2	.5	4.2	3.9	1.0	9.8	14	63	23	0
Depth=4.0ft.	.1	.3	2.6	2.7	1.3	7.2	14	54	32	.2
Depth=5.0ft.	.4	1.1	22	30.7	1.2	57.7	58	23	19	2.3
Depth=6.0ft.	.1	2.2	51.6	39.3	.6	93.8	93	4	3	0

SLUG TEST INFORMATION



	Time Interval sec. (t)	$Y_o/Y(t)$
Well #1	10	.99/.88
Well #2	10	.88/.78
Well #3	10	.85/.45
Well #4	10	.89/.44

HYDRAULIC CONDUCTIVITY CALCULATIONS (Bouwer, 1976)

Slug Test for hydraulic conductivity (K)

$$K = \frac{r_c^2[\mathrm{Ln}\ (Re/r_w)]}{2L} * 1/t\ \mathrm{Ln}(Y_o/Y_t)$$

Where: Re = effective radius over which the head change Y_t is dissipated (ft)

r_w = horizontal distance from well center to original aquifer or 1 + 0.5 = 1.5 inches = 0.125 feet

r_c = radius to well screen or outside of sand pack. Adjusting for the porosity of sand (.37) in the pack we obtain:

$r_c = [(1")^2+0.37((1.5)^2-(1)^2)]^{1/2}$

r_c = 1.21 inches or .101 feet

L = Length of saturated screen (1' to 4')

D = Depth of aquifer approx.40 feet

H = Distance from water table to the bottom of the screen during slug test (page D-57)

t = Time period for change in Y

Y_o = Water level at time = 0

Y_t = Water level at time = t

$1/t\ \mathrm{Ln}(Y_o/Y_t)$ term from plot page D-55

$\mathrm{Ln}(Re/r_w) = 1.1/\mathrm{Ln}(H/r_w)+[(A+B\mathrm{Ln}((D-H)/r_w))/(L/r_w)]^{-1}$

The upper limit for $(D-H)/r_w = 6.0$

So: $\mathrm{Ln}(Re/r_w) = 1.1/\mathrm{Ln}(H/r_w)+[(A+B(1.79))/(L/r_w)]^{-1}$

Where: A and B are dimensionless coefficients which are functions of L/r_w (see page D-57)

HYDRAULIC CONDUCTIVITY CALCULATIONS

(Continued)

BOUWER AND RICE: GROUNDWATER HYDRAULICS

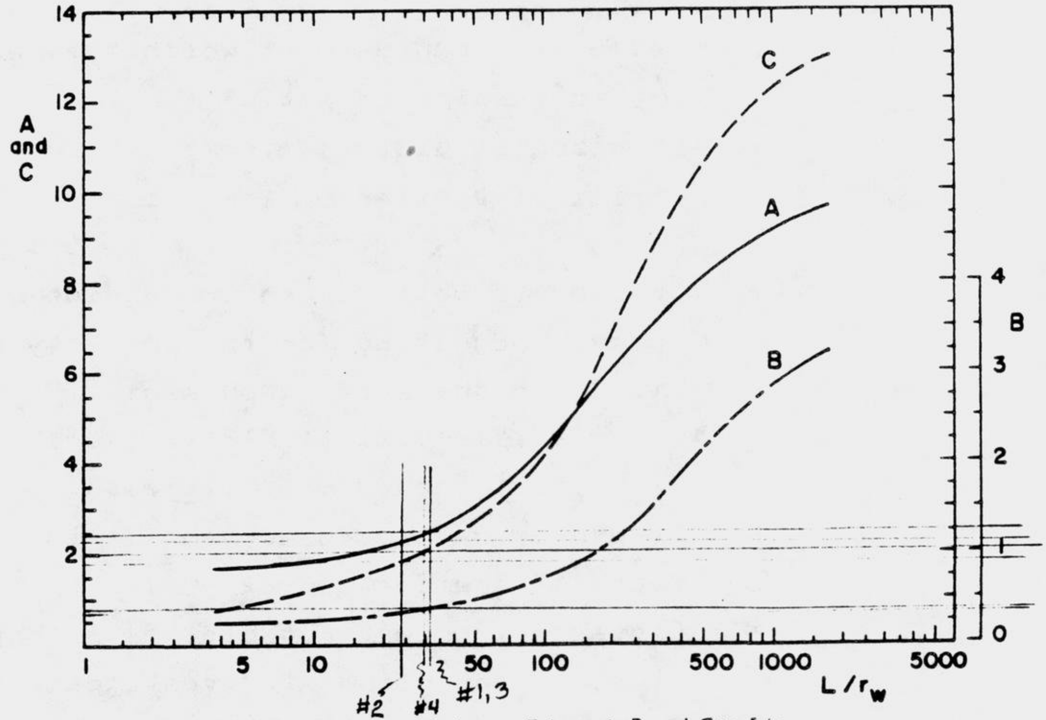


Fig. 3. Curves relating coefficients *A*, *B*, and *C* to L/r_w.

WELL	L/r_w	A	B	C	Y_0(ft) / Y_t(ft)	t (sec)	H (ft)	K cm/s
1	32	2.5	0.4	2.0	.99/.88	10	6.4	$1.2*10^{-3}$
2	24	2.3	0.3	1.8	.88/.78	10	3.0	$5.5*10^{-5}$
3	32	2.5	0.4	2.0	.85/.45	10	4.8	$2.5*10^{-4}$
4	30	2.4	0.4	2.0	.89/.44	10	3.7	$2.9*10^{-4}$

(Example)

$L/r_w = 4/.125$

$\mathrm{Ln}(Re/r_w) = [.279 + (2.4+0.4(1.79))/32]^{-1}$
$= 2.65$

So: $K = [(.101)^2(2.653)/2*4]*(\mathrm{Ln}.99/.88)/10$
$= 3.985*10^{-5}\,\mathrm{ft/s} * .3048$
$= 1.215*10^{-5}\,\mathrm{m/s} = 1.21*10^{-3}\,\mathrm{cm/s}$

VELOCITY CALCULATION

All hydraulic gradient values were calculated from head change /horizontal distance values in Appendices A and B. All hydraulic conductivity values were calculated in Appendix D-57 and converted to appropriate units (ft/s). All combinations using upper and lower bound values of K and dh/dL were then calculated below.

Using Darcy's Law:

V = Average Linear Velocity = -K/n dh/dL

dh/dL range = Hydraulic gradient

= $2.8*10^{-4}$ to $8.5*10^{-4}$ ft/ft

K range = Hydraulic Conductivity

= $3.94*10^{-5}$ to $1.80*10^{-6}$ ft/s

n = porosity

= 30% or 0.3 assumed

Examples:

Combination yielding maximum velocity.

$(3.94*10^{-5} * .00085)/0.3 = 1.12*10^{-7}$

Combinations yielding intermediate velocities.

$(3.94*10^{-5} * .00028)/0.3 = 3.68*10^{-8}$

$(1.80*10^{-6} * .00085)/0.3 = 5.10*10^{-9}$

Combinations yielding minumum velocity.

$(1.80*10^{-6} * .00028)/0.3 = 1.68*10^{-9}$

Calculated Velocities in fps	Theoretical travel time assuming a distance of 16 ft from separator to well 11
$1.12*10^{-7}$	4.5 years
$3.68*10^{-8}$	13.8 years
$5.10*10^{-9}$	99.5 years
$1.68*10^{-9}$	302 years

It is possible that some of the closer wells could have recieved contaminants in the time since separator and petroleum tank discharges began.

STATE LAB OF HYGIENE SAMPLING FORM INFORMATION

Number ___ ___ ___ ___ ___
For Lab Use Only

Detection Limits (ug/l) are indicated in brackets [ ]

			Detected	Not Detected	(ug/l)
☐	007	Acrolein[50]	☐	☐	___ ___ ___ • ___
☐	009	Acrylonitrile[20]	☐	☐	___ ___ ___ • ___
☐	025	Benzene[1.0]	☐	☐	___ ___ ___ • ___
☐	046	Bromobenzene[4.0]	☐	☐	___ ___ ___ • ___
☐	051	Bromodichloromethane[1.5]	☐	☐	___ ___ ___ • ___
☐	053	Bromoform[5.0]	☐	☐	___ ___ ___ • ___
☐	055	Bromomethane[50]	☐	☐	___ ___ ___ • ___
☐	063	n-Butylacetate[0.5]	☐	☐	___ ___ ___ • ___
☐	071	Carbon Disulfide[5.0]	☐	☐	___ ___ ___ • ___
☐	073	Carbon Tetrachloride[1.5]	☐	☐	___ ___ ___ • ___
☐	083	Chlorobenzene[2.0]	☐	☐	___ ___ ___ • ___
☐	087	Chloroethane[20]	☐	☐	___ ___ ___ • ___
☐	093	2-Chloroethylvinyl Ether[4.0]	☐	☐	___ ___ ___ • ___
☐	095	Chloroform[1.0]	☐	☐	___ ___ ___ • ___
☐	108	o-Chlorotoluene[1.0]	☐	☐	___ ___ ___ • ___
☐	110	p-Chlorotoluene[1.0]	☐	☐	___ ___ ___ • ___
☐	147	Dibromochloromethane[2.0]	☐	☐	___ ___ ___ • ___
☐	148	1,2-Dibromo-3-Chloropropane	☐	☐	[not quantified] ___ ___ ___ • ___
☐	153	o-Dichlorobenzene[2.0]	☐	☐	___ ___ ___ • ___
☐	155	m-Dichlorobenzene[2.0]	☐	☐	___ ___ ___ • ___
☐	157	p-Dichlorobenzene[2.0]	☐	☐	___ ___ ___ • ___
☐	165	1,1-Dichloroethane[1.0]	☐	☐	___ ___ ___ • ___
☐	167	1,2-Dichloroethane[1.0]	☐	☐	___ ___ ___ • ___
☐	169	1,1-Dichloroethylene[1.0]	☐	☐	___ ___ ___ • ___
☐	171	1,2-Dichloroethylene[1.0]	☐	☐	___ ___ ___ • ___
☐	174	Dichloroiodomethane	☐	☐	[not quantified] ___ ___ ___ • ___
☐	181	1,2-Dichloropropane[1.0]	☐	☐	___ ___ ___ • ___

Analysis Type (check ✓ one)

☐ GC/MS Screening

☐ Confirmation of GC/MS Screening Sample Number (fill in) ___ ___ ___ ___ ___

☐ Other (Follow Up, Misc.

			Detected	Not Detected	ug/l
☐	183	cis-1,3-Dichloropropene[2.5]	☐	☐	___ ___ ___ • ___
☐	185	trans-1,3-Dichloropropene[2.5]	☐	☐	___ ___ ___ • ___
☐	233	Ethylbenzene[1.0]	☐	☐	___ ___ ___ • ___
☐	427	Fluorotrichloromethane[1.0]	☐	☐	___ ___ ___ • ___
☐	298	Isopropylbenzene[1.0]	☐	☐	___ ___ ___ • ___
☐	319	Methylethylketone (MEK)[12]	☐	☐	___ ___ ___ • ___
☐	393	Styrene[2.0]	☐	☐	___ ___ ___ • ___
☐	396	1,1,1,2-Tetrachloroethane[3.0]	☐	☐	___ ___ ___ • ___
☐	397	1,1,2,2-Tetrachloroethane[3.0]	☐	☐	___ ___ ___ • ___
☐	399	Tetrachloroethylene[1.0]	☐	☐	___ ___ ___ • ___
☐	401	Tetrahydrofuran (THF)[200]	☐	☐	___ ___ ___ • ___
☐	411	Toluene[1.0]	☐	☐	___ ___ ___ • ___
☐	421	1,1,1-Trichloroethane[1.0]	☐	☐	___ ___ ___ • ___
☐	423	1,1,2-Trichloroethane[1.5]	☐	☐	___ ___ ___ • ___
☐	425	Trichloroethylene[1.0]	☐	☐	___ ___ ___ • ___
☐	428	Trichlorotrifluoroethane[3.0]	☐	☐	___ ___ ___ • ___
☐	434	Vinyl Chloride	☐	☐	[not quantified] ___ ___ ___ • ___
☐	437	Xylenes[2.0]	☐	☐	___ ___ ___ • ___
☐		___________________	☐	☐	___ ___ ___ • ___
☐		___________________	☐	☐	___ ___ ___ • ___

Comments ______________________________

____

Date Received and Sample No. ______________________________

VAPOR PRESSURE CALCULATIONS (Lange, 1985)

Equation (1) $\log P = A - (B/(t + C))$

Where: P = vapor pressure in mmHg
t = temperature in °C
A, B and C = constants (below)

Chemical	°C range	A	B	C
Benzene	8-103	6.905	211.033	220.79
Ethylbenzene	26-164	6.957	424.255	213.21
o-Xylene	32-172	6.998	1474.679	213.69
m-Xylene	28-166	7.009	1462.266	215.11
p-Xylene	27-166	6.990	1453.430	215.31
Toluene	6-137	6.954	1344.800	219.48

Chemical	Vapor Pressure (mmHg)
Benzene	95 (agrees closely with published values)
Ethylbenzene	9.5 "
o-Xylene	6.6(calculated)
m-Xylene	8.2 "
p-Xylene	8.75 "
Toluene	28 (agrees closely with published values)

HENRYS LAW CONSTANT

$H = (16.04 * P * M)/ST$

Where: P = vapor pressure in mm Hg
M = molecular wt in g/mole
S = solubility in mg/L
T = Temperature in °K

Values calculated for o, m and p Xylene

Assuming average solubility (S) = 185

ortho-xylene $H = (16.04*6.6*106)/(185*298) = .20$
meta-xylene $H = (16.04*8.2*106)/(185*298) = .25$
para-xylene $H = (16.04*8.75*106)/(185*298) = .27$

Average = .24

SEPARATOR HYDRAULIC CALCULATIONS

Measurements of the separator and water levels inside the separator were used to calculate the active volume of the separator below. Active volume is defined as the volume of wastewater in the tank just before water levels inside rise high enough to produce flow from the separator discharge pipe. Timed field measurements during separator sampling allowed the calculation of inflow rates and detention time.

Field Measurements

Time	Depth(ft)	
0	5.50	
48'30"	4.55	
53'	4.55	Separator Discharging (sample taken)

Inflow $(Q_i) = (.95' * 3.14 * 3'^2)/48.5$ min

$= .55 ft^3/min = 4.1$ gpm

Separator Dimensions

Diameter = 6ft
Volume = 2500 gallons = 334.2 ft^3
Depth to bottom = 11.8ft
Depth to initial wastewater level = 5.5ft
Depth to bottom of discharge pipe is the level of wastewater at discharge = 4.55ft
Height of wastewater (active separator volume) = 7.25ft
Active volume of separator = 205 ft^3 = 1533 gallons

Detention Time = 205/.55 = 373 minutes = 6.2 hrs

INITIAL VOC CONCENTRATIONS

Initial VOC Concentration

Assuming no loss of VOCs to the atmosphere, initial VOC concentrations can be calculated at time equals 48.5 minutes.

Volume of condensate in separator at t = 48.5 minutes

$V = 0.95' * 3.14 * 3^2 = 26.86 ft^3 \quad = 200.9$ gal.

Volume of existing wastewater in separator at t = 0

$V = (11.8-5.50) * 3.14 * 3^2 = 178.1 ft^3 \quad = \underline{1332.4 \text{ gal.}}$

Total volume held at discharge = 1533.3 gal.

Assumptions: The separator is well mixed.
No losses of VOCs through volatilization etc..
Condensate concentrations are constant
Separator liquid has no volatile organics before condensate addition.

Example:

57,000ug/L * 200.9/1533.3 = 7468.4ug/L
1,300ug/L * 200.9/1533.3 = 170.3ug/L
31,000ug/L * 200.9/1533.3 = 4061.8ug/L
4,900ug/L * 200.9/1533.3 = 642.0ug/L

Chemical	Condensate conc.	**Measured** conc. of separator discharge(ppb) not well mixed no steady state	**Calculated** conc. of separator discharge (ppb) well mixed at steady state
Benzene	57,000	180	7,468
E.benzene	1300	9.6	170
Toluene	31,000	61	4,061
Xylene	4900	720	642

MASS BALANCE AND AIR REQUIREMENTS

MASS BALANCE (for the oil/water separator)

$$Q_i C_i = Q_{air} C_{air} + Q_o C_o$$

Where: Q_i = inflow (ft^3per sec)
Q_o = outflow(ft^3per sec)
Q_{air} = airflow(ft^3per sec)
C_i = concentration in condensate inflow
C_o = concentration in separator outflow
C_{air} = concentration in air outflow

Calculations assume air inflow concentration = 0

$H = C_{air}/C_i$ where H = Henrys Law Constant

Substituting we obtain:

$$Q_i C_i = Q_{air} H C_i + Q_o C_o$$

or $(Q_i C_i - Q_o C_o)/HC_i = Q_{air}$ needed for reducing C_i to C_o

To reduce benzene, xylene, toluene and ethylbenzene to the enforcement standard in NR-140 would require the following reductions:

Chemical	Condensate Conc.(C_i)ppb	NR-140 Std(C_o)(ppb)	% Reduction
Benzene	57,000	.67	99.999
Ethyl-benzene	1,300	N/A	N/A
Toluene	31,000	343	98.9
Xylenes	4,900	620	87.3

Assuming that this amount of reduction would be required before discharge, an estimate can be made of air requirement for aeration in the separator under optimum conditions. For each compound we obtain:

(Benzene)[(.55*57000)-(.55*.67)]/(57,000*.22) = 2.5 ft^3/min air
(Toluene)[(.55*31000)-(.55*343)]/(31000*.27) = 2.0 ft^3/min air
(Xylenes)[(.55*4900)-(.55*620)]/(4900*.24) = 2.0 ft^3/min air

This is the minimum amount of air that would normally be required because interferences reduce the rate at which VOCs can enter the liquid phase from the water phase.

LOADING (based on a pure condensate discharge and condensate drainage recorded for 1986, 17,020 gallons)

57lbs/million lbs H_2O (ppm)*.01702MG/yr*8.34 million lbs/million gallons (lbs/gal.) = 8.1 lbs of benzene/yr.

1.3ppm*.01702MG/yr*8.34 lbs/gal = 0.185 lbs of ethylbenzene/yr.

31ppm*.01702MG/yr*8.34 lbs/gal = 4.4 lbs of toluene/yr.

4.9ppm*.01702MG/yr*8.34 lbs/gal = 0.7 lbs of xylene/yr.

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