

DISINFECTION BY-PRODUCT FORMATION BY ALTERNATIVE  
DISINFECTANTS AND REMOVAL BY GRANULAR ACTIVATED CARBON

by

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## FOREWORD

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The Risk Reduction Engineering laboratory is responsible for planning, implementation, and management of research, development, and demonstration programs to provide an authoritative, defensible engineering basis in support of the policies, programs, and regulations of the EPA with respect to drinking water, wastewater, pesticides, toxic substances, solid and hazardous wastes, and Superfund-related activities. This publication is one of the products of that research and provides a vital communication link between the researcher and the user community.

This study reports on a cooperative research effort that examines the formation of halogenated disinfection by-products by the alternative disinfectants and the removal of these by-products and their precursors by granular activated carbon filtration.

E. Timothy Oppelt, Director  
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## ABSTRACT

The effects of the use of the alternative disinfectants on the formation of halogenated disinfection by-products (DBPs) including total organic halide, trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, chloral hydrate, and chloropicrin, were examined along with the ability of granular activated carbon (GAC) to remove these by-products and their precursors. Microbiological information was also obtained on the operating system and included heterotrophic plate count, total coliform, and assimilable organic carbon (AOC). The ability of the alternative disinfectants to inactivate MS2 coliphage was also examined. One other aspect of the project was to provide sampling sites for health effects research by EPA which will be reported elsewhere.

The operating system was comprised of four parallel pilot column process streams consisting of a 30 min contact chamber followed by a sand column in series with a GAC column having a 20 min empty bed contact time. One of four disinfectants, ozone, chlorine dioxide, chlorine, or chloramines, was applied at the beginning of each process stream. A fifth nondisinfected process stream consisting of only a sand column in series with a GAC column was used as a control.

The lowest levels of halogenated DBPs resulted from the combination of preozonation and postchloramination with annual simulated distribution system averages of 27 ug Cl/L for TOX and 12 ug/L for the sum of 18 DBPs when sand filtration was employed. These respective concentrations were further reduced to 13 ug Cl/L and 7 ug/L with subsequent GAC filtration having a 20 min empty bed contact time. While ozonation produced significant levels of AOC, sand filtration resulted in a 77 percent reduction to 39 ug acetate C-eq/L with subsequent GAC filtration further reducing AOC to 4 ug acetate C-eq/L.

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# LIST OF ABBREVIATIONS

AMU	--	atomic mass units
AOC	--	assimilable organic carbon
BAA	--	bromoacetic acid
BCAA	--	bromochloroacetic acid
BCAN	--	bromochloroacetonitrile
$^{\circ}\text{C}$	--	degree centigrade
CAA	--	chloroacetic acid
C-eq/L	--	carbon equivalents per liter
cfu	--	colony forming units
CH	--	chloral hydrate
CP	--	chloropicrin
$\text{Cl}_2$	--	free chlorine
- $\text{Cl}_2$	--	terminal samples treated with free chlorine and incubated at $30^{\circ}\text{C}$ for 5 days
$\text{ClO}_2$	--	chlorine dioxide
$\text{CT}_{10}$	--	residual concentration in mg/L x $T_{10}$ in minutes
DBAA	--	dibromoacetic acid
DBAN	--	dibromacetonitrile
DBP	--	disinfection by-product
DCAA	--	dichloroacetic acid
DCAN	--	dichloroacetonitrile

# LIST OF ABBREVIATIONS

DCP	--	1,1-dichloropropanone
DFTPP	--	decafluorotriphenylphosphine
DO	--	dissolved oxygen
DPD	--	n,n-diethyl-p-phenylenediamine
EBCT	--	empty bed contact time
EPA	--	U. S. Environmental Protection Agency
FAS	--	ferrous ammonium sulfate
FC43	--	perfluorotributylamine
ft	--	foot
GAC	--	granular activated carbon
gal	--	gallon
gpm/ft <sup>2</sup>	--	gallons per minute per square foot
GC/MS	--	gas chromatograph/mass spectrometer
gpm	--	gallons per minute
HAA	--	haloacetic acid
HPC	--	heterotrophic plate count
ID	--	inner diameter
in	--	inch
infl	--	influent
m	--	meter
mgd	--	million gallons per day
mg/L	--	milligram per liter
mg C/L	--	milligrams of carbon per liter

# LIST OF ABBREVIATIONS

min	--	minute
mm	--	millimeter
msec	--	milliseconds
-NH <sub>2</sub> Cl	--	samples treated with ammonia followed by chlorine and incubated at 30°C for 5 days
NH <sub>2</sub> Cl	--	chloramine
ntu	--	nephelometric turbidity unit
O <sub>3</sub>	--	ozone
PRD	--	percent relative deviation
SWTR	--	surface water treatment rule
T <sub>10</sub>	--	the time (minutes) in which 90 percent of the water passing through the column is retained within the column.
TC	--	total coliform
TCAA	--	trichloroacetic acid
TCAN	--	trichloroacetonitrile
TCP	--	1,1,1-trichloropropanone
THM	--	total trihalomethane
TOC	--	total organic carbon
TOX	--	total organic halogen
ug/L	--	microgram per liter
ug Cl/L	--	micrograms of chloride per liter
ul	--	microliter
VOA	--	volatile organics analysis

# METRIC CONVERSION TABLE

ENGLISH UNIT	METRIC EQUIVALENT
1 ft <sup>3</sup>	0.02834 m <sup>3</sup>
1 ft	30.49 centimeter
1 gal	3.788 liter
1 gpm	3.788 liters/min
1 gal/min per ft	40.78 liters/min per m <sup>2</sup>
1 in	2.54 cm
mgd	3788 m <sup>3</sup> /day
1 lb	453.5 g
1 psi	0.1785 kg/cm <sup>2</sup>
1 sq ft	0.0929 m <sup>2</sup>

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## SECTION 1

### INTRODUCTION

Chlorinated disinfectants have historically been widely used throughout the United States in the disinfection of drinking water. During the disinfection process, chlorinated disinfectants have been found to react with naturally occurring organic matter to form a number of halogenated disinfection by-products. Because recent amendments to the Safe Drinking Water Act will require that these by-products be regulated in the near future, this research project was developed to evaluate the formation of disinfection by-products by the alternative disinfectants and their removal by granular activated carbon filtration as well as to evaluate the microbiological quality of the treated water. More specifically, the objectives of this project were:

1. To measure the effects of the alternative disinfectants on the formation of halogenated disinfection by-products including the trihalomethanes, the haloacetic acids, the haloacetonitriles, the haloketones, chloral hydrate, and chloropicrin.
2. To measure the effectiveness of granular activated carbon filtration following sand filtration in removing halogenated disinfection by-products and their precursors.
3. To measure the general microbiological quality of water treated with the alternative disinfectants.
4. To assess the levels of assimilable organic carbon formed during disinfection with ozone and chlorine.
5. To evaluate the effectiveness of the alternative disinfectants in the inactivation of MS2 coliphage.

To meet these objectives, a pilot column system consisting of four disinfected process streams (ozone, chlorine dioxide, chlorine, and chloramine) and a nondisinfected process stream was continually operated for one year beginning in July 1989. This

report contains a complete description of the pilot column system employed, the analytical methods used to monitor the parameters of interest, and the quality assurance associated with the analytical results obtained. A thorough discussion of each parameter is presented relative to the project objectives indicated.



## SECTION 2

### CONCLUSION

1. When high levels of disinfection by-product (DBP) precursors are present, the level of halogenated DBPs reaching the consumer is primarily dependent upon the type of postdisinfectant (chlorine or chloramine) used in the distribution system as opposed to the predisinfectant or filtration process employed.
2. The combination of pre- and postdisinfectants which resulted in the lowest levels of halogenated DBPs reaching the consumer was preozonation and postchloramination which produced annual distribution system averages of 27 ug Cl/L for TOX and 12 ug/L for total halogenated DBPs when sand filtration was employed. With subsequent GAC filtration having a 20 min empty bed contact time, these annual averages were reduced to 13 ug Cl/L TOX and 7 ug/L total halogenated DBPs indicating that, even with annual GAC replacement or reactivation, GAC filtration would not be very beneficial for DBP removal in a chloraminated distribution system.
3. The use of postchlorination following sand filtration and preozonation completely negated any beneficial effects of ozonation due to the high level of DBP precursors present, producing annual distribution system averages of 330 ug Cl/L for TOX and 309 ug/L for total halogenated DBPs, 50% of which were THMs. Even with GAC filtration following preozonation and sand filtration, postchlorination produced annual distribution system averages for TOX and total halogenated DBPs of 127 and 138 ug/L, respectively. In order to maintain THM levels below 50 ug/L using this process, GAC replacement or reactivation would be required approximately every 100 days.
4. Pretreatment with chlorine dioxide followed by sand filtration and postchloramination produced only slightly higher DBP levels than pretreatment with ozone which had

an annual halogenated DBP level of 19 ug/L. However, chlorine dioxide pretreatment also produced an annual average TOX level of 80 ug/L which was three times that observed for ozone pretreatment, as well as a chlorite residual of 0.5 ug/L (chlorate was not measured).

5. Relatively high levels of assimilable organic carbon (AOC) were observed following ozone pretreatment ranging from 50-270 ug acetate C-eq/L with an annual average of 170 ug acetate C-eq/L. These AOC levels correlated with changes in water temperature, with the lowest AOC levels being produced at the lowest water temperature. The biologically active ozone sand column reduced AOC levels by 77 percent to an average of 30 ug acetate C-eq/L with subsequent GAC filtration reducing the AOC level to 4 ug acetate C-eq/L. Chlorination produced only a slight reduction in the nondisinfected influent AOC which averaged 10 ug acetate C-eq/L, while subsequent GAC filtration reduced the AOC level to 3 ug acetate C-eq/L.
6. Reductions of MS2 coliphage of greater than 6 logs occurred across the ozone contact chamber with  $CT_{10}$  values ranging from 3-5 mg/L-min while those across the chlorine dioxide and chlorine contact chambers were equal to or greater than 5 logs with respective  $CT_{10}$  values ranging from 7-10 mg/L-min and 14-20 mg/L-min. Relatively low coliphage removals of 0.2-1.8 logs occurred across the chloramine contact chamber with  $CT_{10}$  values ranging from 22-31 mg/L-min.
7. High heterotrophic plate counts (HPC) were observed in the ozone sand column effluent averaging 28,000 cfu/mL and in the GAC effluents of all process streams averaging 2,000-16,000 cfu/mL. This indicated that free chlorine contact of a relatively short duration would be required to reduce the HPC to an acceptable level before the addition of ammonia to form chloramine and thereby minimize DBP formation in the distribution system.
8. A relatively good correlation with a coefficient of 0.88 and a standard deviation of 26 ug Cl/L, was observed between TOX and the sum of 18 DBPs for the terminally chlorinated distribution simulation. Correlations within the treatment train were highly variable due to the short disinfectant contact times employed and the variations in reaction rates observed for TOX and the DBPs. The use of TOX as a DBP surrogate in a chloraminated distribution system was determined to be impractical since the correlation coefficient would vary dramatically with the free chlorine contact time employed in the treatment process.

### SECTION 3

#### RECOMMENDATIONS

1. Further studies of ozone disinfection should be conducted with regard to the formation of AOC and specific nonhalogenated ozone by-products at various ozone dosages and their reductions across various filtration medias over a range of hydraulic loadings.
2. The effects of AOC on distribution system regrowth should be thoroughly investigated particularly with regard to the presence of excess ammonia from chloramine generation and phosphate from corrosion inhibitors.
3. The free chlorine contact time required to produce an acceptable heterotrophic plate count level following ozonation and GAC filtration should be assessed for a chloraminated distribution system along with the subsequent levels of halogenated disinfection by-products formed.
4. Further studies of virus inactivation in natural waters should be conducted for the alternative disinfectants to confirm the higher log removals observed in this study.

## SECTION 4

### PILOT COLUMN CONFIGURATION AND OPERATION

Lower Mississippi River water entering the 34 mgd Permutit treatment plant was dosed with 1-6 mg/L diallyldimethylammonium chloride and/or dimethylamine polyelectrolyte polymers for clarification, 0.1-0.3 mg/L fluosilicic acid (as fluoride) for fluoridation, and 2 mg/L powdered activated carbon for spill prevention. After clarification via Permutit upflow precipitators, a small portion of clarified water was diverted to the pilot column system and was filtered through one of two pressure sand filters at a hydraulic loading of 1.7 gpm/ft<sup>2</sup>. Each sand filter contained 30 in of 0.45 mm filter sand and provided an average nondisinfected sand filtered water flow of 8.5 gpm to the rest of the pilot column system as indicated in Figure 1. The filtered water was then split into five process streams, one for each of the four disinfectants and a nondisinfected process stream which was used as a control. Each disinfected process stream consisted of a 30 min disinfectant contact chamber followed by series filtration through a sand column and a granular activated carbon (GAC) column, while the nondisinfected process stream consisted of only a sand column in series with the GAC column.

Each disinfection contact chamber was constructed using a 12 in diameter stainless steel pipe and was 10 ft in height, except for the ozone contact chamber which was 11 ft high. The sand and GAC columns were constructed from 10 ft sections of 6 in diameter glass pipe. All pilot column components were constructed from stainless steel, glass, and teflon. Further details of pilot column construction have been presented in a previous report.<sup>1</sup> The sand columns were charged with 30 in of 0.45 mm filter sand while the GAC columns were charged with 6.8 ft of 12 x 40 mesh GAC to achieve a 20 min empty bed contact time (EBCT) at a flow of 0.5 gpm as indicated in Table 1. Each column was backwashed only when necessary to achieve the desired flow rate. No media loss was observed during backwashing. The GAC used in this study was Cecarbon GAC 40 and was selected after a thorough evaluation of various types of GAC as previously reported.<sup>1</sup>

The average water quality of the nondisinfected water

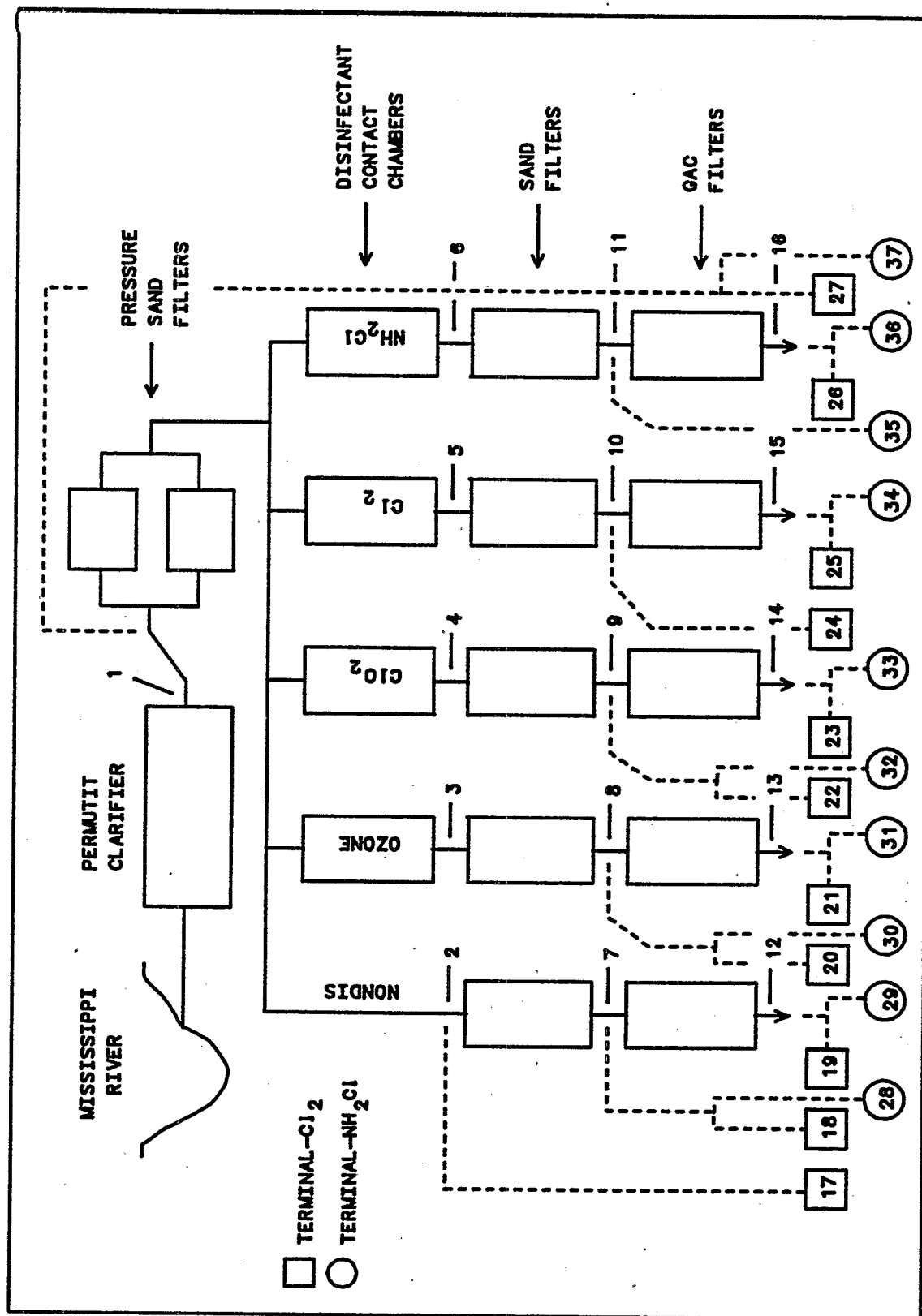


Figure 1. Pilot Column System Configuration.

TABLE 1: Physical Pilot Column Operating Conditions

	Average Flow Rate (gpm)	Average Hydraulic Loading (gal/min /ft <sup>2</sup> )	Average GAC EBCT (min)	Total Volume Filtered (gal x10 <sup>3</sup> )	Number of Backwashes	
					Sand	GAC
non- disinfected	0.50	2.5	20	251	5	1
ozone	0.50	2.5	20	239	3	1
chlorine dioxide	0.50	2.5	20	252	2	0
chloramine	0.50	2.5	20	252	2	0
chlorine	0.50	2.5	20	251	6	0

entering the five pilot column process streams after sand filtration is indicated in Table 2. During the course of the operational period, water temperature fluctuations were observed from 3-29°C as indicated in Figure 2. After the addition of the various disinfectants, slight variations in pH were observed due to the acids and bases contained in the disinfectant solutions. On the average, the pH of the chlorine dioxide contact chamber effluent decreased 0.6 units to pH 7.0 while that for the chlorine and chloramine contact chambers increased 0.1 & 0.2 units to pH 7.7 & 7.8, respectively. No change in pH was observed for the ozone process stream. Chlorine dioxide was generated with a 96% yield by the in-line mixing of hypochlorite/chlorite and sulfuric acid solutions prior to injection into the process stream. Chloramines were formed within the process stream with the injection of hypochlorite followed within a few seconds by that of ammonia hydroxide. The average 30 min demands for each disinfectant determined during the operational period are compared in Table 3 along with their respective average disinfectant contact chamber effluent residual concentrations. While all residual concentrations were measured as chlorine using the DPD titrimetric method, all residual concentrations are reported as the specific disinfectant indicated, and not as free chlorine. With the exception of the ozone demand, these demands were determined by the difference in the 30 min residual readings of the various disinfectants applied at the same dosages to deionized water and nondisinfected influent water. The ozone demand was determined by measuring the

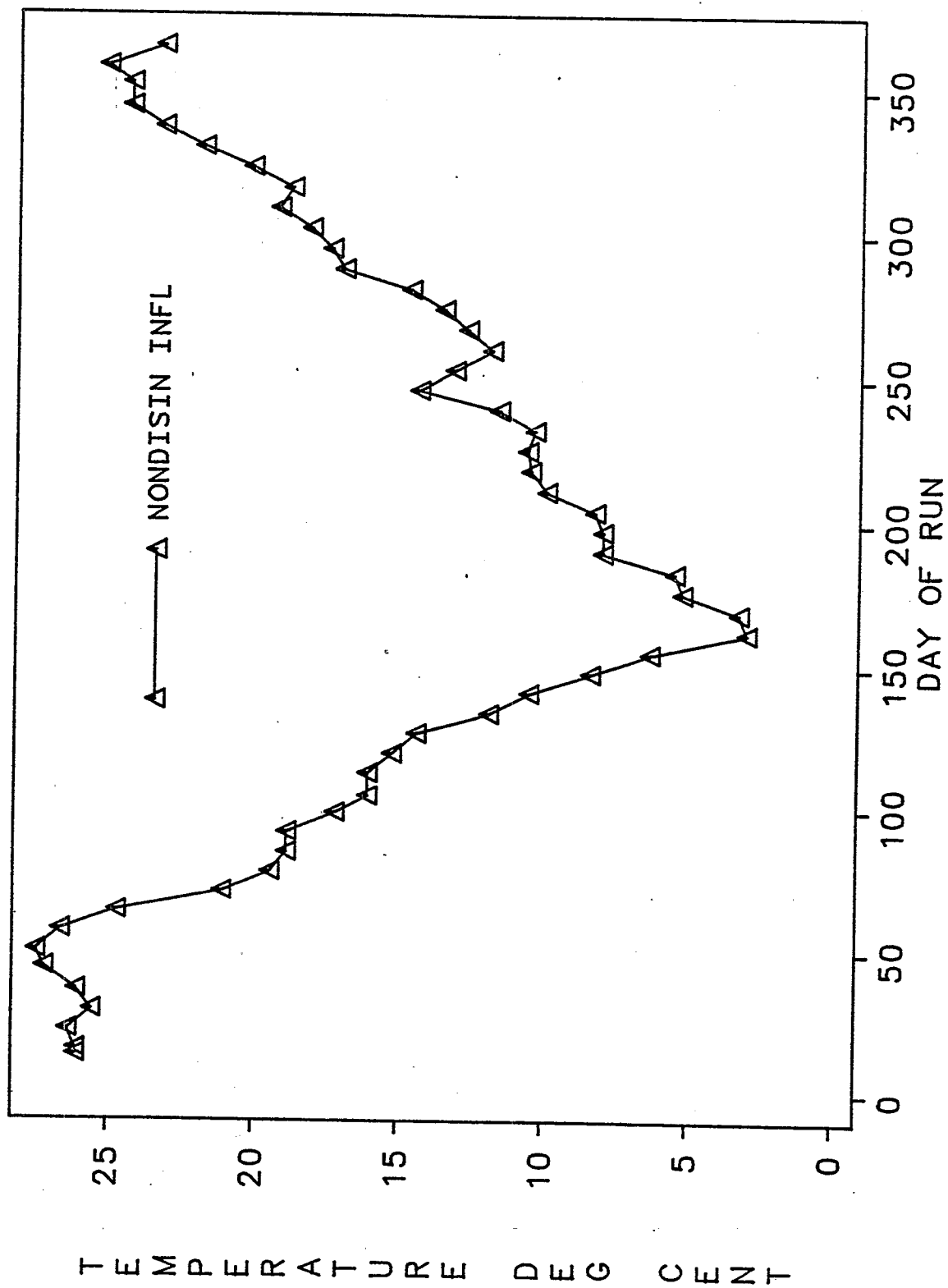


Figure 2. Water Temperature of the Pilot Column System Influent.

TABLE 2: Average Nondisinfected Influent Water Quality

carbonates (mg/L as $\text{CaCO}_3$ )	0	calcium (mg/L as $\text{CaCO}_3$ )	39
bicarbonates (mg/L as $\text{CaCO}_3$ )	88	chlorides (mg/L)	28
hardness (mg/L as $\text{CaCO}_3$ )	131	turbidity (ntu)	0.3
pH	7.6	temperature ( $^{\circ}\text{C}$ )	19.4

TABLE 3: Average Disinfectant Contact Chamber Demands and Residuals

	Average 30 Minute Disinfectant Demand Determinations (mg/L)	Process Stream Average Disinfectant Contact Time (min)	Process Stream Average Disinfectant Residuals (mg/L)
ozone	2.5	30	0.5
chlorine dioxide	0.7	30	0.5
chlorine	1.8	30	1.0
monochloramine	0	30	2.2

difference in the concentration of ozone in the gas entering and exiting the ozone contact chamber and subtracting the ozone residual after making the appropriate corrections for gas and water flows through the ozone contact chamber. The highest demand was observed for ozone at 2.5 mg/L followed by chlorine at 1.8 mg/L and chlorine dioxide at 0.7 mg/L. Essentially no 30 min demand was observed for chloramine, however significant demands of 1-1.5 mg/L were observed after several days of storage at a temperature of  $30^{\circ}\text{C}$ . The average concentrations of residual disinfectant species observed in the contact chamber and sand column effluents are presented in Table 4. While the ozone residual dissipated completely across the sand column, the other three disinfectant residuals were only slightly reduced. No residual species of any disinfectant were observed in the



TABLE 4: Average Disinfectant Contact Chamber and Sand  
Column Effluent Residuals

<u>Process Stream</u>	<u>Disinfectant Species</u>	<u>Contact Chamber Effluent (mg/L)</u>	<u>Sand Columns Effluent (mg/L)</u>
ozone	ozone	0.5	0.0
chlorine dioxide	chlorine dioxide	0.5	0.3
	chlorite	0.3	0.4
	mono-chloramine	0.2	0.0
	dichloramine	0.2	0.1
	chlorine	0.0	0.0
chloramine	mono-chloramine	2.2	1.7
	dichloramine	0.1	0.3
	chlorine	0.0	0.0
chlorine	chlorine	1.0	0.9
	dichloramine	0.2	0.2
	mono-chloramine	0.1	0.1

effluent of the GAC columns during the one year operational period.

## SECTION 5

### SAMPLING, ANALYSIS, AND QUALITY ASSURANCE

#### Sampling, Preservation, and Storage

The sampling and analysis schedule for the pilot column system during the one year operational period is indicated in Table 5 with the numbered sampling point locations corresponding to those in Figure 1. Those analyses performed included total organic carbon (TOC), total organic halide (TOX), volatile organics (VOC), haloacetic acids (HAA), chlorinated disinfection by-products (CDBP), heterotrophic plate count (HPC), total coliform (TC), assimilable organic carbon (AOC), MS2 coliphage, dissolved oxygen (DO), disinfectant residuals, pH, and temperature. The CDBP analysis included such chlorinated by-products as the haloacetoneitriles, halo ketones, chloral hydrate, and chloropicrin. Qualitative confirmatory GC/MS analysis was performed for the THMs, HAAs, and the CDBPs on the influent to each process stream (the nondisinfected influent and the disinfectant contact chamber effluents), as well as on the chlorinated terminal formation potential samples collected at these locations. Those sampling locations in Figure 1 designated 17-36 were terminal formation potential samples which were dosed in the laboratory with chlorine or chloramine and held for 5 days at 30°C in order to simulate the maximum formation of by-products in the distribution system as well as to obtain a measure of the level of disinfection by-product precursors present. The chlorinated terminal formation potential samples ( $-Cl_2$ ) were spiked with varying amounts of chlorine dependent upon the level of demand in the sample. Over the course of the project, the precipitator and nondisinfected influent and sand filter effluent were spiked with 8-12 mg/L chlorine, all other sand filter effluents were spiked with 6-7 mg/L, and all GAC effluents were spiked with 4-4.5 mg/L. The chloraminated terminal formation potential samples ( $-NH_2Cl$ ), having a considerably lower demand, were spiked with 5 mg/L ammonia-nitrogen followed by 4 mg/L chlorine at all locations. After the five day storage period at 30°C had elapsed, all terminal samples were quenched with sodium thiosulfate (VOC), sodium sulfite (TOX), or ammonium chloride (HAA & CDBP) and stored at 4°C until analyzed. This same quenching and storage procedure was also used for all

Table 5. Sampling and Analysis Schedule

Sampling Location

Analysis	No. per Week	Sampling Location																												
		Week 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
TOC	15	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
TOX	21	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
VOC	21	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
HAA	21	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
CDBP	21	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
GC/MS-THM	5	-	W	W	W	W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GC/MS-HAA	5	-	W	W	W	W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
GC/MS-HAN	5	-	W	W	W	W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
HPC	48	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
TC	48	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T	T
AOC	2	-	M	M	-	-	M	-	M	-	M	-	M	-	M	-	M	-	M	-	M	-	M	-	M	-	M	-	M	-
Coliphage	1	-	M	M	M	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
DO	36	-	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
Disin. Resid	28	-	-	F	F	F	F	-	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W	W
pH	5	-	W	W	W	W	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
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W: 1/week X: 2/week T: 3/week M: Monthly F: 5 days/week

instantaneous samples. No preservative was used for TOC other than immediate storage at 4°C. All organics samples were collected in duplicate with the duplicate being analyzed when the original result was suspected of being in error based on the existing data trend, as determined by the section analyst. HPC and TC samples were both collected and analyzed in duplicate and the average value reported.

### Analytical Procedures

#### Total Organic Carbon (TOC)--

EMSL Method 415.2 was used for TOC analysis with the exception that the samples were stored at 4°C without preservative and a linearity check was performed on a weekly basis.

#### Total Organic Halide (TOX)--

EMSL Method 450.1 was used for TOX analysis without modification.

#### Disinfection By-Products--

Those volatile organics and disinfection by-products monitored during this project are listed in Tables 6, 7, and 8 along with their respective method detection limits and, where applicable, their percent recoveries. For the HAA and CDBP methods, which were still under development at the time of this study, the detection limit was defined as the lowest concentration at which the method response was still linear. This process is exemplified in Figure 3 which compares the true and reported concentrations of trichloro- and dichloro-acetonitrile with respective detection limits of 0.0016 and 0.0032 ug/L.

EMSL Method 502.2 was used for VOC analysis with the following exceptions:

- The analytical column was a 30 m x 0.53 mm I.D. DB-624 column which was held initially at 33°C for 4 min, ramped at 2.4°C/min to 40°C, held 1 min, ramped at 6°C/min to 160°C, and held for 10 min.
- The 25 cm x 2.7 mm I.D. trap was comprised of equal volumes of Tenax, silica gel, and charcoal.
- The internal standard used was 1,2-dichloropropane.

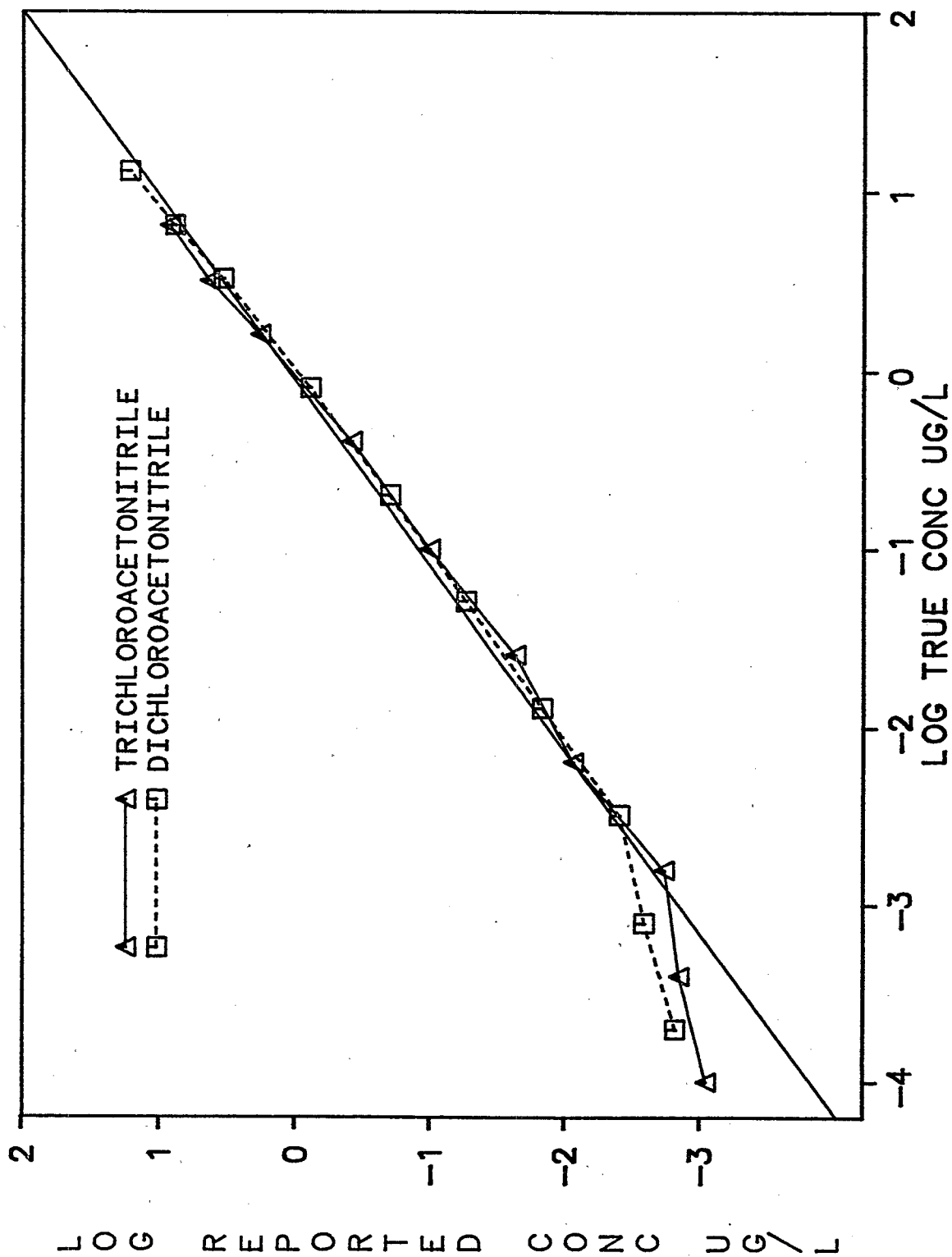


Figure 3. Method Recoveries for Di- and Trichloroacetonitrile.

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Table 6. Gas Chromatography Detection Limits for VOC Analysis

<u>Compound</u>	<u>Standard Conc, ug/L</u>	<u>Method Detection Limit, ug/L</u>
dichloromethane	2.1	.003
1,2-dichloroethylene	5.0	0.5*
chloroform	2.4	.001
tetrachloromethane	2.6	.005
1,2-dichloroethane	3.0	0.01
1,1,2-trichloroethylene	3.5	0.005
bromodichloromethane	3.2	0.02
1,1,2-trichloroethane	2.3	0.008
chlorodibromomethane	5.9	0.017
bromoform	11.6	0.04

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\*Interference from methyl-t-butylether used as the extraction solvent in methods 551 & 552.

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EMSL Draft Method 552 was used for the analysis of the haloacetic acids with the following exceptions:

- The DB-210 column was used as the analytical column and was held at 32°C for 10 min and ramped at 10°C/min to 200°C with a final hold of 5 min. The injection port temperature was 160°C and a splitless injection with a 20 sec delay was employed.

EMSL Draft Method 551 was used for the analysis of chlorinated disinfection by-products which included the haloacetonitriles, halo ketones, chloral hydrate, and chloropicrin, with the following exceptions:

- A 30m x 0.325 mm I.D. DB-210 column with a 0.5 um film thickness was used as the analytical column and was

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Table 7. Gas Chromatography Detection Limits for HAA Analysis

<u>Compound</u>	<u>Standard Conc, ug/l</u>	<u>Method Detection Limit, ug/L</u>	<u>Method Recovery %</u>
monochloro- acetic acid	3.0	0.1	46.2
dichloro- acetic acid	3.5	0.012	83.1
monobromo- acetic acid	3.0	0.01	63.0
trichloro- acetic acid	1.0	0.01	71.6
bromochloro- acetic acid	2.0	0.02	43.9
dibromo- acetic acid	0.25	0.0025	62.4
2,4,6-trichloro- phenol	1.5	0.02	87.8
2,4-dichloro- phenol	25	4.0*	70.0
2-chloro- phenol	100	0.81	101

\*Method contaminant interference

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programmed as previously indicated for Method 552.

#### Confirmatory GC/MS Analysis--

The standard concentrations and method detection limits for those volatile organics and disinfection by-products that were qualitatively confirmed by GC/MS analysis are indicated in Table 9.

EMSL method 624 was used for VOC confirmatory analysis by

Table 8. Gas Chromatography Detection Limits for CDBP Analysis

Compound	Standard Conc, ug/l	Method Detection Limit, ug/l	Method Recovery %
dichloroaceto- nitrile	.20	.0032	97.3
trichloroaceto- nitrile	.10	.0016	89.1
bromochloroaceto- nitrile	.15	.0024	99.3
dibromoaceto- nitrile	.20	.0032	1.19
chloral hydrate	.40	.0256	55.2
chloropicrin	.15	.0024	96.3
1,1-dichloro- propanone	.20	.008	62.5
1,1,1-trichloro- propanone	.5	.004	91.6

GC/MS with the following exceptions:

- 20mL aliquots were spiked with internal standards (2-bromo-1-chloropropane, fluorobenzene, and bromofluorobenzene) and purged for 15 min at a helium flow of 40 mL/min on to a Tenex and silica gel trap.

The trap was rapidly heated to 180°C, desorbed for 4 min at 30 mL/min, and then vented to atmosphere and purged for an additional 110 min.

- A 60 m x 0.25 mm ID DB-5 capillary column with a 25 micron coating thickness was used for analysis. A 20:1 split ratio was employed during injection.
- Spectra were acquired on a Finnigan 4023C GC/MS in the full scan mode from 35-260 amu each second. A compound was considered confirmed if the signal-to-noise ratio was greater than 5 and the spectrum obtained met an



Table 9. Confirmatory GC/MS Standard Concentrations and Qualitative Detection Limits

Compound	Standard Concentration, ug/L	Method Detection Limit, ug/L
chloroform	8.0	0.05
bromodichloromethane	8.0	0.10
chlorodibromomethane	8.0	0.10
bromoform	8.0	0.30
monochloroacetic acid	30	0.10
dichloroacetic acid	3.5	0.05
monobromoacetic acid	3.0	0.10
trichloroacetic acid	1.0	0.10
bromochloroacetic acid	1.0	0.05
dibromoacetic acid	0.25	0.10
2,4,6-trichlorophenol	25	0.60
2,4-dichlorophenol	1.5	0.04
2-chlorophenol	100	0.25
dichloroacetonitrile	0.20	0.05
trichloroacetonitrile	0.10	0.03
bromochloroacetonitrile	0.15	0.10
dibromoacetonitrile	0.20	0.10
chloral hydrate	0.40	0.10
chloropicrin	0.15	0.07
1,1-dichloropropanone	0.50	0.20
1,1,1-trichloropropanone	0.25	0.15

acceptable fit criteria (usually >850) when compared to external standard spectra. The GC/MS was calibrated each day with FC43 and verified with the bromofluorobenzene in each sample. The other two internal standards were used to assess compound recovery.

EMSL Draft Method 551 & 552 were used for the initial extraction and concentration of the chlorinated disinfection by-products and haloacetic acids with further processing for GC/MS confirmation as follows:

- After GC analysis, the remaining extracts were sealed and stored along with their corresponding standards and blanks at 4°C until GC/MS analysis was performed. A 200 uL aliquot of the haloacetic acid and chlorinated disinfection by-product extracts of each sample were combined and blown down by gentle air stream to 5 uL. A 2 uL aliquot of this concentrate was injected splitless onto a 60 m x 0.25 mm diameter DB-5 capillary column with a 25 micron film thickness, held for 5 min at 40°C,

and programmed to 70°C at 3°C/min and then to 200°C at 6.5°C/min. Spectra were generated using multiple ion detection (MID) with eight MID descriptors which were sequentially changed during the chromatographic run. Each descriptor scanned up to 24 different masses in one second scans. Each mass  $\pm 0.1$  amu was scanned in 12 msec to maximize signal-to-noise. The instrument was calibrated daily with FC43 and periodically checked for agreement with DFTPP tuning specifications. The sample spectra obtained were then compared to those of external standards and blanks and were confirmed if the sample response was significantly greater than that of the blank, the signal-to-noise ratio was greater than 5, and an acceptable fit, usually  $>850$ , was obtained.

Heterotrophic Plate Count (HPC), Total Coliform (TC), and Dissolved Oxygen (DO)--

Analysis for HPC, TC, and DO were performed using Parts 907C, 909A, and 421F of the 16th Edition of Standard Methods<sup>2</sup>.

Assimilable Organic Carbon (AOC)--

Samples were collected in 45 mL vials which were prewashed with detergent, rinsed 5 times with hot water, acid rinsed with 0.1 N HCl, rinsed 3 times with carbon-free deionized water, dried, capped with foil, and heated to 550°C for 6 hours. The teflon-lined silicone septa were soaked in a 10% potassium persulfate solution at 60°C for one hour and then rinsed with carbon-free deionized, distilled water.

After collection, samples were returned to the laboratory where they were quenched with 10% sodium thiosulfate and placed in a 70°C waterbath for 30 min. The samples were then cooled to 15°C and inoculated with a culture of Pseudomonas P-17 to achieve an initial plate count of 50-500 cfu/mL. After subsequent incubation at 15°C for 7, 8, and 9 days, three vials from each location were assayed using the standard spread plate technique<sup>2</sup>. Each vial was assayed using two dilutions in triplicate. The viable counts for the three days were then averaged and the AOC concentration determined using the Vander Kooij yield factor<sup>3</sup>.

MS2 Coliphage--

The initial MS2 coliphage culture was received from EPA in Cincinnati in a tryptone yeast extract broth (10 g bacto tryptone, 8 g sodium chloride, 1 g glucose, & 1 g yeast extract/L

distilled water) with a titer of approximately  $10^{10}$  plaque forming units (pfu) per mL. The stock culture was prepared from the original culture by plating four 20 mL agar plates with a  $10^{-6}$  dilution as indicated below. These plates were then harvested by mixing the contents of the plates with 200 mL tryptone yeast extract broth, adding 0.28 g of disodium EDTA and 0.026 g of lysozyme for each 100 mL of agar-broth mixture, stirring for 30 min, centrifuging at 2200 rpm for 30 min, and collecting the supernatant. Each month, the stock culture was prepared in this manner from the previous month's stock culture and consistently contained  $3-6 \times 10^{10}$  pfu/mL. The stock culture was subsequently diluted 1:10 in sodium chloride-calcium chloride diluent (8.5 g sodium chloride and 0.22 g calcium chloride/L distilled water) to produce 2 L of phage seed solution containing  $10^9$  pfu/mL. This seed solution was metered into the nondisinfected water entering the pilot column system such that the final concentration was  $10^4-10^5$  pfu/mL. After feeding the seed solution a minimum of 2-3 hours to ensure saturation of the contact chambers, 200 mL samples were collected dropwise from each location over a period of 10 min. This was accomplished by inserting a small capillary tube into the side of a section of latex tubing attached to the sample spigot and slightly restricting the 0.8 gpm flow in the latex tubing such that a dropwise flow was obtained at the capillary.

Prior to sample collection, petri dishes were prepared with 15-20 mL of bottom agar (10 g bacto tryptone, 10 g bacto agar, 2.5 g sodium chloride, 2.5 g potassium chloride, and 1 mL 1 M calcium chloride/L distilled water) and refrigerated. A host E. coli solution (ATCC 15597) was prepared by inoculation of 10-2 mL of tryptone yeast extract broth in a 20 mL test tube and incubating at 35°C. Top agar (10 g bacto tryptone, 8 g sodium chloride, 8 g bacto agar, 1 g glucose, 1 g yeast extract/L distilled water) was also prepared and refrigerated.

After sample collection, 3 mL of melted top agar was dispensed into a test tube and held at 44°C in a water bath. Sample dilutions were made with sodium chloride-calcium chloride diluent and one mL of the diluted sample was added to the test tube along with 4 drops of host E. coli solution. After thorough mixing, the test tube solution was added to the petri dish on top of the bottom agar. The petri dish was then swirled, allowed to stand for 15 min, inverted, and incubated at 35°C for 18-24 hours. The plates were then read and the number of plaque forming units recorded.

#### Disinfectant Residuals--

All disinfectant residuals were measured via the LaMotte-Palin DPD-FAS Method using a LaMotte Model DT Laboratory

titration kit available from LaMotte Chemical Products, Chestertown, MD. The stock standard solution of ferrous ammonium sulfate (FAS) was freshly prepared each month and standardized against a primary standard dichromate solution as indicated in Part 408D of the 16th Edition of Standards Methods<sup>2</sup>.

#### Temperature and pH--

Temperature and pH measurements were made in accordance with Parts 212 and 423 of the 16th Edition of Standard Methods<sup>2</sup>.

#### Quality Assurance

Precision was assessed for all organic analyses by comparing the results of duplicate samples. One duplicate sample was analyzed each week for TOC, TOX, VOC, HAA, and CDBP analyses. The sample which was analyzed in duplicate was the first and the last sample to be analyzed within each weekly sample set. In this manner, the precision determined was indicative of the entire sample set over the time period in which the sample set was analyzed. The average precision observed for each organic parameter monitored during the operational period is indicated in Table 10 along with the concentration range and the number of duplicate samples analyzed. The number of observations for each parameter varied with sampling frequency and detectability. The percent relative deviation (PRD) of each duplicate was calculated by determining the percent difference between the higher of the two data points (H) and their mean (X), i.e.  $PRD = 100 (H-X)/X$ . The average PRD represents the average of all PRD's determined during the one year operational period. The PRD for all parameters monitored were within 10% except for monochloroacetic acid, monobromoacetic acid, dibromoacetic acid, trichloroacetonitrile, and dibromoacetonitrile which were within 20%. The higher PRD's observed for these substances resulted from the very low concentrations observed, which were in most cases, below the method detection limit.

Accuracy was assessed through the evaluation of the relative error determined for the internal quality control samples obtained from EPA and through performance audits conducted by EPA. Unfortunately, quality control samples for the HAA and CDBP methods were not available during the project and they were not included in the EPA performance audits until the very end of the operational period in May, 1990. Hence, the subsequent performance evaluation in November, 1990 has been included to further qualify the data presented in this report. Internal quality control samples were introduced approximately once each month while EPA performance evaluations were conducted every six months. The average percent relative error observed for the internal quality control samples, which were only available for

Table 10. Analytical Precision as Measured by Duplicate Sample Analysis

<u>Parameter</u>	<u>Conc. Range</u>	<u>No. of Observ.</u>	<u>Average Percent Relative Deviation</u>
TOC, mg/L	2.497-4.405	52	4.6
TOX, ug/L	68.8-129.5	50	4.4
chloroform, ug/L	0.967-7.830	50	5.2
dichlorobromo- methane, ug/L	0.131-1.808	50	5.1
1,2-dichloro- ethane, ug/L	0.009-0.207	12	5.8
carbon tetra- chloride, ug/L	0.007-0.681	6	3.6
1,1,1-trichloro- ethene, ug/L	0.004-0.314	7	3.1
monochloro- acetic acid, ug/L	0.018-0.938	53	17.2
dichloro- acetic acid, ug/L	0.870-6.111	53	8.6
trichloro- acetic acid, ug/L	0.264-2.119	53	9.4
monobromo- acetic acid, ug/L	0.006-0.658	29	13.0
dibromo- acetic acid, ug/L	0.005-0.064	53	11.5
bromochloro- acetic acid, ug/L	0.193-1.723	43	7.1
chloral hydrate, ug/L	0.027-2.911	53	8.9
dichloro- acetonitrile, ug/L	0.078-3.557	53	4.3
trichloro- acetonitrile, ug/L	0.001-0.125	49	17.7
chloropicrin, ug/L	0.007-1.182	53	6.2
1,1-dichloro- propanone, ug/L	0.256-1.502	53	4.9
1,1,1-trichloro- propanone, ug/L	0.037-0.179	53	4.7
bromochloro- acetonitrile, ug/L	0.008-0.566	53	6.1
dibromo- acetonitrile, ug/L	0.0003-0.029	53	12.5

TOC and VOC analyses, were at or below 10% (Table 11). In the EPA performance evaluations, the acceptance range was -18% to 39% for TOC and  $\pm 20\%$  for the VOC's as indicated in Tables 12-16. The performance evaluations for these substances were acceptable for the most part except that chloroform and bromoform were occasionally just outside the upper acceptance limit. The average relative error determined for chloroform in the performance evaluations averaged 16% while that for bromoform averaged 7%. The acceptance ranges for those substances analyzed by the HAA and CDBP methods varied by compound and were quite broad, ranging from the detection limit (DL) to over 100% (Tables 15 & 16). The performance evaluations for all HAA and CDBP compounds were acceptable except for one trichloroacetic acid result which slightly exceeded the upper acceptance range. Those unacceptable results indicated for dibromoacetic acid, dichloroacetic acid, monochloroacetic acid, and monobromoacetic acid were considered invalid because sample No. 1 did not contain these compounds. Sample No. 2 was accurately analyzed at the same time and with the same method as sample No. 1. However, sample No. 1 contained no measurable chromatographic peaks even though the concentration was only one-sixth to one-third that of Sample No. 2 and was 80-500 times that of the method detection limits (Table 7).

#### GC/MS Qualitative Confirmation

Qualitative confirmation by GC/MS analysis was performed for the trihalomethanes, haloacetic acids, haloacetonitriles, haloketones, chloral hydrate, and chloropicrin. Those locations confirmed by GC/MS were the influent of each process stream after 30 min of disinfectant contact time and the terminally chlorinated sand filter effluents of the nondisinfected, ozone, chlorine dioxide, and chlorine process streams as well as the terminally chloraminated sand filter effluent of the chloramine process stream. The percentage of possible GC/MS confirmation and the average mass spectral fit for each compound are presented in Table 17 for the process stream influents and in Table 18 for the terminal distribution system simulation. A value of 1000 for the mass spectral fit would indicate that the compound spectra of the sample matched perfectly with that of the computer based mass spectral library derived from external standards.

In general, higher levels of confirmation were observed in the terminal distribution system simulation than in the process stream influents due to the significantly higher concentrations observed in the terminal samples. Those low confirmation levels observed for the process stream influents resulted from the low concentrations observed and the significantly lower detection limits of the gas chromatography methods (Tables 6, 7, & 8) as compared to those of the GC/MS confirmatory procedure (Table 9).

Table 11. Analytical Accuracy as Measured by Internal Quality Control Sample Analysis

<u>Parameter</u>	<u>Concentration Range ug/L</u>	<u>No. of Observ.</u>	<u>Average % Relative Error</u>
TOC	23.0 - 61.4	10	8.36
chloroform	10 - 45	6	7.0
bromodichloro- methane	20	2	2.45
chlorodibromo- methane	20	2	6.2
bromoform	20	2	10.3
carbon tetra- chloride	10	1	6.0
1,1,1-trichloro- ethylene	10	1	10.0

Table 12. USEPA Performance Evaluation DMR009, April 1989

<u>Parameter</u>	<u>True Value mg/L</u>	<u>Reported Value mg/L</u>	<u>Acceptance Limit mg/L</u>	<u>Performance Evaluation</u>
TOC	11.5	13.1	9.45-16.0	acceptable

Those low confirmation levels observed for the terminal distribution system simulation resulted, for the most part, from the low levels observed with average concentrations at or below the GC/MS detection limits.

Table 13. USEPA Performance Evaluation WS024, May 1989

<u>Parameter</u>	<u>Sample No.</u>	<u>True Value ug/L</u>	<u>Reported Value ug/L</u>	<u>Acceptance Limit ug/L</u>	<u>Performance Evaluation</u>
bromodichloro- methane	1	22.5	22.2	18.0-27.0	acceptable
	2	57.8	49.8	46.2-69.4	acceptable
bromoform	1	12.3	12.8	9.84-14.8	acceptable
	2	66.9	69.2	53.5-80.3	acceptable
chlorodibromo- methane	1	7.66	8.40	6.13-9.19	acceptable
	2	80.5	69.5	64.4-96.6	acceptable
chloroform	1	10.6	12.3	8.48-12.7	acceptable
	2	63.8	50.8	51.0-76.6	unacceptable
total trihalomethane	1	53.1	55.7	42.5-63.7	acceptable
	2	269	239	215-323	acceptable

Table 14. USEPA Performance Evaluation WS025, November 1989

<u>Parameter</u>	<u>Sample No.</u>	<u>True Value ug/L</u>	<u>Reported Value ug/L</u>	<u>Acceptance Limit ug/L</u>	<u>Performance Evaluation</u>
bromodichloro- methane	1	71.4	75.0	57.1-85.7	acceptable
	2	8.40	9.28	6.72-10.1	acceptable
bromoform	1	48.1	47.9	38.5-57.7	acceptable
	2	9.12	11.3	7.30-110.9	unacceptable
chlorodibromo- methane	1	47.8	47.8	38.2-57.4	acceptable
	2	15.6	17.3	12.5-18.7	acceptable
chloroform	1	77.8	82.5	62.2-93.4	acceptable
	2	24.4	30.2	19.5-29.3	unacceptable
total trihalomethane	1	245.1	253.2	196-294	acceptable
	2	57.5	68.1	46.0-69.0	acceptable



Table 15. USEPA Performance Evaluation WS026, May 1990

<u>Parameter</u>	<u>Sample No.</u>	<u>True Value ug/L</u>	<u>Reported Value ug/L</u>	<u>Acceptance Limit ug/L</u>	<u>Performance Evaluation</u>
bromodichloro- methane	1	25.8	26.46	20.6-31.0	acceptable
	2	60.5	65.12	48.4-72.6	acceptable
bromoform	1	15.4	17.43	12.3-18.5	acceptable
	2	77.4	74.38	61.9-92.9	acceptable
chlorodibromo- methane	1	22.1	24.43	17.7-26.5	acceptable
	2	72.9	71.54	58.3-87.5	acceptable
chloroform	1	7.53	10.10	6.02-9.04	unacceptable
	2	59.1	63.92	47.3-70.9	acceptable
total trihalomethane	1	70.8	78.42	46.6-85.0	acceptable
	2	270	275.0	216-324	acceptable
dibromoacetic acid	1	1.27	----	D.L.-4.98	unacceptable*
	2	6.77	3.81	D.L.-21.2	acceptable
dichloroacetic acid	1	2.58	----	.0212-4.12	unacceptable*
	2	12.0	10.4	D.L.-22.5	acceptable
monobromoacetic acid	1	4.10	----	1.30-4.01	unacceptable*
	2	13.9	11.8	D.L.-18.4	acceptable
monochloroacetic acid	1	8.33	----	D.L.-8.00	unacceptable*
	2	16.7	18.5	D.L.-20.6	acceptable
trichloroacetic acid	1	1.10	0.767	D.L.-1.58	acceptable
	2	5.87	5.38	D.L.-0.01	acceptable
2,4,6-trichloro- phenol	1	5.04	3.85	D.L.-11.2	acceptable
	2	12.6	11.6	D.L.-28.1	acceptable
bromochloro- acetonitrile	3	0.671	0.571	0.201-1.37	acceptable
	4	4.58	4.38	3.55-6.27	acceptable
dibromoaceto- nitrile	3	0.762	0.642	0.309-1.03	acceptable
	4	2.37	2.34	1.01-3.17	acceptable

Table 15. USEPA Performance Evaluation WS026, May 1990 (Cont.)

<u>Parameter</u>	<u>Sample No.</u>	<u>True Value ug/L</u>	<u>Reported Value ug/L</u>	<u>Acceptance Limit ug/L</u>	<u>Performance Evaluation</u>
1,1-dichloro-propanone	3	0.692	0.587	0.313-1.09	acceptable
	4	4.04	3.47	2.22-7.23	acceptable
trichloro-acetonitrile	3	0.393	0.295	0.075-0.72	acceptable
	4	2.84	2.05	0.271-5.13	acceptable
1,1,1-trichloro-propanone	3	0.452	0.372	0.136-0.753	acceptable
	4	7.68	5.41	D.L.-14.5	acceptable

\*suspect performance evaluation samples.

Table 16. USEPA Performance Evaluation WS027, November 1990

<u>Parameter</u>	<u>Sample No.</u>	<u>True Value ug/L</u>	<u>Reported Value ug/L</u>	<u>Acceptance Limit ug/L</u>	<u>Performance Evaluation</u>
bromodichloro-methane	1	32.4	29.5	25.9-38.9	acceptable
bromoform	1	22.7	23.28	18.2-27.2	acceptable
chlorodibromo methane	1	30.8	30.35	24.6-37.0	acceptable
chloroform	1	87.0	82.85	69.6-104	acceptable
total trihalomethane	1	172.9	166.0	138-207	acceptable
dibromoacetic acid	1	4.84	2.45	D.L.-16.4	acceptable
dichloroacetic acid	1	6.96	5.57	D.L.-13.5	acceptable

Table 16. USEPA performance Evaluation WS027, November 1990  
(Cont.)

<u>Parameter</u>	<u>Sample No.</u>	<u>True Value ug/L</u>	<u>Reported Value ug/L</u>	<u>Acceptance Limit ug/L</u>	<u>Performance Evaluation</u>
monobromoacetic acid	1	8.40	4.22	D.L.-10.7	acceptable
monochloroacetic acid	1	10.5	10.97	D.L.-15.9	acceptable
trichloroacetic acid	1	8.33	16.09	D.L.-14.6	unacceptable
2,4,6-trichloro-phenol	1	7.32	6.80	D.L.-16.6	acceptable
bromochloro-acetonitrile	2	1.98	1.72	D.L.-4.33	acceptable
dibromo-acetonitrile	2	5.33	5.38	0.0846-6.90	acceptable
dichloro-acetonitrile	2	----	0.075	D.L.-D.L.	unacceptable
1,1-dichloro-propanone	2	1.33	1.29	0.67-2.07	acceptable
trichloro-acetonitrile	2	1.76	1.81	0.442-3.14	acceptable
1,1,1-trichloro-propanone	2	0.989	0.93	0.118-1.35	acceptable

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Table 17. Percent GC/MS confirmation and Average Mass Spectral Fit for the Influent of each Process Stream.

	Nondis	Ozone	ClO <sub>2</sub>	NH <sub>2</sub> Cl	Chlorine
<u>Compound</u>	<u>%/Fit</u>	<u>%/Fit</u>	<u>%/Fit</u>	<u>%/Fit</u>	<u>%/Fit</u>
chloroform	92/962	98/956	96/967	100/983	96/996
bromodichloro- methane	83/889	68/913	83/901	96/956	96/999
chlorodibromo- methane	57/931	56/925	56/890	58/897	98/984
monochloro- acetic acid	100/982	100/986	97/987	94/990	94/986
dichloroacetic acid	96/979	98/981	98/980	98/980	96/982
monobromoacetic acid	30/932	93/978	77/943	47/923	100/969
trichloroacetic acid	98/990	98/989	98/987	100/989	98/990
bromochloro- acetic acid	95/986	96/986	98/994	98/996	98/998
dibromoacetic acid	39/952	100/986	98/994	60/982	98/997
dichloroaceto- nitrile	78/996	83/995	89/995	96/998	98/998
trichloroaceto- nitrile	23/979	24/922	29/960	30/959	70/966
bromochloro- acetonitrile	13/971	15/954	27/949	56/975	96/996
dibromoaceto- nitrile	70/980	62/975	58/974	62/969	98/991
chloral hydrate	28/907	24/853	31/906	83/909	96/952
chloropicrin	32/958	20/944	40/936	60/959	96/985
1,1-dichloropro- panone	47/969	28/953	51/962	85/971	96/972
1,1,1-trichloro- propanone	16/964	21/966	36/969	69/975	94/985

Table 18. Percent GC/MS Confirmation and Average mass Spectral Fit for Terminal Sand Filtered Distribution System Simulation.

	Nondis-Cl <sub>2</sub>	Ozone-Cl <sub>2</sub>	ClO <sub>2</sub> -Cl <sub>2</sub>	Cl <sub>2</sub> -Cl <sub>2</sub>	NH <sub>2</sub> Cl-NH <sub>2</sub> Cl
Compound	%/Fit	%/Fit	%/Fit	%/Fit	%/Fit
chloroform	100/996	100/994	100/993	100/992	100/998
bromodichloro- methane	100/998	77/998	100/998	91/999	100/999
chlorodibromo- methane	100/978	92/994	100/999	100/998	100/999
monochloro- acetic acid	98/994	99/992	100/971	100/995	100/972
dichloroacetic acid	100/974	100/968	100/977	100/969	100/972
monobromoacetic acid	100/999	100/999	100/999	100/999	100/999
trichloroacetic acid	100/963	100/982	100/986	100/976	100/970
bromochloro- acetic acid	100/995	100/995	100/997	100/997	100/996
dibromoacetic acid	100/999	100/999	100/999	100/999	100/999
dichloroaceto- nitrile	100/989	92/989	100/997	100/995	92/995
trichloroaceto- nitrile	63/953	45/967	72/973	91/972	54/953
bromochloro- acetonitrile	92/973	92/994	92/993	91/988	92/997
dibromoaceto- nitrile	92/973	92/994	92/993	91/988	92/997
chloral hydrate	92/946	92/947	92/944	100/946	92/951
chloropicrin	100/991	100/988	100/988	100/984	92/987
1,1-dichloro- propane	42/962	50/981	58/955	36/967	42/959
1,1,1-trichloro- propane	89/961	92/967	92/982	100/978	92/982

## SECTION 6

### RESULTS AND DISCUSSION

#### DISINFECTION BY-PRODUCTS

##### Total Organic Carbon (TOC)--

While TOC itself is not a disinfection by-product (DBP), it is a general measure of the amount of precursor material available for DBP formation. Seasonal variations of total organic carbon levels in the influent of each process stream are indicated in Figure 4. The average TOC levels in the contact chamber effluents across the one year operational period were 3.12, 2.86, 3.18, 3.23, and 3.15 mg C/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively. As expected, sand filtration had no effect on TOC in the precipitator water entering the pilot column system which averaged 3.16 mg C/L. Relative to the nondisinfected influent, ozonation produced an average TOC reduction of 0.26 mg C/L (8%) while an additional removal averaging 0.56 mg C/L (18%) occurred across the ozone sand column (Figure 5) for a total removal of 0.82 mg C/L (26%) prior to GAC filtration. Based on the levels of heterotrophic bacteria in the effluents of the ozone contactor chamber and ozone sand column which are discussed later in this report, the reduction of TOC across the ozone contact chamber appears to have resulted primarily from oxidation while that across the ozone sand column can be attributed to biodegradation. Essentially no reductions in TOC attributable to predisinfection or sand filtration were observed for the other process streams.

TOC removals across the GAC columns were very similar for the nondisinfected, chlorine dioxide, chloramine, and chlorine process streams (Figure 6) with each column reaching steady state on day 200. Average removals relative to the respective sand column effluents of 22-23% were observed after steady-state was reached with average GAC effluent concentrations of 2.5-2.6 mg C/L. The ozone GAC column also reached steady-state on day 200 with a subsequent average removal of 26% relative to the ozone sand column effluent and an average GAC effluent concentration of 1.8 mg C/L. The overall TOC removal observed for ozonation

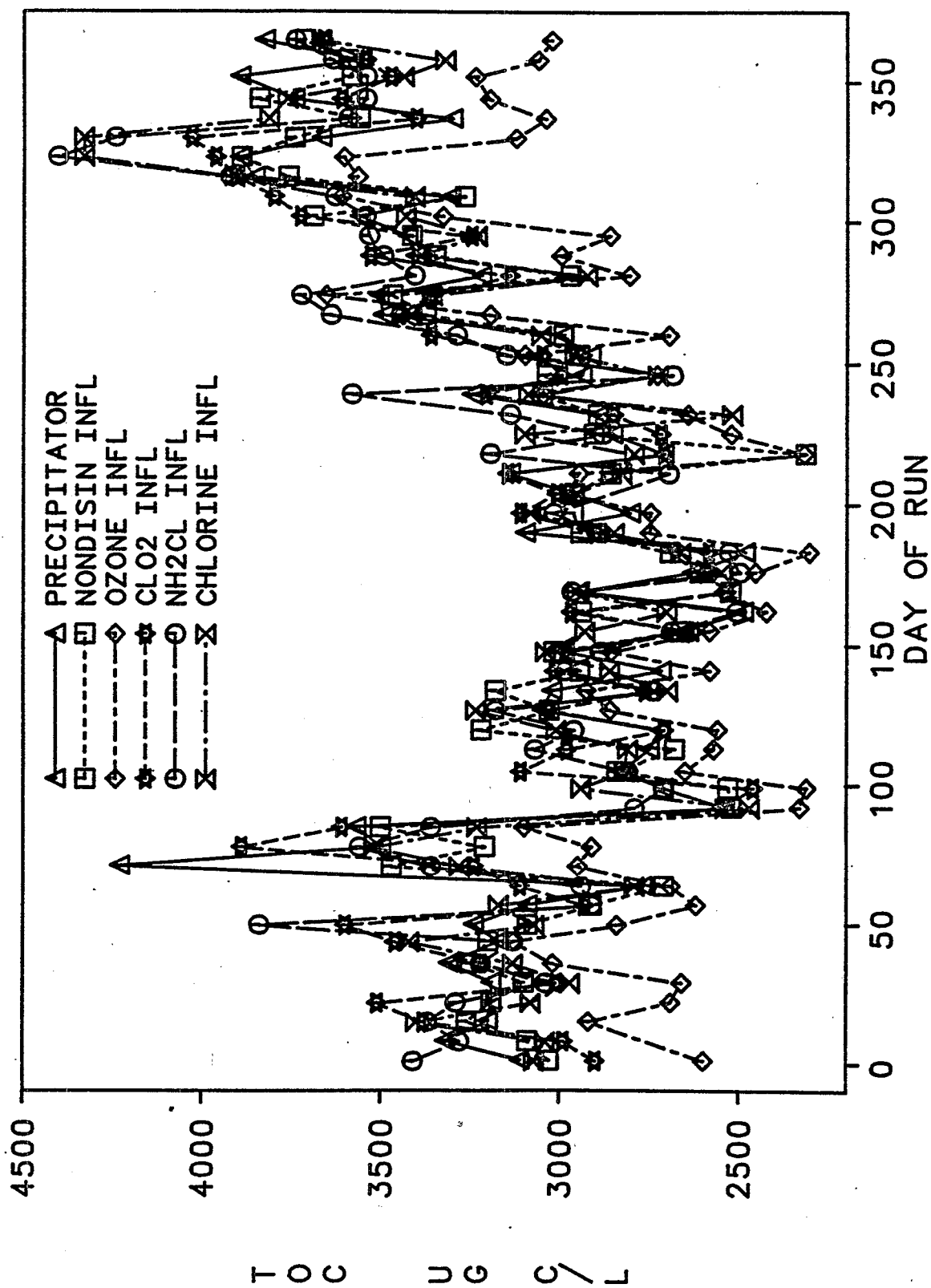


Figure 4. Comparison of TOC levels in the Influent of each Process Stream.

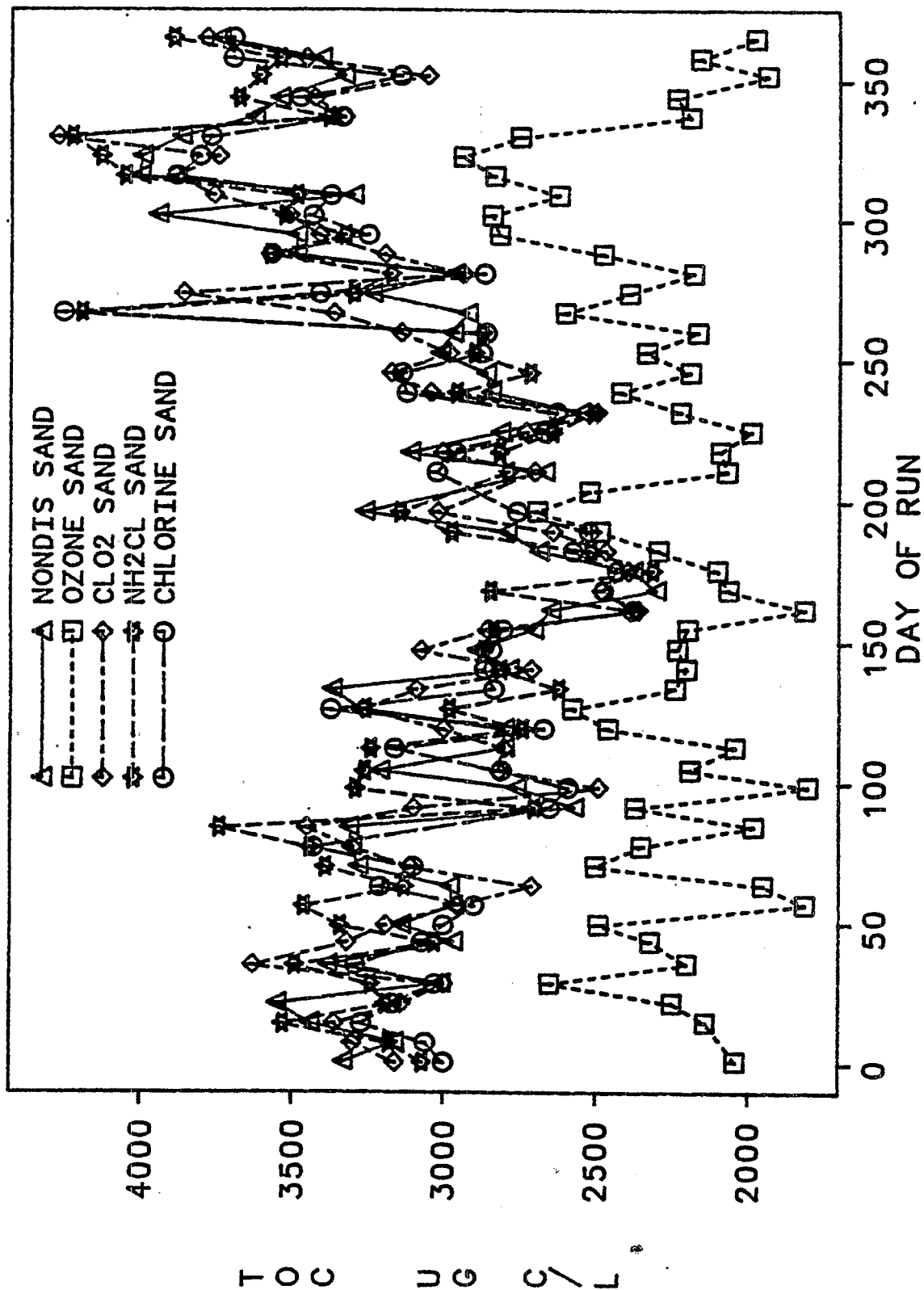


Figure 5. Comparison of TOC Levels in the Sand Column Effluent of each Process Stream.



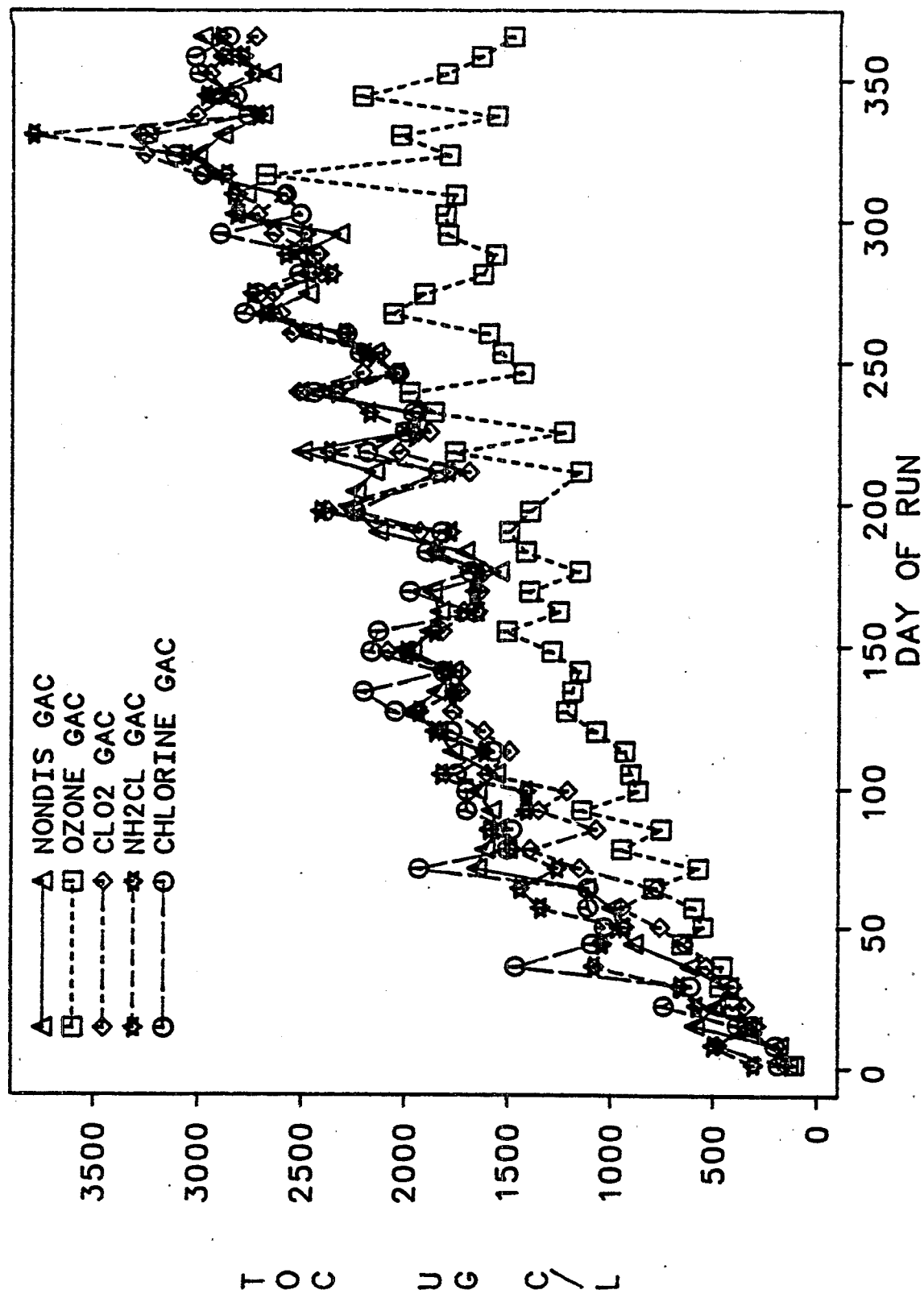


Figure 6. Comparison of TOC Levels in the GAC Column Effluent of each Process Stream.

followed by sand filtration and subsequent GAC filtration after steady-state was reached on day 200 was 47%.

#### Total Organic Halide (TOX)--

With an average nondisinfected influent concentration of 25 ug Cl/L, TOX levels increased significantly after 30 min of disinfectant contact time across the chlorine dioxide, chloramine, and chlorine contact chambers to 86, 99, & 246 ug Cl/L, respectively (Figure 7). A reduction in TOX averaging 33% occurred across the ozone contact chamber with an average effluent concentration of 16 ug Cl/L. Further reduction to an average concentration of 11 ug Cl/L was observed across the ozone sand column for a combined reduction of approximately 50% for ozonation followed by sand filtration (Figure 8). While some variation was observed due to experimental error, no significant change in TOX was observed across the sand columns of the chlorine dioxide, chloramine, and chlorine process streams.

Treatment of the sand filtered effluents with free chlorine followed by 5-day storage (TOX-Cl<sub>2</sub>) significantly increased TOX levels for all process streams as indicated in Figure 9. Similar TOX-Cl<sub>2</sub> levels were observed for the precipitator and the nondisinfected and chlorine sand column effluents with respective averages of 585, 557, and 540 ug Cl/L. Predisinfection with ozone and chlorine dioxide reduced the levels of TOX-Cl<sub>2</sub> by 39 & 32 percent, respectively, relative to the nondisinfected sand column effluent with average TOX-Cl<sub>2</sub> levels of 339 and 379 ug Cl/L, respectively.

Treatment of the sand filtered effluents with chloramine followed by 5-day storage (TOX-NH<sub>2</sub>Cl) resulted in an increase to an average of 27 ug Cl/L for the ozone process stream, while that for the chlorine dioxide process stream remained relatively constant at 89 ug Cl/L (Figure 10). Similar treatment in the chloramine process stream resulted in a reduction of 32% to 59 ug Cl/L relative to the sand column effluent. This unusual reduction in TOX for the chloramine process stream has been observed from terminally stored samples in previous studies and is, as yet, unexplained. The TOX-NH<sub>2</sub>Cl levels observed for the precipitator and nondisinfected sand column effluent were essentially the same as that observed for the chloramine sand column effluent with respective averages of 54 and 44 ug Cl/L.

GAC filtration with a 20 min empty bed contact time resulted in TOX levels of less than 30 ug Cl/L over the one year operational period for all process streams except for the chlorine process stream (Figure 11). The nondisinfected and ozone GAC columns reached apparent steady-state conditions on day 100 and day 130, respectively, achieving average percent removals

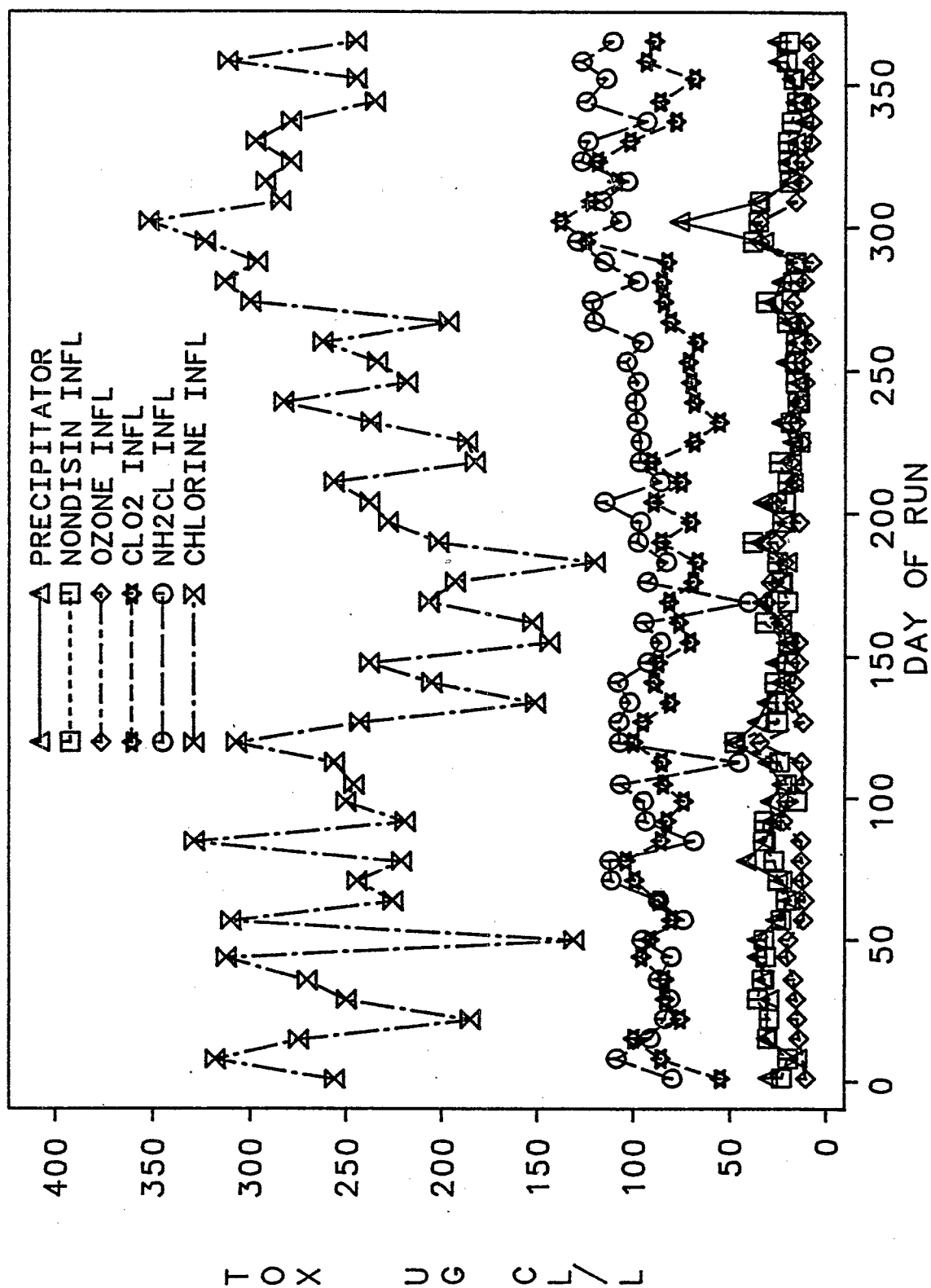


Figure 7. Comparison of the TOX Levels in the Disinfectant Contact Chamber Effluent of each Process Stream.

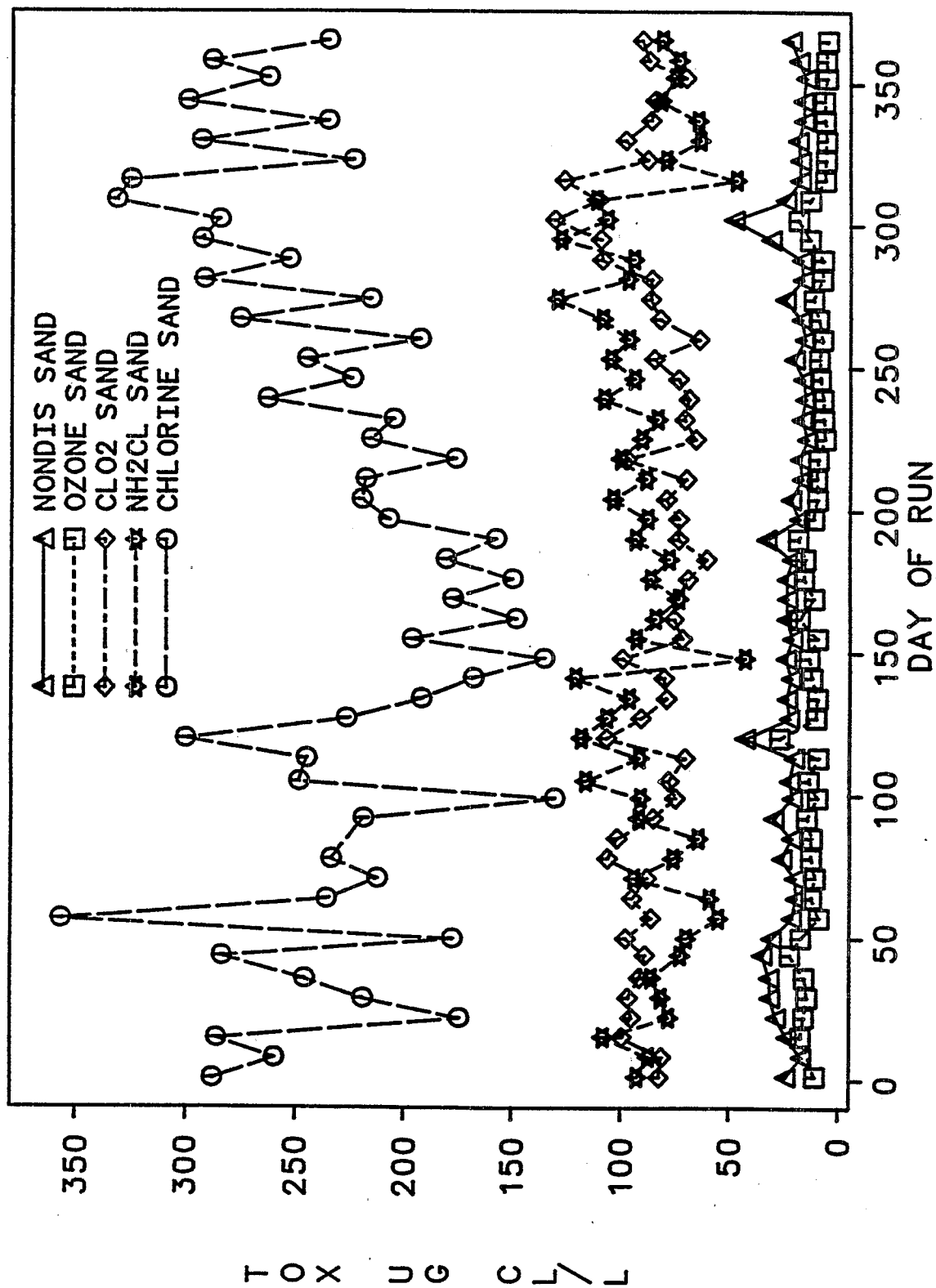


Figure 8. Comparison of the TOX Levels in the Sand Column Effluent of each Process Stream.

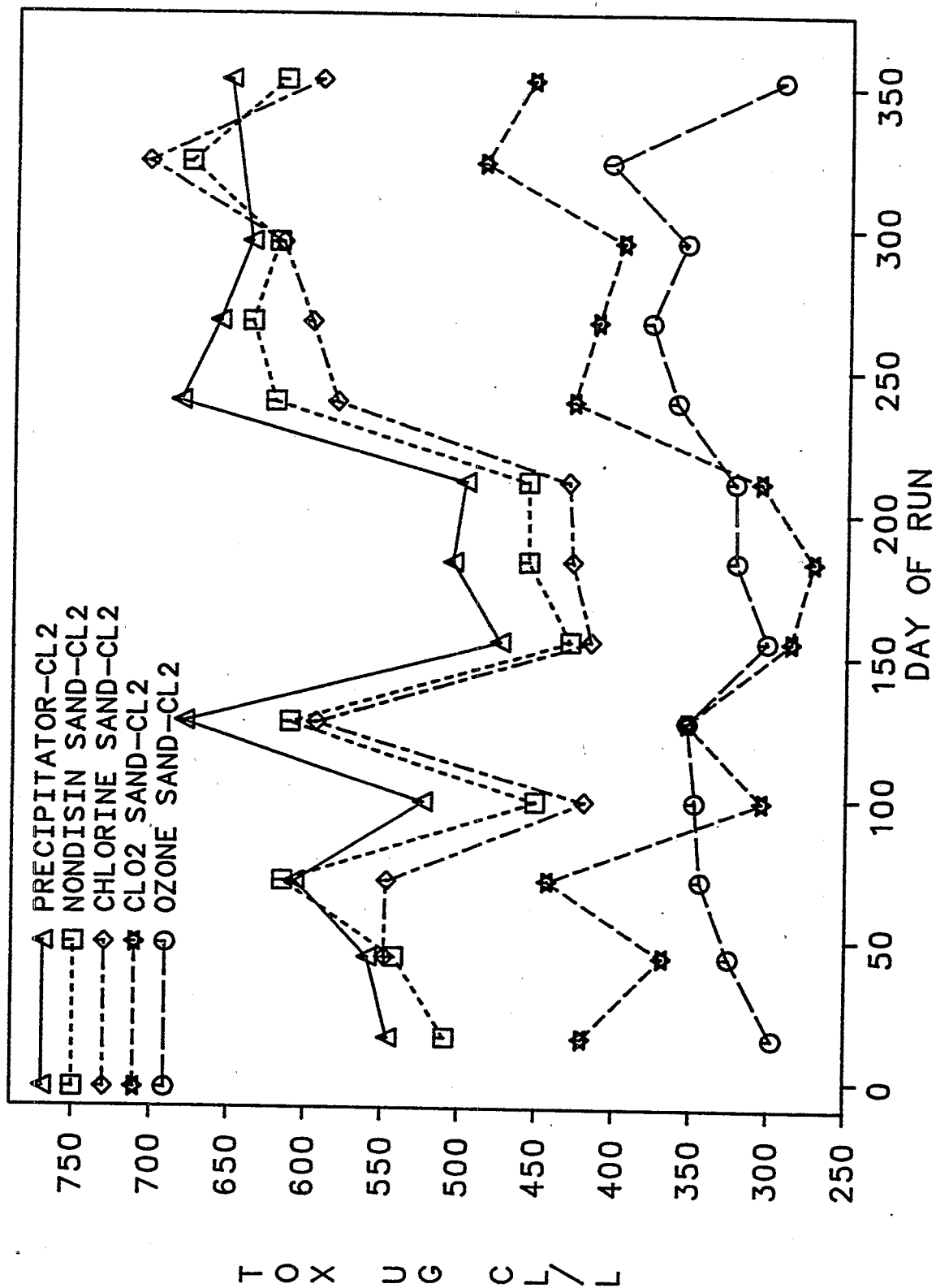


Figure 9. Comparison of the TOX-CL<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

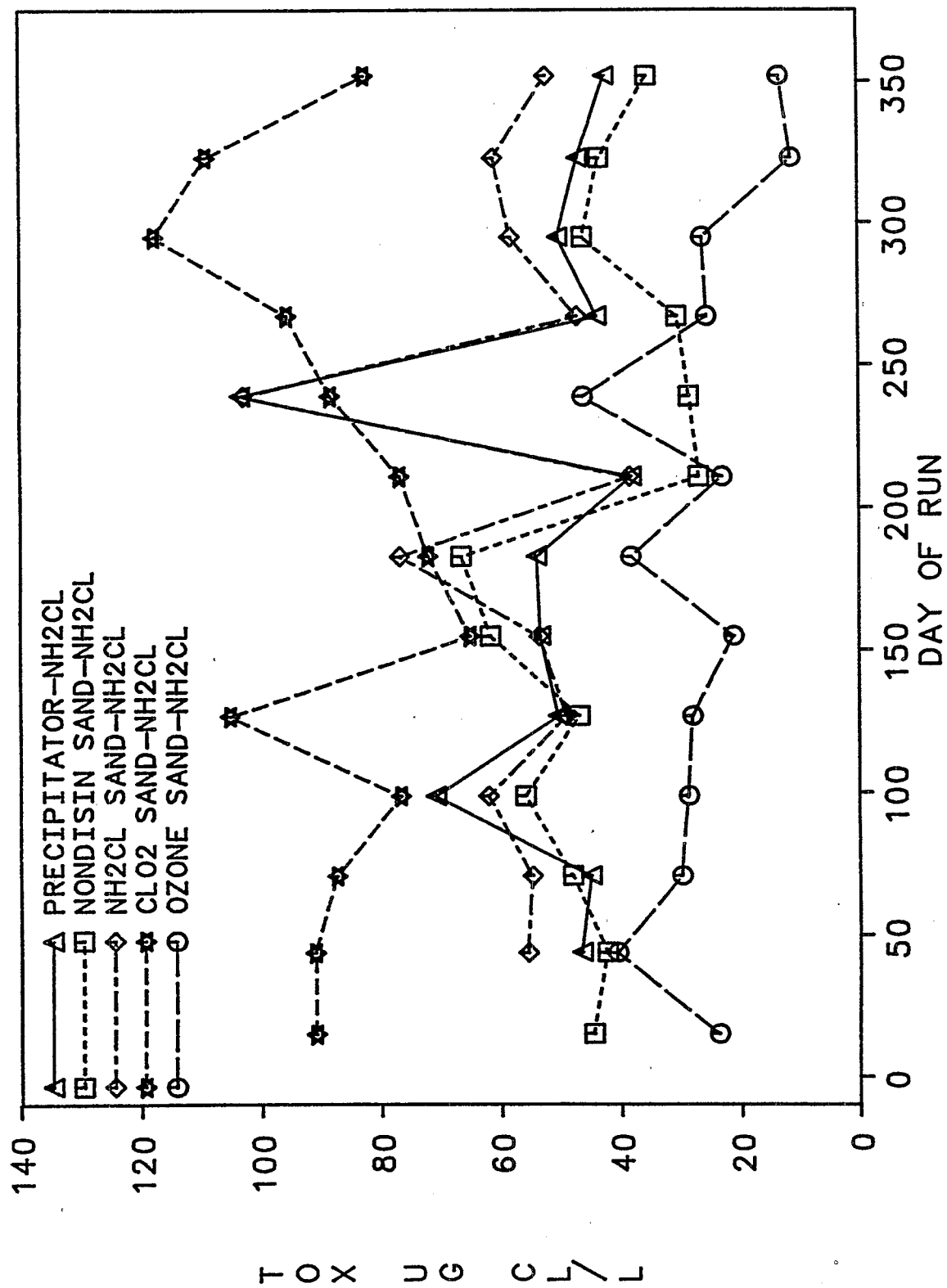


Figure 10. Comparison of the TOX-NH<sub>2</sub>CL Levels in the Sand Column Effluent of each Process Stream.

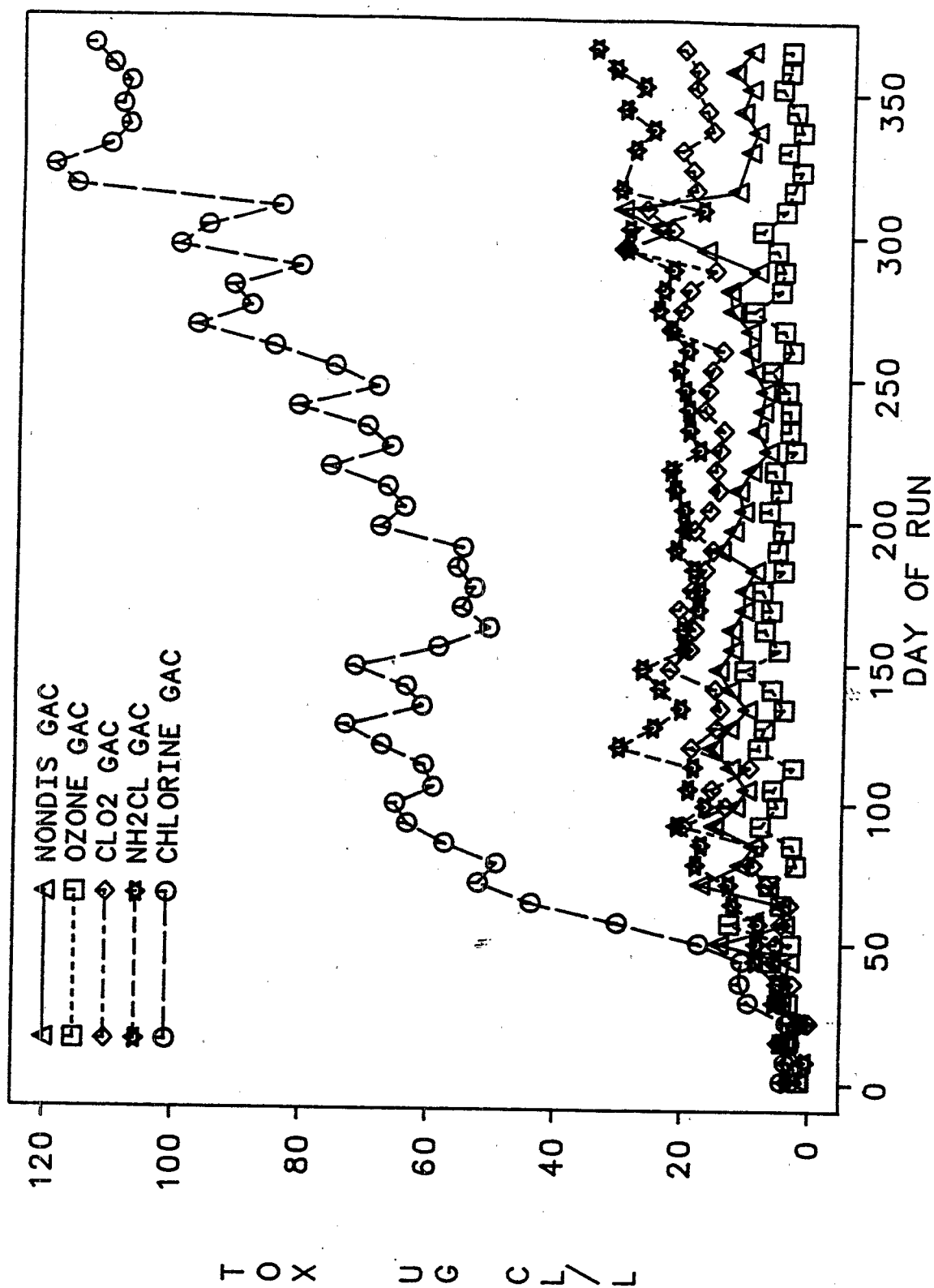


Figure 11. Comparison of the TOX Levels in the GAC Column Effluent of each Process Stream.

after steady-state of 41% for both columns with respective average effluent TOX concentrations after steady-state of 13 and 6 ug Cl/L. Steady-state was reached about day 150 for the chlorine dioxide GAC column with an average percent removal and average effluent concentration after steady-state of 77% and 19 ug Cl/L. The chloramine GAC column reached steady-state about day 100 while that for the chlorine GAC column occurred on day 120. Their respective average removals after steady-state were 74 and 65 percent with corresponding average effluent concentrations of 24 and 82 ug Cl/L. Thus after one year of operation, GAC filtration continued to produce significant TOX removals in all process streams.

As with the sand filtered effluents, treatment of the GAC column effluents with free chlorine followed by 5-day storage (TOX-Cl<sub>2</sub>) significantly increased TOX levels in all process streams as indicated in Figure 12. All GAC columns reached steady-state on about day 150 with average TOX-Cl<sub>2</sub> steady-state effluent concentrations of 290, 280, and 310 ug<sup>2</sup> Cl/L for the nondisinfected, chlorine dioxide, and chlorine GAC columns, respectively. The average TOX-Cl<sub>2</sub> level of 310 ug Cl/L in the chlorine GAC effluent was comprised of approximately 27 percent (84 ug Cl/L) TOX breakthrough and 73 percent (226 ug Cl/L) unreacted TOX precursors. The ozonated sand filtered water entering the GAC column contained a lower level of TOX-Cl<sub>2</sub> (Figure 8) and resulted in subsequently lower GAC effluent concentrations averaging 167 ug Cl/L TOX-Cl<sub>2</sub> after reaching steady-state on day 150. While TOX-Cl<sub>2</sub> levels in the chlorine dioxide sand filter effluent were similar to those of the ozone sand filter effluent, significantly higher levels of TOX-Cl<sub>2</sub> were observed in the chlorine dioxide GAC effluent as compared to the ozone GAC effluent. Despite the higher levels of TOX-Cl<sub>2</sub> observed in the GAC effluents, significant TOX-Cl<sub>2</sub> reductions were still evident after steady-state was reached with respective average removals of 49, 51, 26 & 43% for the nondisinfected, ozone, chlorine dioxide, and chlorine GAC columns. The TOX-Cl<sub>2</sub> levels in the chloramine GAC column effluent were similar to those of the nondisinfected and chlorine process streams indicating similar levels of TOX-Cl<sub>2</sub> removal.

Treatment of the GAC column effluents with chloramine followed by storage for 5 days (TOX-NH<sub>2</sub>Cl) resulted in minimal increases in TOX as indicated in Figure 13. Average increases over the TOX levels in the GAC column effluents (Figure 11) of 17, 7, 11, & 12 ug Cl/L were observed for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams with respective average TOX-NH<sub>2</sub>Cl levels of 29, 13, 26, & 32 ug Cl/L. Essentially no increase was observed in the chlorine process stream with an average TOX-NH<sub>2</sub>Cl concentration of 69 ug Cl/L, all of which was derived from the TOX breakthrough on the GAC column. Comparison of these average TOX-NH<sub>2</sub>Cl GAC effluent levels to



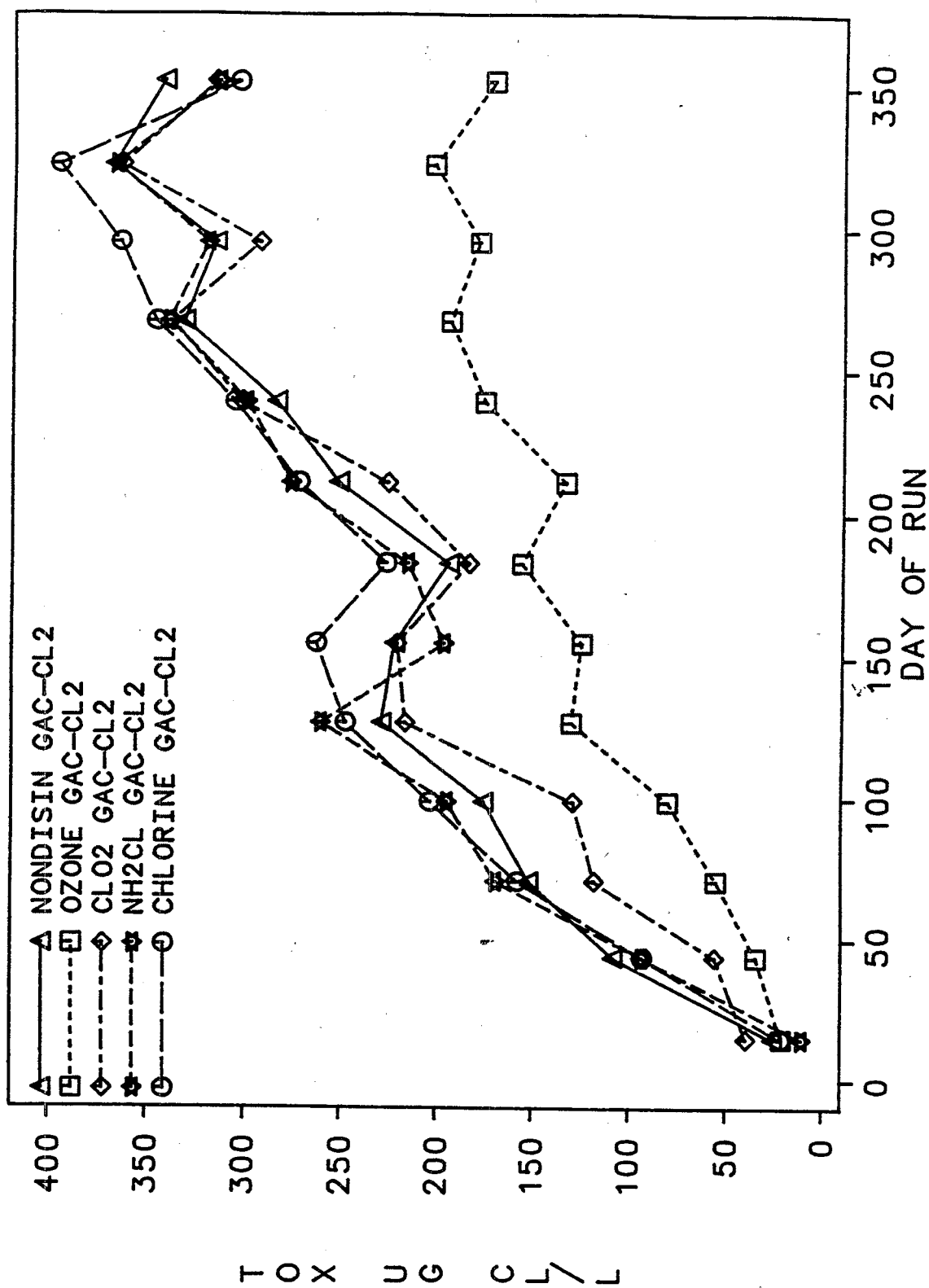


Figure 12. Comparison of the TOX-CL2 Levels in the GAC Column Effluent of each Process Stream.

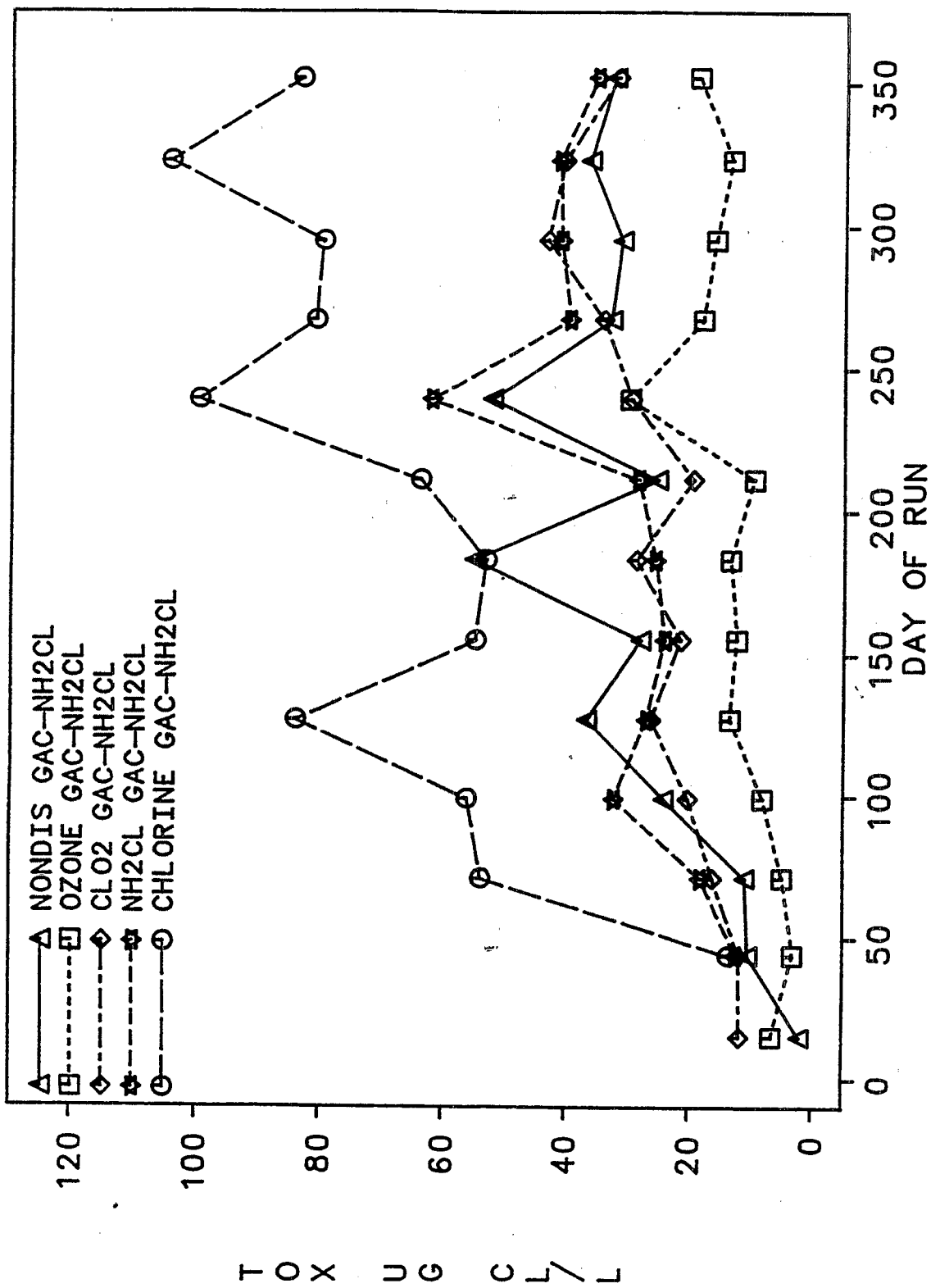


Figure 13. Comparison of the TOX-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

those of the sand columns (Figure 10) across the project period indicates that GAC filtration resulted in average reductions of 34, 52, 71, and 46% for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams.

#### Trihalomethanes (THM)--

Chloroform was the most abundant THM formed accounting for approximately 83% of the total followed by bromodichloromethane with 15% and dibromochloromethane with the remaining 2%. Bromoform was rarely observed, even in the free chlorine formation potential samples.

No significant levels of THMs were observed in the disinfectant contact chamber and sand column effluents of the nondisinfected, ozone, and chlorine dioxide process streams with concentrations averaging 1 ug/L. An average THM level of 3 ug/L occurred in the chloramine disinfectant contact chamber and sand column effluents while that in the chlorine contact chamber effluent averaging 39 ug/L, increased 10 ug/L (25%) to 49 ug/L across the chlorine sand column due to the additional contact time of approximately 30 min across the sand column (Figure 14). Treatment of the sand column effluents with chloramine followed by storage for 5 days at 30°C resulted in slightly elevated terminal THM levels (THM-NH<sub>2</sub>Cl) averaging 8.5, 3.2, 4.2, and 9.4 ug/L for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams (Figure 15). Similar treatment and storage of the sand column effluents with free chlorine produced relatively high terminal THM levels (THM-Cl<sub>2</sub>) with average concentrations of 236 and 225 ug/L for the nondisinfected and chlorine process streams (Figure 16). Average reductions of 35 and 41 percent relative to the nondisinfected sand column effluent were observed for pretreatment with ozone and chlorine dioxide resulting in average THM-Cl<sub>2</sub> levels of 154 and 138 ug/L, respectively.

The THM concentrations in the GAC column effluents, compared in Figure 17, all reached saturation in 60-80 days. In each case, saturation was preceded by a rise and a subsequent fall in the sand column effluent concentration (Figure 14) exemplifying a chromatographic effect. The chlorine, chloramine, and chlorine dioxide GAC columns all reached saturation on day 60 with the nondisinfected and ozone GAC columns reaching saturation on days 70 and 80, respectively. The average GAC effluent concentrations observed after saturation was reached were 1.2, 1.0, 1.4, 4.1, and 43 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine and chlorine process streams. While the GAC effluent levels after saturation equaled their respective influent or sand column effluent levels in the chlorine process stream, those in the other process streams exceeded their respective influent

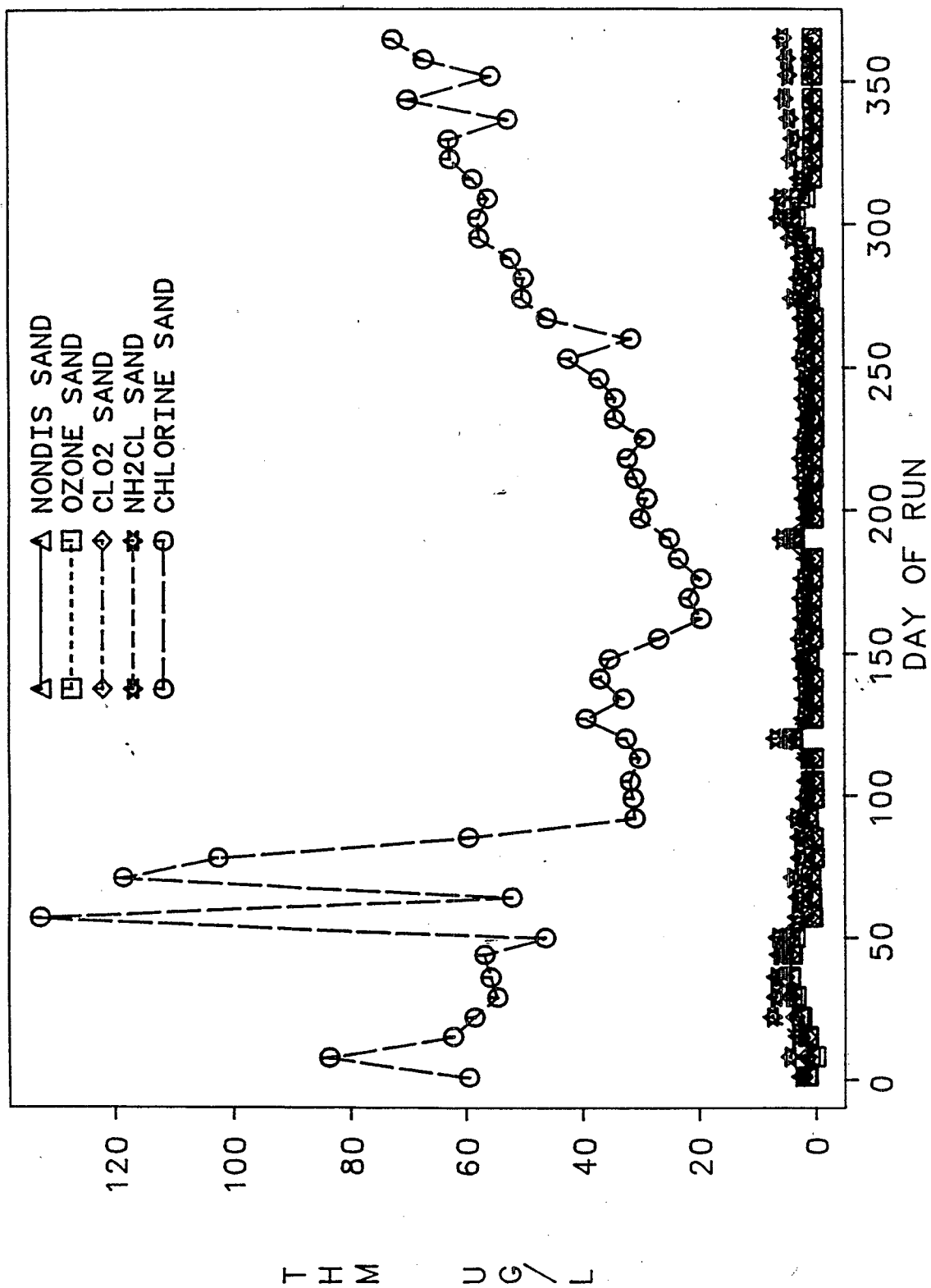


Figure 14. Comparison of the THM Levels in the Sand Column Effluent of each Process Stream.

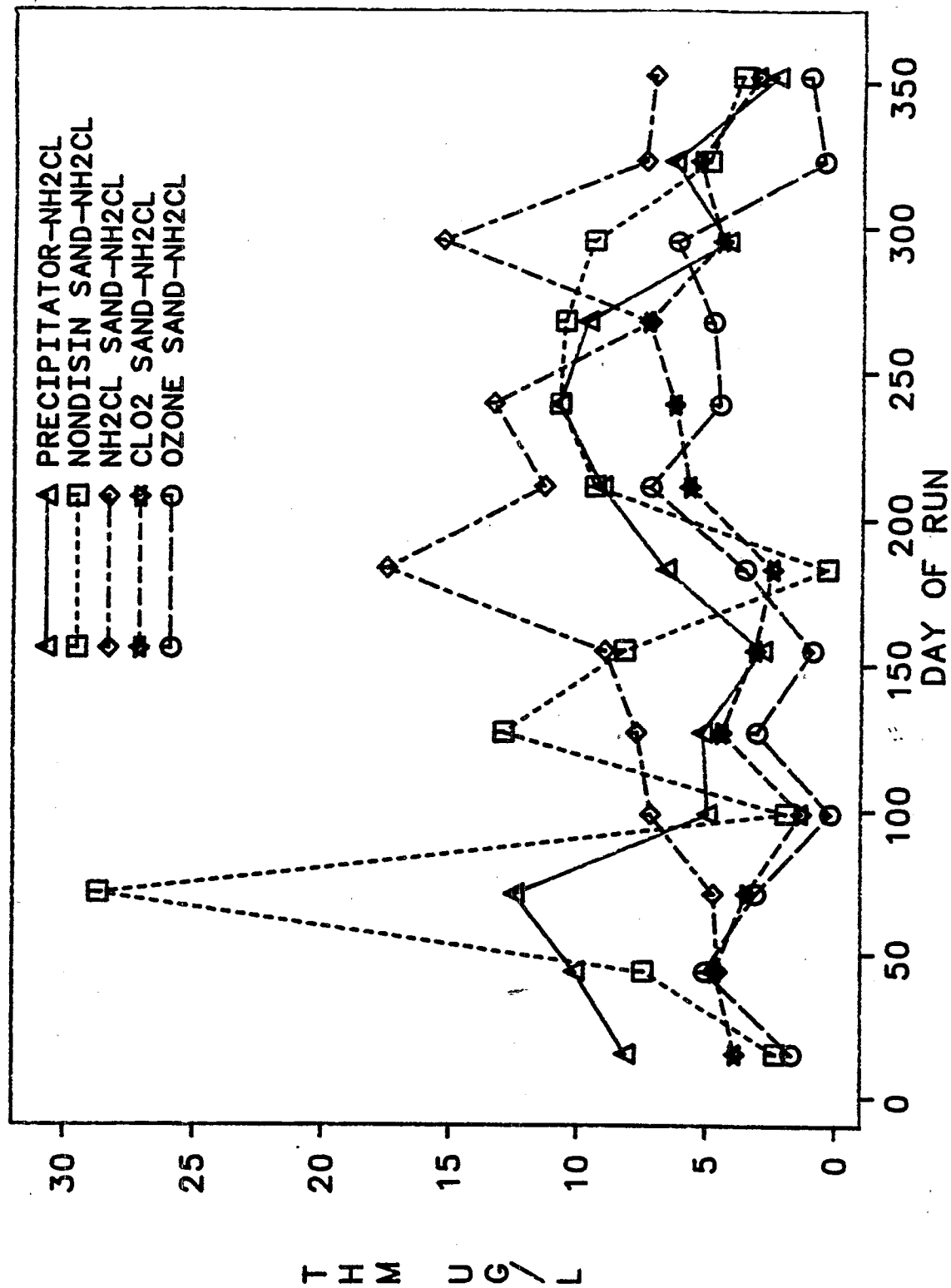


Figure 15. Comparison of the THM-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

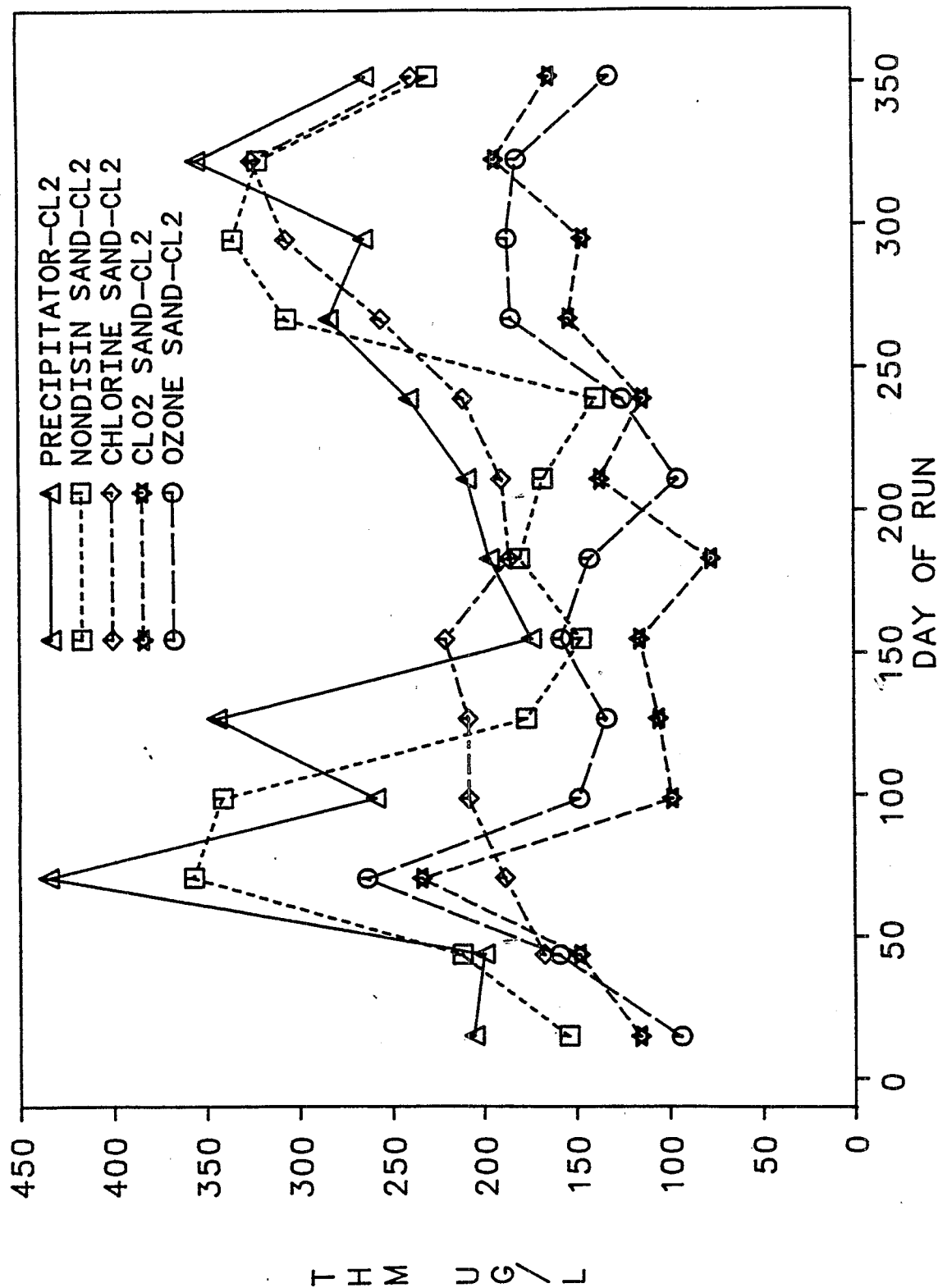


Figure 16. Comparison of the THM-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

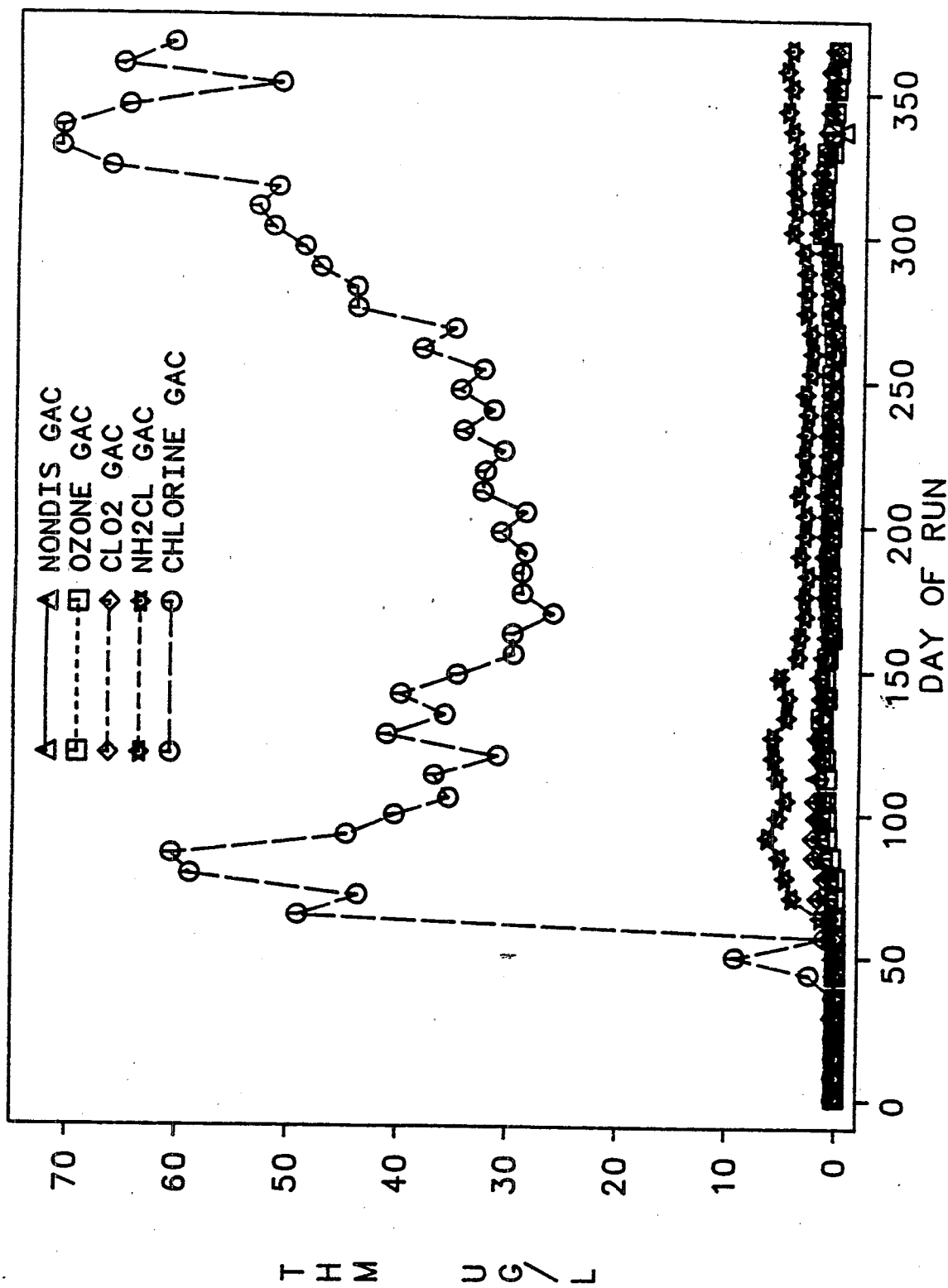


Figure 17. Comparison of the THM Levels in the GAC Column Effluent of each Process Stream.

concentrations by 41-73 percent exhibiting a significant level of desorption. A typical breakthrough profile followed by desorption is presented in Figure 18 for the chlorine dioxide process stream.

Treatment of the GAC column effluents with free chlorine and subsequent storage for 5 days at 30°C resulted in THM-Cl<sub>2</sub> levels which were significantly lower than those of similarly<sup>2</sup> treated sand column effluents (Figure 19). Steady-state was reached on day 150 for the chlorine GAC column with an average steady-state THM-Cl<sub>2</sub> concentration of 161 ug/L which was comprised of approximately 27 percent (43 ug/L) THM breakthrough and 73 percent (118 ug/L) unreacted THM precursors, which coincidentally, were the same percentages observed for TOX-Cl<sub>2</sub>. Both the nondisinfected and chlorine dioxide GAC columns reached steady-state on day 130 with steady-state THM-Cl<sub>2</sub> levels of 118 and 105 ug/L resulting in steady-state THM-Cl<sub>2</sub> removals of 48 and 24 percent, respectively. The ozone GAC column did not reach steady-state until day 180 with an average steady-state effluent concentration of 95 ug/L which was indicative of an average THM-Cl<sub>2</sub> removal of 37 percent. The THM-Cl<sub>2</sub> levels observed in the chloramine GAC effluent were similar to those of the nondisinfected GAC effluent indicating a similar THM-Cl<sub>2</sub> removal.

Treatment of the GAC column effluents of each process stream with chloramine and subsequent storage for 5 days produced only slight increases in THMs relative to the GAC column effluents, which were also slight decreases in THM-NH<sub>2</sub>Cl when compared to similarly treated sand column effluents. The average THM-NH<sub>2</sub>Cl levels observed across the operational period in the nondisinfected, ozone, chlorine dioxide, and chloramine GAC column effluents were 5.2, 2.2, 2.2, and 5.5 ug/L, respectively (Figure 20). A significantly higher THM-NH<sub>2</sub>Cl concentration was observed for the chlorine GAC effluent which reached 60 ug/L by the end of the operational period. However, this was due solely to the GAC breakthrough of THMs formed during predisinfection with chlorine.

#### Haloacetic Acids (HAA)--

The highest levels of the haloacetic acids were formed using free chlorine with primary constituents of dichloroacetic acid (DCAA), trichloroacetic acid (TCCA), and bromochloroacetic acid (BCAA). Chloroacetic acid (CAA), bromoacetic acid (BAA), and dibromoacetic acid (DBAA) were also formed to some extent, but were very minor constituents. Halophenols were also analyzed via the haloacetic acid method, but were not found. Despite the additional disinfectant contact time observed across the sand columns, no increase was observed for any of the haloacetic acids



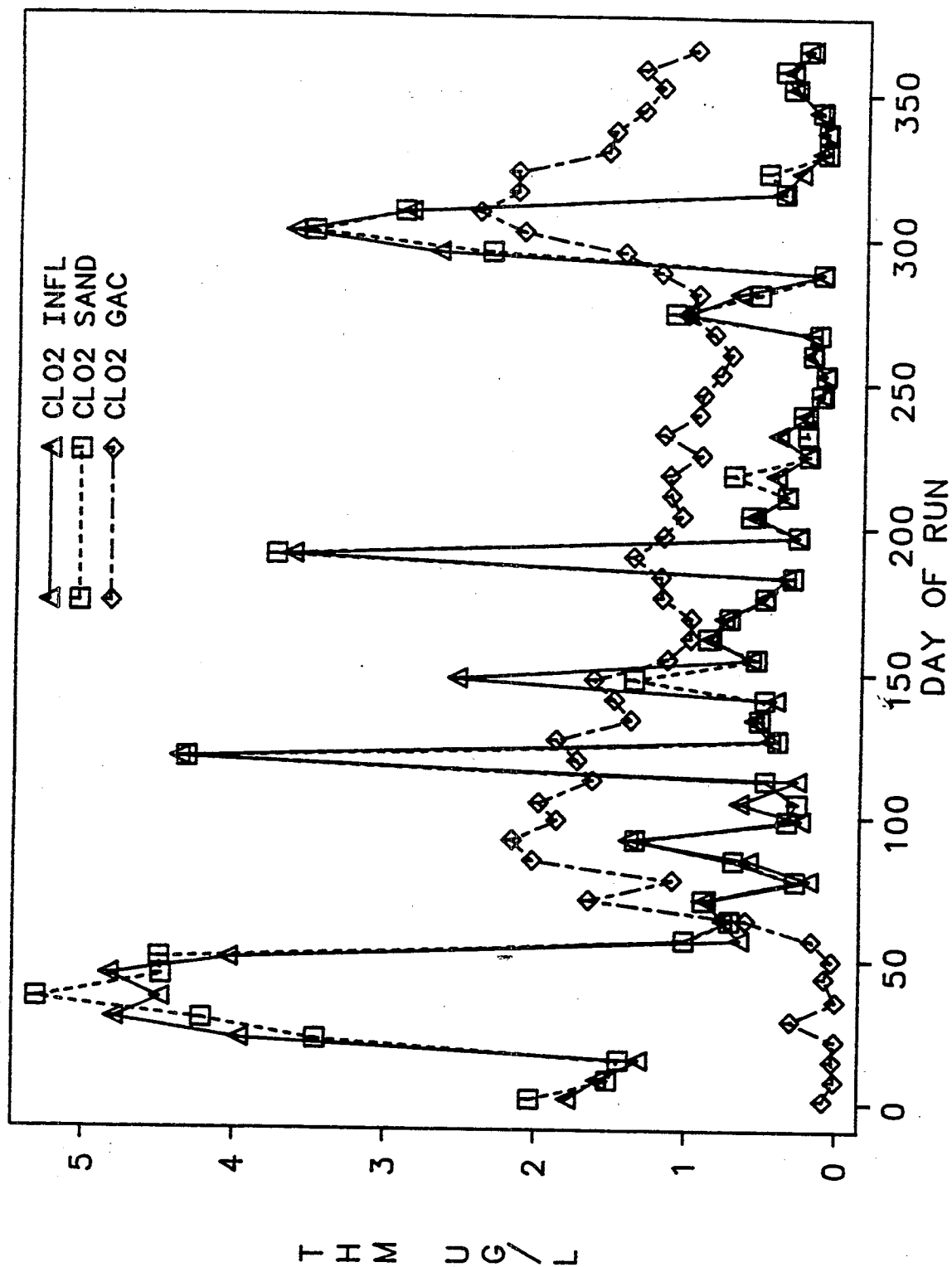


Figure 18. THM Breakthrough Profile for the Chlorine Dioxide Process Stream.

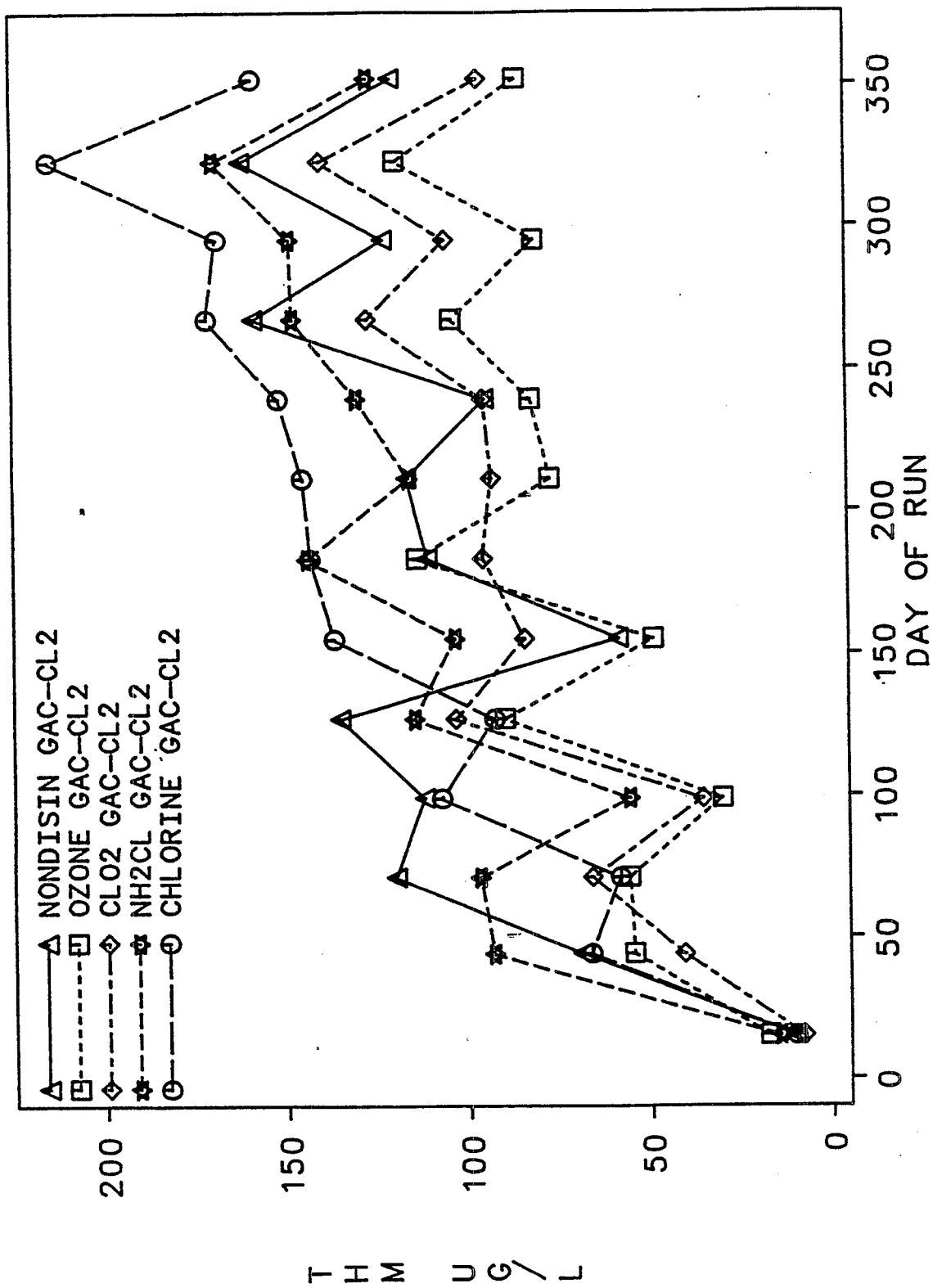


Figure 19. Comparison of the THM-CL<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

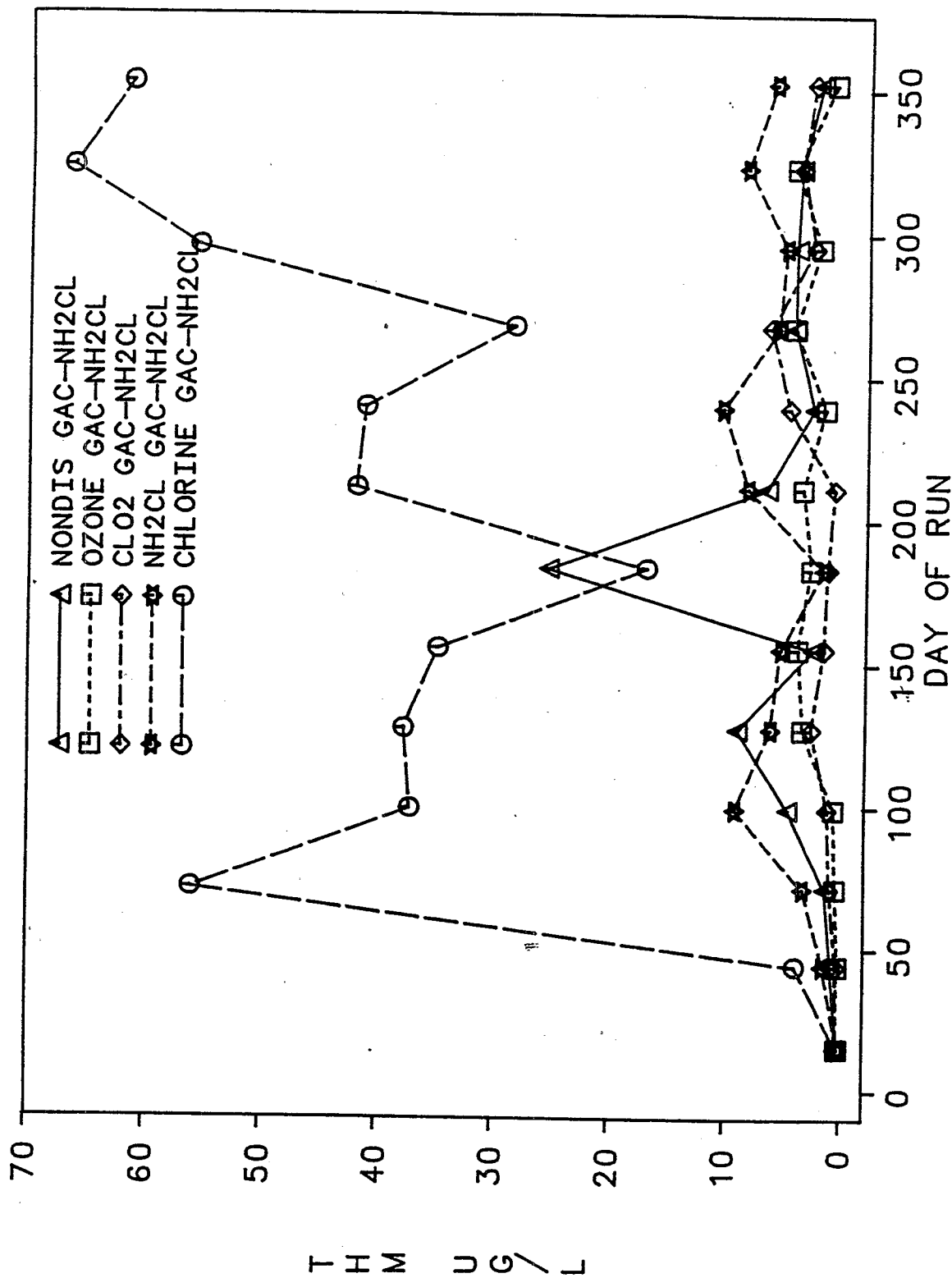


Figure 20. Comparison of the THM-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

in the chlorine, chloramine, and chlorine dioxide process streams. While some indication of biodegradation was observed across the nondisinfected and ozone sand columns, significantly higher removals occurred across the GAC columns at steady-state which may be attributed to an adsorption/biodegradation process.

One of the more prevalent haloacetic acids observed following the use of a chlorinated disinfectant was dichloroacetic acid (DCAA). Contact chamber and sand column effluent concentrations averaged 1.7, 3.7, and 13 ug/L for the chlorine dioxide, chloramine, and chlorine process streams, respectively (Figure 21). Minor reductions in DCAA attributable to biodegradation were observed across the nondisinfected and ozone sand columns with average respective influent concentrations of 0.9 and 1.1 ug/L and a corresponding effluent concentration of 0.6 ug/L for both columns (Figure 22). Treatment of the sand column effluents with free chlorine followed by 5-day storage indicated that the DCAA-Cl<sub>2</sub> levels entering the pilot column system averaged approximately 65 ug/L (Figure 23) with little change occurring across the nondisinfected and chlorine sand columns. Reductions in DCAA-Cl<sub>2</sub> of 27% (to 44 ug/L) and 26% (to 38 ug/L) were observed for chlorine dioxide and ozone pretreatment followed by sand filtration. Similar treatment of the sand filter effluents with chloramine and a 5-day storage period resulted in only slightly elevated DCAA levels (Figure 24) with DCAA-NH<sub>2</sub>Cl concentrations averaging 5.6, 7.3, 8.6, and 9.2 ug/L for the ozone, nondisinfected, chlorine dioxide, and chloramine process streams, respectively. Although these DCAA-NH<sub>2</sub>Cl levels were, respectively, 9, 13, 5, and 3 times that of their average sand column effluent levels, they were very similar to the levels of THMs formed during similar treatment with chloramine suggesting that both were formed by reaction with free chlorine during the in situ formation of chloramine.

GAC filtration resulted in significant DCAA removal efficiencies throughout the operational period (Figure 25) with continued removals of 80% or greater after steady-state was reached, which occurred about day 150 for all process streams. Steady-state effluent concentrations were proportionate to their respective influent concentrations. With steady-state influent concentrations of 13, 3.7, and 0.6 ug/L and effluent concentrations of 2, 0.55, and 0.07 ug/L, respectively, the chlorine, chloramine, and ozone GAC columns achieved 86% removal after steady-state was reached. A steady-state removal of 80% was observed for both the chlorine dioxide and nondisinfected GAC columns with respective influent concentrations of 1.7 and 0.6 ug/L and corresponding effluent concentrations averaging 0.3 and 0.1 ug/L. Similar GAC breakthrough profiles were observed for the DCAA-Cl<sub>2</sub> levels in all process streams except for that of ozone (Figure 26). Steady-state was reached around day 250 for all process streams at a DCAA-Cl<sub>2</sub> effluent concentration of 40

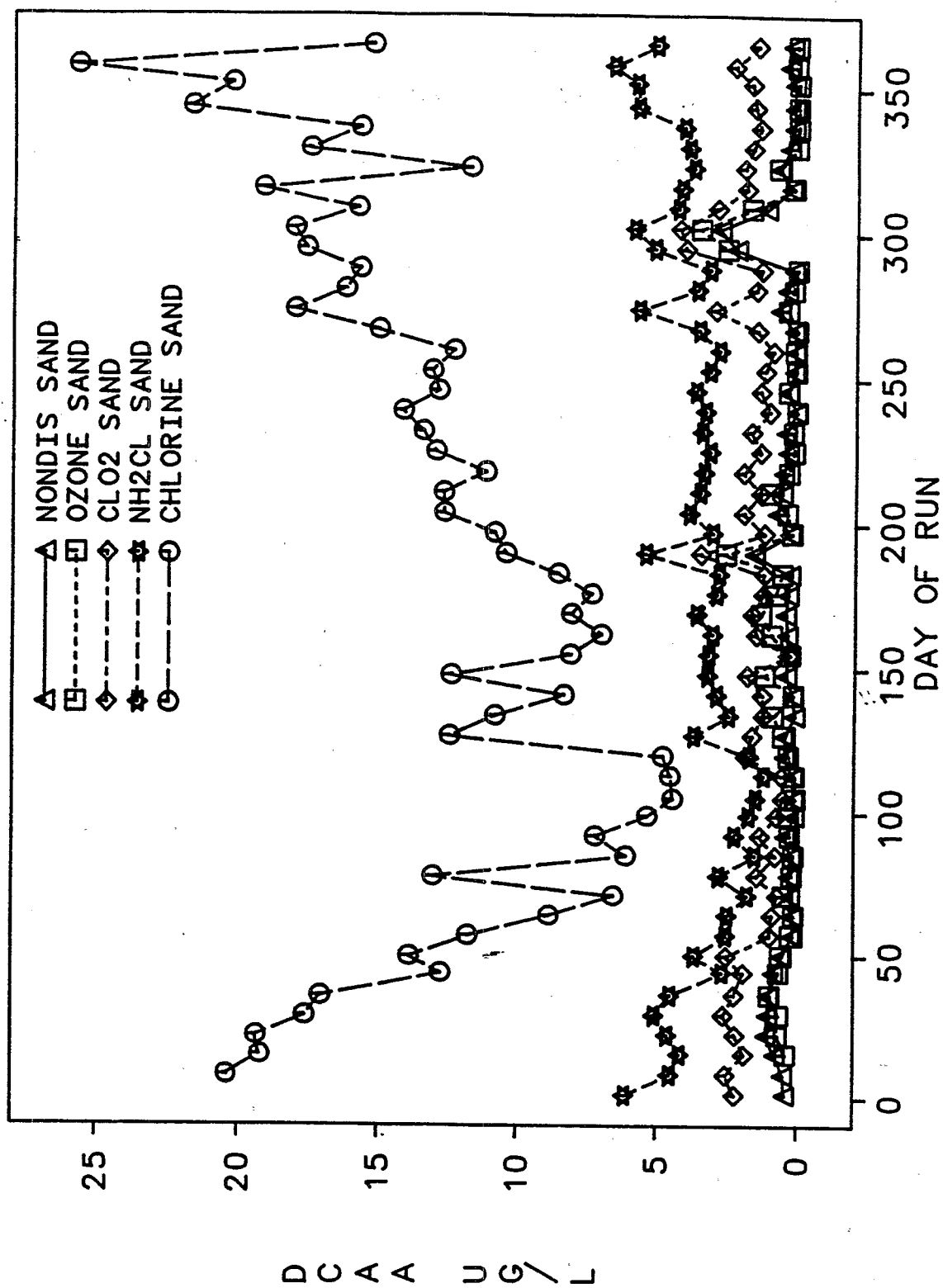


Figure 21. Comparison of DCAA Levels in the Sand Column Effluent of each Process Stream.

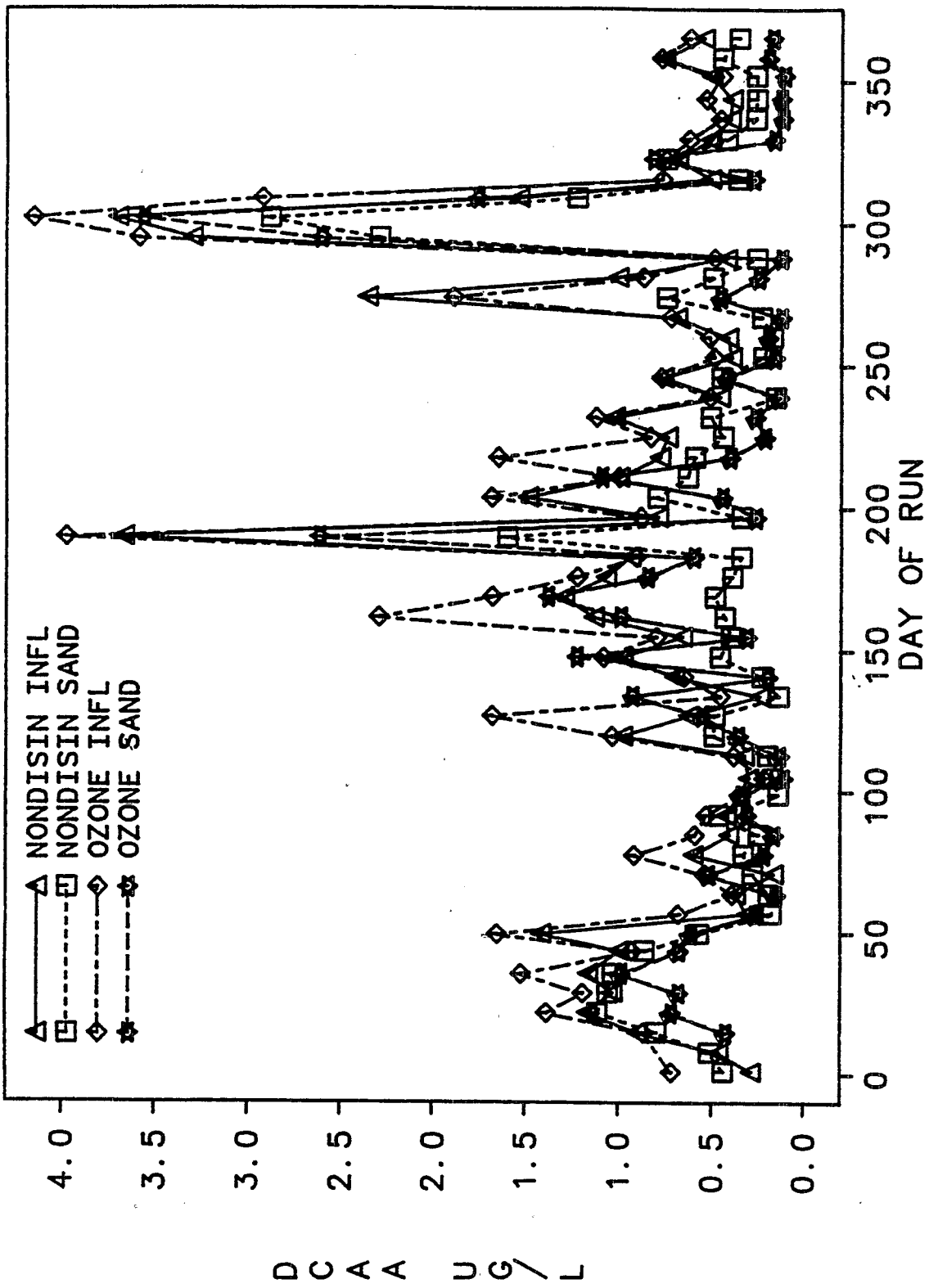


Figure 22. Comparison of Influent and Effluent DCAA Levels for the Nondisinfected and Ozone Sand Columns.

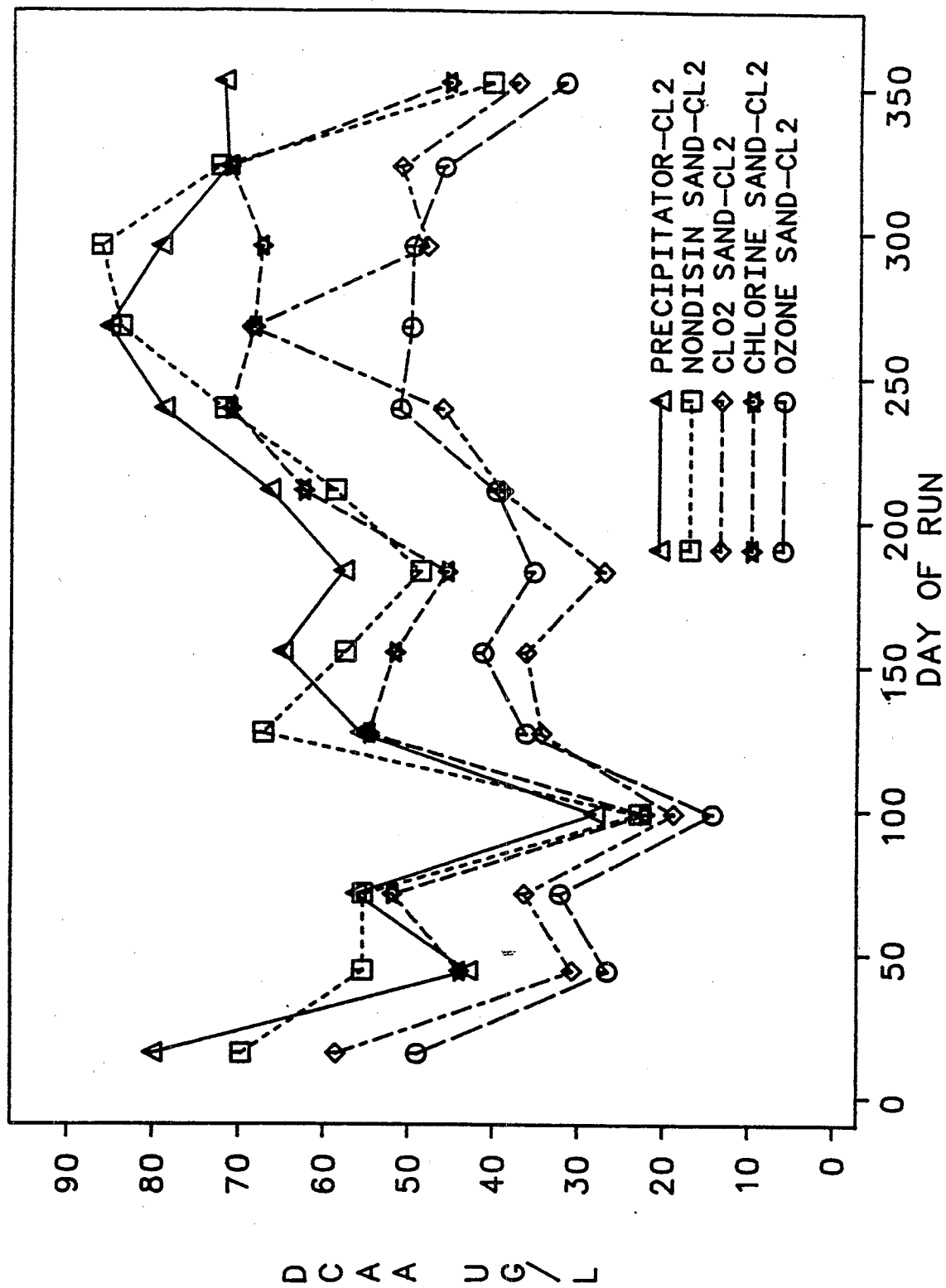


Figure 23. Comparison of DCAA-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

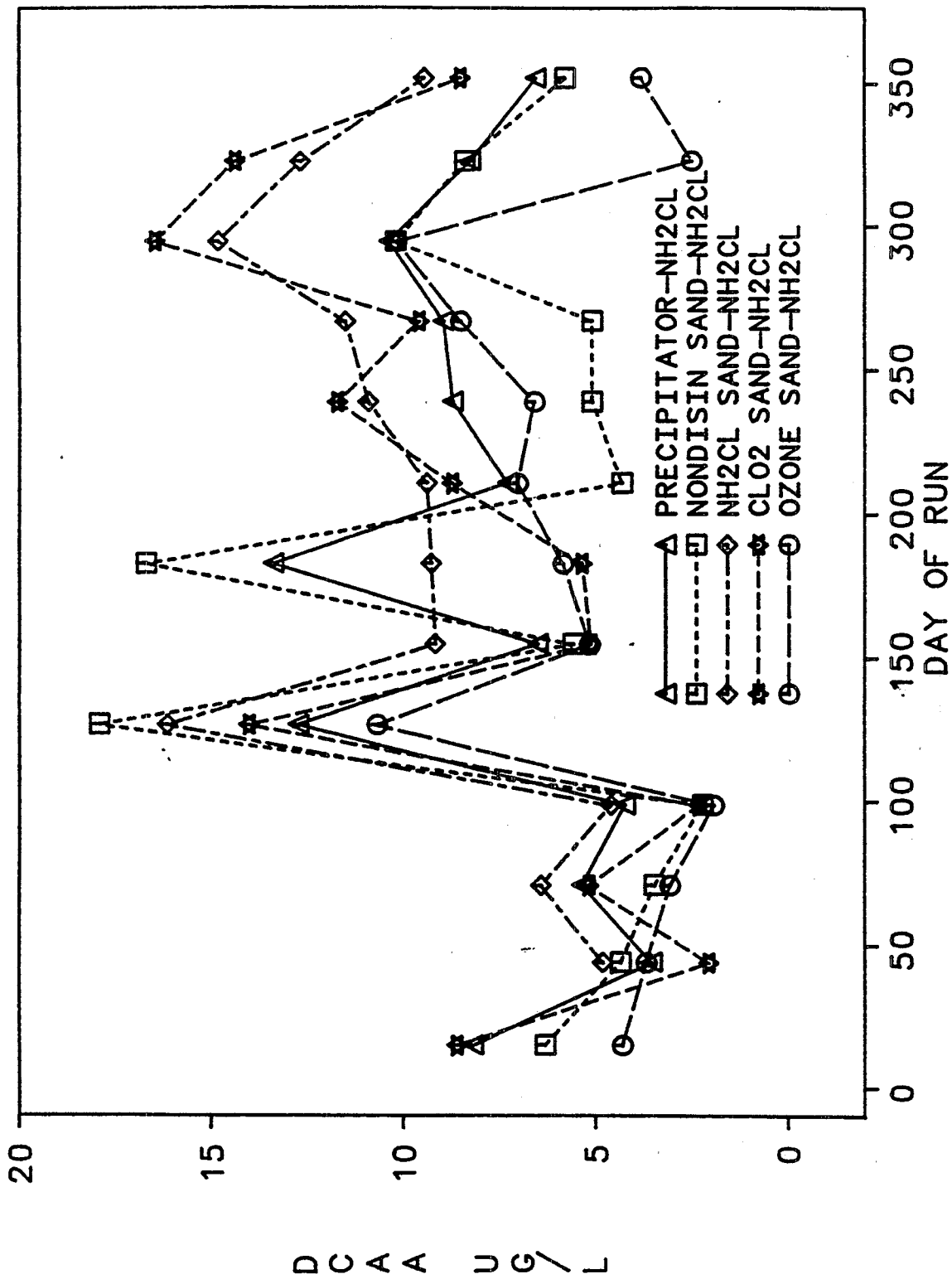


Figure 24. Comparison of DCAA-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.



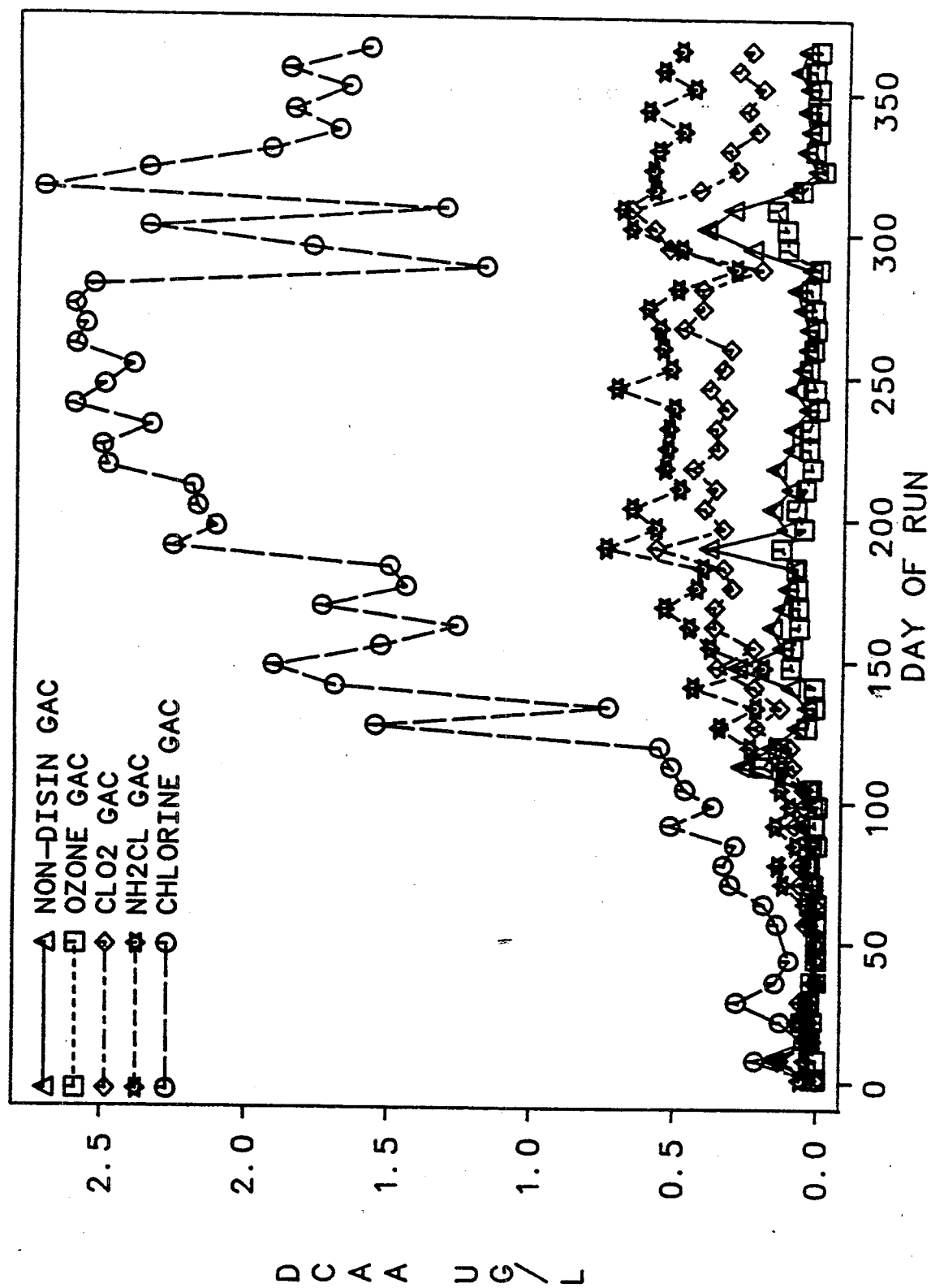


Figure 25. Comparison of DCAA Levels in the GAC Column Effluent of each Process Stream.

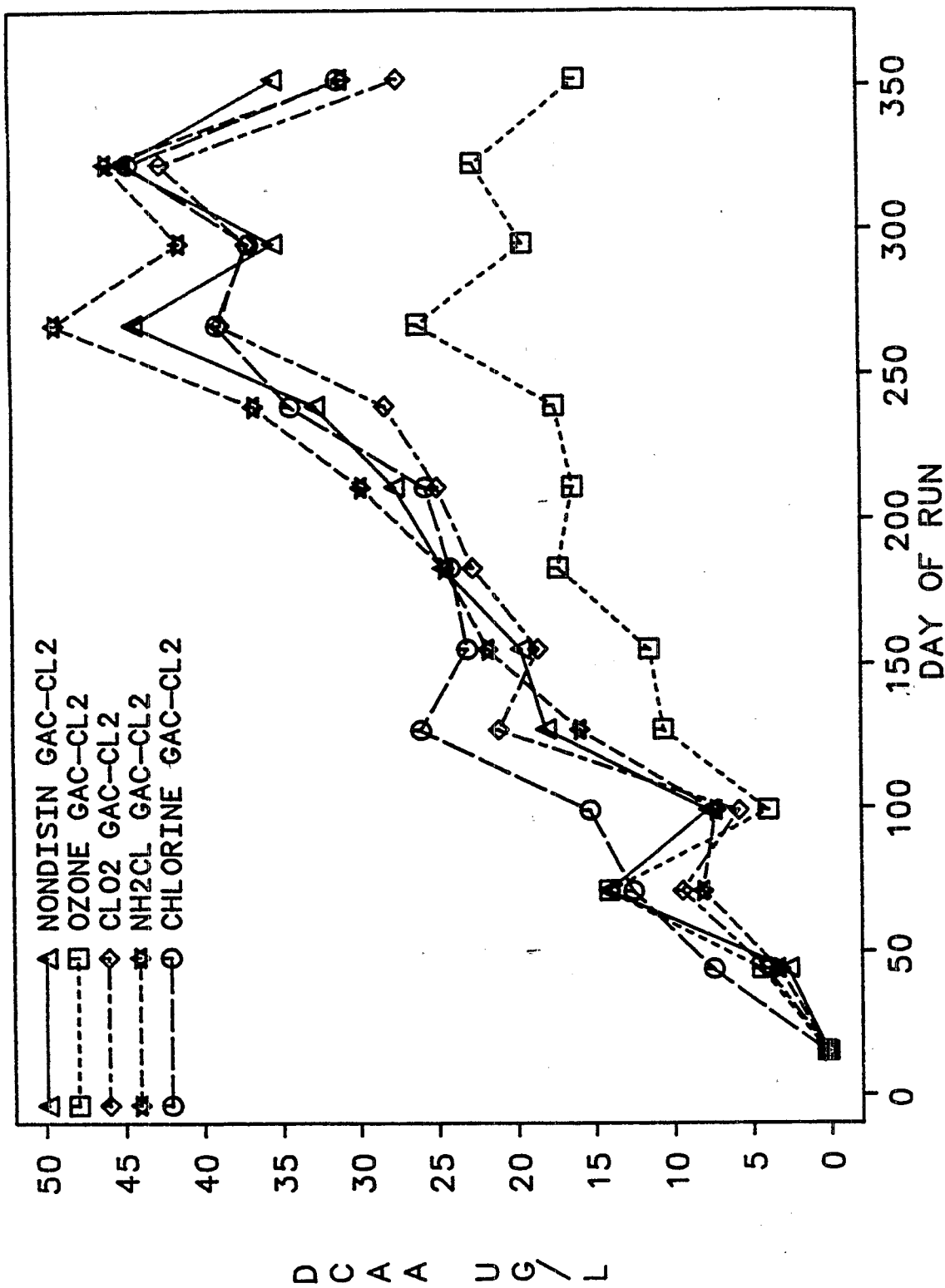


Figure 26. Comparison of DCAA-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

ug/L except for the ozone process stream which had an average steady-state effluent concentration of 20 ug/L. Average GAC DCAA-Cl<sub>2</sub> removals of 63, 79, 67, 61, and 62 percent relative to the precipitator influent were observed for DCAA over the one year operational period for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams. Respective removals of 48, 73, 53, 46, and 51 percent continued after steady-state was reached. Treatment of the GAC column effluents with chloramine and subsequent storage for 5 days resulted in average DCAA-NH<sub>2</sub>Cl reductions of 53-56% (Figure 27) relative to the similarly treated sand filter effluents (Figure 24). Average DCAA-NH<sub>2</sub>Cl levels ranged from 2.5-4.8 ug/L over the project period with steady-state concentrations ranging from 4-7 ug/L after day 250.

Trichloroacetic acid (TCAA) was an equally prominent haloacetic acid with equivalent contact chamber and sand column effluent concentrations averaging 0.6, 0.9, and 10 ug/L for the chlorine dioxide, chloramine, and chlorine process streams (Figure 28). Unlike DCAA, almost negligible reductions of TCAA were observed across the nondisinfected and ozone sand columns with respective influent levels averaging 0.5 and 0.6 ug/L, and average effluent concentrations of 0.4 and 0.5 ug/L. The levels of TCAA-Cl<sub>2</sub> in the precipitator effluent entering the pilot column system ranged from 30-120 ug/L with an average of 74 ug/L. Little change in TCAA-Cl<sub>2</sub> levels were observed across the nondisinfected and chlorine sand columns while average reductions of 32% and 58% occurred for the chlorine dioxide and ozone sand columns relative to the nondisinfected influent (Figure 29). Treatment of the sand column effluents with chloramine followed by storage for 5 days produced similarly elevated TCAA levels for all process streams (Figure 30) with operational period averages of 2 ug/L or less.

As with DCAA, excellent removals across the GAC columns were observed for TCAA throughout the operational period. Steady-state occurred on or about day 150 in all process streams (Figure 31) with subsequent removals of 85, 87, 73, 77, and 94 percent through the remainder of the operational period for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine GAC columns with average effluent concentrations of 0.07, 0.06, 0.15, 0.23, and 0.68 ug/L. Similar TCAA-Cl<sub>2</sub> breakthrough profiles were observed for all process streams except that of ozone (Figure 32). As with DCAA-Cl<sub>2</sub>, steady-state was reached around day 250 at a TCAA-Cl<sub>2</sub> level of about 60 ug/L for all process streams except that of ozone which was 20 ug/L. Average percent removals of TCAA-Cl<sub>2</sub> relative to the precipitator influent of 57, 83, 60, 54, and 58 percent were observed across the operational period for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams with continued removals averaging 43, 79, 47, 39, and 48 percent after

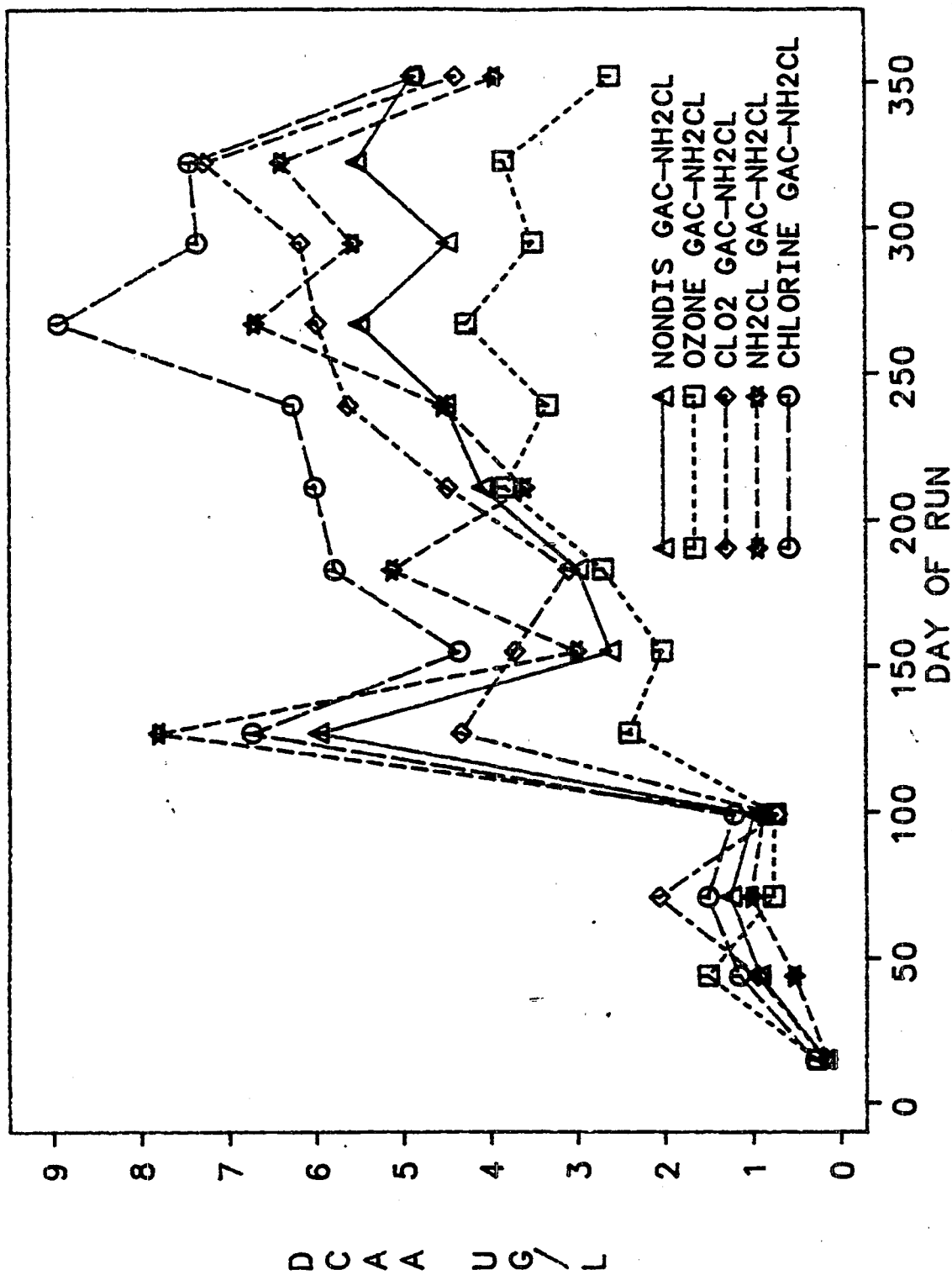


Figure 27. Comparison of DCAA-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

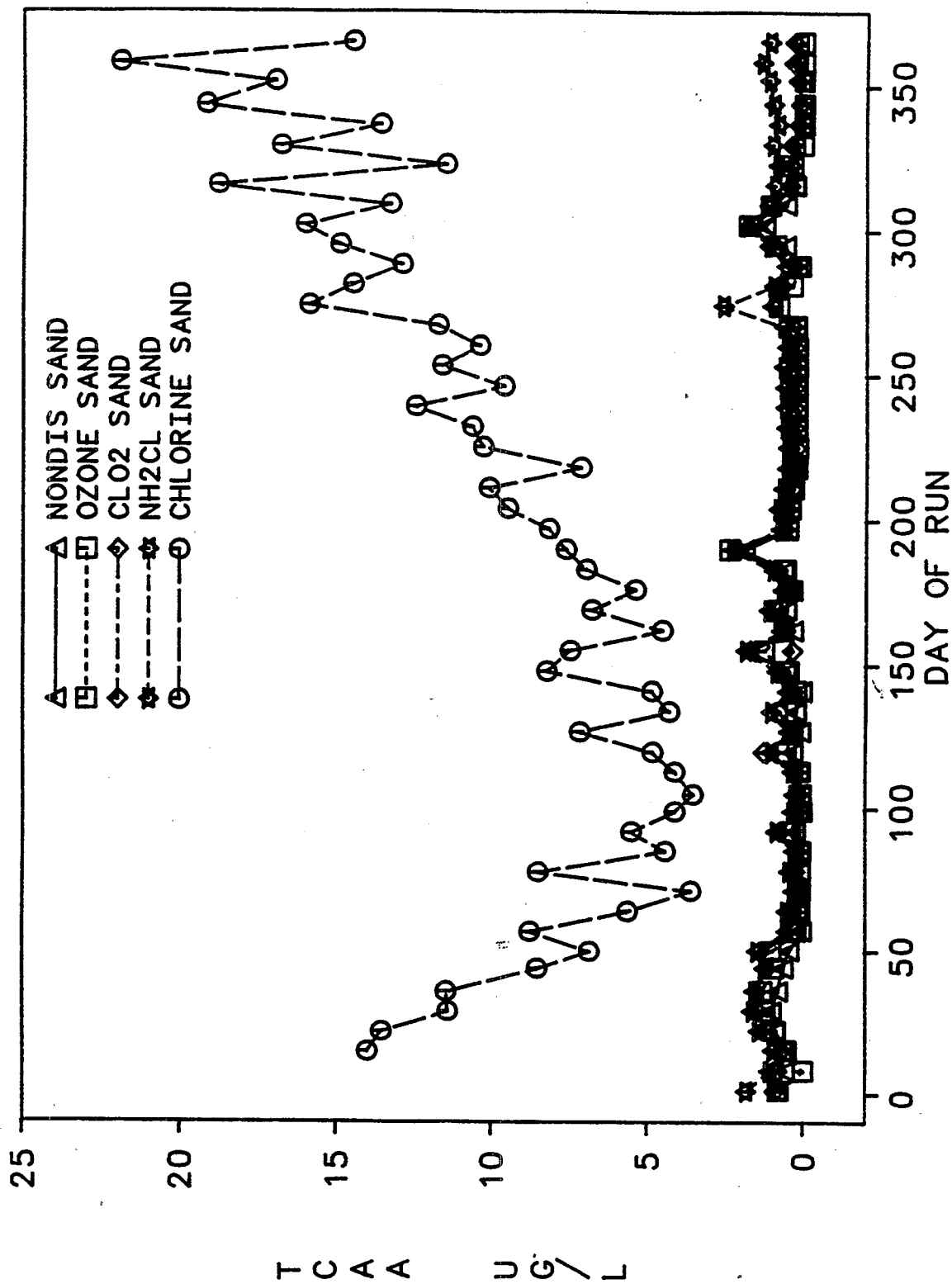


Figure 28. Comparison of TCAA Levels in the Sand Column Effluent of each Process Stream.

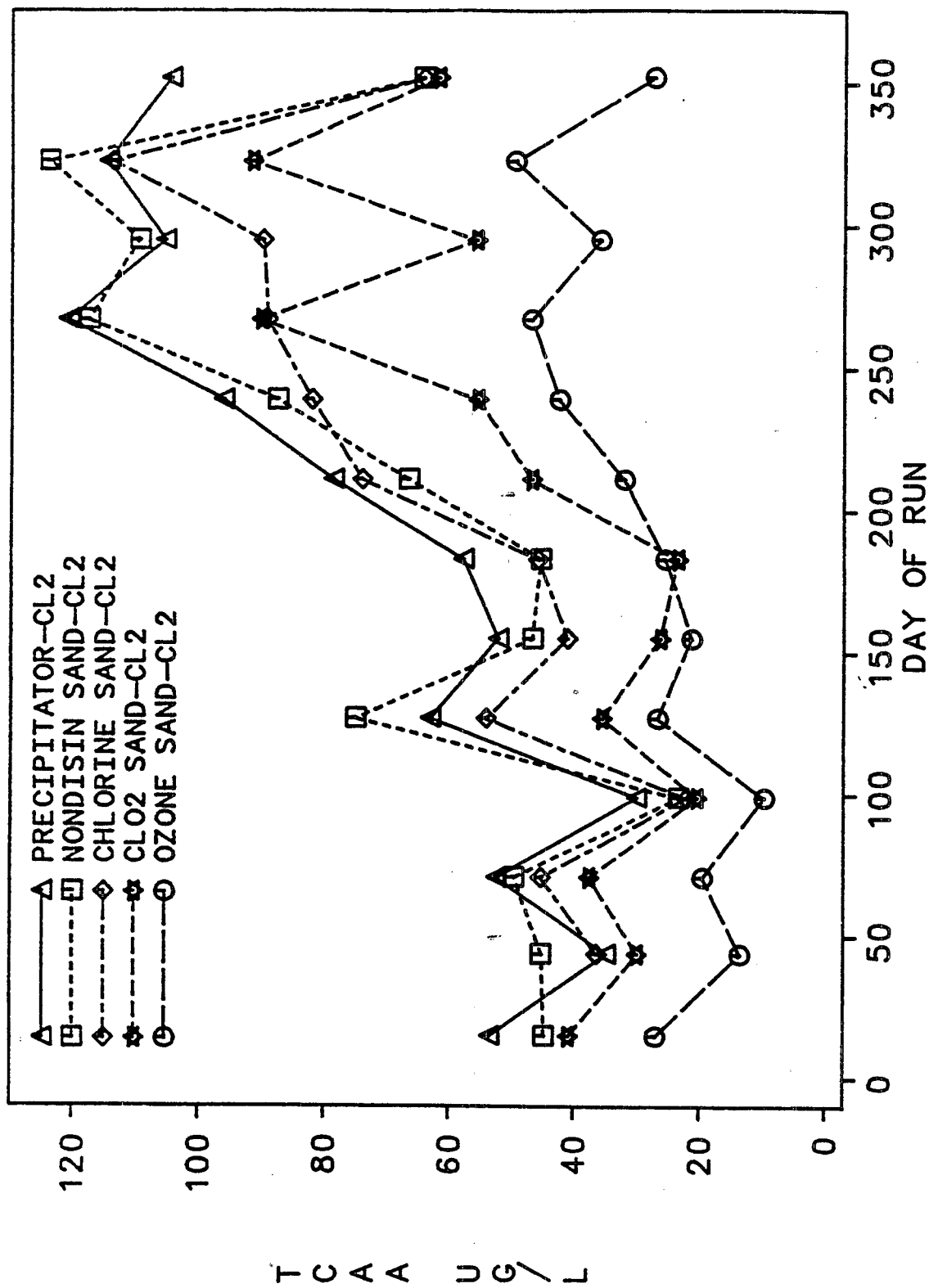


Figure 29. Comparison of TCAA-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

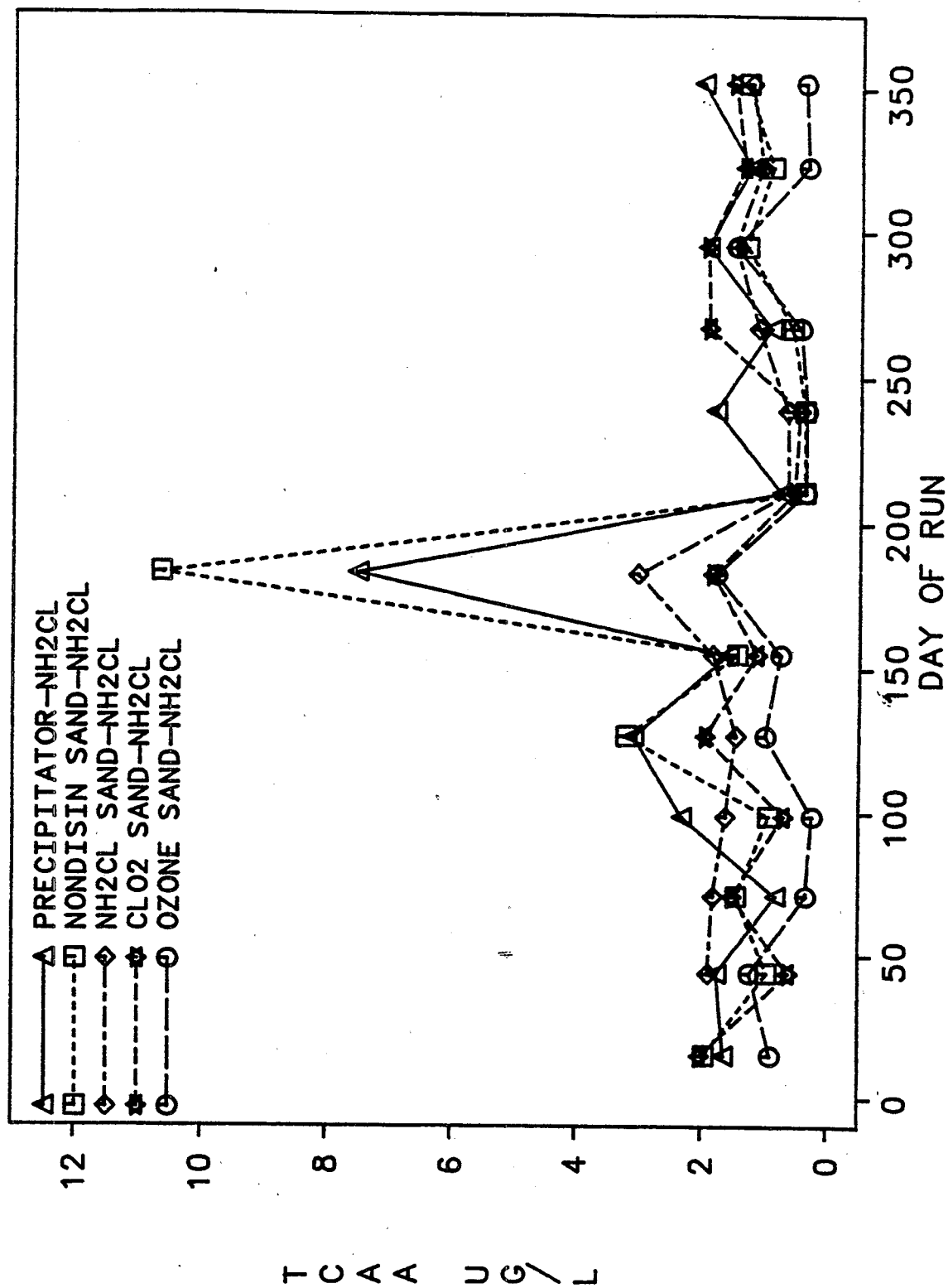


Figure 30. Comparison of TCAA-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

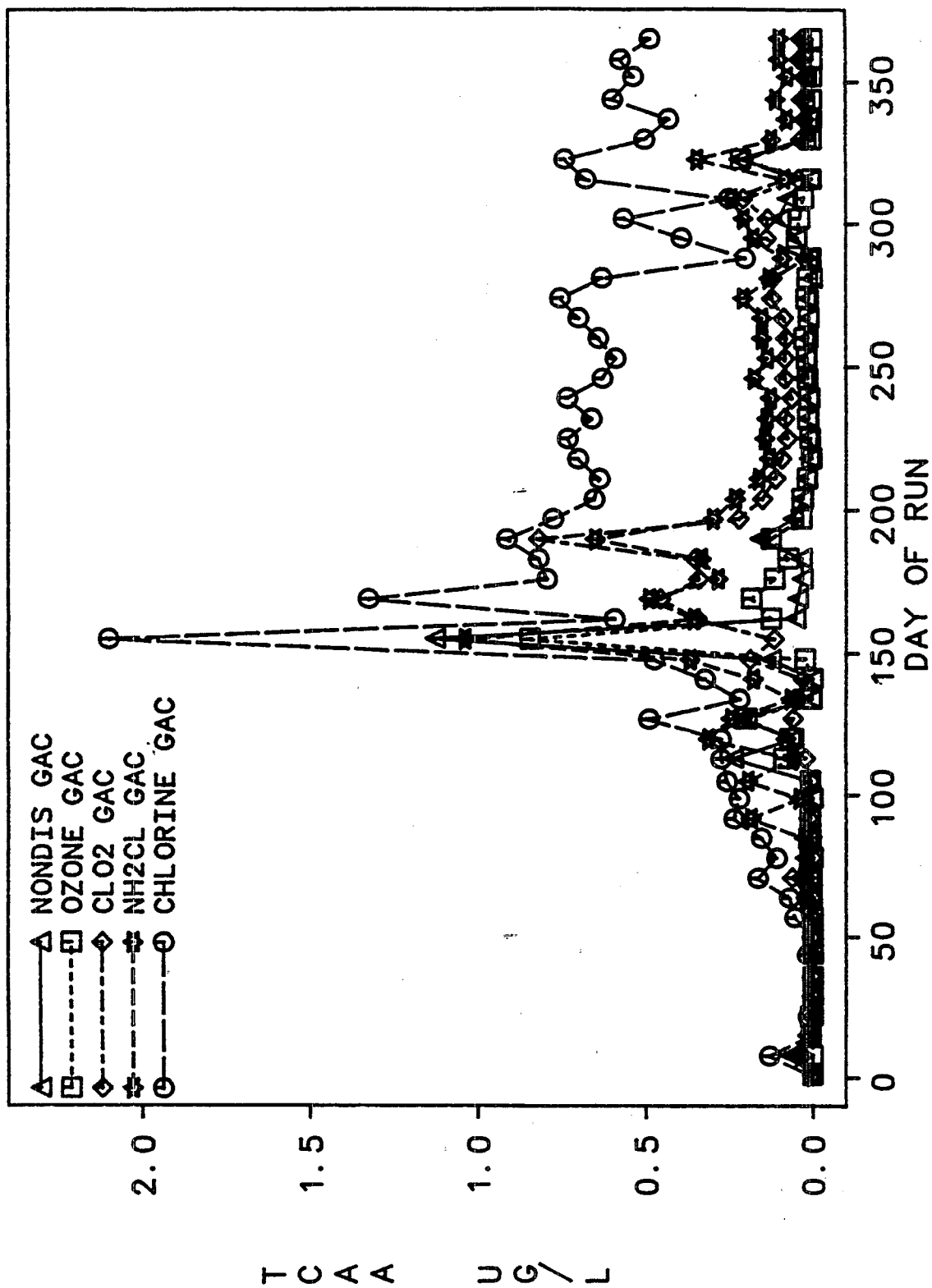


Figure 31. Comparison of TCAA Levels in the GAC Column Effluent of each Process Stream.



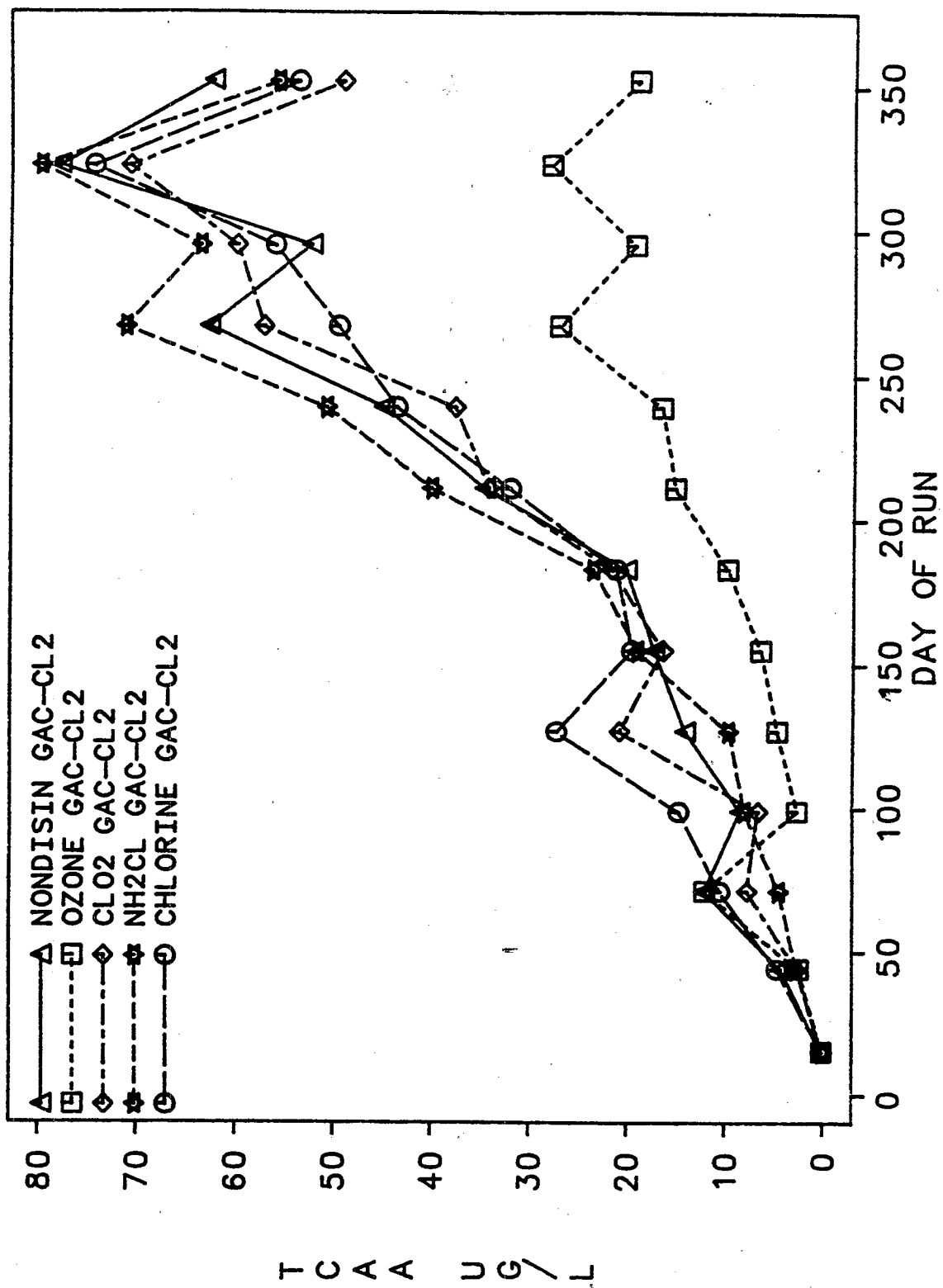


Figure 32. Comparison of TCAA-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

steady-state was reached. Post disinfection using chloramine with a 5-day hold produced consistently low TCAA-NH<sub>2</sub>Cl levels averaging from 0.3-0.8 ug/L across the project period (Figure 33). Steady-state concentrations after day 250 averaged only slightly higher at 0.4-0.9 ug/L.

Bromochloroacetic acid (BCAA) was also formed to a significant extent during the disinfection process. Contact chamber and sand column effluent concentrations were essentially identical for the chlorine dioxide, chloramine, and chlorine process streams with respective averages of 1, 0.8, and 6 ug/L (Figure 34). Low level reductions attributable to biodegradation were observed across the nondisinfected and ozone sand columns with respective average influent concentrations of 0.21 and 0.26 ug/L and average effluent levels of 0.13 and 0.12 ug/L. Treatment of aliquots of process stream water with free chlorine followed by 5-day incubation indicated that the BCAA-Cl<sub>2</sub> levels in the precipitator effluent entering the pilot column system ranged from 10-30 ug/L with an average of 17 ug/L (Figure 35). Essentially identical BCAA-Cl<sub>2</sub> levels were observed for the nondisinfected, ozone, chlorine dioxide, and chlorine sand columns with overall averages of 17, 14, 18, & 16 ug/L, respectively. Similar treatment of sand column aliquots with chloramine and subsequent 5-day storage again resulted in increases which were 3-13 times that of the sand column effluents with average BCAA-NH<sub>2</sub>Cl levels of 1.7, 1.0, 3.1, and 2.0 ug/L for the nondisinfected, ozone, chlorine dioxide, and chloramine sand column effluents (Figure 36).

As with the previous haloacetic acids, relatively good removals of BCAA were observed across the GAC columns throughout the operational period. The average BCAA removals observed across the project period for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine GAC columns were, respectively, 74, 79, 90, 91, and 93 percent with average effluent concentrations of 0.02, 0.01, 0.07, 0.06, and 0.34 ug/L (Figure 37). Steady-state was not readily observable for the nondisinfected and ozone GAC columns due to their relatively low influent concentrations which averaged 0.13 ug/L. As with the previous haloacetic acids, steady-state was again observed on day 150 for the chlorine dioxide, chloramine, and chlorine GAC columns. The percent removals observed for these three GAC columns after steady-state averaged, respectively, 87, 88, and 89 percent with average effluent concentrations of 0.10, 0.07, and 0.46 ug/L BCAA. Free chlorine treatment of the GAC effluents produced similar BCAA-Cl<sub>2</sub> breakthrough profiles across each GAC column (Figure 38). A relatively rapid breakthrough occurred to a 'quasi' steady-state on or about day 50 in all process streams at a removal of 35-45% which slowly decreased to 0% by the end of the project period. The average BCAA-Cl<sub>2</sub> removals observed across the project period were similar for all process streams

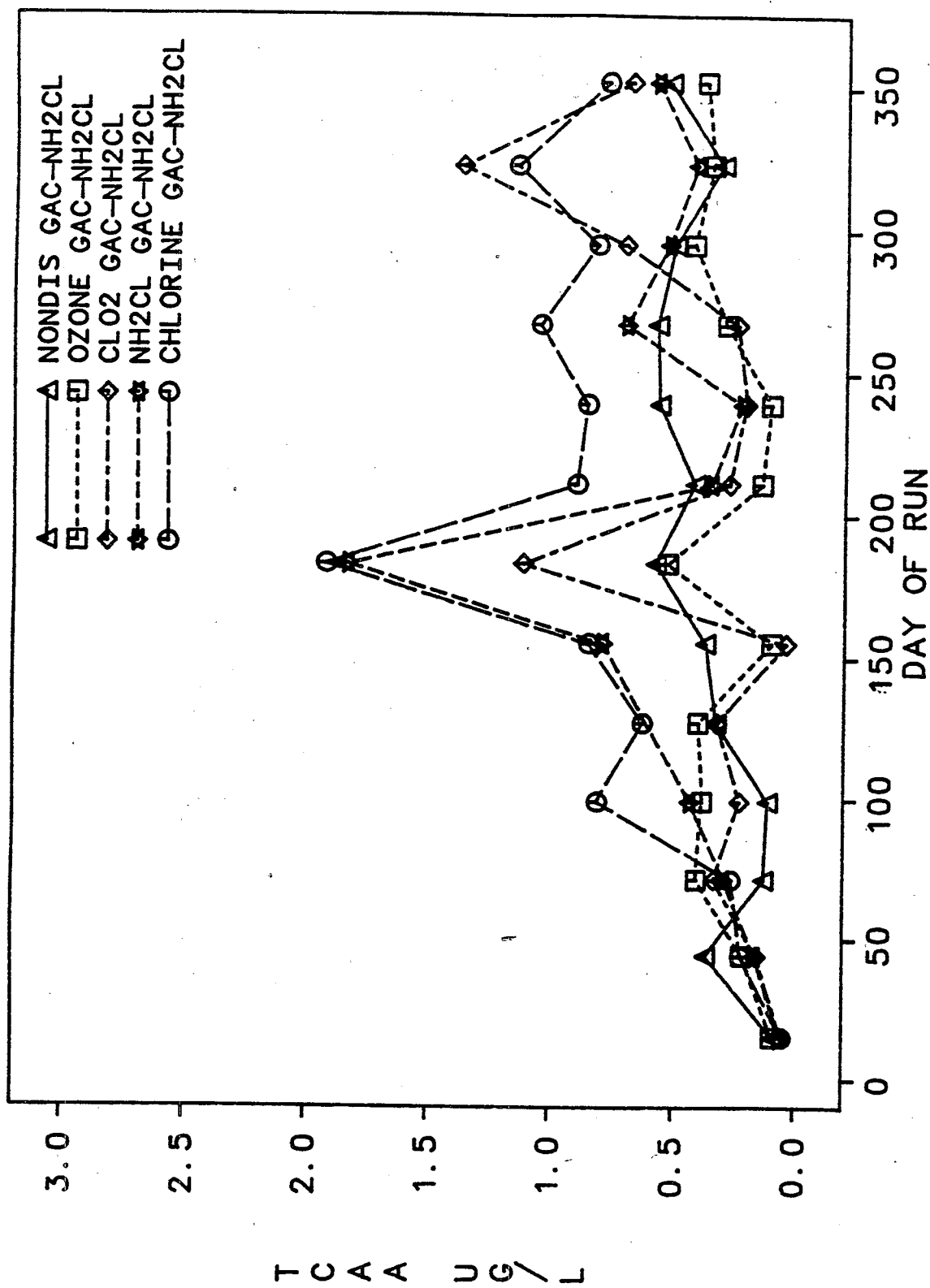


Figure 33. Comparison of TCAA-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

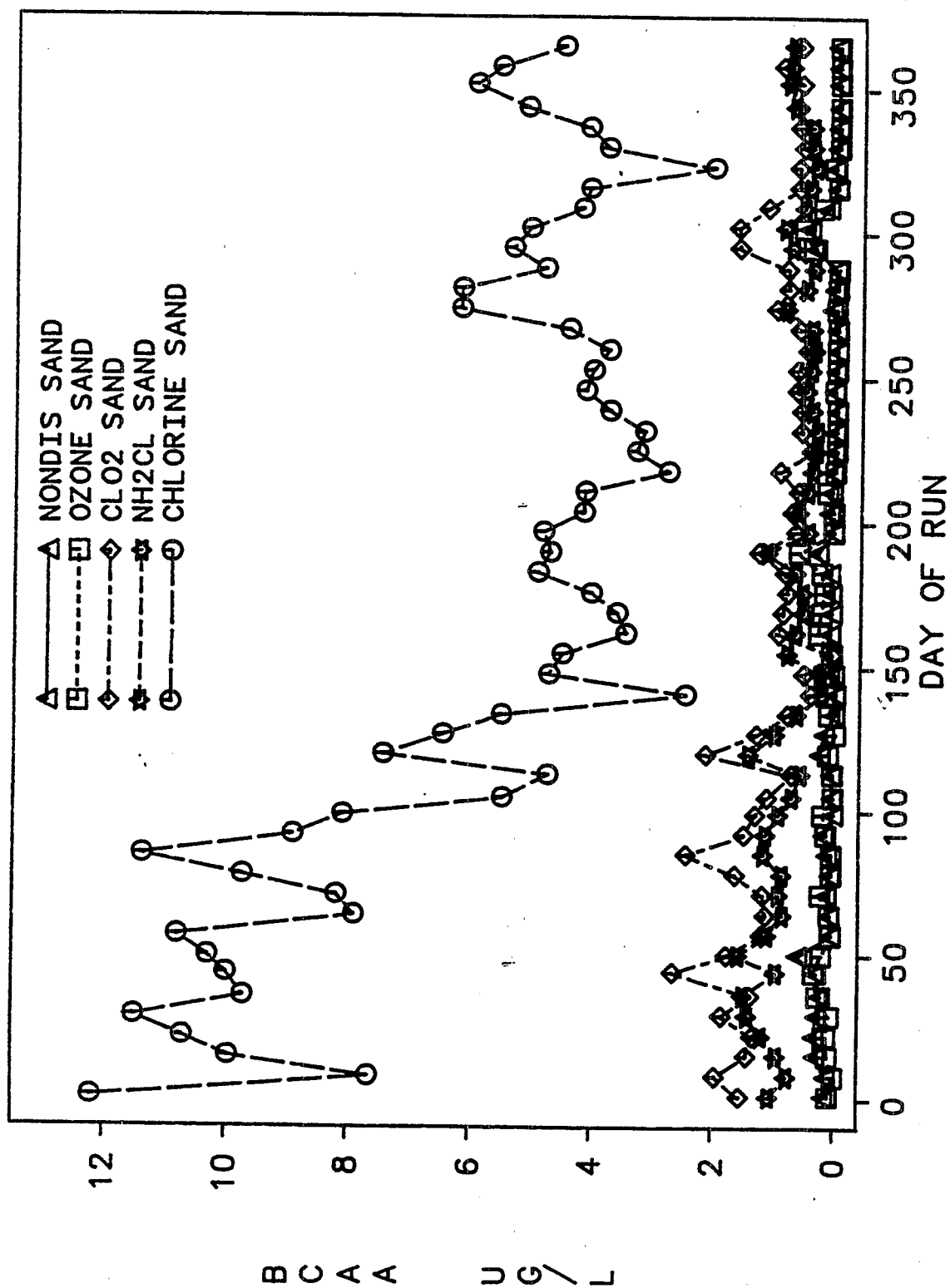


Figure 34. Comparison of the BCAA Levels in the Sand Column Effluent of each Process Stream.

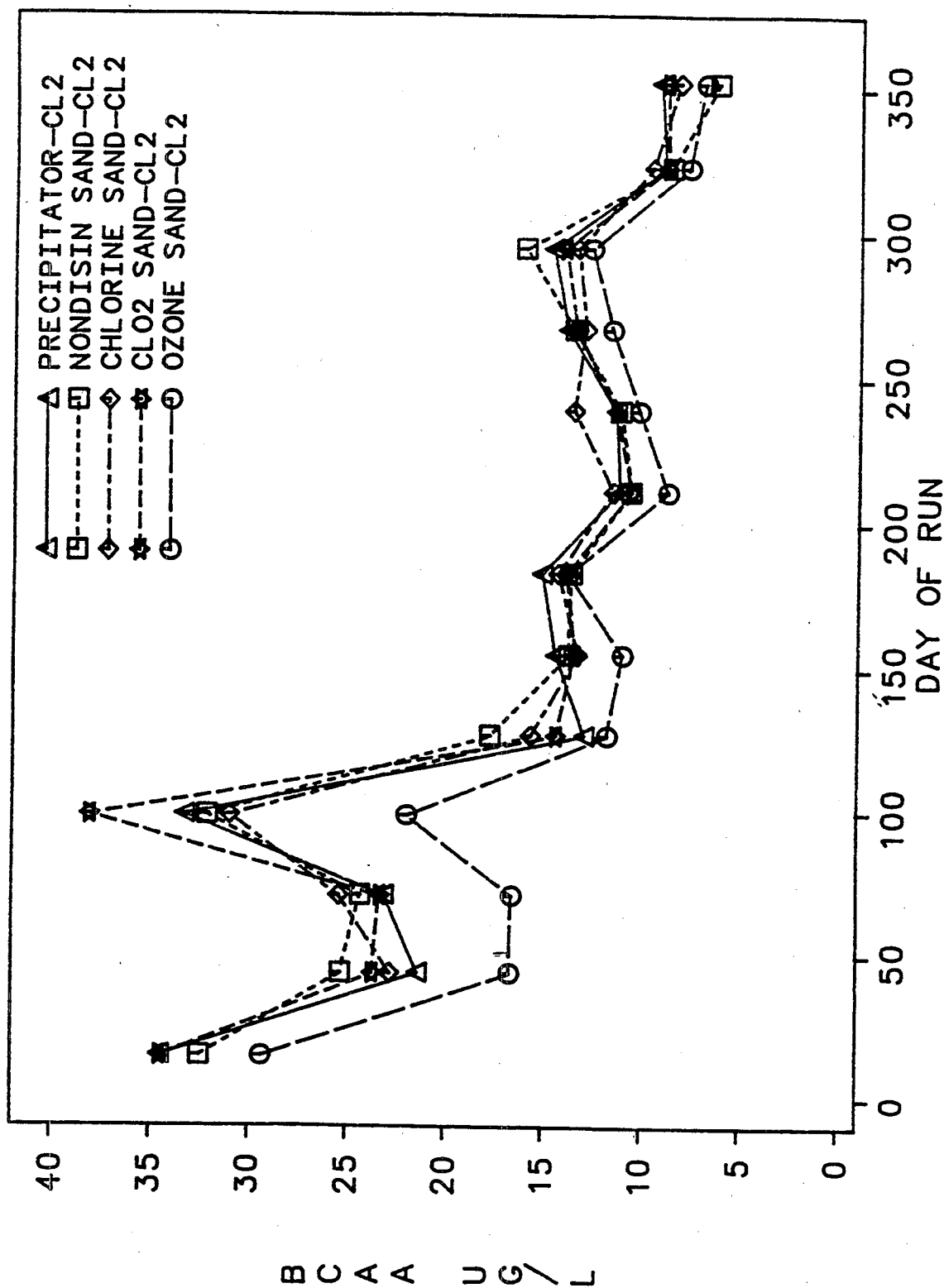


Figure 35. Comparison of the BCAA-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

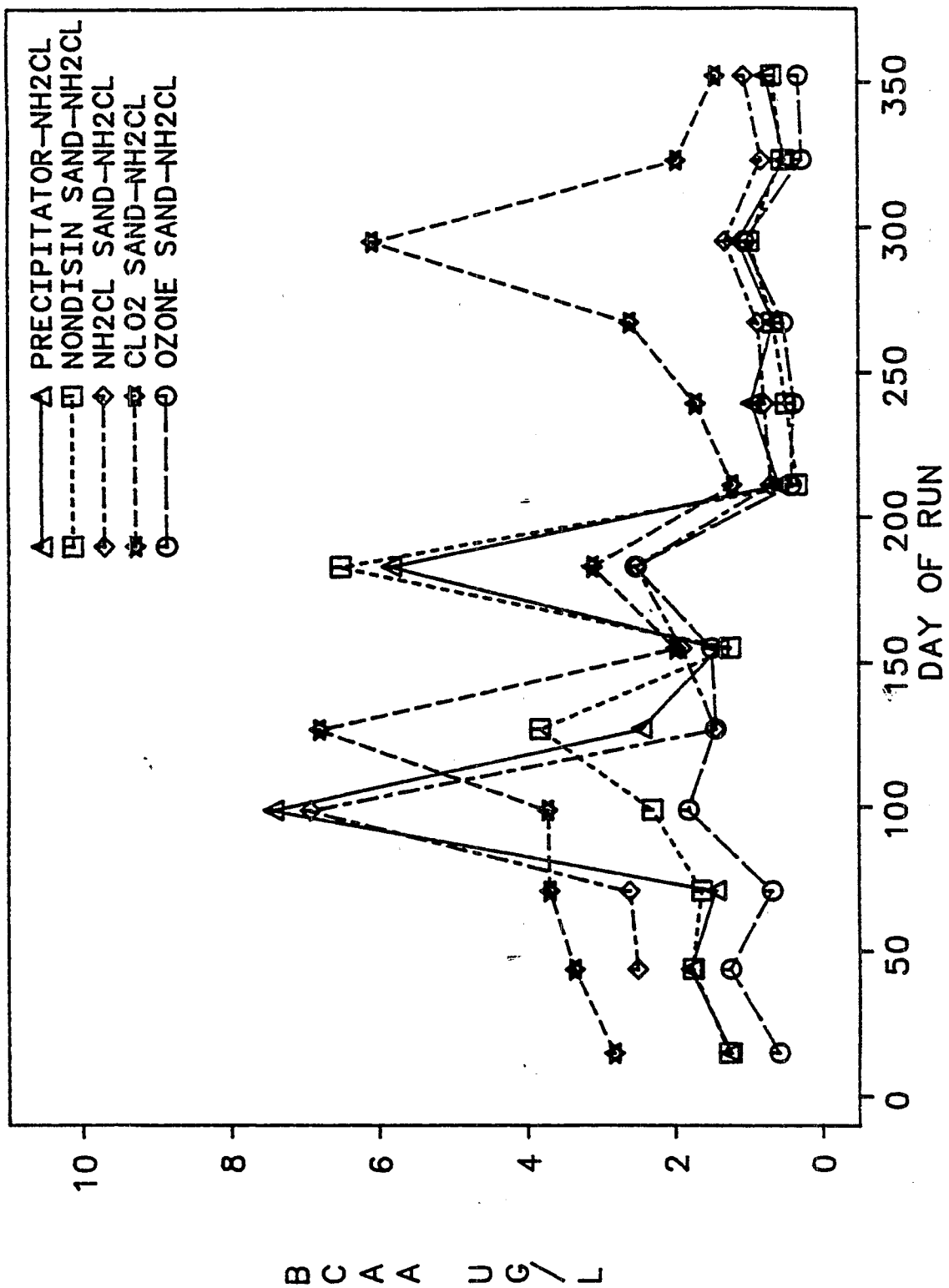


Figure 36. Comparison of the BCAA-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

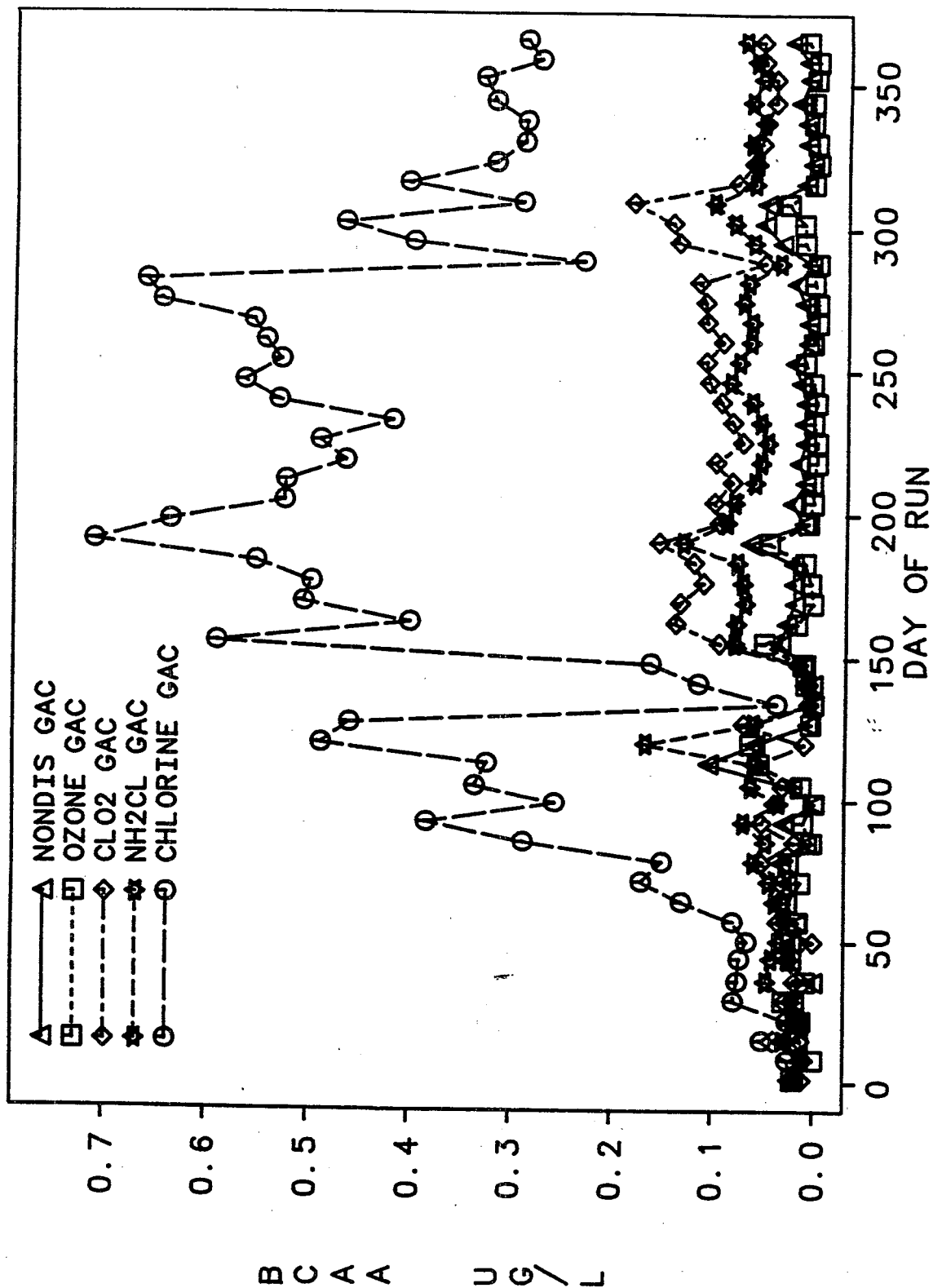


Figure 37. Comparison of the BCAA Levels in the GAC Column Effluent of each Process Stream.

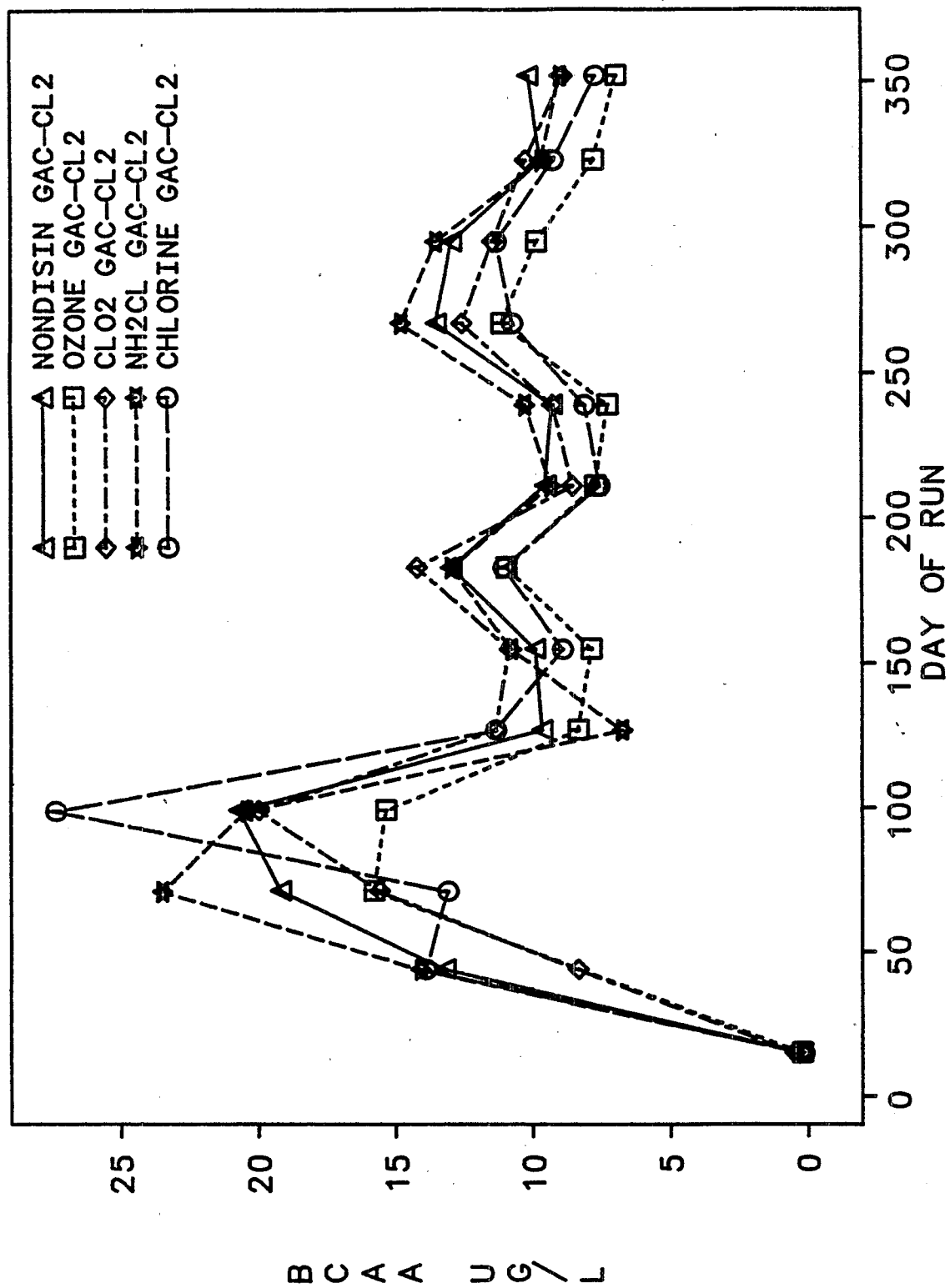


Figure 38. Comparison of the BCAA-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.



ranging from 2J-25% with average precursor effluent concentrations ranging from 9-12 ug/L. Chloramine treatment of the GAC column effluents and subsequent storage for 5 days resulted in similar average BCAA-NH<sub>2</sub>Cl effluent levels of 0.6, 0.8, 1.7, 1.6, and 1.2 ug/L across the project period for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams (Figure 39). Comparison to similarly treated sand filtered effluents indicates that GAC filtration produced BCAA-NH<sub>2</sub>Cl removals of 64, 24, 45, and 20 percent in the nondisinfected, ozone, chlorine dioxide, and chloramine process streams.

Chloroacetic acid (CAA) was a minor constituent with an observed maximum average of approximately 0.5 ug/L in the process stream effluents and 1.7 ug/L in the free chlorine terminal CAA-Cl<sub>2</sub> determinations. The CAA data obtained was somewhat erratic because the CAA chromatographic peak was usually a small peak which was not completely separable from that of a rather larger impurity requiring a somewhat subjective integration. The contact chamber and sand column effluent concentrations were essentially equivalent for the chlorine dioxide, chloramine, and chlorine process streams with respective averages of 0.12, 0.20, and 0.59 ug/L (Figure 40). In the effluents of the nondisinfected and ozone process streams, CAA was detected in less than 50 percent of the samples analyzed at levels averaging 0.07 and 0.09 ug/L, respectively. Terminal CAA-Cl<sub>2</sub> levels were similar in the sand column effluents of all process streams ranging from 2-6 ug/L (Figure 41) and averaging 3-4 ug/L. Similar CAA-NH<sub>2</sub>Cl levels were also observed for the sand column aliquots treated with chloramine and stored for 5 days with averages ranging from 0.9-1.2 ug/L (Figure 42). As with several of the haloacetic acids previously discussed, these levels were 5-15 times those of the sand column effluents suggesting that some reaction between free chlorine and the CAA precursors had occurred during the in situ formation of chloramine.

The only GAC column effluent in which CAA was consistently detected was that of the chlorine process stream (Figure 43). By the end of the project period (days 300-365) effluent CAA levels were averaging 0.07 ug/L resulting in CAA removals averaging 92% with respect to the sand column effluent. While influent concentration spikes caused temporary breakthroughs in the process streams (day 127), no consistent CAA breakthrough was observed in the GAC effluents of the other process streams. In contrast, significant CAA precursor breakthrough occurred for all GAC columns as indicated by the CAA-Cl<sub>2</sub> levels depicted in Figure 44. The average CAA-Cl<sub>2</sub> levels in the GAC effluents of the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams were essentially identically at 1.5, 1.1, 1.3, 1.4 and 1.6 ug/L. The GAC removal of CAA precursor diminished across the operational period with continued removals of 31, 53,

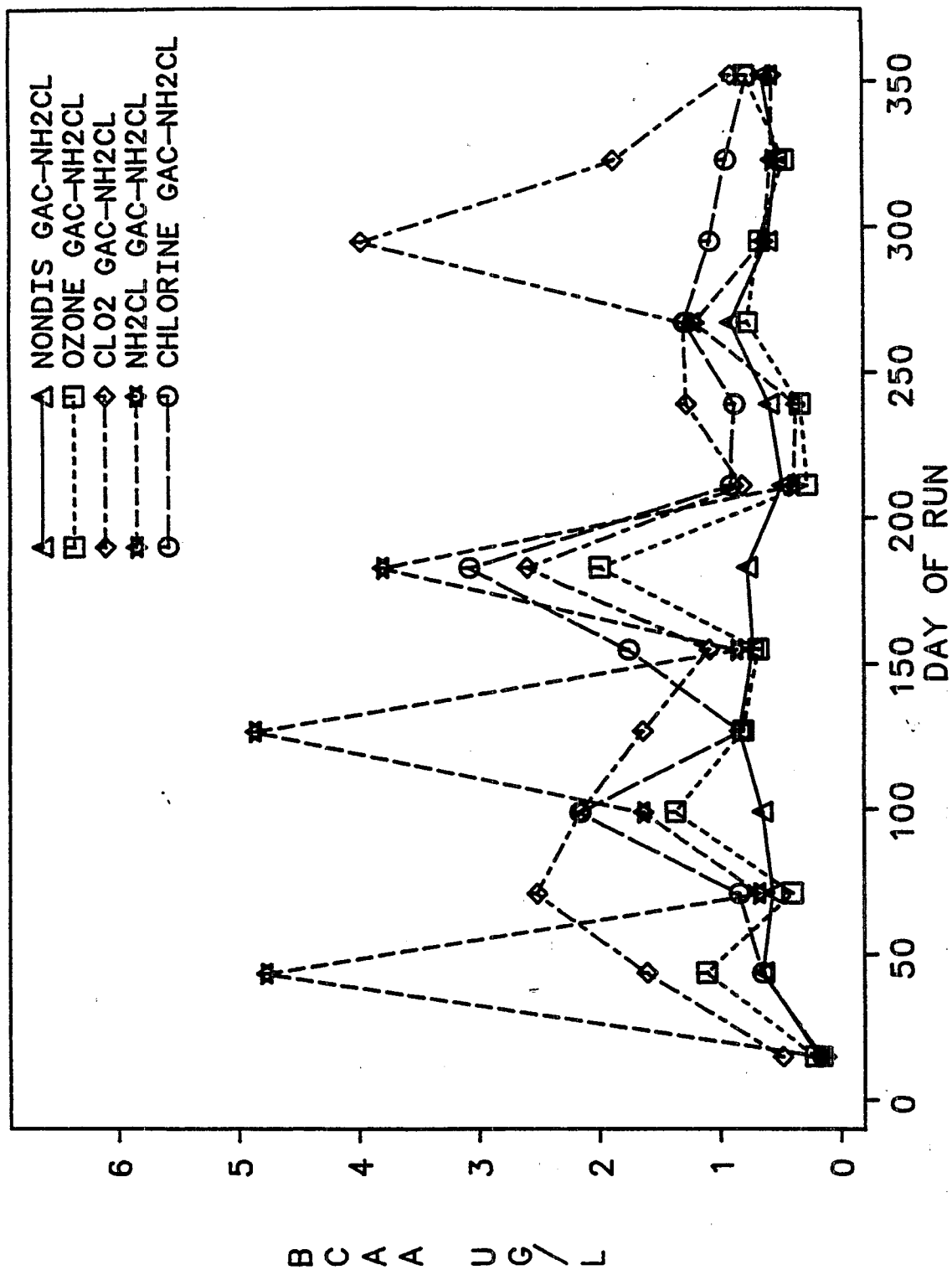


Figure 39. Comparison of the BCAA-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

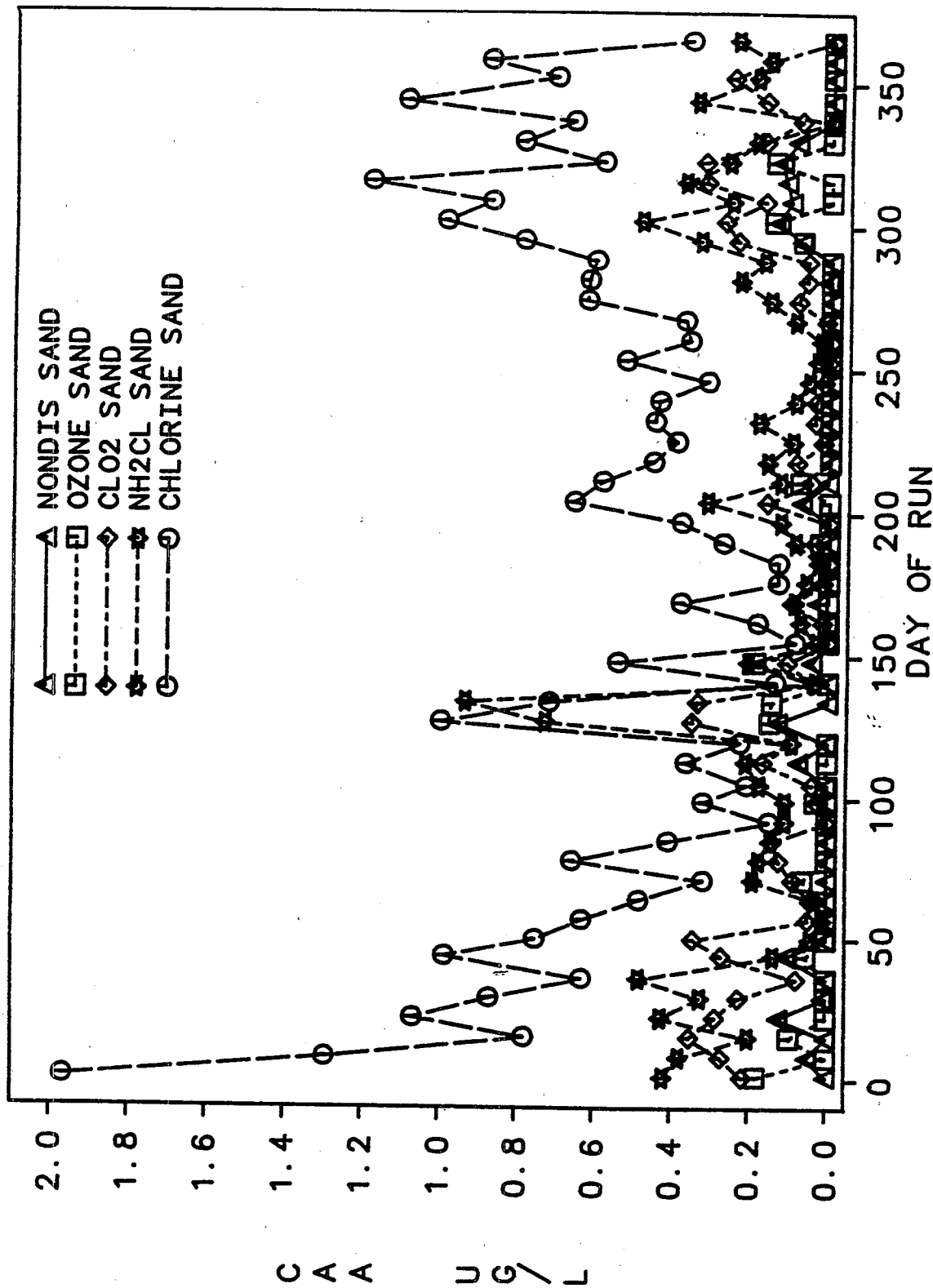


Figure 40. Comparison of the CAA Levels in the Sand Column Effluent of each Process Stream.

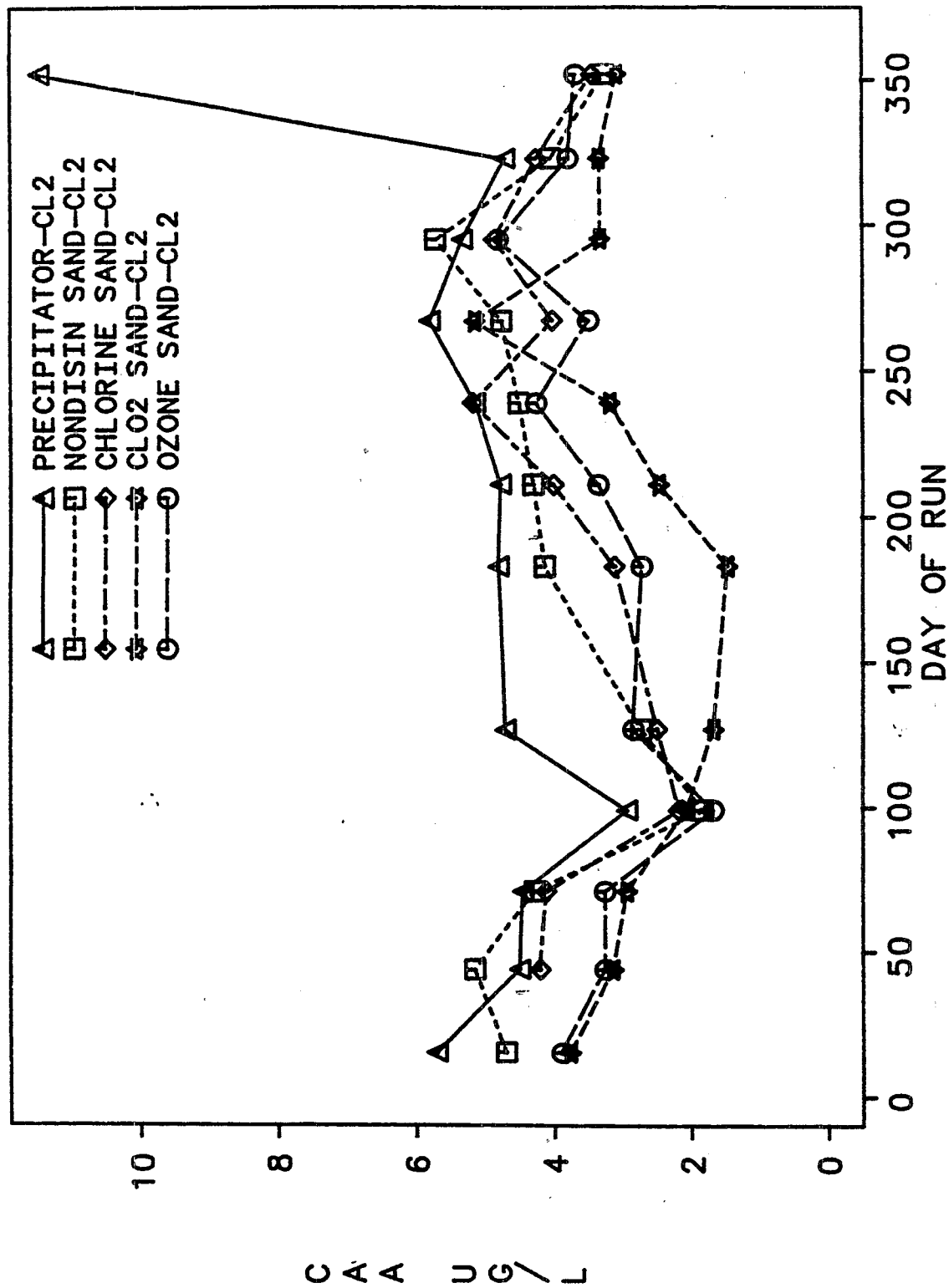


Figure 41. Comparison of the CAA-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

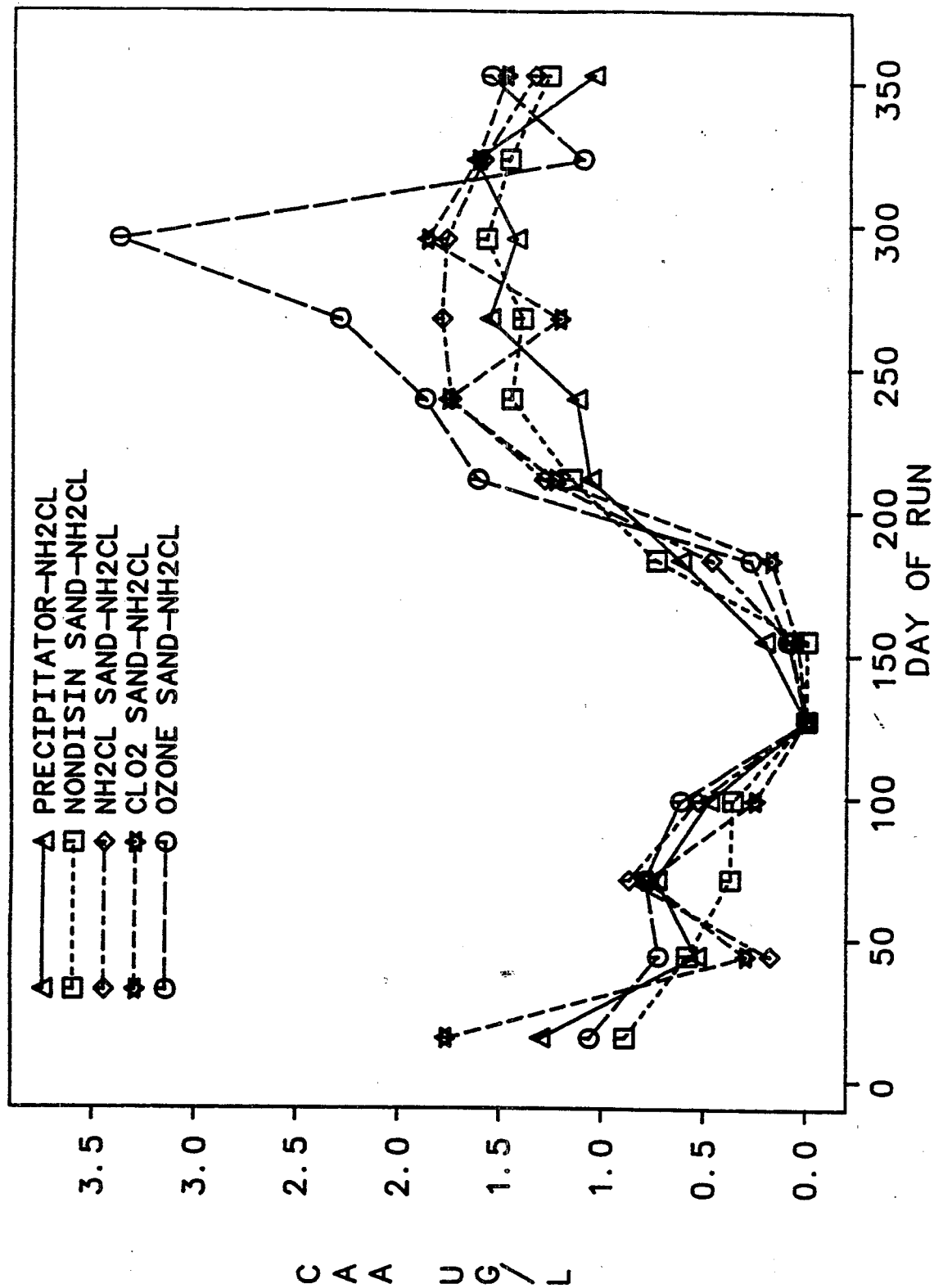


Figure 42. Comparison of the CAA-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

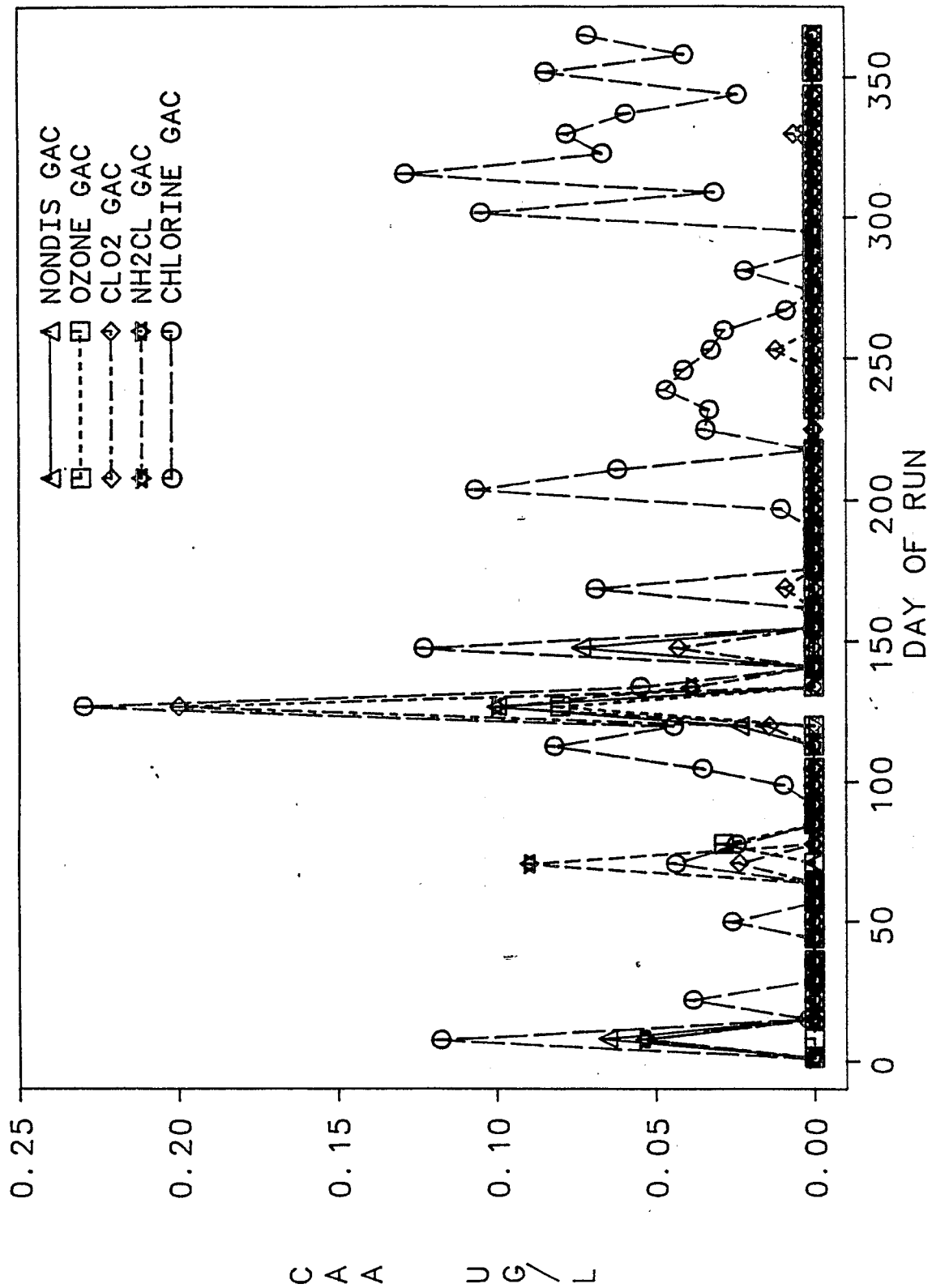


Figure 43. Comparison of the CAA Levels in the GAC Column Effluent of each Process Stream.

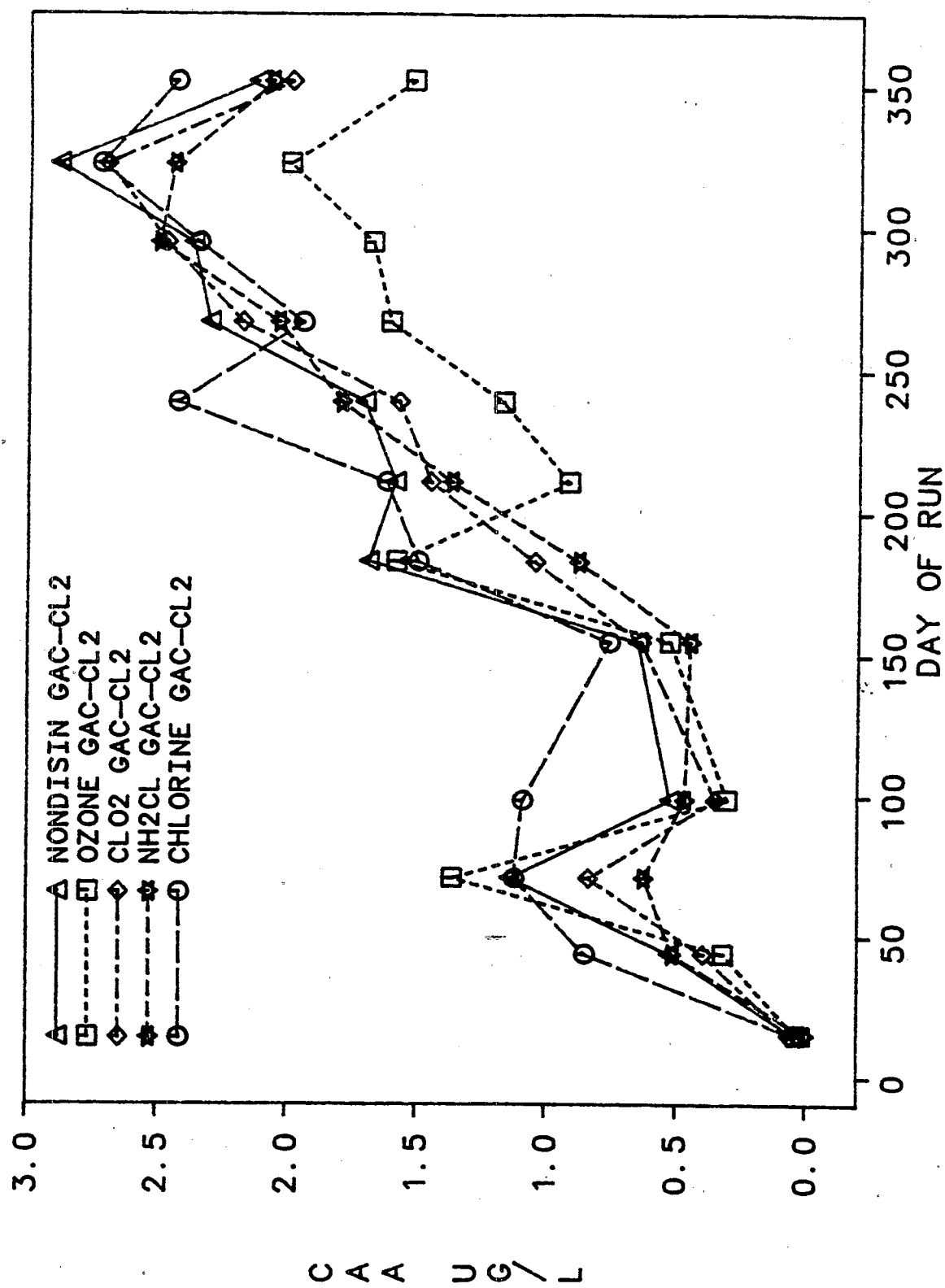


Figure 44. Comparison of the CAA-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

27, and 33 percent on days 320-360 for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams as compared to similarly treated sand column effluents. Since the chloramine GAC column exhibited similar CAA-Cl<sub>2</sub> effluent concentrations, similar CAA precursor removal was assumed. Chloramine treatment of the GAC effluents and subsequent 5-day storage resulted in similar CAA-NH<sub>2</sub>Cl concentrations for all process streams with project period averages ranging from 0.3-0.5 ug/L (Figure 45). Comparison to similarly treated sand column effluents indicated that average removals of 60-70% were produced by GAC filtration over the one year operational period with removals diminishing to 27-53% by the end of the year (days 320-360).

Dibromoacetic acid (DBAA) was another minor constituent with a maximum average process stream concentration of 0.3 ug/L and an maximum average terminal DBAA-Cl<sub>2</sub> concentration of 1.1 ug/L. Unlike CAA, reasonably good precision was obtained for DBAA in the 0.02-0.1 ug/L range as evidenced by the comparison of the chlorine dioxide influent and sand effluent in Figure 46. As exemplified for the chlorine dioxide process stream, the contact chamber and sand column effluent concentrations were essentially identical for all process streams except that of ozone. Ozonation generated additional DBAA apparently resulting from the presence of trace amounts of bromide in the raw water, increasing the average nondisinfected concentration from 0.007 to 0.088 ug/L (Figure 47). After passage through the ozone sand column, the average DBAA concentration was reduced to 0.037 ug/L, presumably due to biodegradation. The average DBAA levels in the sand column effluents of the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams were, respectively, 0.004, 0.037, 0.096, 0.018, and 0.33 ug/L (Figure 48). The level of terminal DBAA-Cl<sub>2</sub> entering the pilot column system averaged 0.6 ug/L. Increases of approximately 65% were observed for both chlorine dioxide and ozone resulting in DBAA-Cl<sub>2</sub> levels averaging 1.0 ug/L (Figure 49). The addition of chloramine and storage for 5 days produced moderate increases in DBAA levels of approximately 2-3 times that of the sand column effluent for the ozone, chlorine dioxide, and chloramine process streams with respective averages of 0.10, 0.22, and 0.06 ug/L (Figure 50). Similar treatment of nondisinfected sand filtered water resulted in an average DBAA-NH<sub>2</sub>Cl concentration of 0.08 ug/L which was 20 times that of the initial average nondisinfected sand column concentration of 0.004 ug/L.

Significant levels of DBAA breakthrough occurred across the GAC columns of the chlorine and chlorine dioxide process streams while relatively minor intermittent breakthrough was observed for the nondisinfected, ozone, and chloramine GAC columns at the 0.002 ug/L level (Figure 51). The average DBAA removals observed for the chlorine and chlorine dioxide GAC columns were both 94% relative to their respective sand column influents. Both of



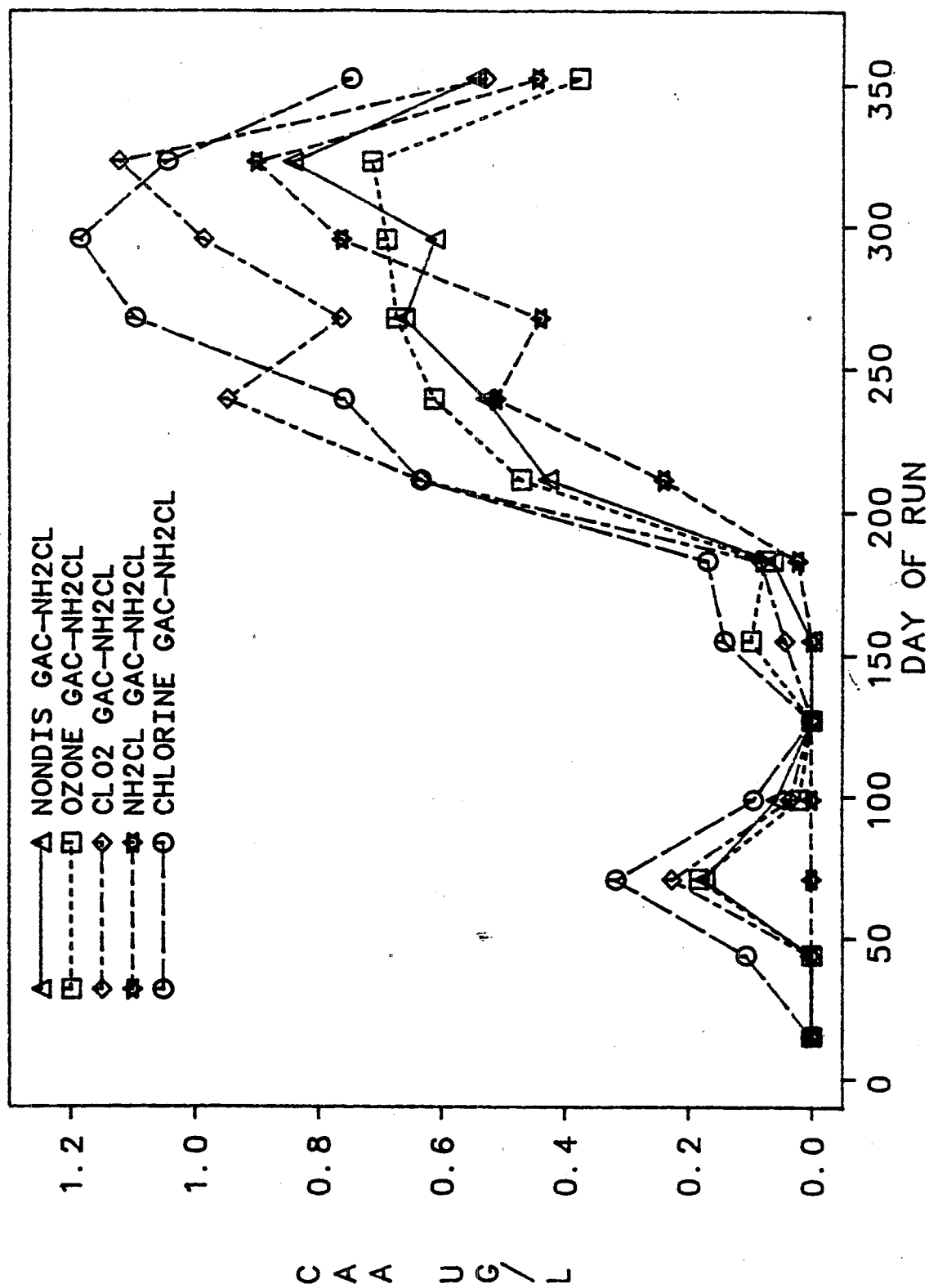


Figure 45. Comparison of the CAA-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

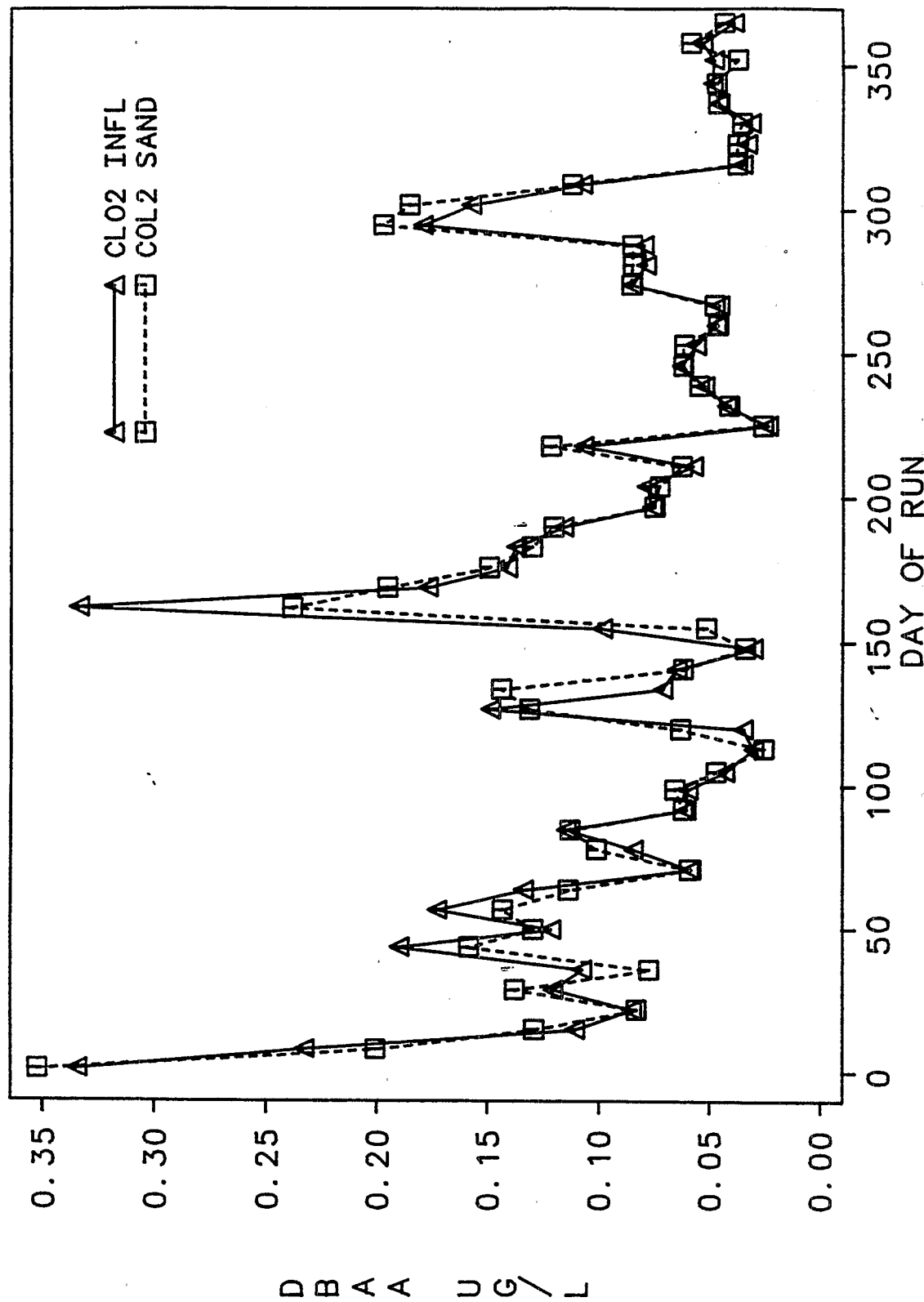


Figure 46. Comparison of the DBAA Levels in the Chlorine Dioxide Contact Chamber and Sand Column Effluents.

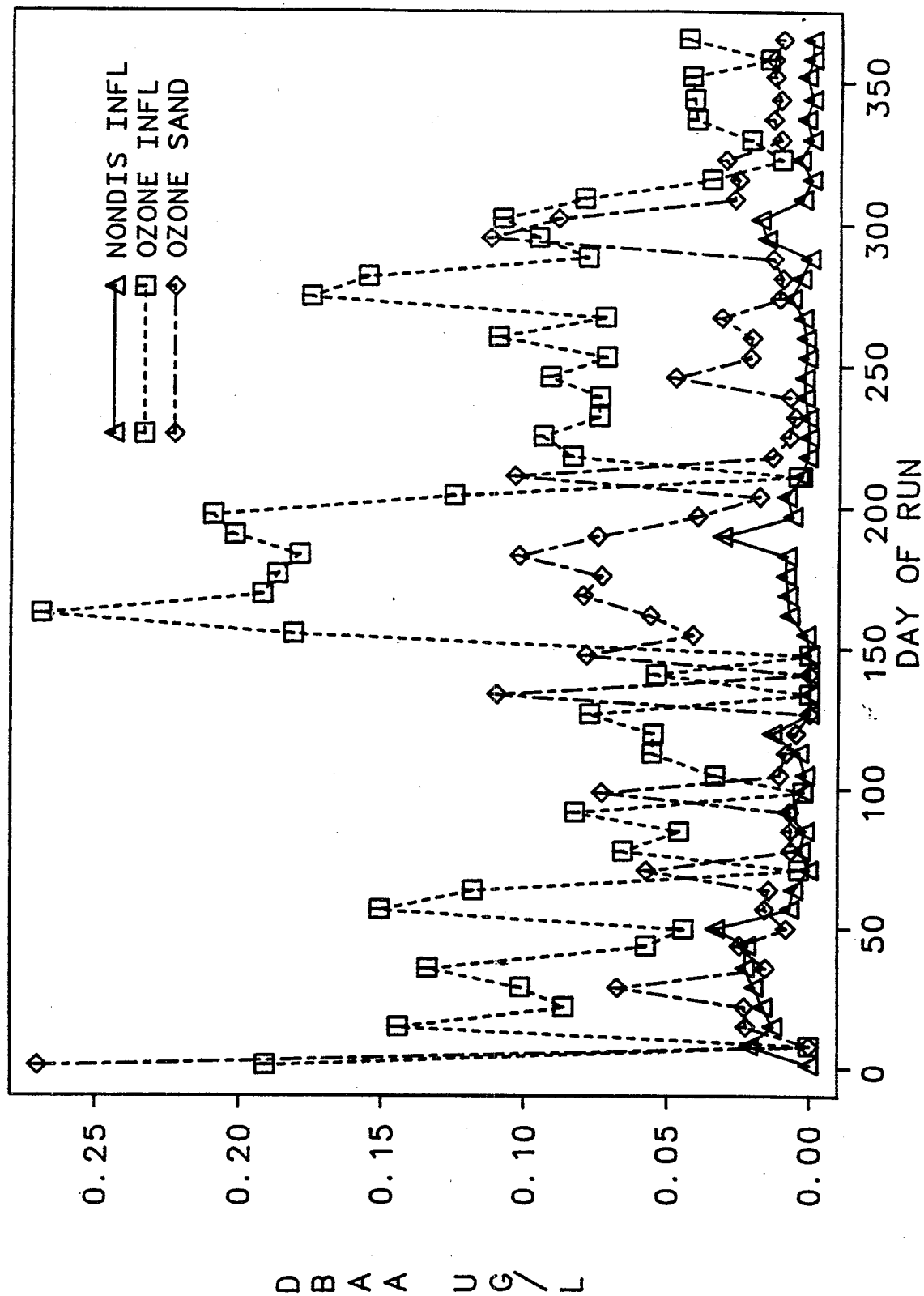


Figure 47. Comparison of the DBAA Levels in the Nondisinfected and Ozone Contact Chamber and Sand Column Effluents.

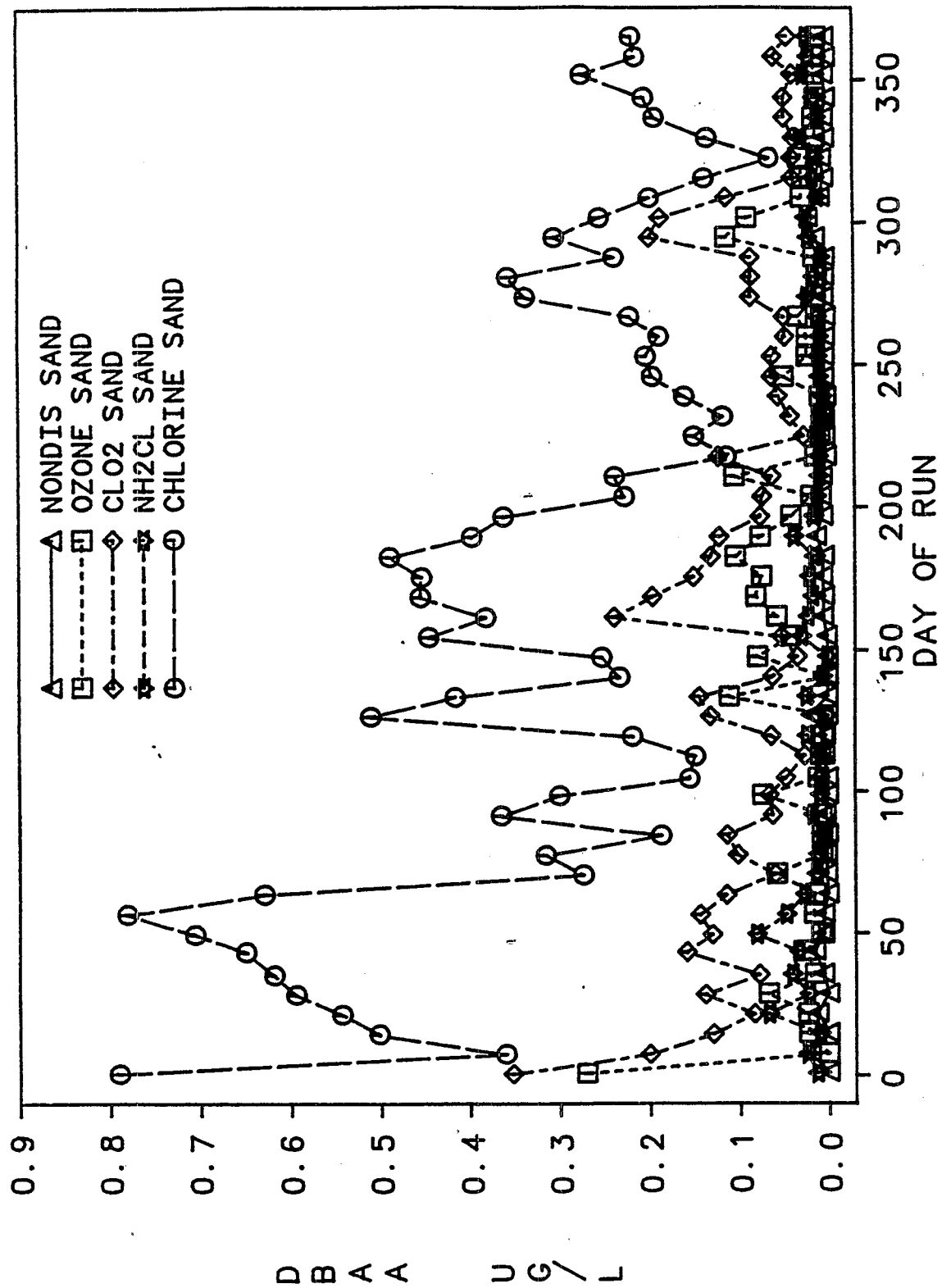


Figure 48. Comparison of the DBAA Levels in the Sand Column Effluent of each Process Stream.

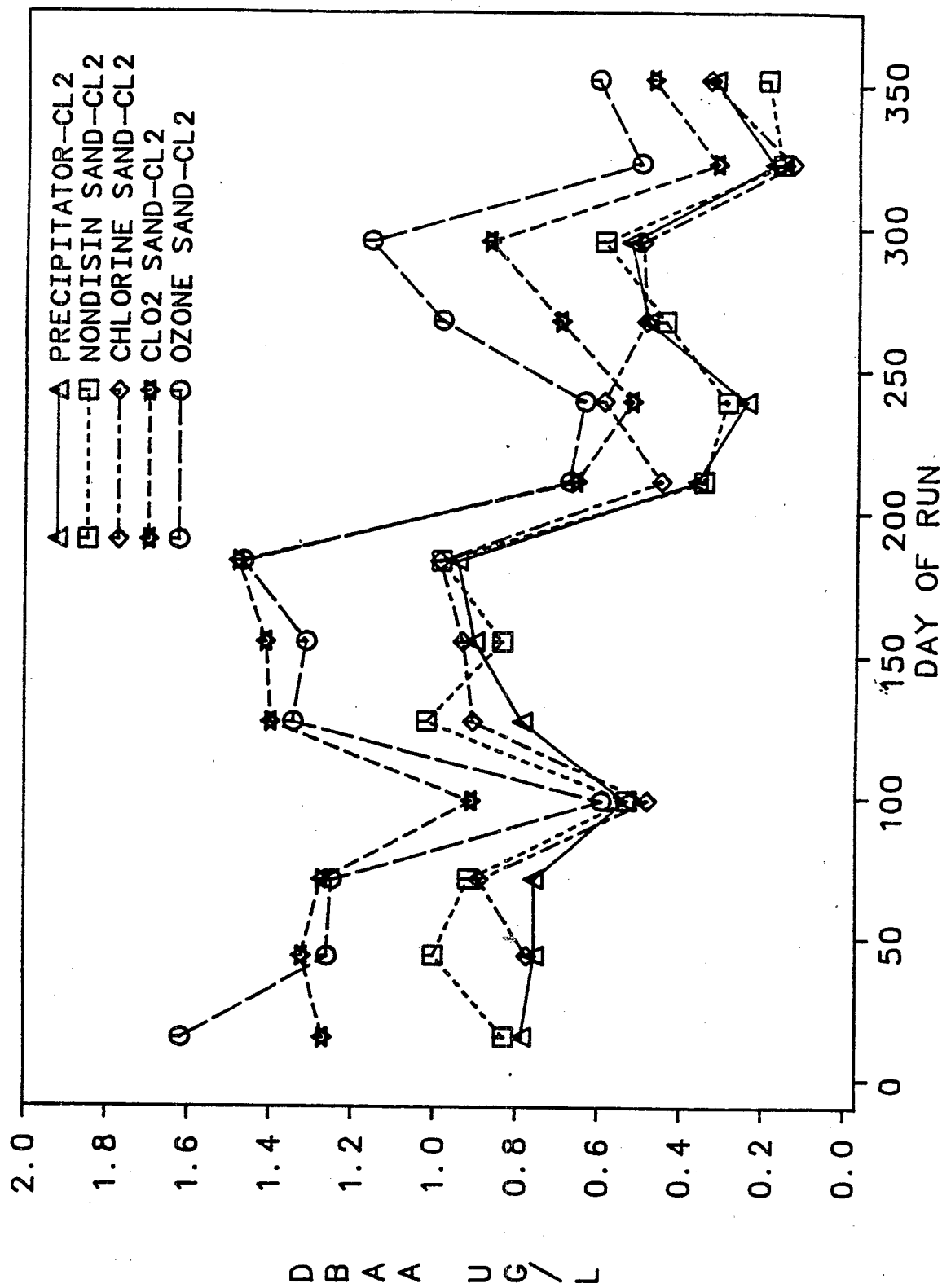


Figure 49. Comparison of the DBAA-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

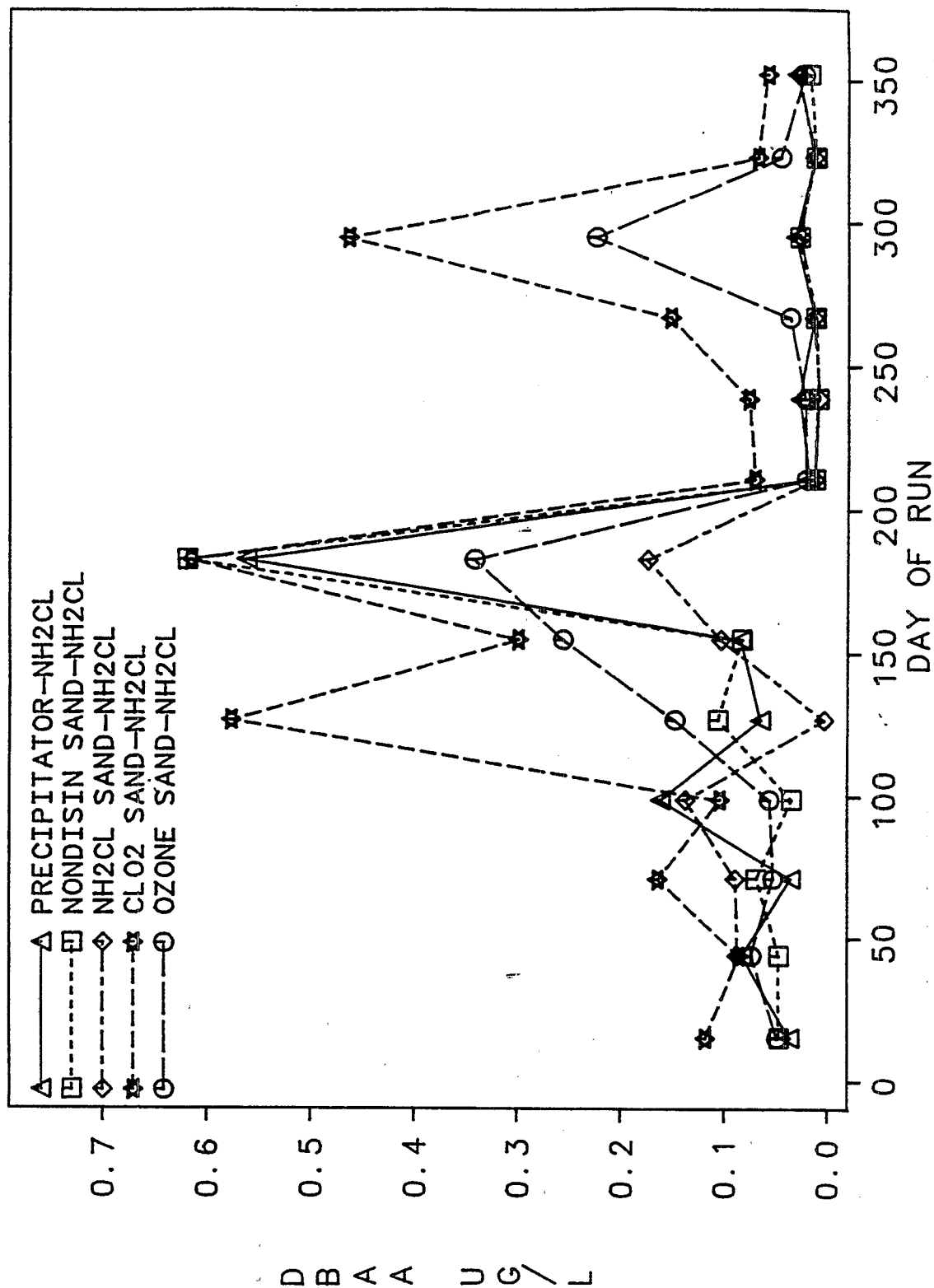


Figure 50. Comparison of the DBAA-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

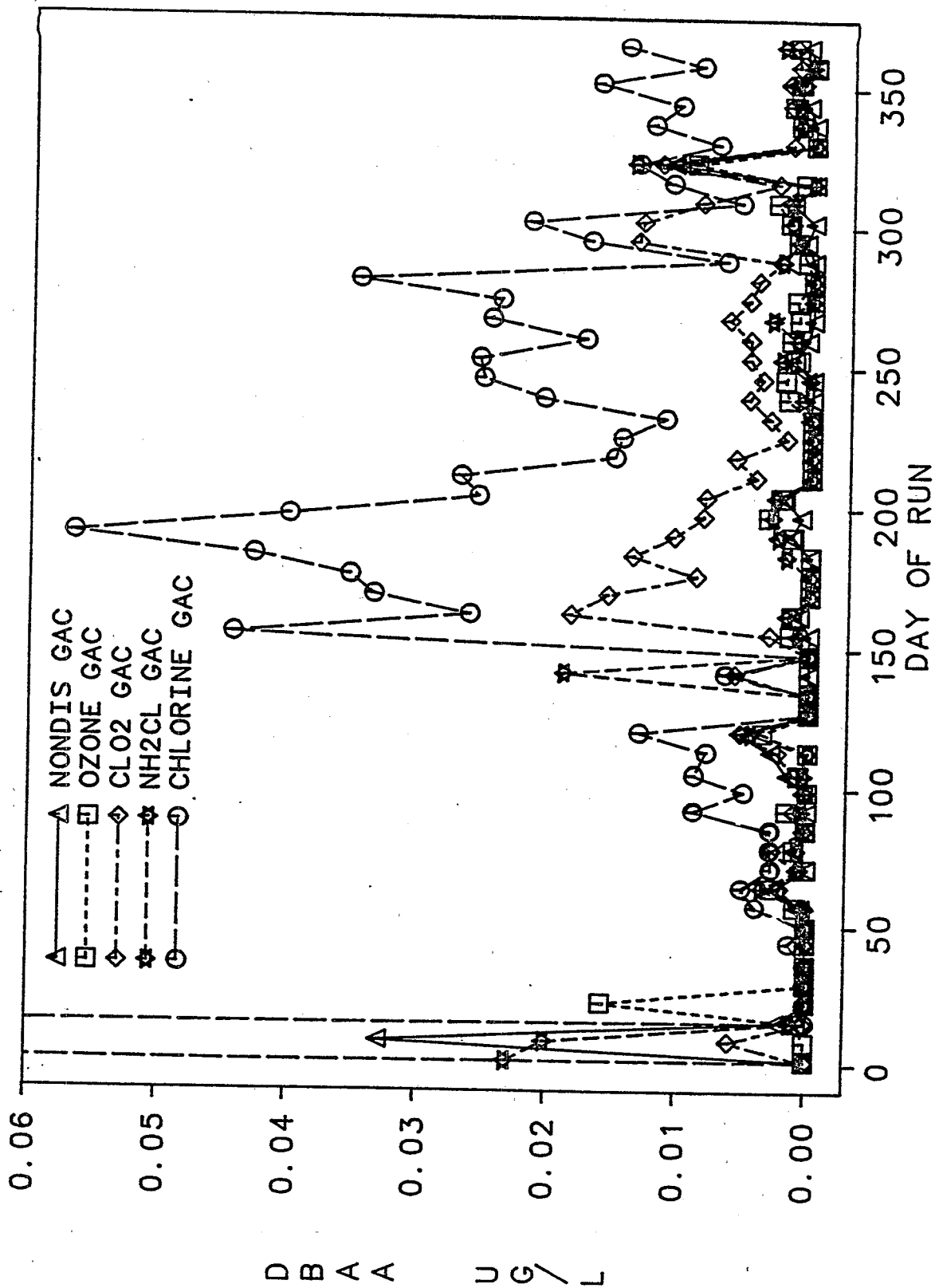


Figure 51. Comparison of the DBAA Levels in the GAC Column Effluent of each Process Stream.

these GAC columns reached apparent steady state about day 200 with respective average steady-state removals of 92 and 93% and average effluent concentrations of 0.017 and 0.005 ug/L. The average GAC effluent concentrations observed across the operational period for the nondisinfected, ozone, and chloramine process streams were 0.001, 0.001, and 0.002 ug/L. Similar GAC breakthrough profiles were observed for DBAA-Cl<sub>2</sub> in all process streams with a very rapid breakthrough to an apparent steady state prior to day 50 (Figure 52). DBAA-Cl<sub>2</sub> steady-state effluent concentrations averaging 0.97, 1.25, 1.13, 1.03 and 0.96 ug/L were observed for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine GAC columns, respectively. These DBAA-Cl<sub>2</sub> levels were 59, 30, 19, and 55 percent greater than those of similarly treated sand filter effluents in the nondisinfected, ozone, chlorine dioxide, and chlorine process streams. No explanation for this increase was apparent. Chloramine treatment of GAC filtered water followed by 5-day storage resulted in average DBAA-NH<sub>2</sub>Cl concentrations of 0.02, 0.11, 0.17, 0.12, and 0.08 ug/L for the nondisinfected ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively (Figure 53). The cause of the relatively erratic data obtained for the chloramine treated samples could not be determined and may have resulted from slight variations in free chlorine contact.

Bromoacetic acid was also a minor component of the total haloacetic acid concentration ranging from nondetectable in many samples to a maximum average concentration of 0.25 ug/L in the chlorine sand column effluent and 1.5 ug/L in the terminal free chlorine formational potential determinations (BAA-Cl<sub>2</sub>). Like chloroacetic acid, the low-level BAA data obtained was considerably erratic due to interference from other chromatographic peaks, between which BAA eluted, with quantitation dependent on somewhat subjective integration. In many instances, BAA could not be quantitated due to variations in chromatographic conditions. BAA was detected at a frequency of only 60% in the influent of the pilot column system at an approximate concentration of 0.01 ug/L. The frequency of detection and approximate average concentration in the contact chamber and sand column effluents were very similar for all process streams (Figure 54) except that of ozone, with 95% and 0.10 ug/L for the chlorine dioxide process stream, 55% and 0.02 ug/L for the chloramine process stream, and 85% and 0.25 ug/L for the chlorine process stream. BAA was detected in the ozone contact chamber effluent at a frequency of 96% and an average concentration of 0.22 ug/L (Figure 55), while that for the ozone sand column was 88% and 0.07 ug/L suggesting that some biodegradation had occurred. BAA was detected in less than 50% of the GAC effluent samples with breakthrough to an apparent steady-state occurring on approximately day 120 for all locations (Figure 56). The BAA levels after steady-state were below 0.02 ug/L on all GAC



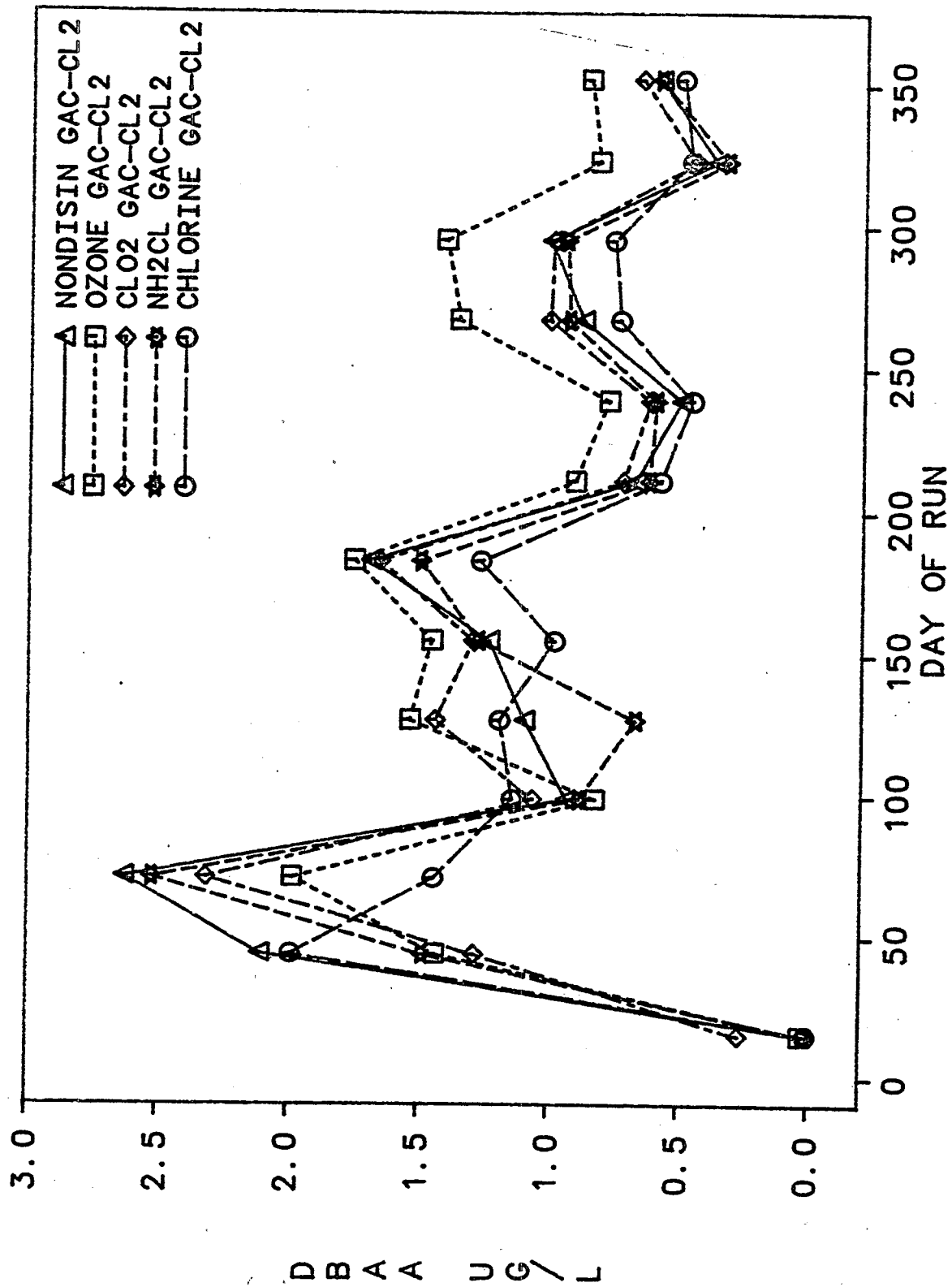


Figure 52. Comparison of the DBAA-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

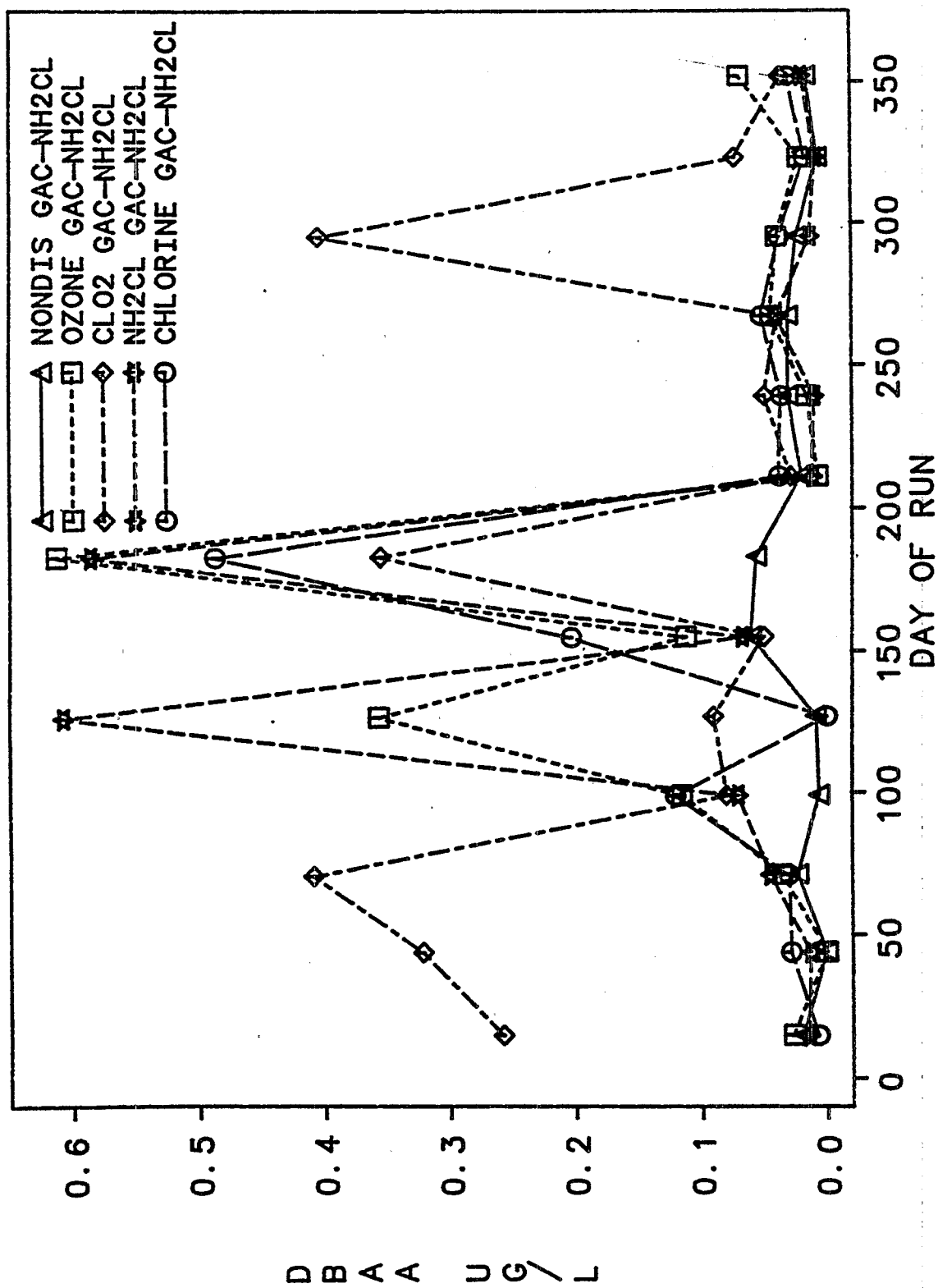


Figure 53. Comparison of the DBAA-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

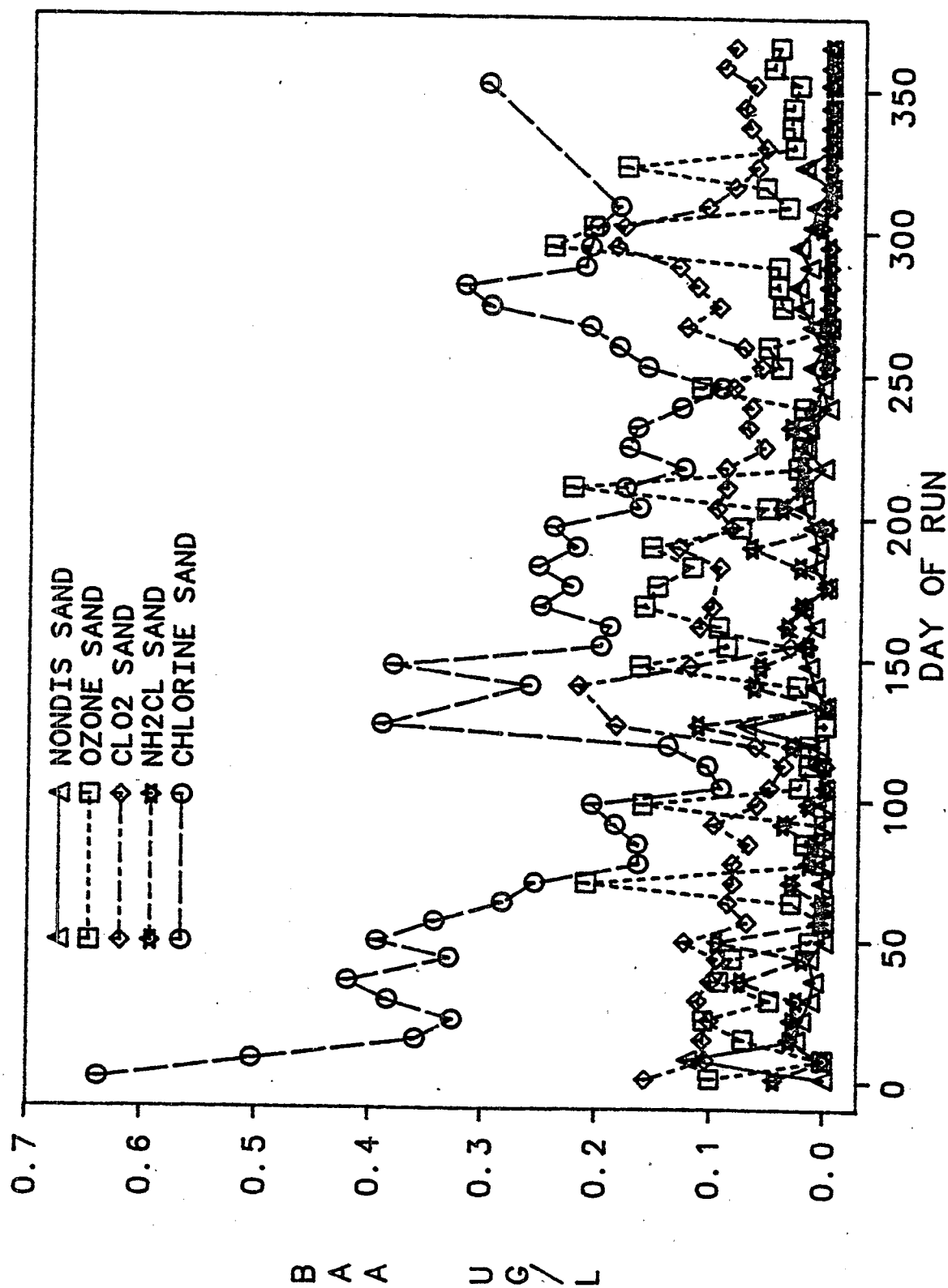


Figure 54. Comparison of the BAA Levels in the Sand Column Effluent of each Process Stream.

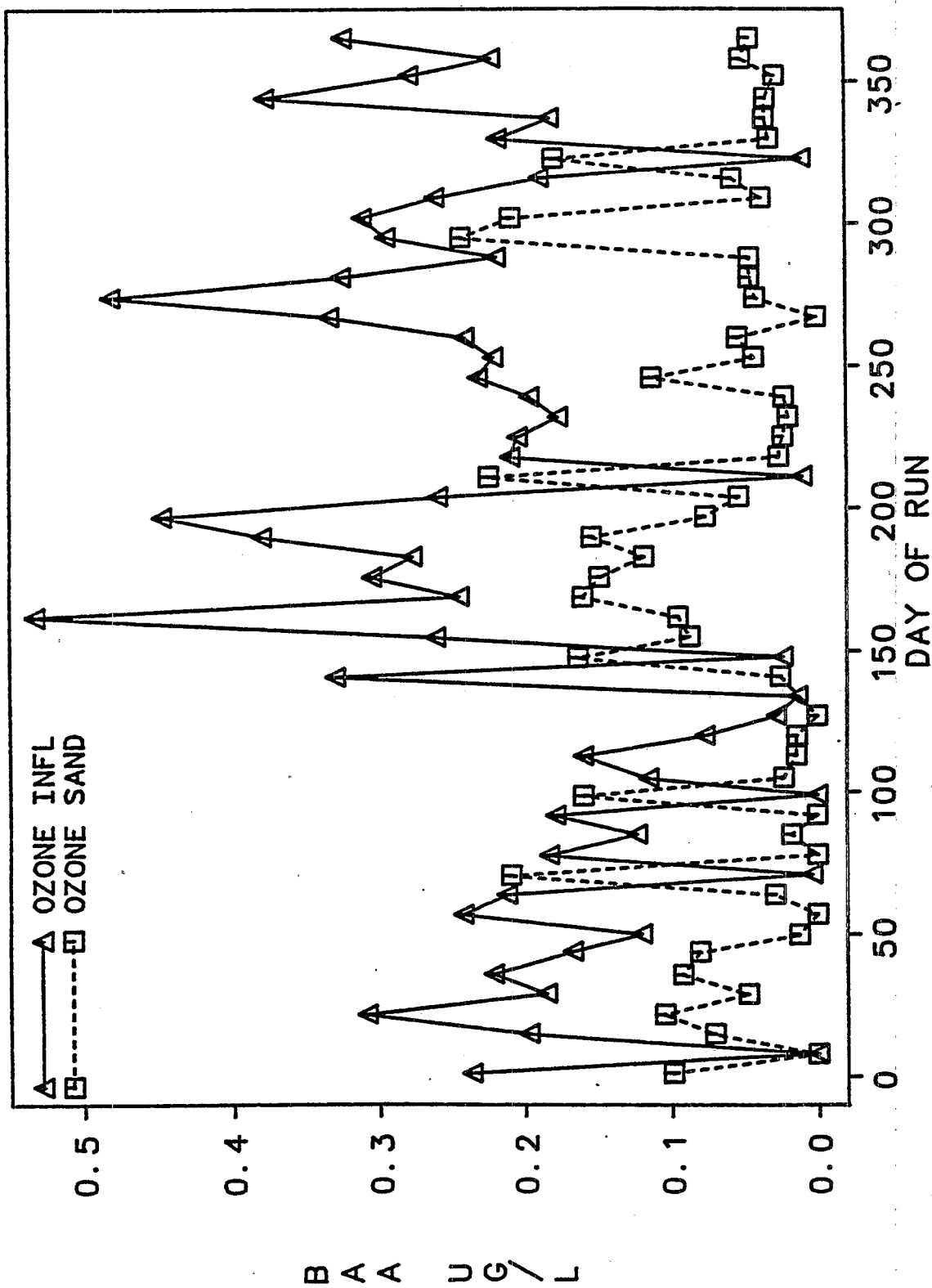


Figure 55. Comparison of the BAA Levels in the Ozone Contact Chamber and Sand Column Effluents.

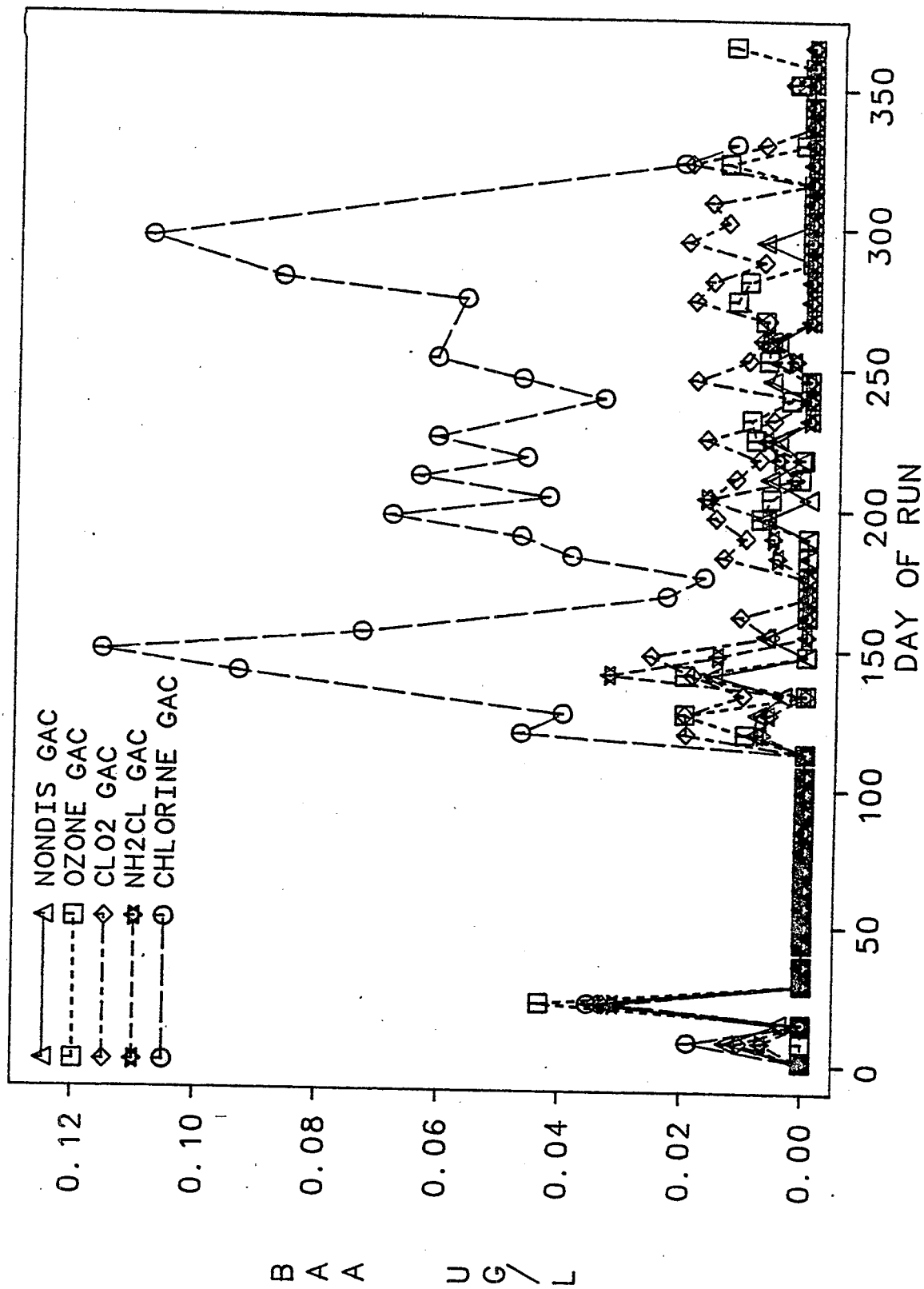


Figure 56. Comparison of the BAA Levels in the GAC Column Effluent of each Process Stream.

effluents except that of the chlorine process stream which averaged approximately 0.05 ug/L. A greater number of interferences with BAA quantitation occurred in all formation potential samples such that only 20-60% of the data was quantifiable at all locations. From the data obtained, it would appear that all process streams exhibited similar BAA-Cl<sub>2</sub> and BAA-NH<sub>2</sub>Cl levels. For BAA-Cl<sub>2</sub>, quantifiable data ranged from 0.5-3 ug/L in the sand effluents while that for the GAC effluents ranged from 0.4-1.5 ug/L. Comparable quantifiable data for BAA-NH<sub>2</sub>Cl ranged from 0.02-0.5 ug/L both before and after GAC filtration.

#### Chloral Hydrate (CH)--

Chloral hydrate (CH) was formed predominantly in the chlorine process stream with an average contact chamber effluent concentration of 2.9 ug/L which increased 55% to 4.5 ug/L across the sand column due to an additional 30 min of chlorine contact time (Figure 57). The CH levels in the effluent of the chloramine contact chamber and sand column were identical averaging 0.25 ug/L. CH was detected intermittently in the contactor chamber and sand column effluents of the chlorine dioxide, ozone, and nondisinfected process streams at respective frequencies of 56, 32, and 26 percent with similar average concentrations ranging from 0.01-0.07 ug/L. Treatment of the sand column effluents with free chlorine and storage for 5 days produced CH-Cl<sub>2</sub> levels averaging 79, 55, 45, and 75 ug/L (Figure 58) for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams, respectively. Treated precipitator water had essentially an identical CH-Cl<sub>2</sub> content as the nondisinfected sand column effluent. Similar treatment with chloramine resulted in average CH-NH<sub>2</sub>Cl levels of 0.03 ug/L for the nondisinfected and ozonated sand column effluents, and, 0.08 & 0.3 ug/L for the chloramine and chlorine dioxide sand column effluents (Figure 59).

Granular activated carbon filtration resulted in 100 percent removal of CH throughout the one year project period in all process streams. Essentially no chloral hydrate was detected in any GAC effluent greater than 0.001 ug/L. Similar breakthrough profiles for terminal CH-Cl<sub>2</sub> were observed across the GAC columns in each process stream (Figure 60). Steady-state was reached about day 150 for CH-Cl<sub>2</sub> in all process streams. Steady-state removals relative to the sand column effluents ranged from 42% and 50% for the chlorine dioxide and chlorine GAC columns, to 60% for the nondisinfected and ozone GAC columns with respective average steady state CH-Cl<sub>2</sub> concentrations of 35, 41, 36, and 28 ug/L. Treatment of the GAC column effluents with chloramine followed by 5-day storage produced essentially the same CH-NH<sub>2</sub>Cl levels in each process stream ranging from 0.1-0.3 ug/L (Figure 61). These levels were essentially the same as those obtained for the similarly treated sand column effluents.

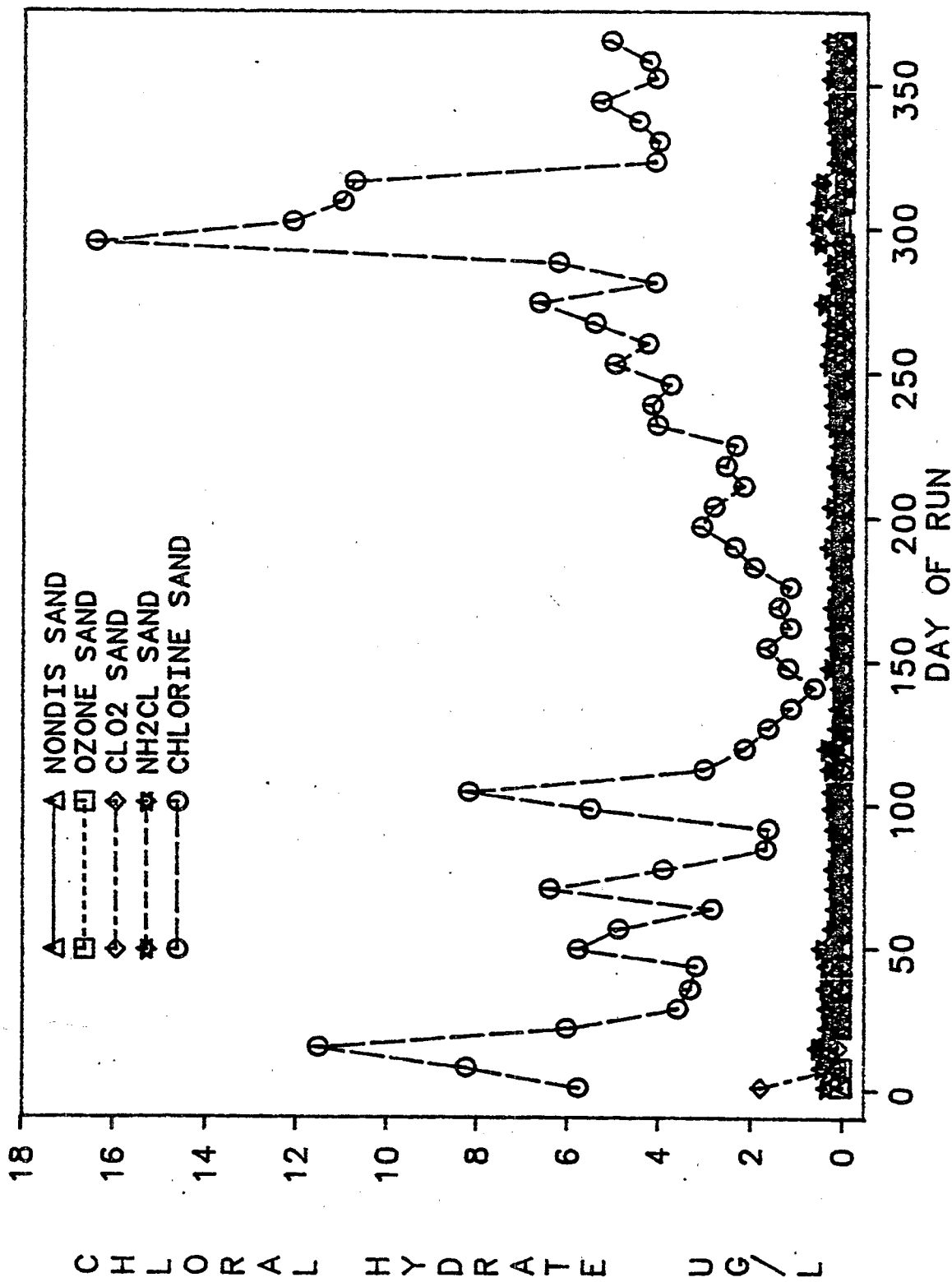


Figure 57. Comparison of the CH Levels in the Sand Column Effluent of each Process Stream.

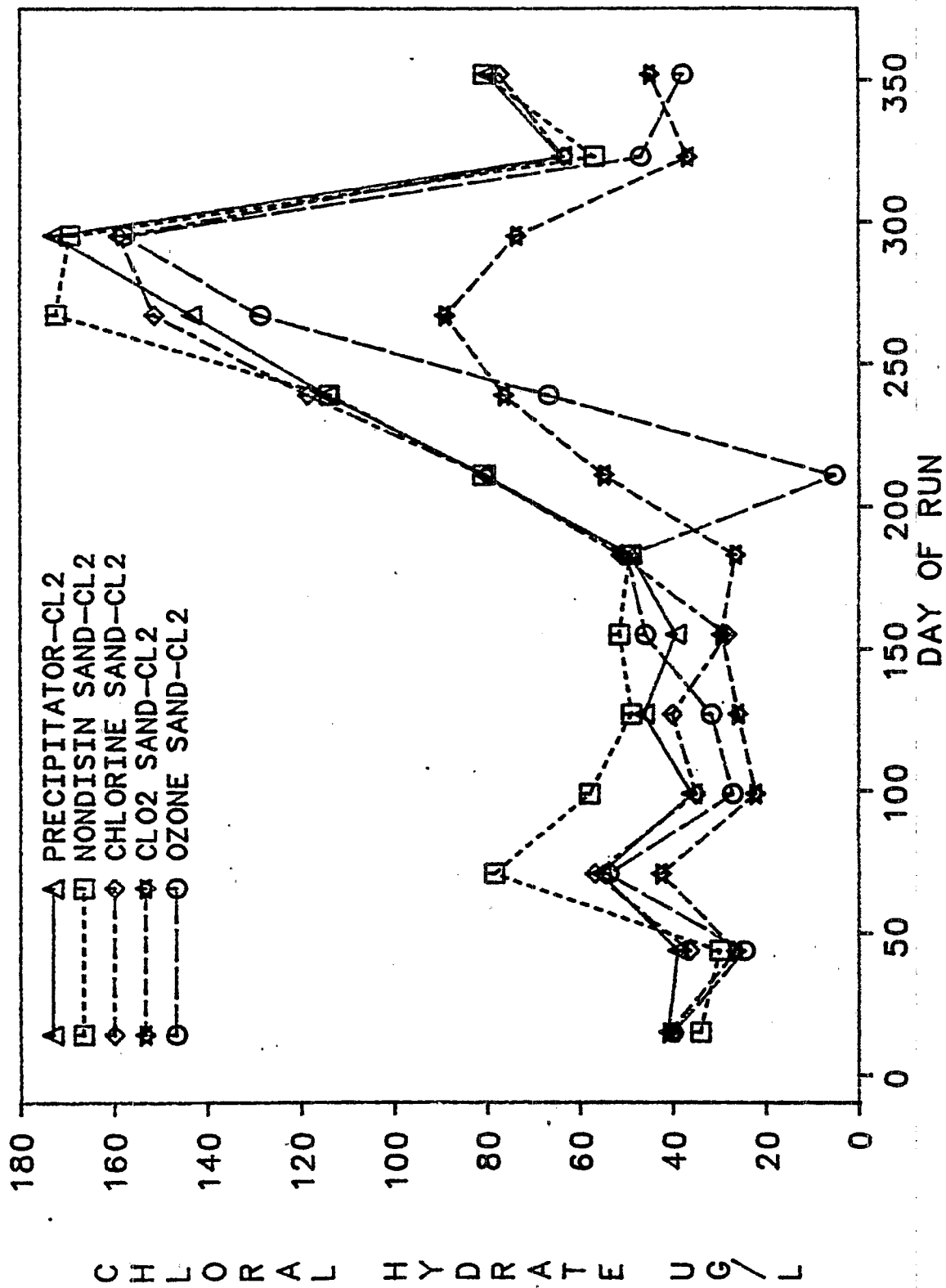


Figure 58. Comparison of the CH-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.



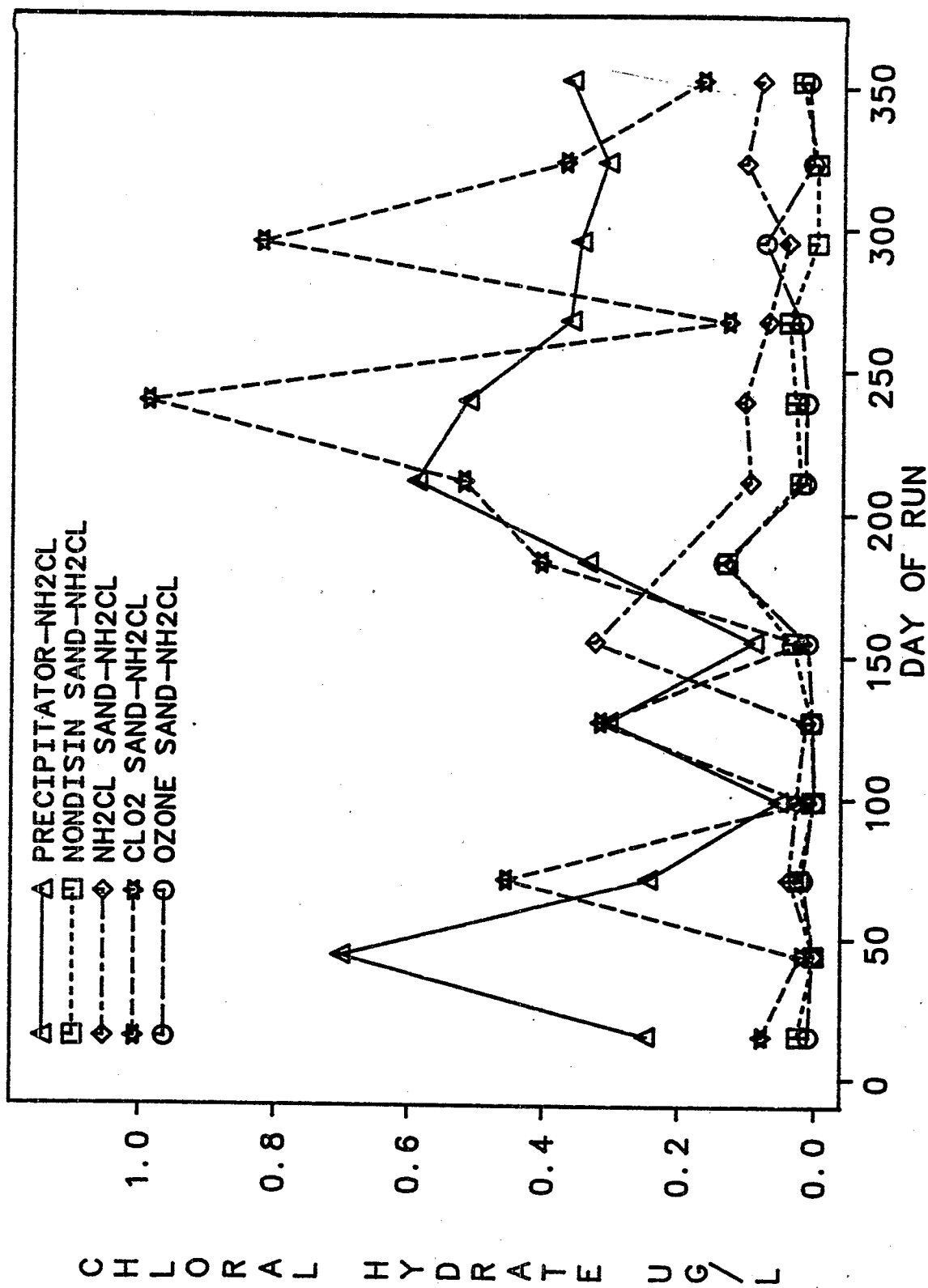


Figure 59. Comparison of the CH-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

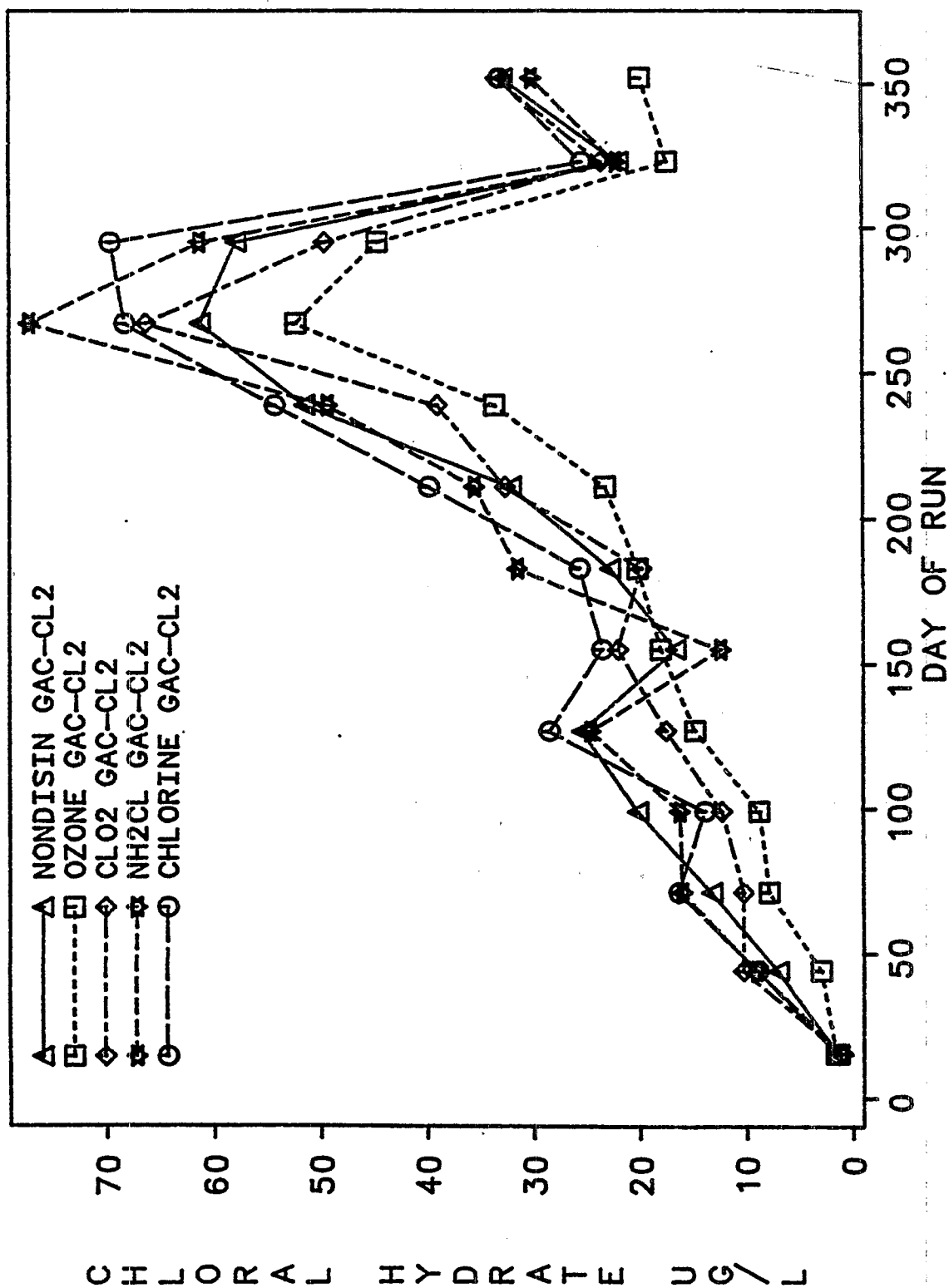


Figure 60. Comparison of the CH-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

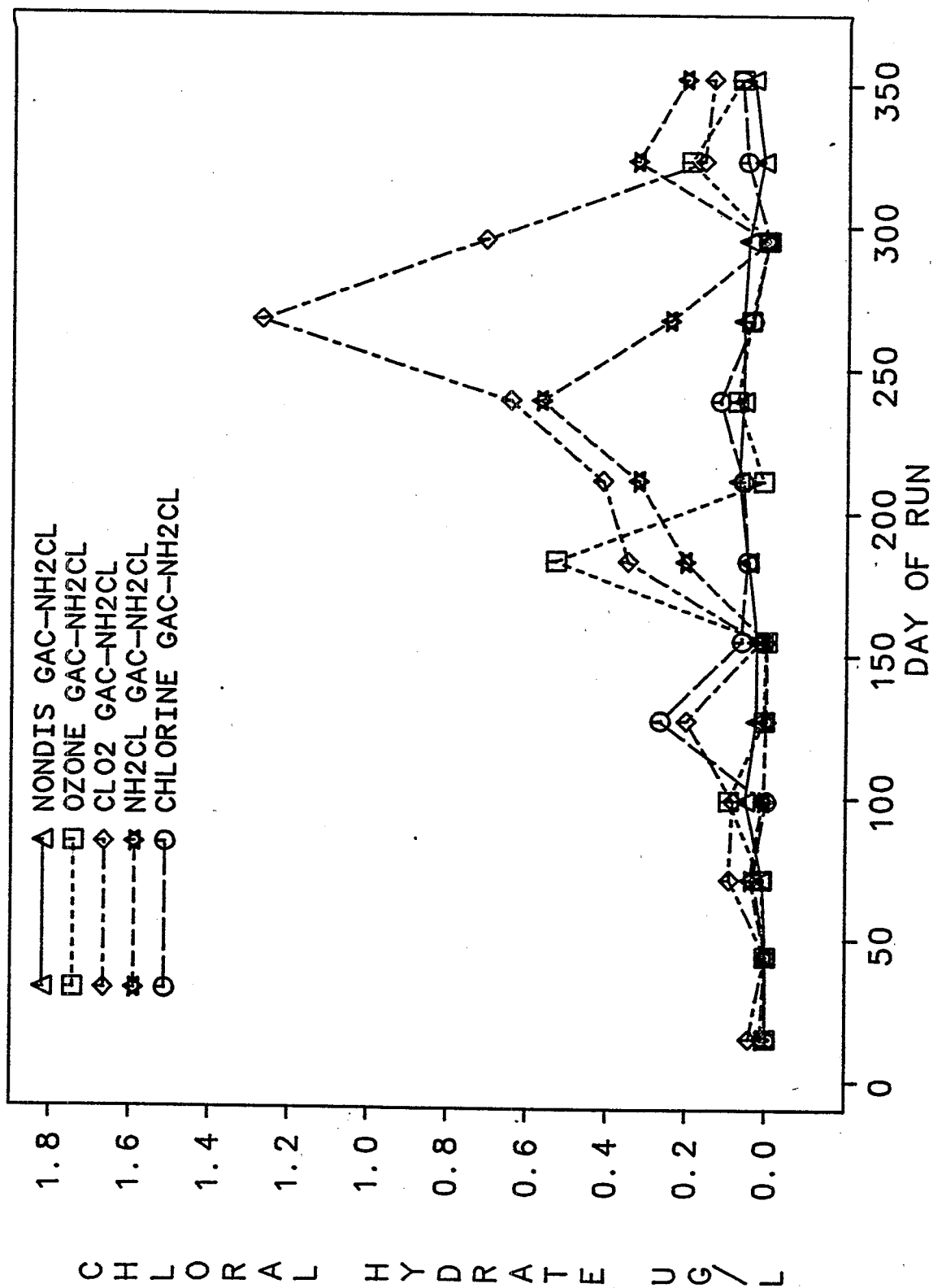


Figure 61. Comparison of the CH-NH<sub>2</sub>CL Levels in the GAC Column Effluent of each Process Stream.

## Haloacetonitriles--

Relatively low levels of the haloacetonitriles were formed across each process stream with the chlorine process stream producing the highest levels averaging 3.1 ug/L total haloacetonitriles. Levels of haloacetonitriles averaging less than 1 ug/L were observed across the other process streams. The predominant haloacetonitrile (HAN) was dichloroacetonitrile (DCAN) followed by bromochloroacetonitrile (BCAN), dibromoacetonitrile (DBAN), and trichloroacetonitrile (TCAN). No consistent breakthrough of the HANs was observed through any GAC column except that of the chlorine process stream, which was still removing over 95% of the influent HANs by the end of the one year operational period.

Dichloroacetonitrile (DCAN) was primarily formed in the chlorine process stream with an average influent concentration of 1.5 ug/L which increased 30% to 1.9 ug/L across the chlorine sand column. The contact chamber and sand column effluents of the chloramine, chlorine dioxide, and nondisinfected process streams were essentially identical with respective sand column effluent concentrations averaging 0.2, 0.1, and 0.05 ug/L (Figure 62). Some evidence of biodegradation across the ozone sand column was observed with respective average influent and effluent concentrations of 0.07 & 0.02 ug/L. Treatment of the chlorine sand column effluent with additional free chlorine and subsequent 5-day storage produced an average DCAN-Cl<sub>2</sub> concentration of 1.9 ug/L (Figure 63) which was the same as that of DCAN in the sand column effluent indicating that all DCAN precursors had reacted across the chlorine contact chamber and sand column. Similar treatment of the nondisinfected, ozone, and chlorine dioxide sand column effluents produced respective DCAN-Cl<sub>2</sub> levels averaging 1.3, 1.6, & 4.1 ug/L suggesting that significantly higher levels of DCAN precursors were formed by pretreatment with chlorine dioxide. Similar treatment of the sand column effluents with chloramine followed by 5-day storage produced respective average DCAN-NH<sub>2</sub>Cl levels of 0.03, 0.02, 0.21, and 0.04 ug/L for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams (Figure 64). Comparison of these DCAN-NH<sub>2</sub>Cl levels to corresponding DCAN levels present in the sand column effluent indicated that the addition of chloramine had essentially no effect on the DCAN levels of the nondisinfected and ozone sand column effluents while it increased the DCAN in the chlorine dioxide sand column effluent by a factor of three to an average of 0.21 ug/L, again suggesting the formation of DCAN precursors by chlorine dioxide pretreatment. The further addition of chloramine to the chloramine sand column effluent resulted in an average DCAN reduction of approximately 80 percent after 5 days of storage. This reduction was similar to that observed for TOX after 5-day chloramine treatment.

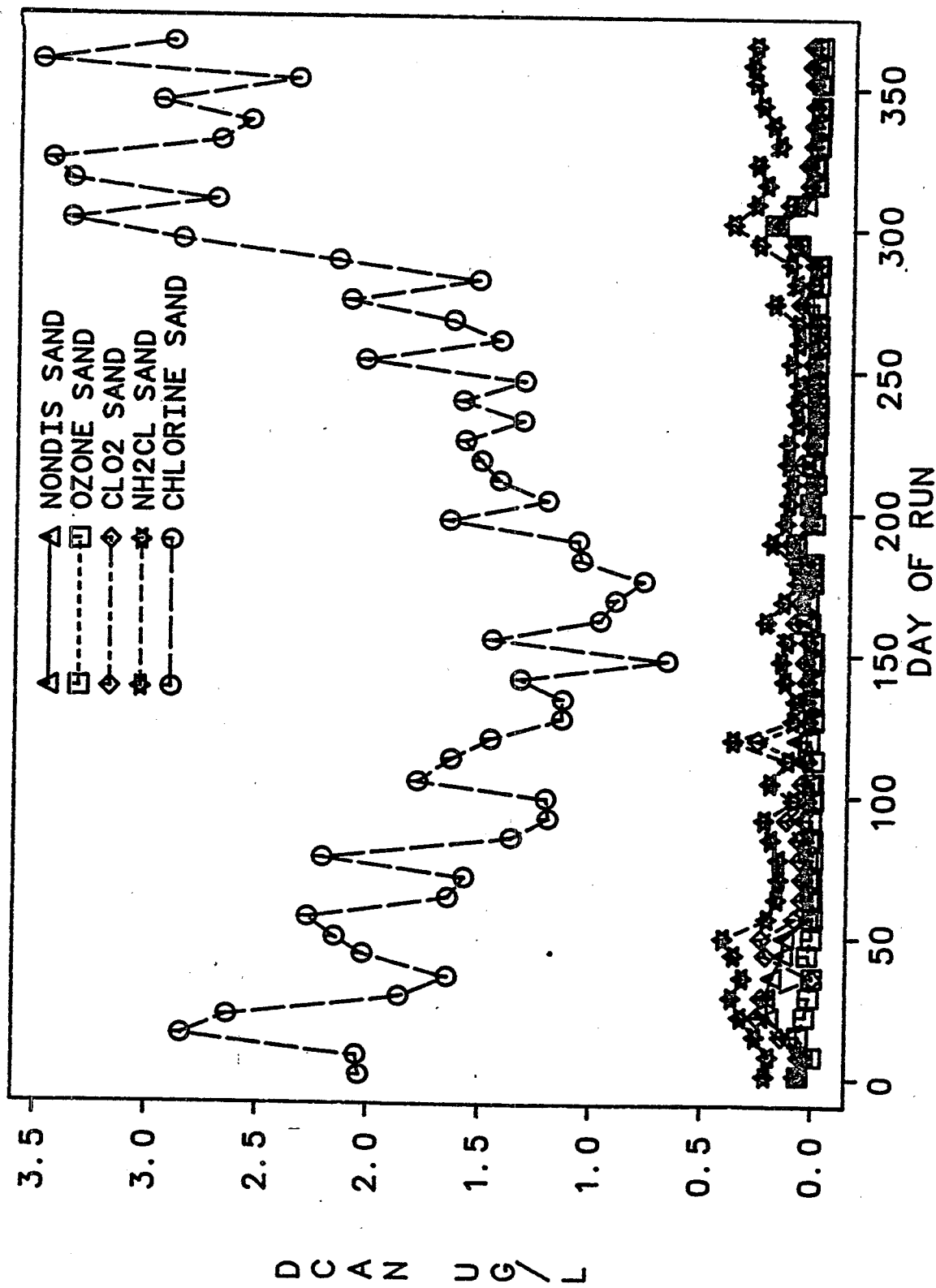


Figure 62. Comparison of the DCAN Levels in the Sand Column Effluent of each Process Stream.

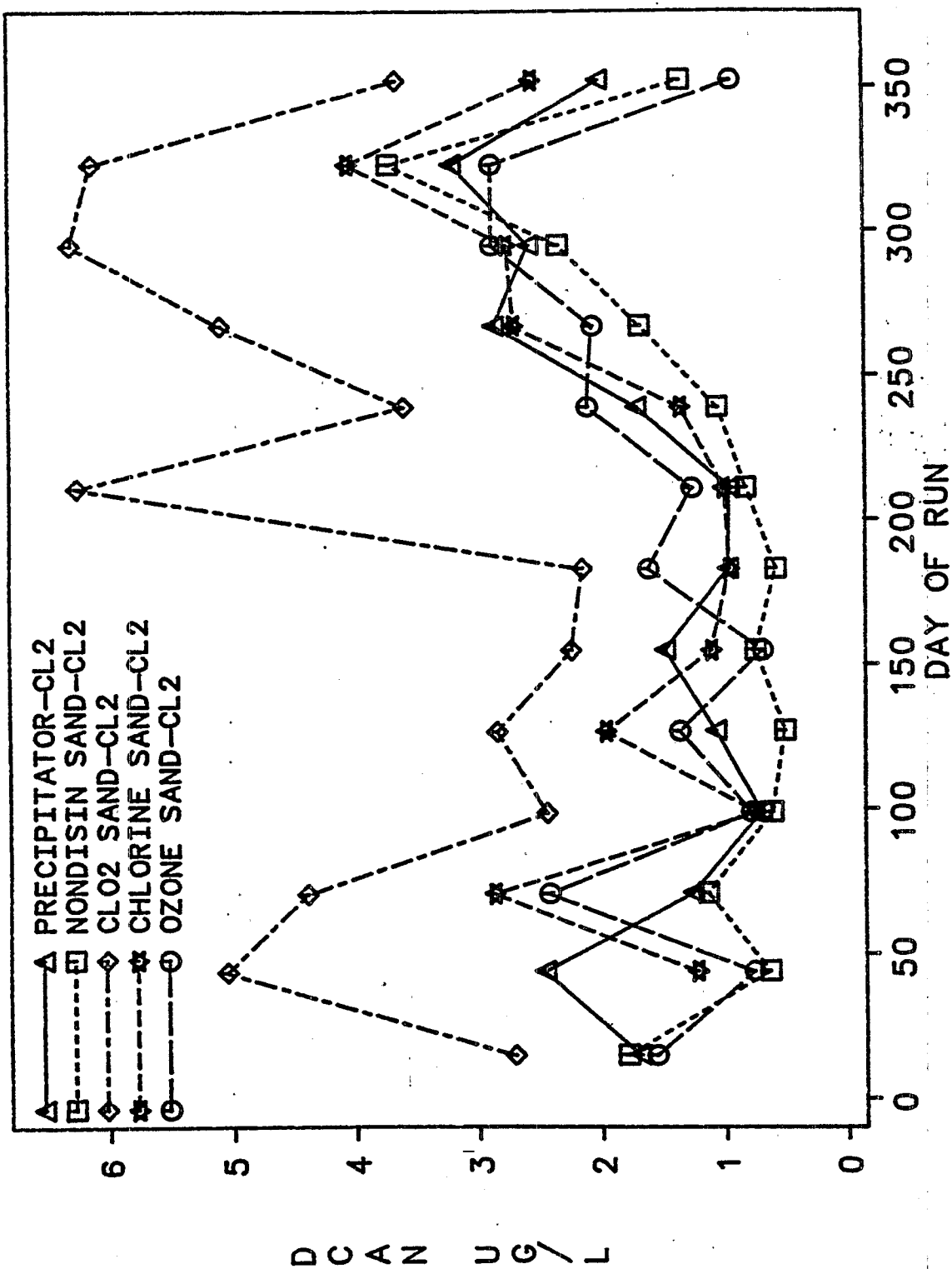


Figure 63. Comparison of the DCAN-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

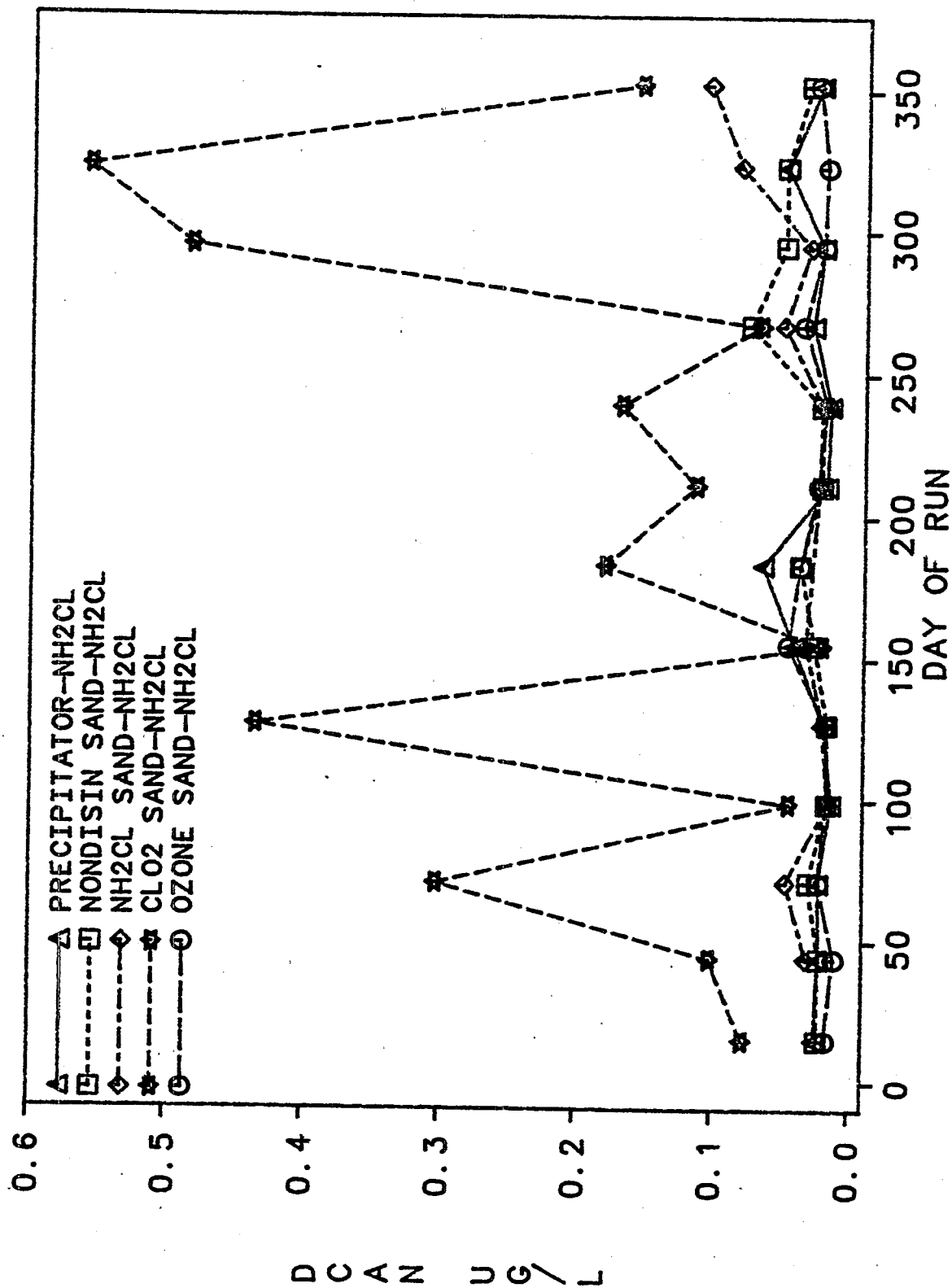


Figure 64. Comparison of the DCAN-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

No consistent breakthrough of DCAN was observed across the GAC column of any process stream other than chlorine (Figure 65). Breakthrough on the chlorine GAC column occurred on day 70 with an increasing effluent concentration until steady-state was reached after 140 days of operation. The average effluent concentration after reaching steady-state was 0.05 ug/L for an average steady-state removal of 98 percent. Treatment of the GAC column effluents with free chlorine and storage for 5 days resulted in average DCAN-Cl<sub>2</sub> of 2.4, 1.1, 2.9, 2.3, and 2.0 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively (Figure 66). Comparison of these data with those of the similarly treated sand column effluents indicated that in the ozone and chlorine dioxide process streams, saturation was reached on approximately days 140 & 150 with subsequent effluent levels essentially equal to their respective influent levels. In contrast, after a relatively rapid precursor breakthrough to saturation on day 80, DCAN-Cl<sub>2</sub> levels in the nondisinfected GAC effluent were consistently greater by an average of approximately 80% (Figure 67). A similar anomaly occurred in the chlorine process stream as indicated in Figure 68. The DCAN and terminal DCAN-Cl<sub>2</sub> levels in the sand column effluent were essentially identical indicating that all DCAN precursors present had reacted to form DCAN. Since the DCAN levels in the GAC effluent were essentially zero, the DCAN-Cl<sub>2</sub> levels in the GAC effluent should also have been nonexistent. However, concentrations from 0.5 - 5 ug/L DCAN-Cl<sub>2</sub> were observed in the chlorine GAC effluent. Saturation was reached on day 180 with the DCAN-Cl<sub>2</sub> levels in the chlorine GAC effluent averaging 42% higher than those in the sand column effluent, similar to that observed for the nondisinfected GAC effluent. These increases in precursor concentration were also observed for bromochloroacetonitrile and dibromoacetonitrile, as indicated in subsequent sections, suggesting that these precursors are being formed on or released from the GAC columns.

Treatment of the GAC column effluents with chloramine followed by 5-day storage resulted in average DCAN-NH<sub>2</sub>Cl levels of 0.02, 0.03, 0.2, 0.03, and 0.02 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively (Figure 69). No significant difference between the DCAN-NH<sub>2</sub>Cl levels of the sand and GAC column effluents was observed in any process stream, with the DCAN-NH<sub>2</sub>Cl levels in the chlorine GAC column effluent being essentially identical to those of the chloramine GAC column.

Bromochloroacetonitrile (BCAN) was the second most abundant haloacetonitrile formed primarily in the chlorine process stream with an average contact chamber effluent concentration of 0.70 ug/L which increased 25% to 0.88 ug/L across the chlorine sand column. A similar increase of 35% was observed across the chloramine sand column raising the average concentration from



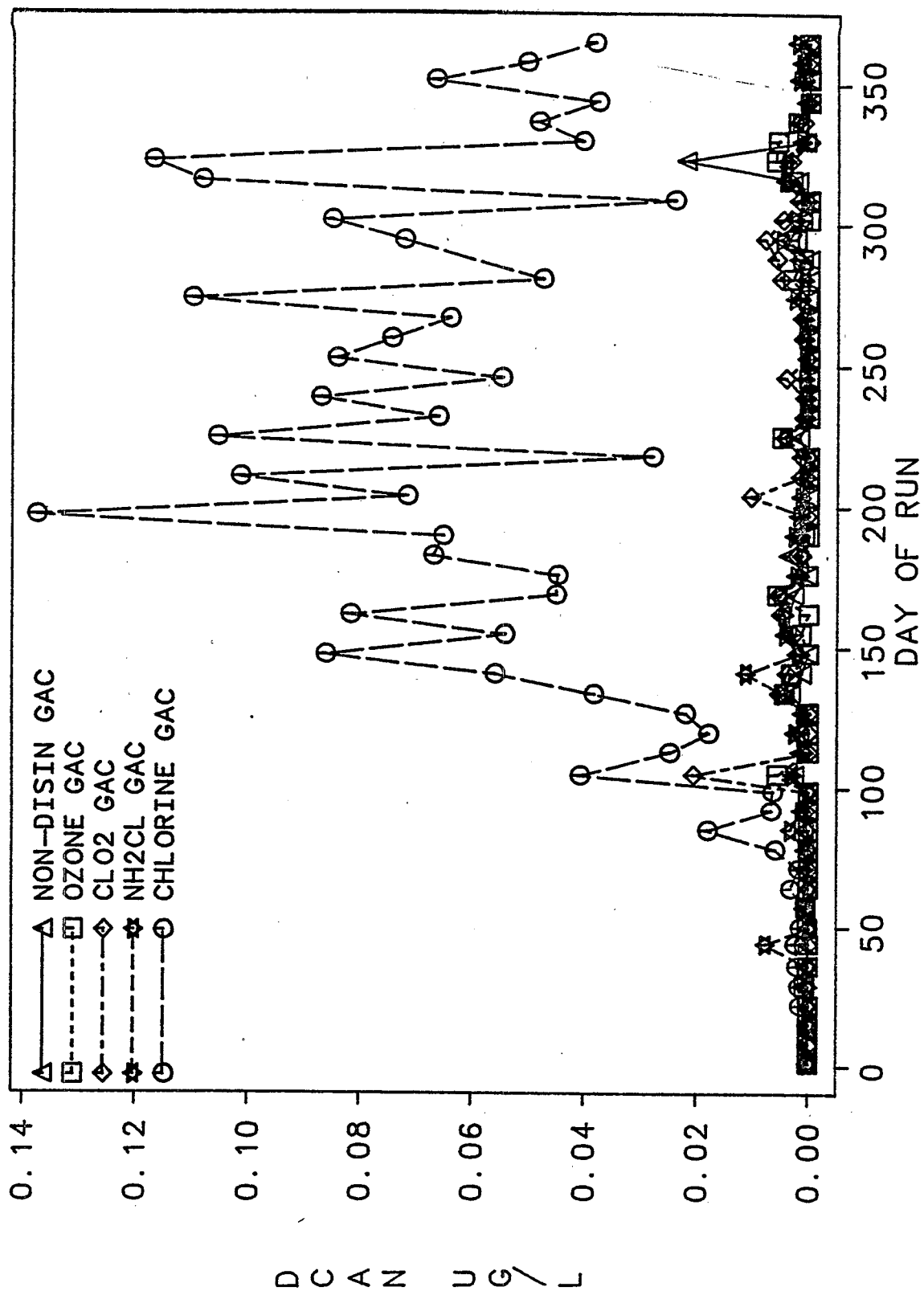


Figure 65. Comparison of the DCAN Levels in the GAC Column Effluent of each Process Stream.

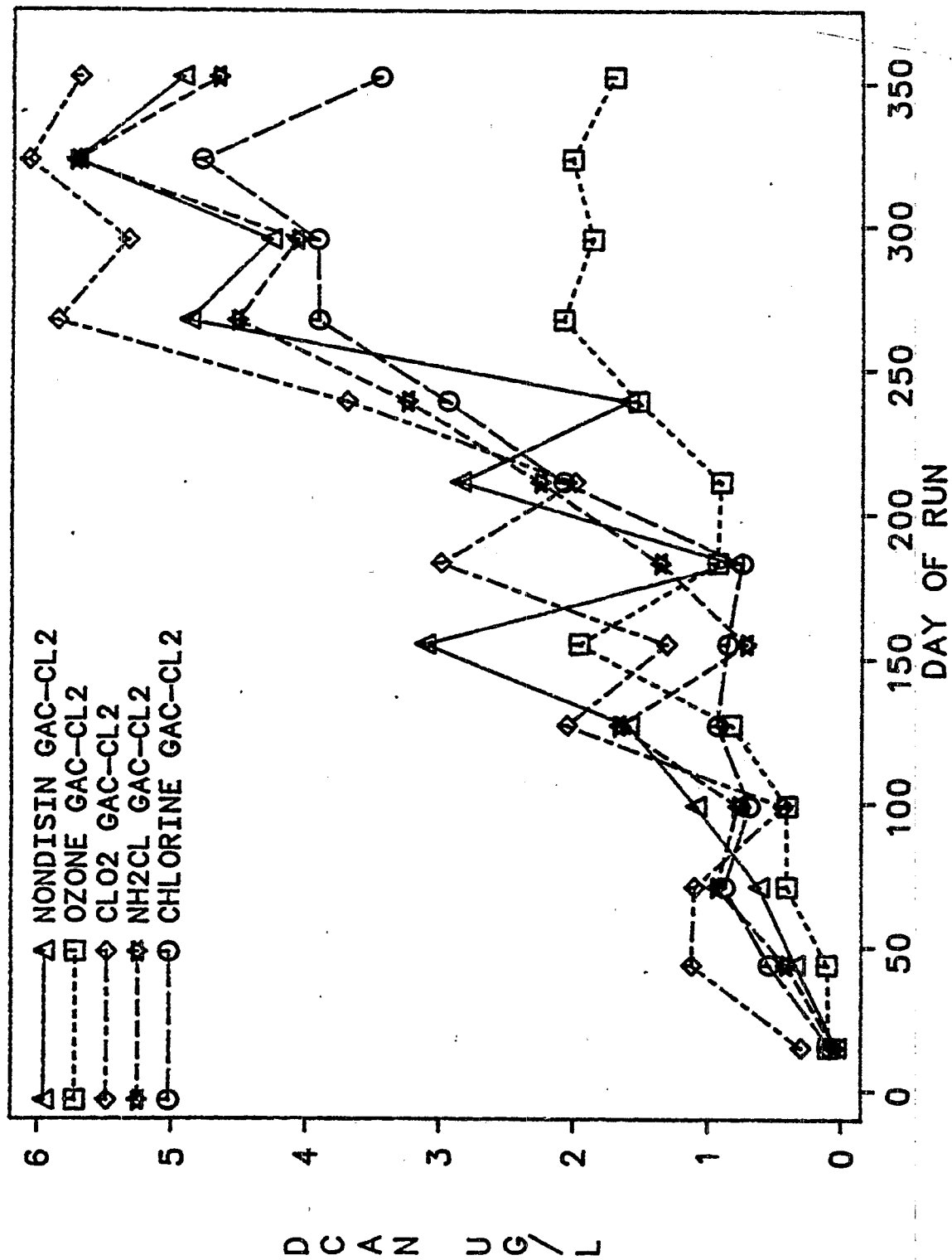


Figure 66. Comparison of the DCAN-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

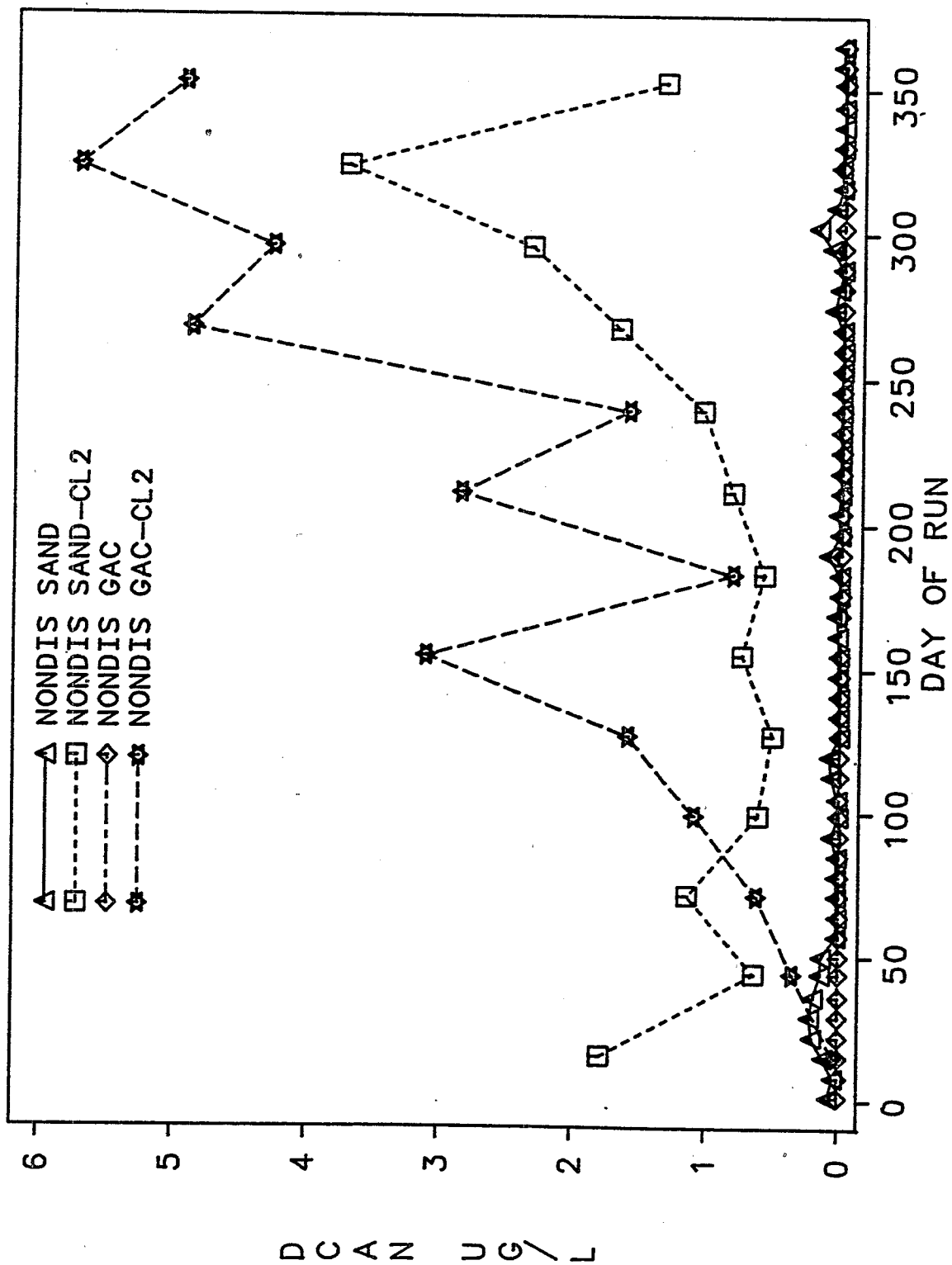


Figure 67. Comparison of DCAN and DCAN-Cl<sub>2</sub> Levels in the Nondisinfected Process Stream.

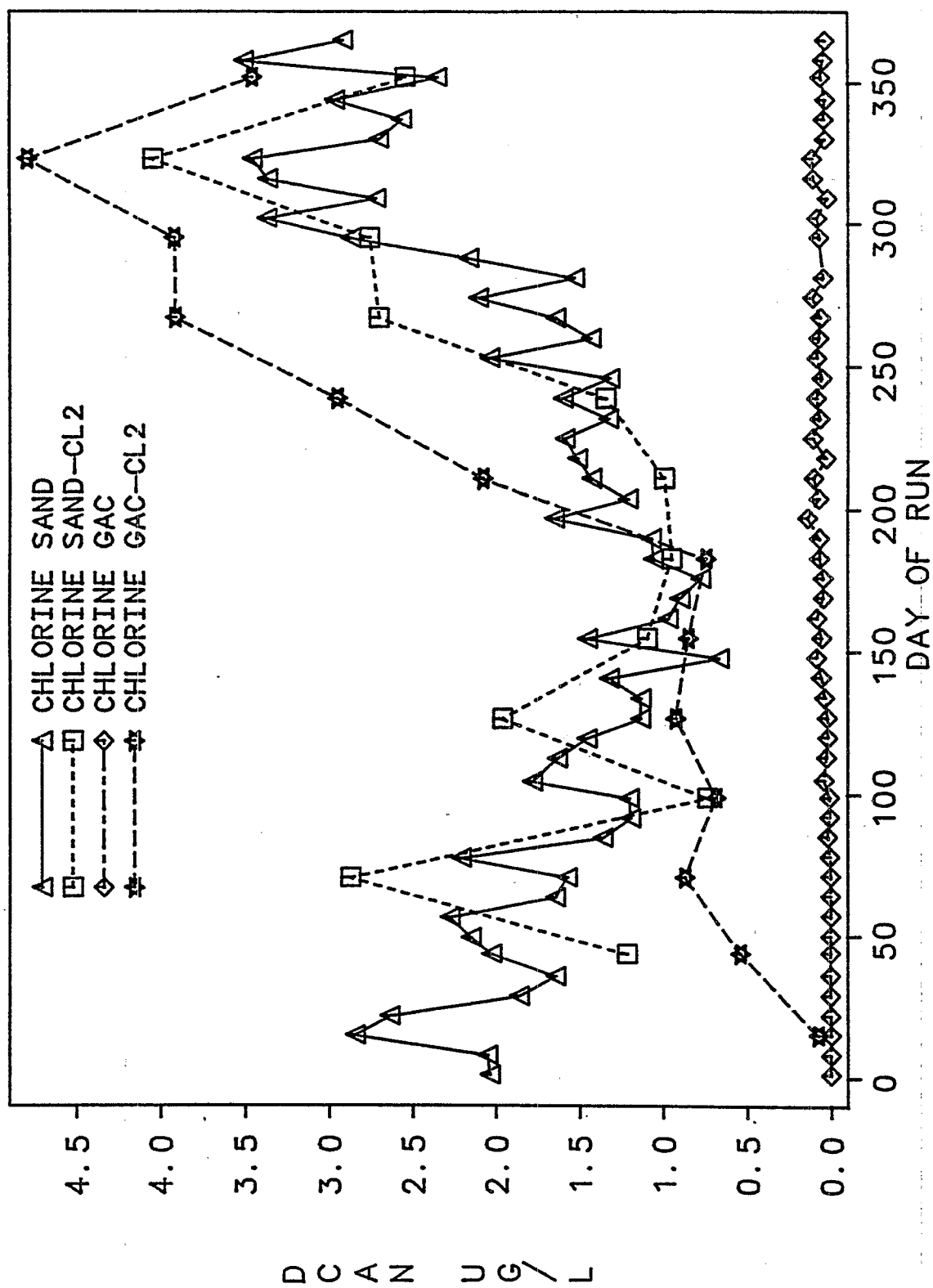


Figure 68. Comparison of DCAN and DCAN-Cl<sub>2</sub> Levels in the Chlorine Process Stream.

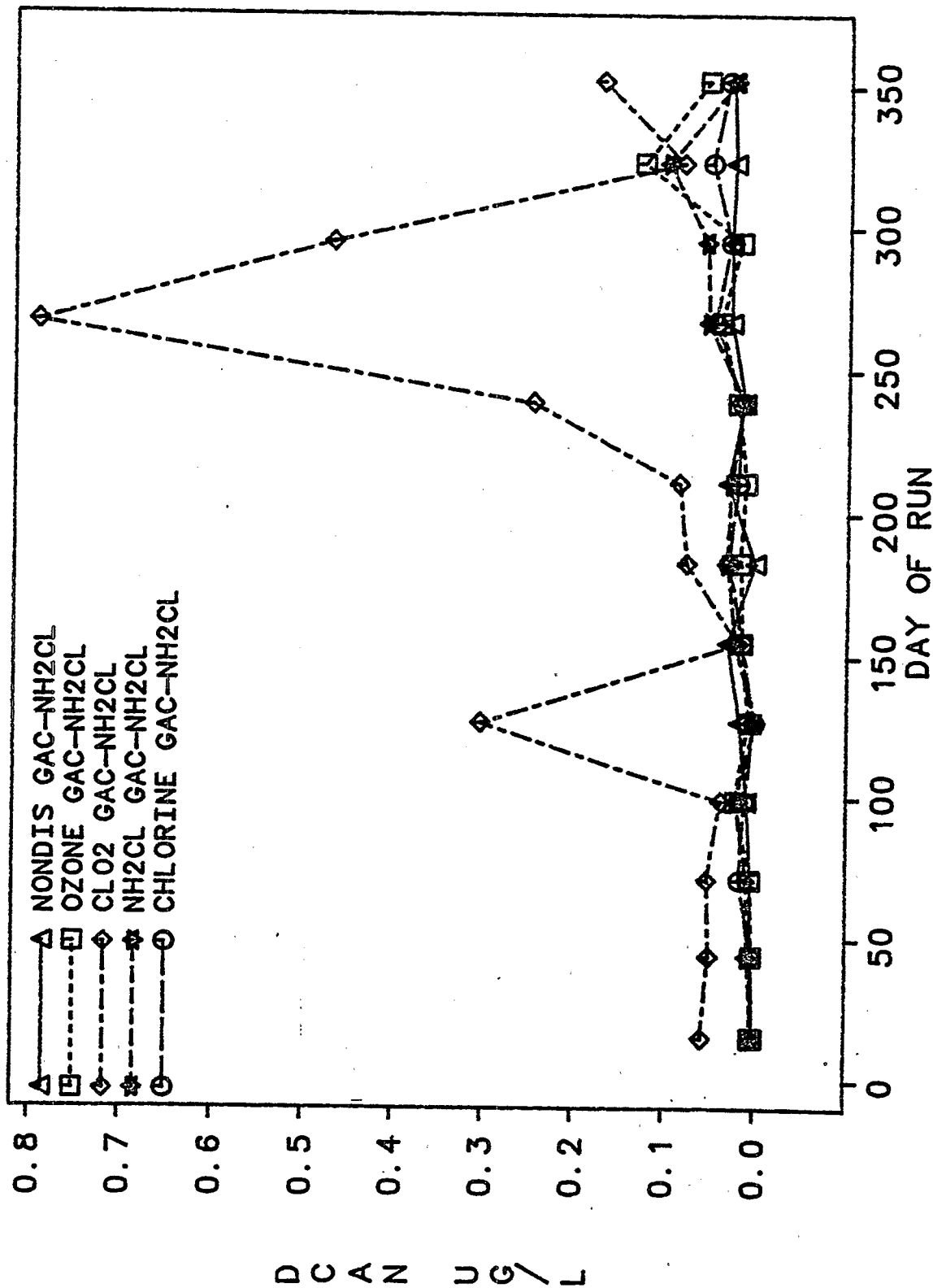


Figure 69. Comparison of DCAN-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

0.031 to 0.042 ug/L. The sand column effluent concentrations of BCAN compared in Figure 70, averaged 0.006, 0.002, 0.019, 0.042, and 0.88 ug/L, respectively, for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams. Evidence of BCAN biodegradation was observed across the nondisinfected and ozone sand columns. An average removal of 80% was observed across the ozone sand column with average influent and effluent concentrations of 0.014 and 0.002 ug/L. A lower removal of 20% occurred across the nondisinfected sand column with average influent and effluent concentrations of 0.012 and 0.006 ug/L. No change in BCAN concentration was observed across the chlorine dioxide sand column. Treatment of the sand column effluents with free chlorine followed by storage for 5 days produced respective average BCAN-Cl<sub>2</sub> levels of 0.44, 0.66, 1.39, and 0.61 ug/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams (Figure 71), again indicating elevated levels in the chlorine dioxide process stream. Treatment of the sand column effluents with chloramine followed by 5-day storage also produced slightly elevated levels in the chlorine dioxide process stream with average BCAN-NH<sub>2</sub>Cl levels of 0.006, 0.007, 0.05, and 0.008 ug/L for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams (Figure 72). In comparison to the BCAN levels in the sand column effluents, slight increases were observed for BCAN-NH<sub>2</sub>Cl in the chlorine dioxide and ozone process streams with no change in the nondisinfected process stream. The chloramine process stream again exhibited lower (80%) BCAN-NH<sub>2</sub>Cl levels than the BCAN-NH<sub>2</sub>Cl in the sand filter effluent after the additional chloramination and 5-day storage.

Filtration through GAC with a 20 minute EBCT removed essentially 100% BCAN in every process stream except that of chlorine (Figure 73). Breakthrough above 0.001 ug/L was observed on day 75 with steady-state occurring on day 150 at the 0.015 ug/L level. Relative to the sand filtered effluent, an average removal of 98% was observed after steady-state was reached. Treatment of the GAC filter effluent with free chlorine and subsequent storage for 5 days resulted in respective average BCAN-Cl<sub>2</sub> levels of 1.1, 0.8, 1.2, 1.1, and 0.9 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams. These levels were equivalent or slightly greater than those BCAN-Cl<sub>2</sub> levels in the similarly treated sand column effluents indicating that precursor breakthrough to saturation occurred fairly rapidly, within the first 50 days (Figure 74). As indicated previously for DCAN, increased precursor levels were observed across the nondisinfected and chlorine GAC columns. The average BCAN-Cl<sub>2</sub> concentration after saturation in the nondisinfected GAC column effluent at 1.3 ug/L was more than 3 times that of the sand column effluent at 0.4 ug/L (Figure 75). With equivalent chlorine sand column effluent BCAN and BCAN-Cl<sub>2</sub> levels indicating that essentially no

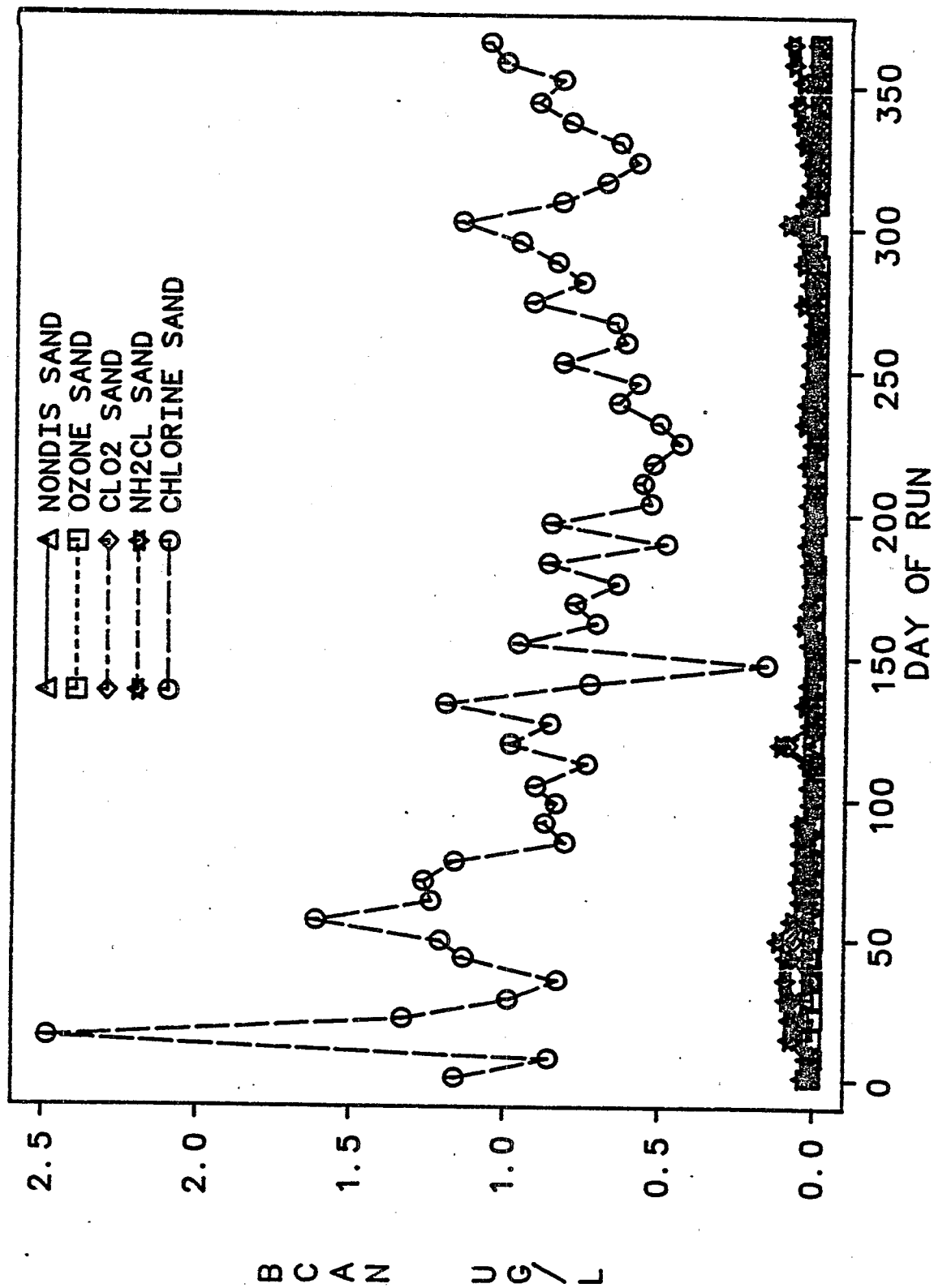


Figure 70. Comparison of BCAN Levels in the Sand Column Effluent of each Process Stream.

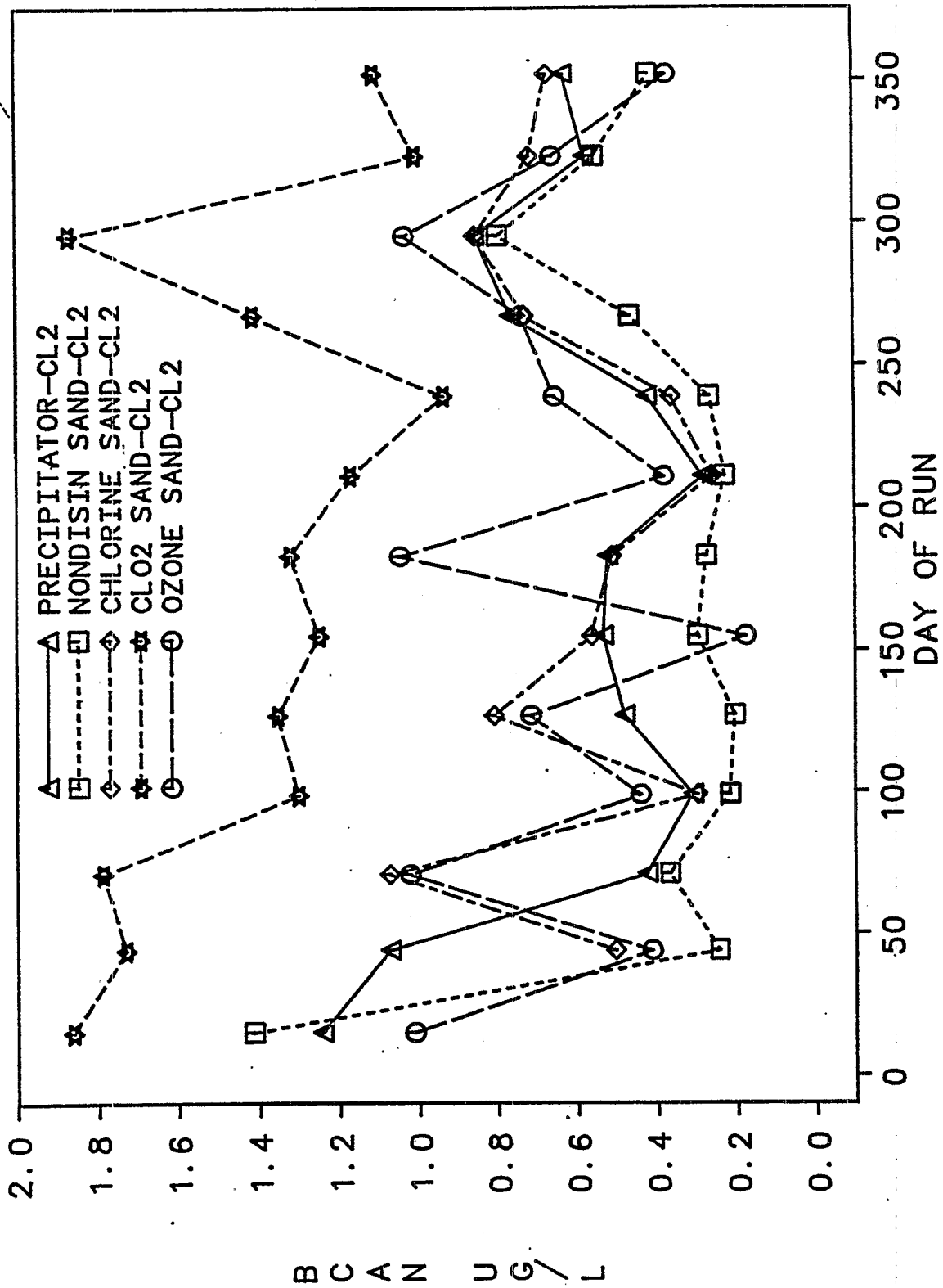


Figure 71. Comparison of BCAN-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.



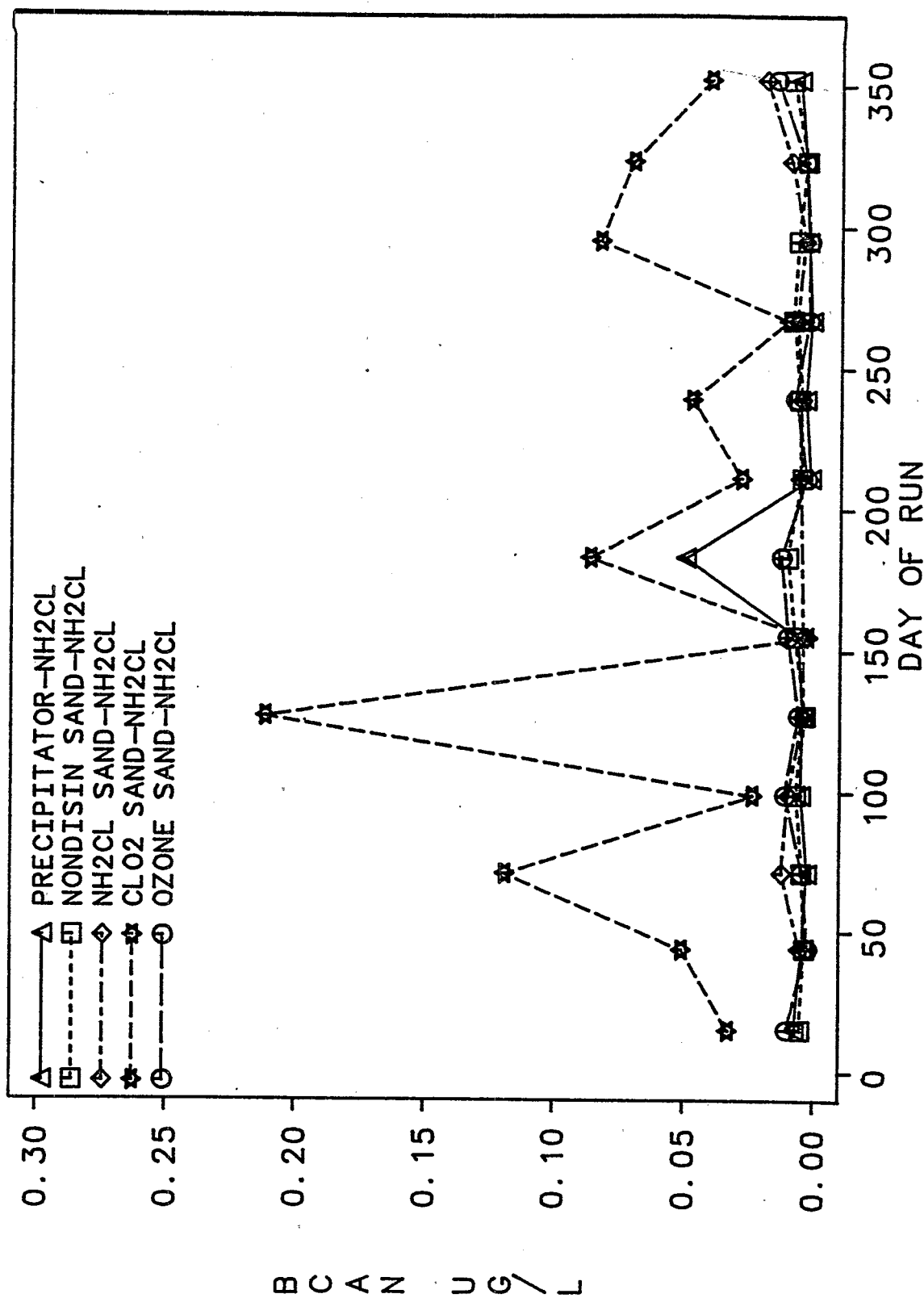


Figure 72. Comparison of BCAN-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

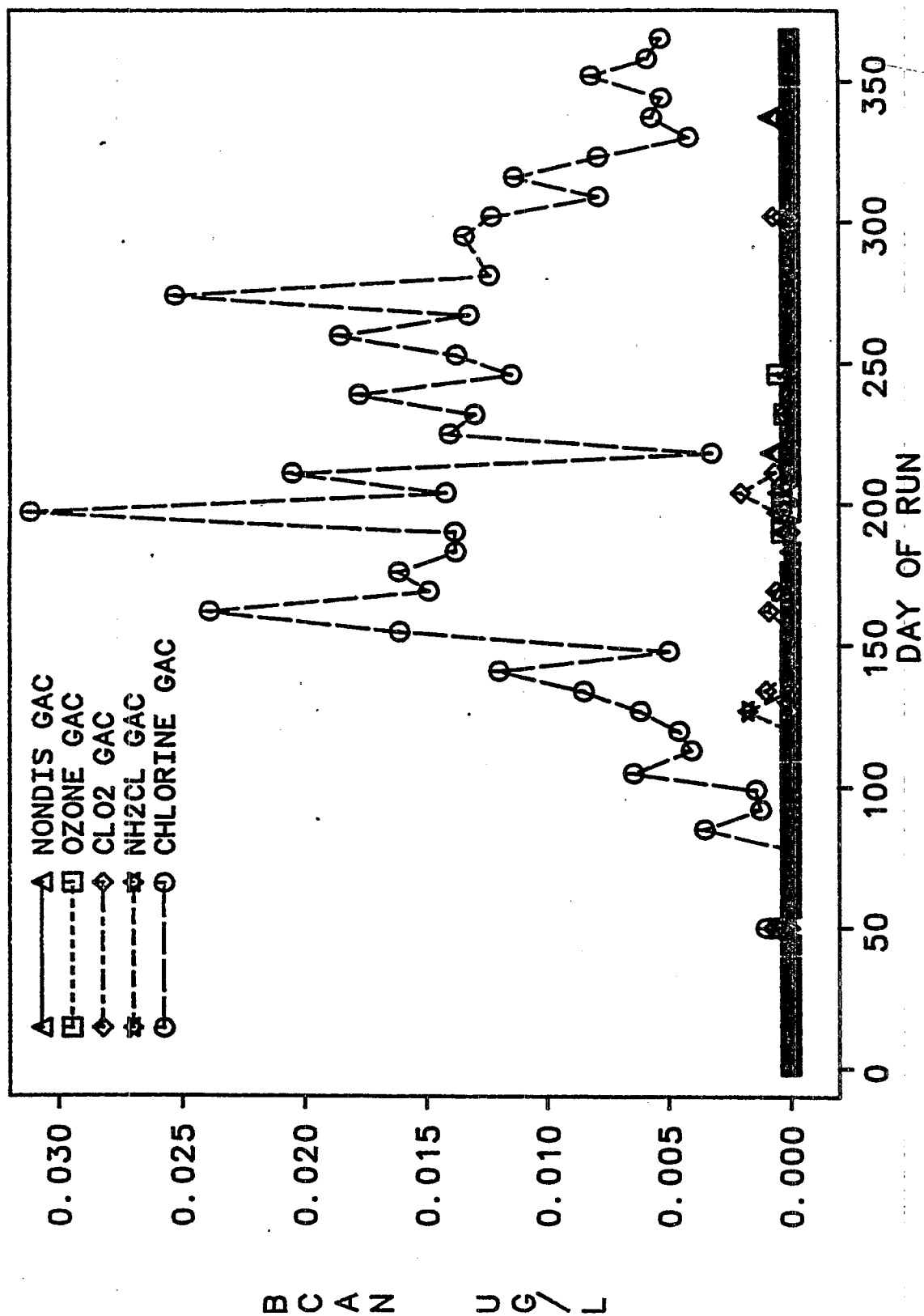


Figure 73. Comparison of BCAN Levels in the GAC Column Effluent of each Process Stream.

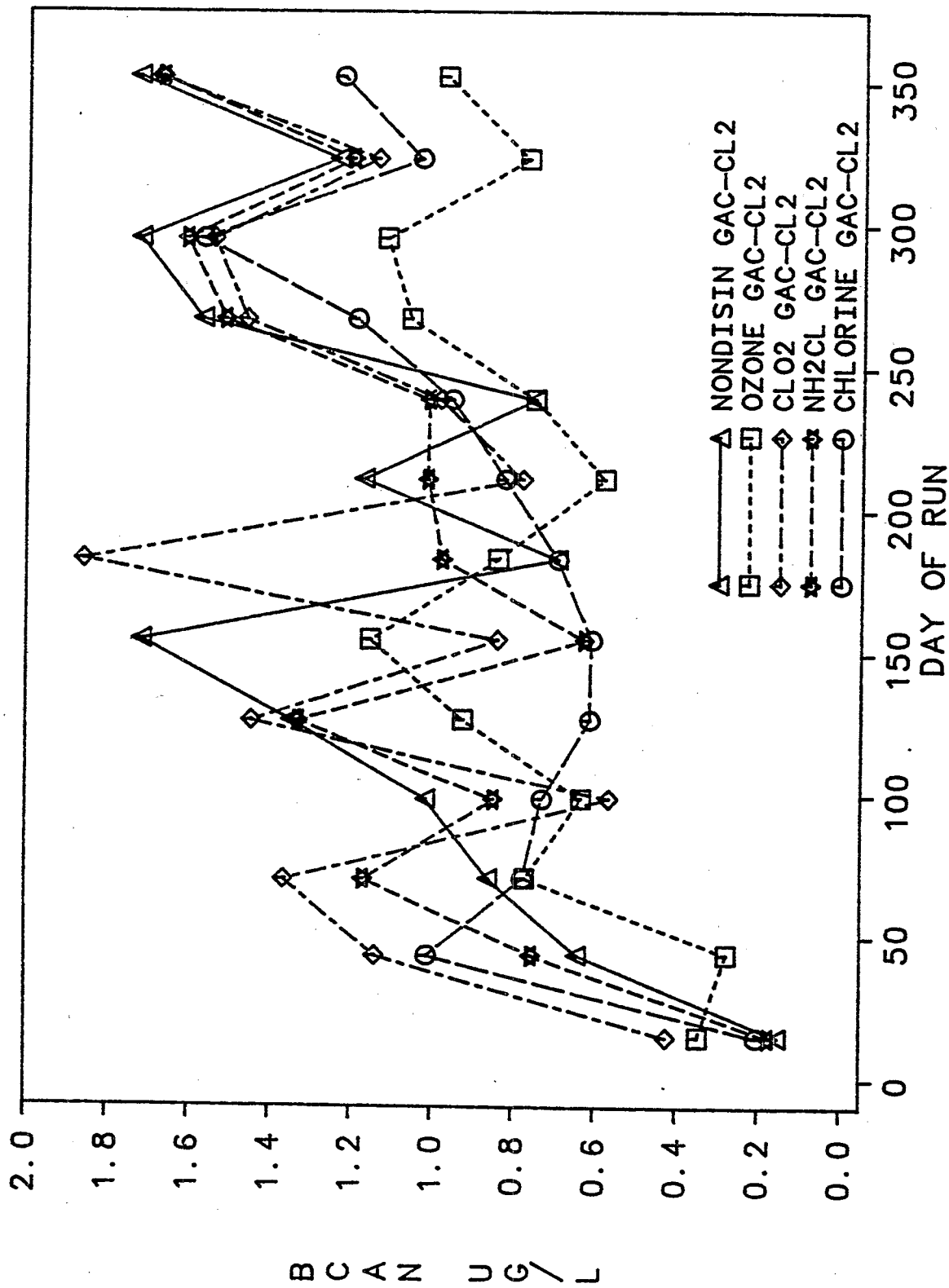


Figure 74. Comparison of BCAN-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

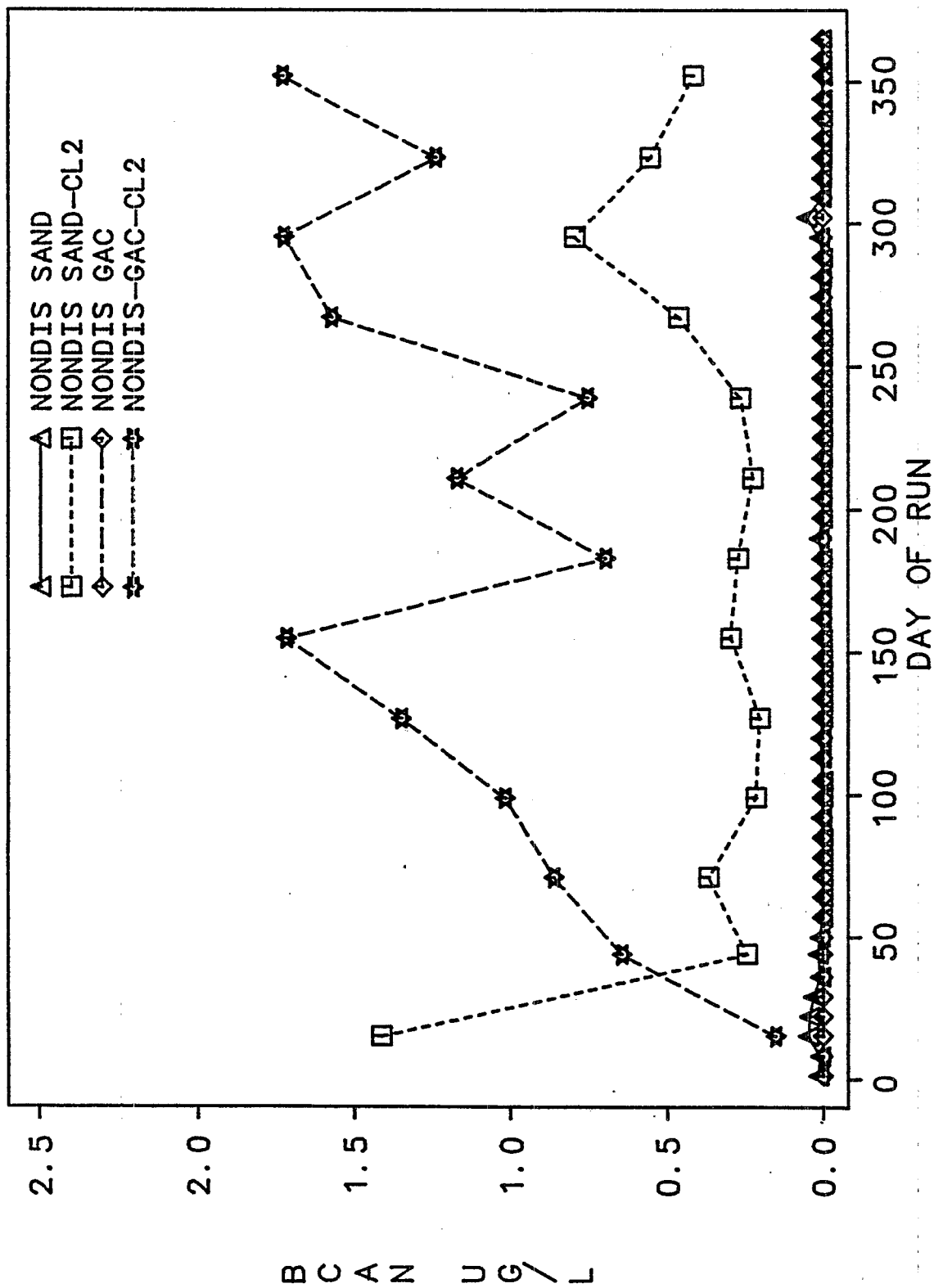


Figure 75. Comparison of BCAN and BCAN-Cl<sub>2</sub> Levels in the Nondisinfected Process Stream.

precursors were entering the GAC column, and with all BCAN in the chlorine sand column effluent being removed by GAC filtration, it would be expected that the BCAN-Cl<sub>2</sub> levels in the chlorine GAC effluent would be essentially nonexistent (Figure 76). However, the actual BCAN-Cl<sub>2</sub> levels in the chlorine GAC effluent were equal to or greater than those of the sand column effluent implying that the GAC column was the source of the precursors, possibly through some form of microbiological transformation. The addition of chloramines to the GAC filter effluent followed by 5-day storage produced respective average BCAN-NH<sub>2</sub>Cl levels of 0.005, 0.008, 0.11, 0.009, and 0.006 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams which were essentially equivalent to those of the similarly treated sand column effluents (Figure 77).

Contact chamber effluent concentrations of dibromoacetonitrile (DBAN) were equivalent for the chlorine and ozone process streams averaging 0.26 ug/L (Figure 78). Lower levels averaging 0.007, 0.027, and 0.03 ug/L were observed for the nondisinfected influent and the chlorine dioxide and chloramine contact chamber effluents. While no change in DBAN was observed across the chlorine sand column (Figure 79), an average reduction of 90% occurred across the ozone sand column resulting in an average effluent concentration of 0.027 ug/L (Figure 80). The average sand column effluent concentrations for the nondisinfected, chlorine dioxide, and chloramine process streams at 0.006, 0.033, and 0.07 ug/L were essentially equivalent to their respective contact chamber effluent concentrations. Chlorination of the sand column effluents and storage for 5 days resulted in similar average DBAN-Cl<sub>2</sub> levels of 0.23, 0.39, 0.45, and 0.26 ug/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams, respectively (Figure 81). Similar treatment of the sand column effluents with chloramine resulted in average DBAN-NH<sub>2</sub>Cl levels of 0.005, 0.011, 0.026, and 0.007 ug/L for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams (Figure 82). Other than in a few instances during the operational period, these DBAN-NH<sub>2</sub>Cl levels were essentially the same as the DBAN levels in the respective sand column effluents, except for the chloramine process stream which exhibited a reduction of 87%, similar to that observed for TOX (Figure 83).

GAC filtration reduced the average DBAN levels in all process streams to .003-.005 ug/L with intermittent breakthrough observed at or below the .05 ug/L level (Figure 84). The breakthrough of DBAN across the chlorine GAC column was more or less continuous after day 40 with an average steady state concentration of 0.006 ug/L resulting in a 98% removal. Chlorination of the GAC effluent followed by 5-day storage resulted in essentially the same DBAN-Cl<sub>2</sub> levels in all process streams with respective average concentrations of 0.45, 0.53, 0.50, 0.45, and 0.41 for the nondisinfected, ozone, chlorine dioxide, chloramine, and

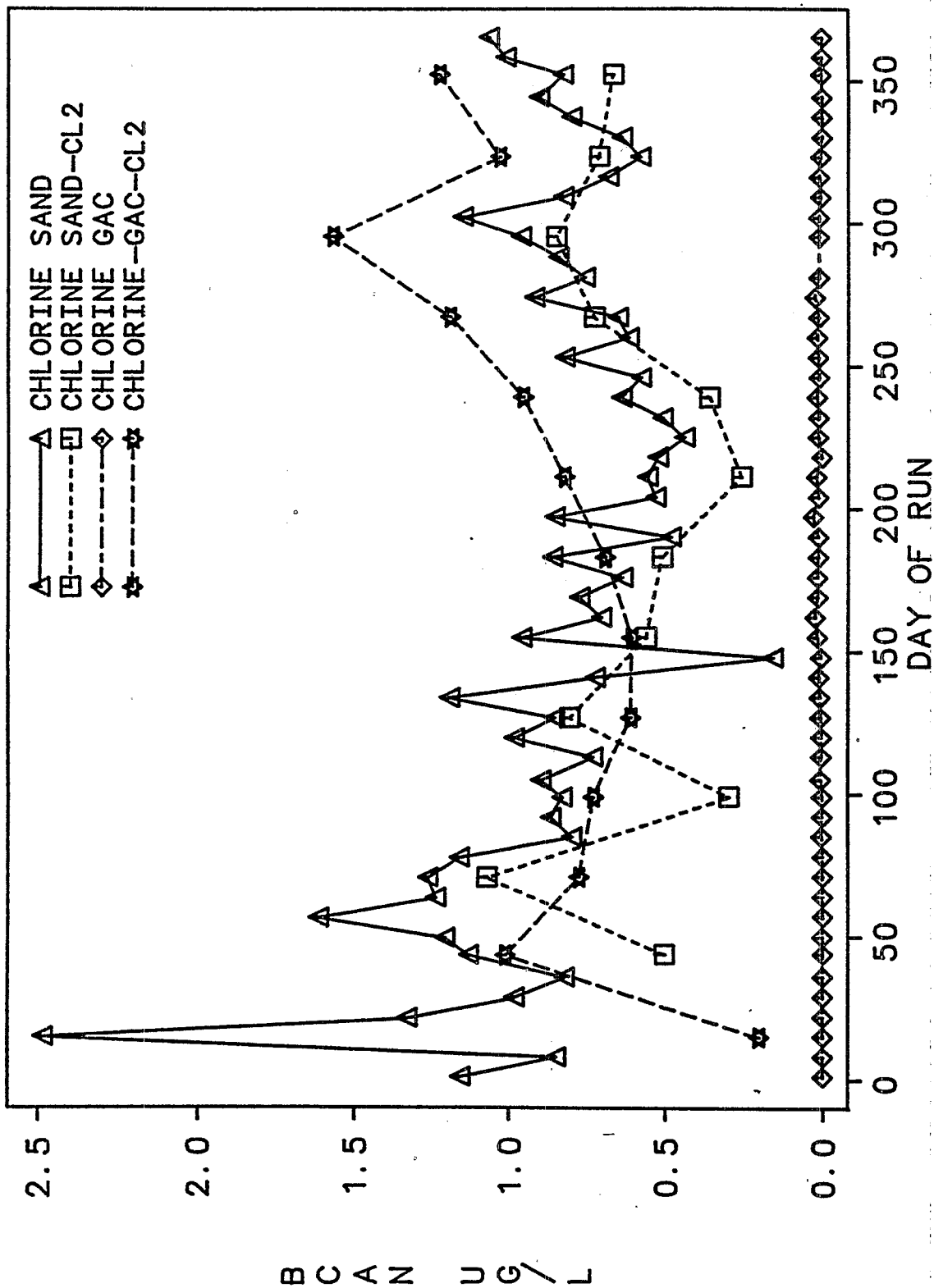


Figure 76. Comparison of BCAN and BCL2 Levels in the Chlorine Process Stream.

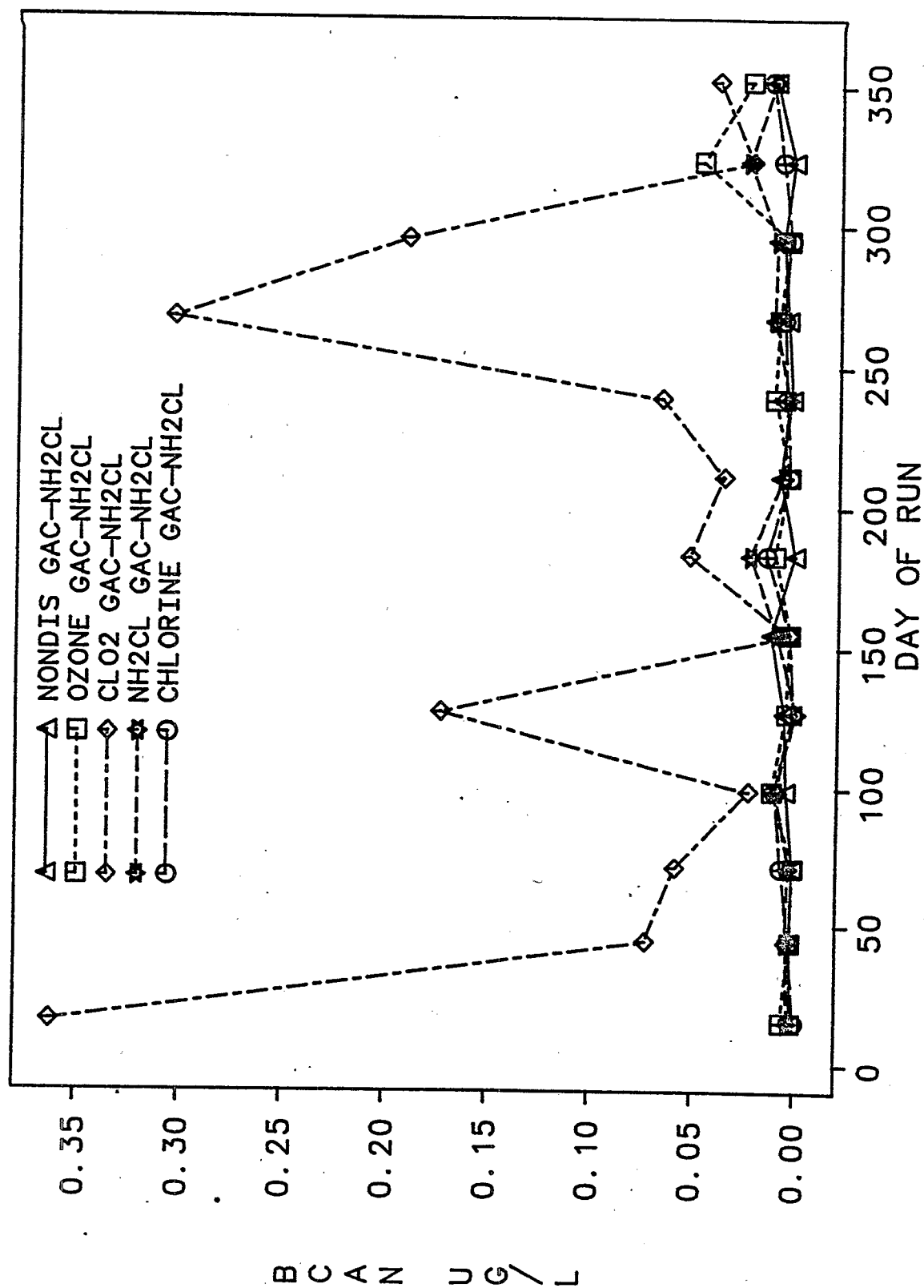


Figure 77. Comparison of BCAN-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

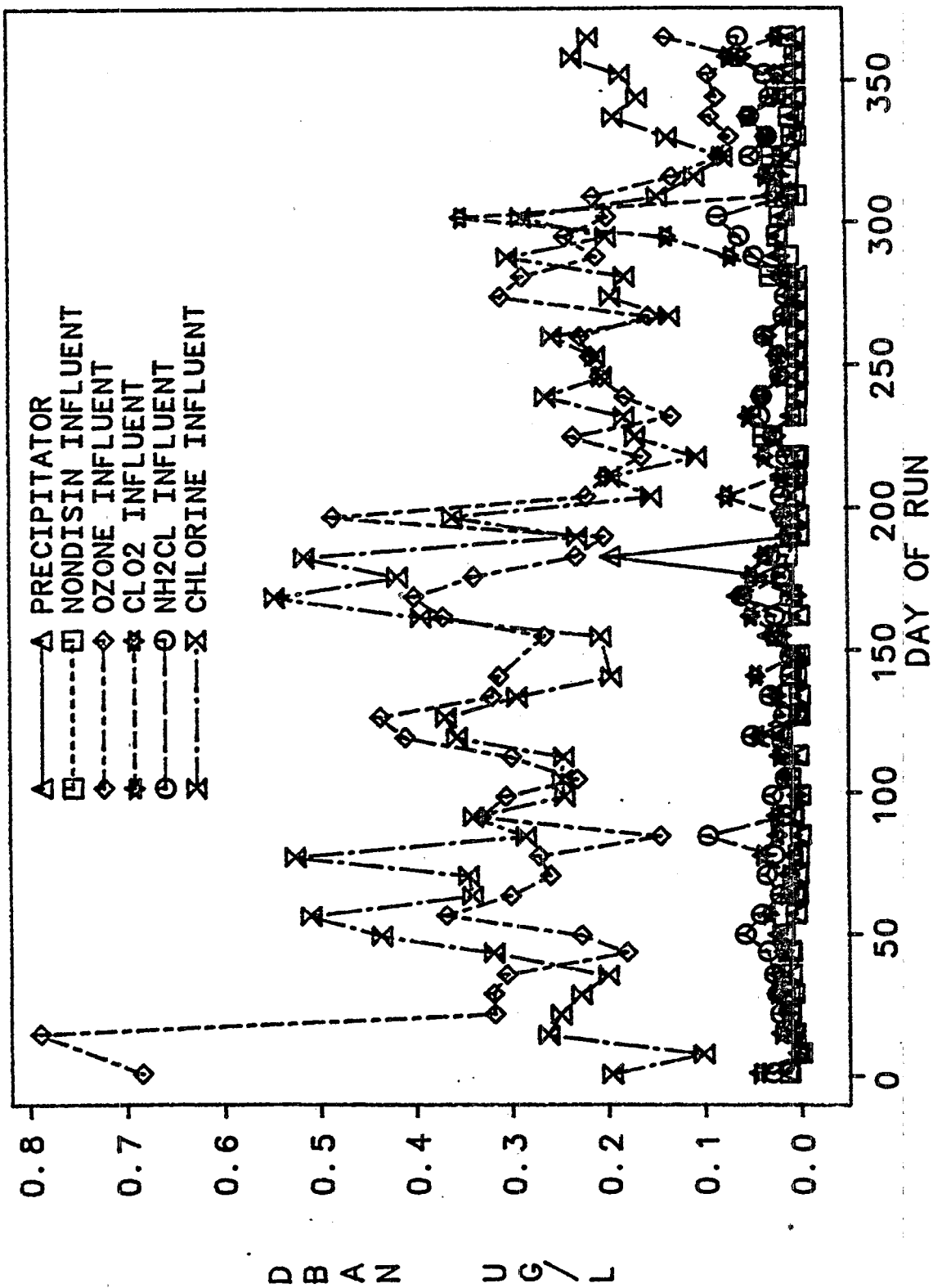


Figure 78. Comparison of DBAN Levels in the Contact Chamber Effluent of each Process Stream.



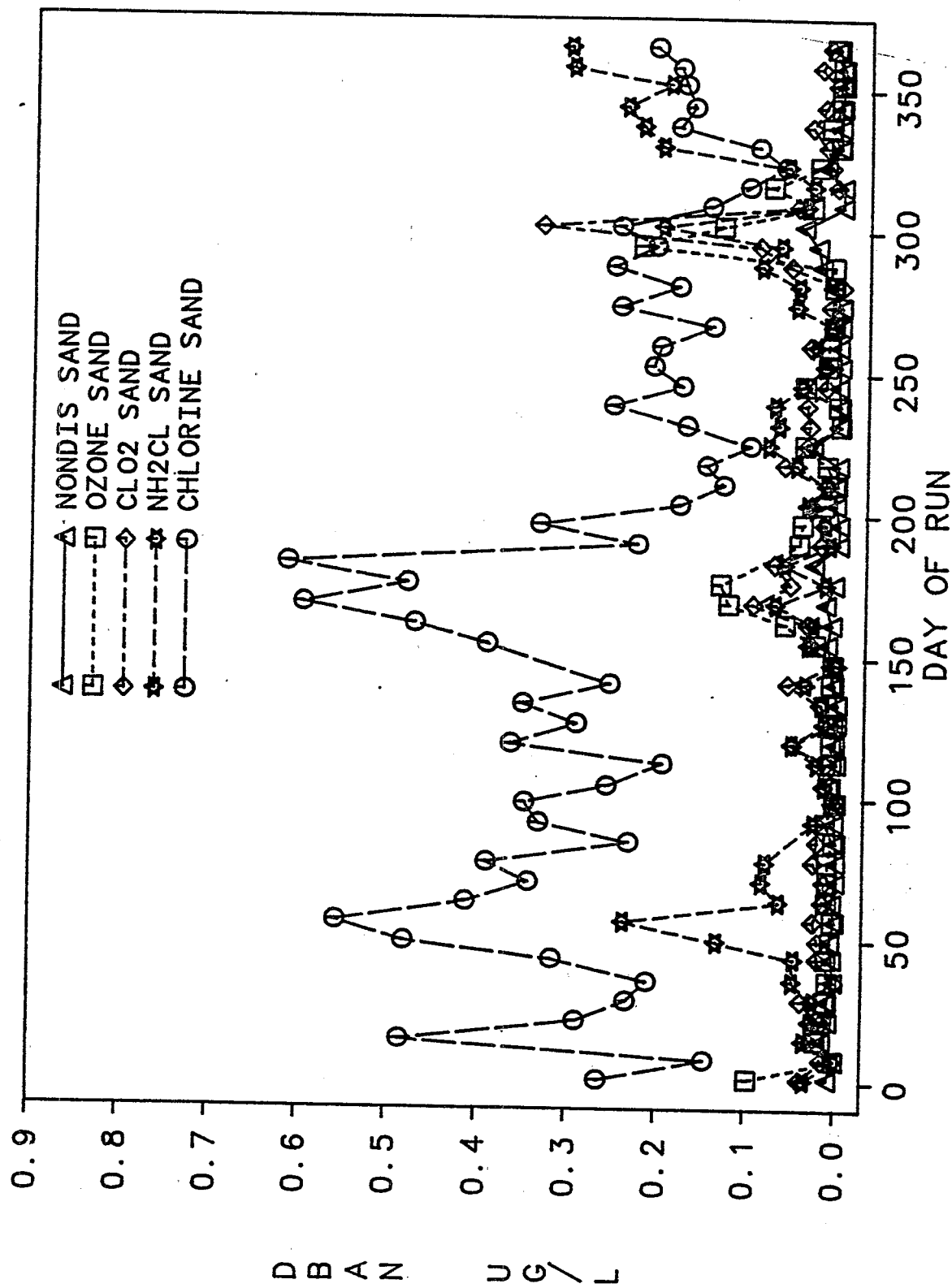


Figure 79. Comparison of DBAN Levels in the Sand Column Effluent of each Process Stream.

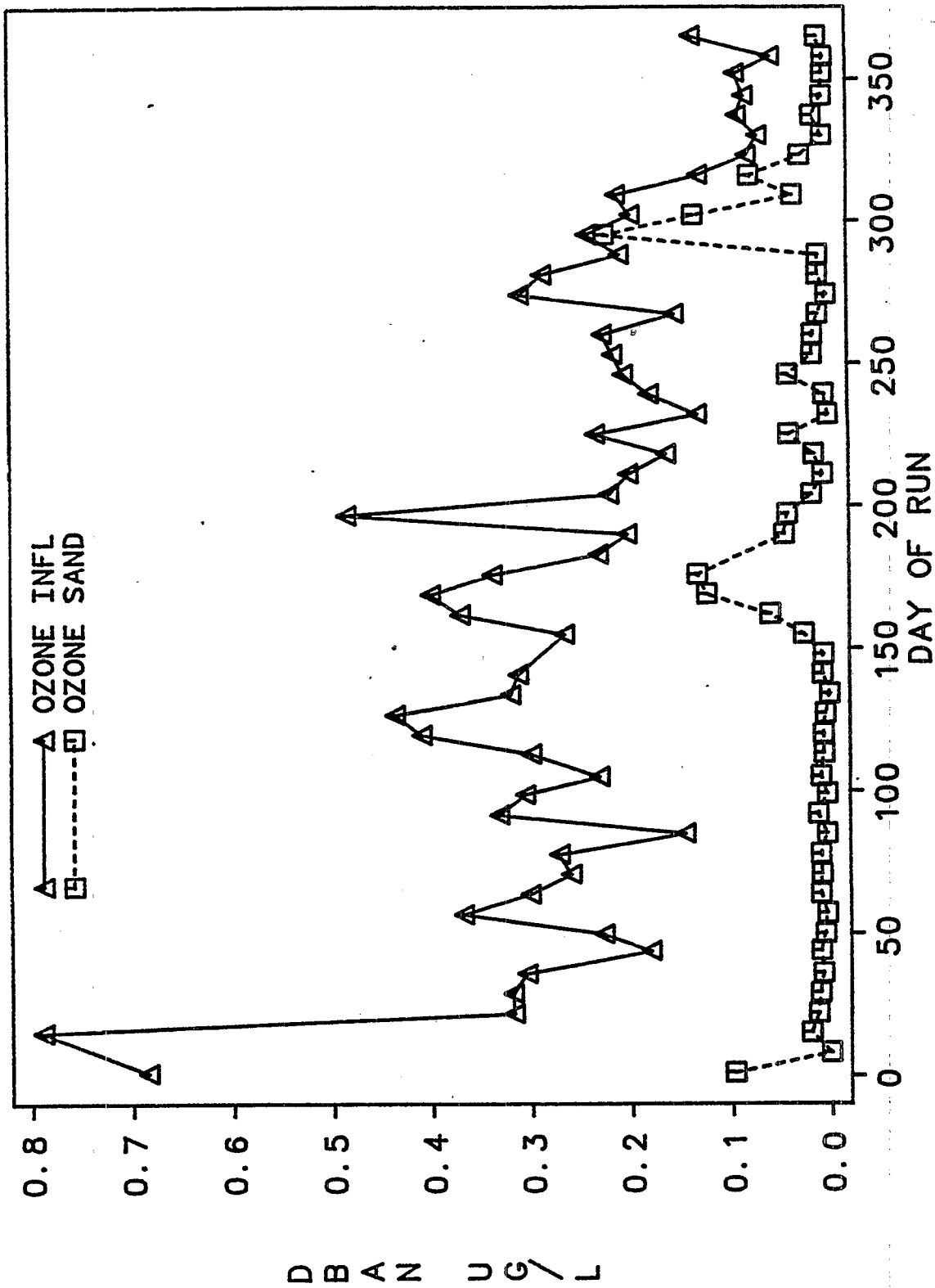


Figure 80. Comparison of DBAN Levels in the Ozone Contact Chamber and Sand Column Effluents.

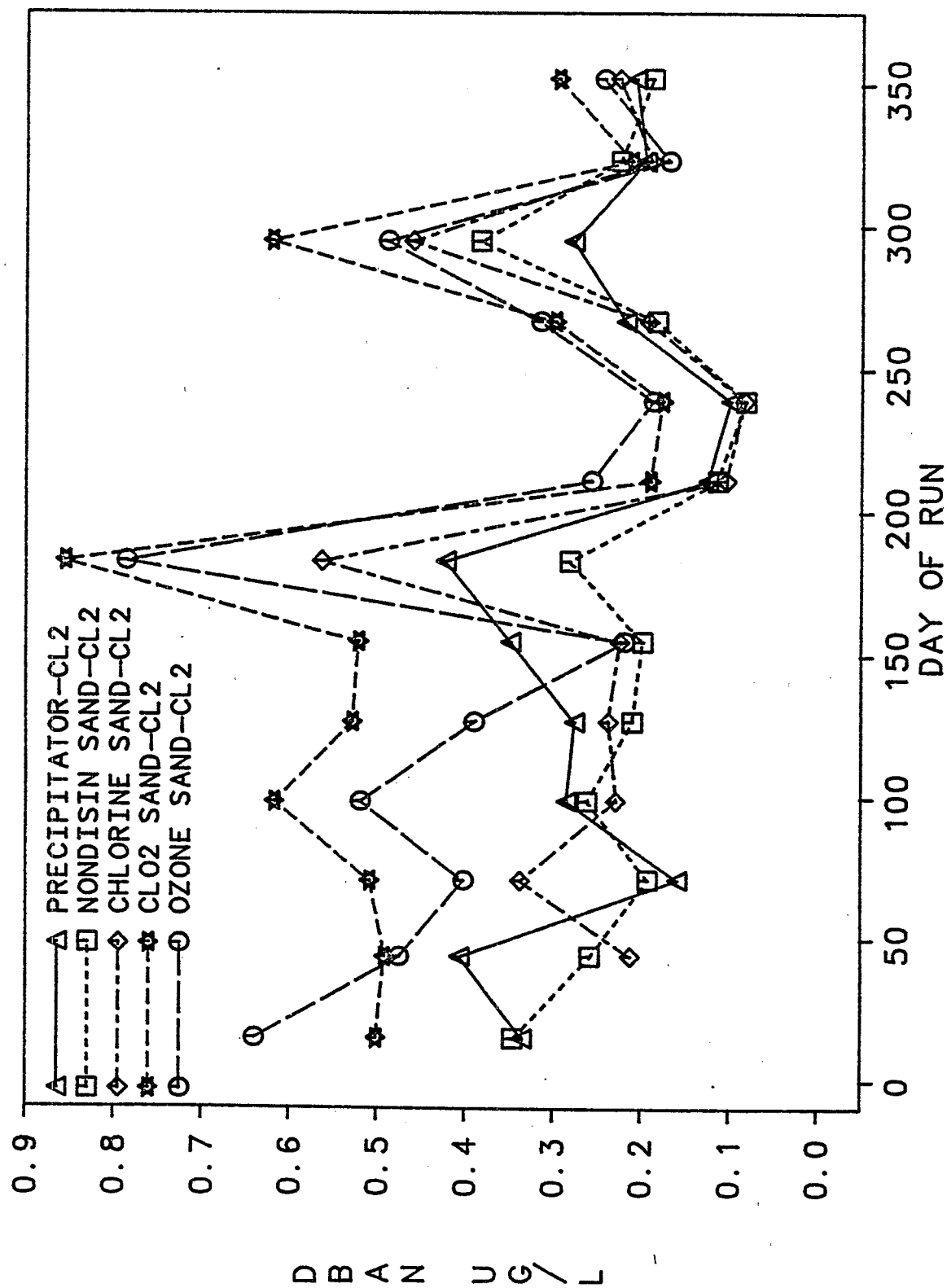


Figure 81. Comparison of DBAN-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

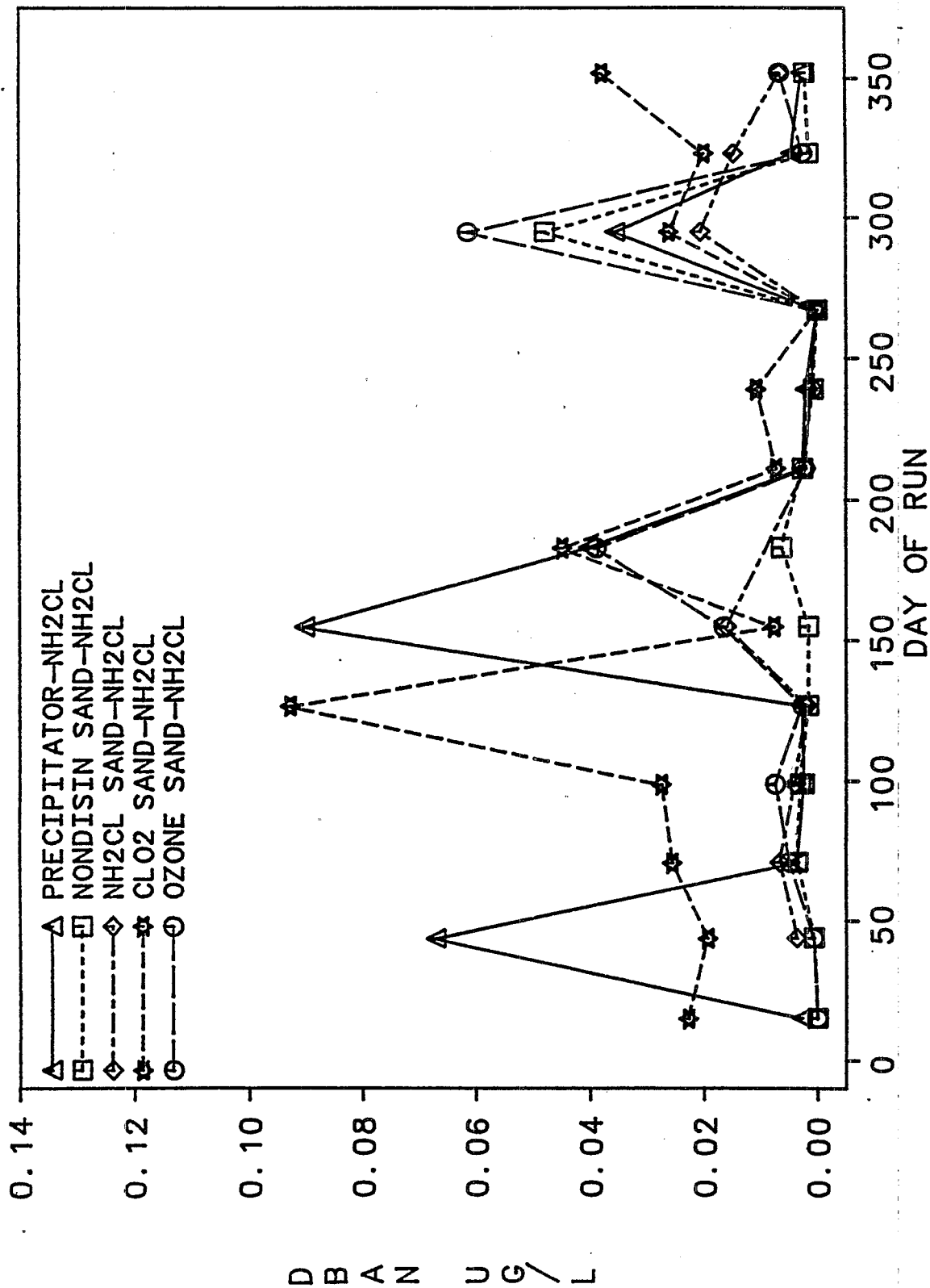


Figure 82. Comparison of DBAN-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

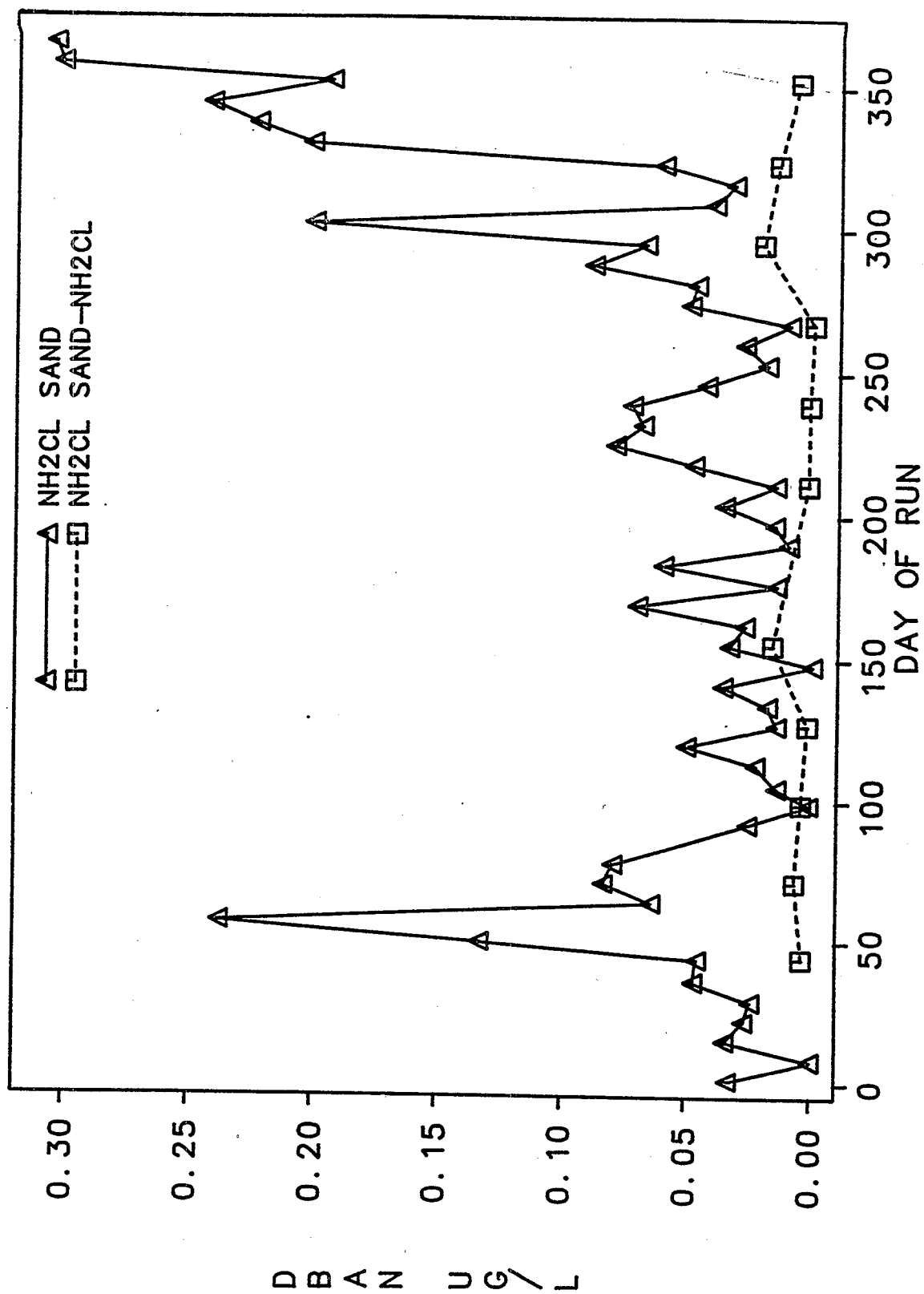


Figure 83. Comparison of DBAN and DBAN-NH<sub>2</sub>Cl Levels in the Chloramine Sand Column Effluent.

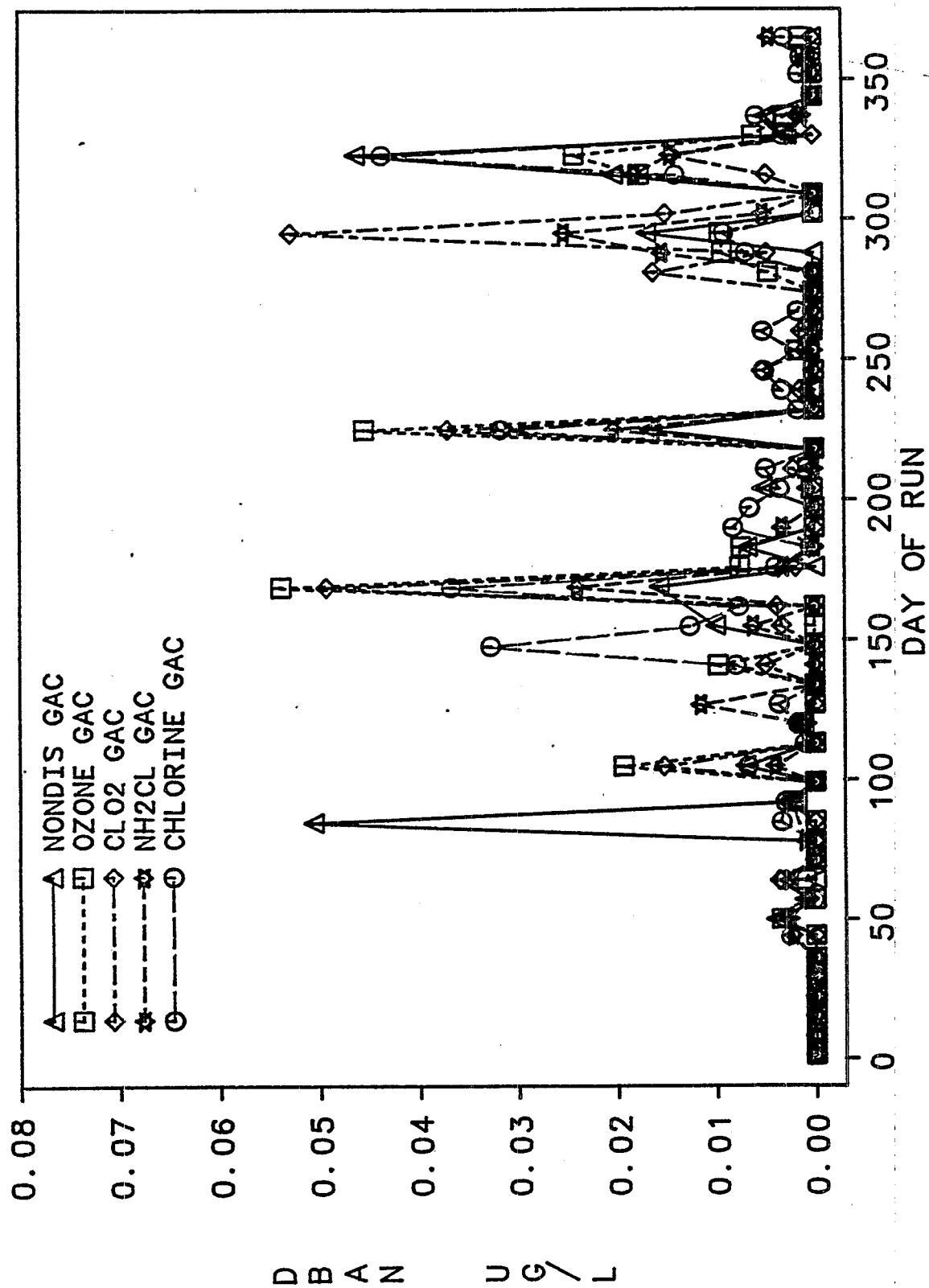


Figure 84. Comparison of DBAN Levels in the GAC Column Effluent of each Process Stream.

chlorine process streams (Figure 85).

Precursor breakthrough to steady-state for all process streams occurred very rapidly, prior to day 40. As indicated for the previous acetonitriles, the DBAN-Cl<sub>2</sub> levels in the nondisinfected GAC column effluent were more than twice those of the nondisinfected sand column effluent (Figure 86). Also, the DBAN and DBAN-Cl<sub>2</sub> levels in the chlorine sand column effluent were equivalent indicating the absence of DBAN precursors in the chlorine GAC influent. Yet the levels of DBAN-Cl<sub>2</sub> were significantly higher than the DBAN levels in the chlorine GAC effluent indicating the presence of additional precursors (Figure 87). Similar treatment of the GAC effluents with chloramine and subsequent 5-day storage produced significantly lower levels with respective average DBAN-NH<sub>2</sub>Cl concentrations of 0.010, 0.012, 0.034, 0.012, and 0.005 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams (Figure 88). These DBAN-NH<sub>2</sub>Cl levels were essentially the same as those of the respective sand column effluents.

The average concentrations of trichloroacetonitrile (TCAN) in the sand column effluents were equivalent to those of the respective disinfectant contact chambers in all process streams except for that of chlorine which increased 86% across the sand column to 0.066 ug/L due to increased contact time. The TCAN sand column effluent concentrations for the nondisinfected, ozone, chlorine dioxide, and chloramine process streams were very similar averaging 0.001, 0.001, 0.002, and 0.004 ug/L, respectively (Figure 89). Chlorination of the sand column effluents and subsequent 5-day storage produced similar TCAN-Cl<sub>2</sub> levels for all process streams with respective averages of 0.062, 0.058, 0.104, and 0.054 for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams (Figure 90). The higher average level for the chlorine dioxide process stream resulted from two somewhat erratic data points at the beginning of the operational period. Treatment of the sand column effluents with chloramine followed by 5 days of storage produced TCAN-NH<sub>2</sub>Cl levels less than 0.001 ug/L in the nondisinfected, ozone, chlorine dioxide, and chloramine process streams.

No consistent breakthrough of TCAN was observed across the GAC columns of the nondisinfected, ozone, chlorine dioxide, and chloramine process streams with average concentrations of 0.001 ug/L or less. A relatively consistent breakthrough of TCAN was observed across the chlorine GAC column after day 50 with an average concentration of 0.003 ug/L (Figure 91). Chlorination of the GAC column effluents followed by 5-day storage produced TCAN-Cl<sub>2</sub> levels slightly lower than the similarly treated sand column effluents. TCAN-Cl<sub>2</sub> levels averaged 0.043, 0.034, 0.070, 0.036, and 0.046 in the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams (Figure 92). Similar

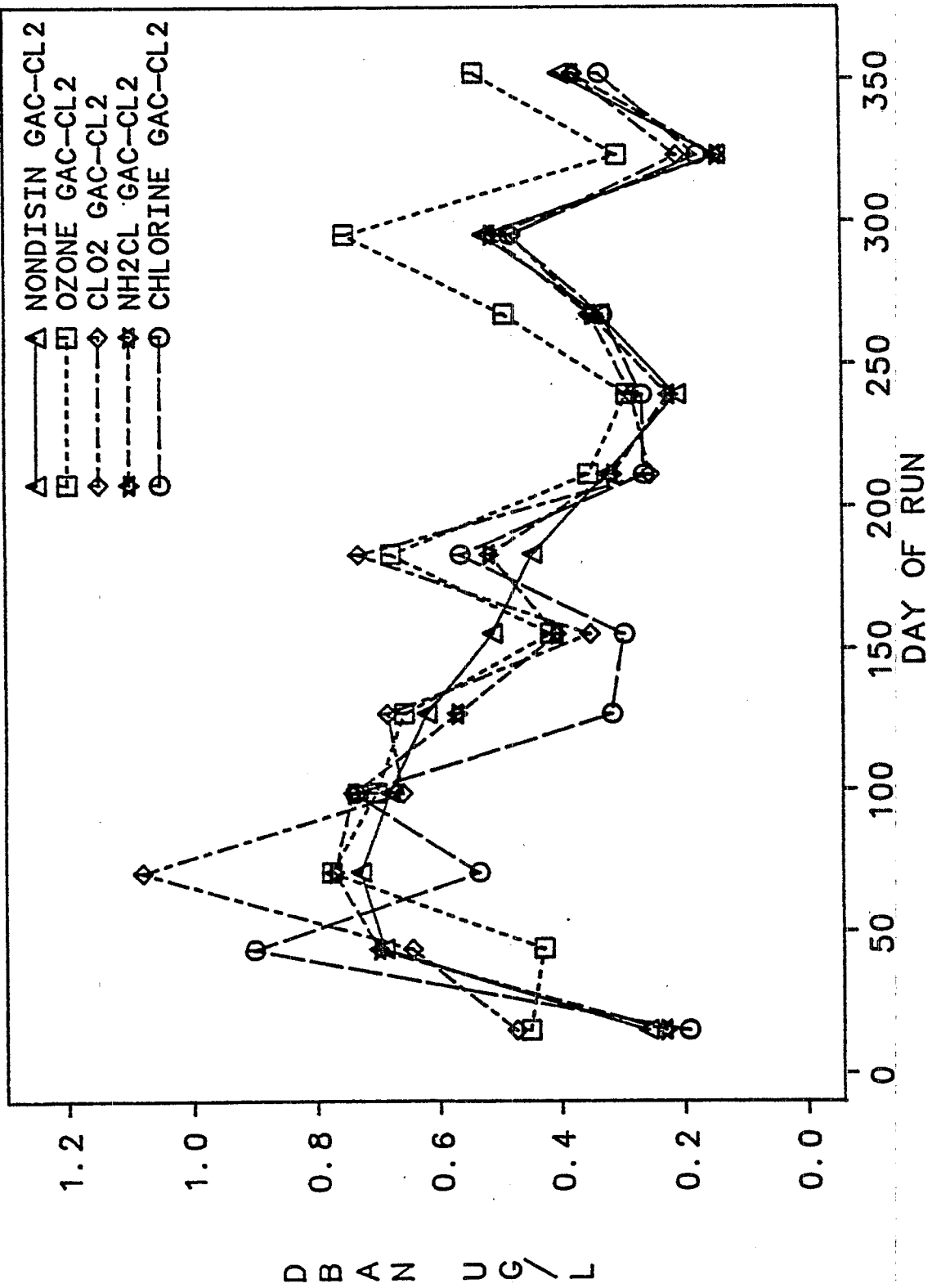


Figure 85. Comparison of DBAN-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.



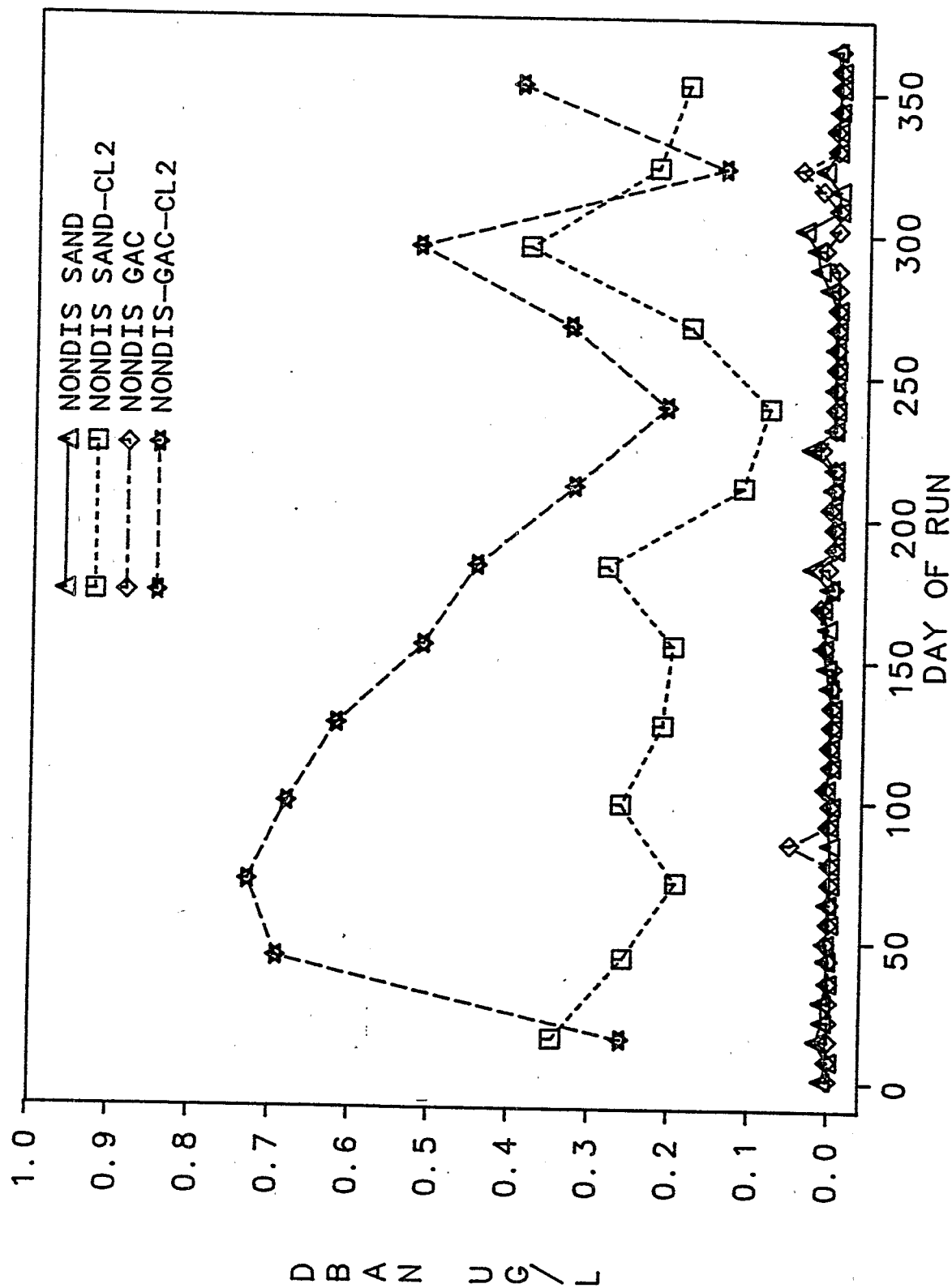


Figure 86. Comparison of DBAN and DBAN-Cl<sub>2</sub> Levels in the Nontreated Process Stream.

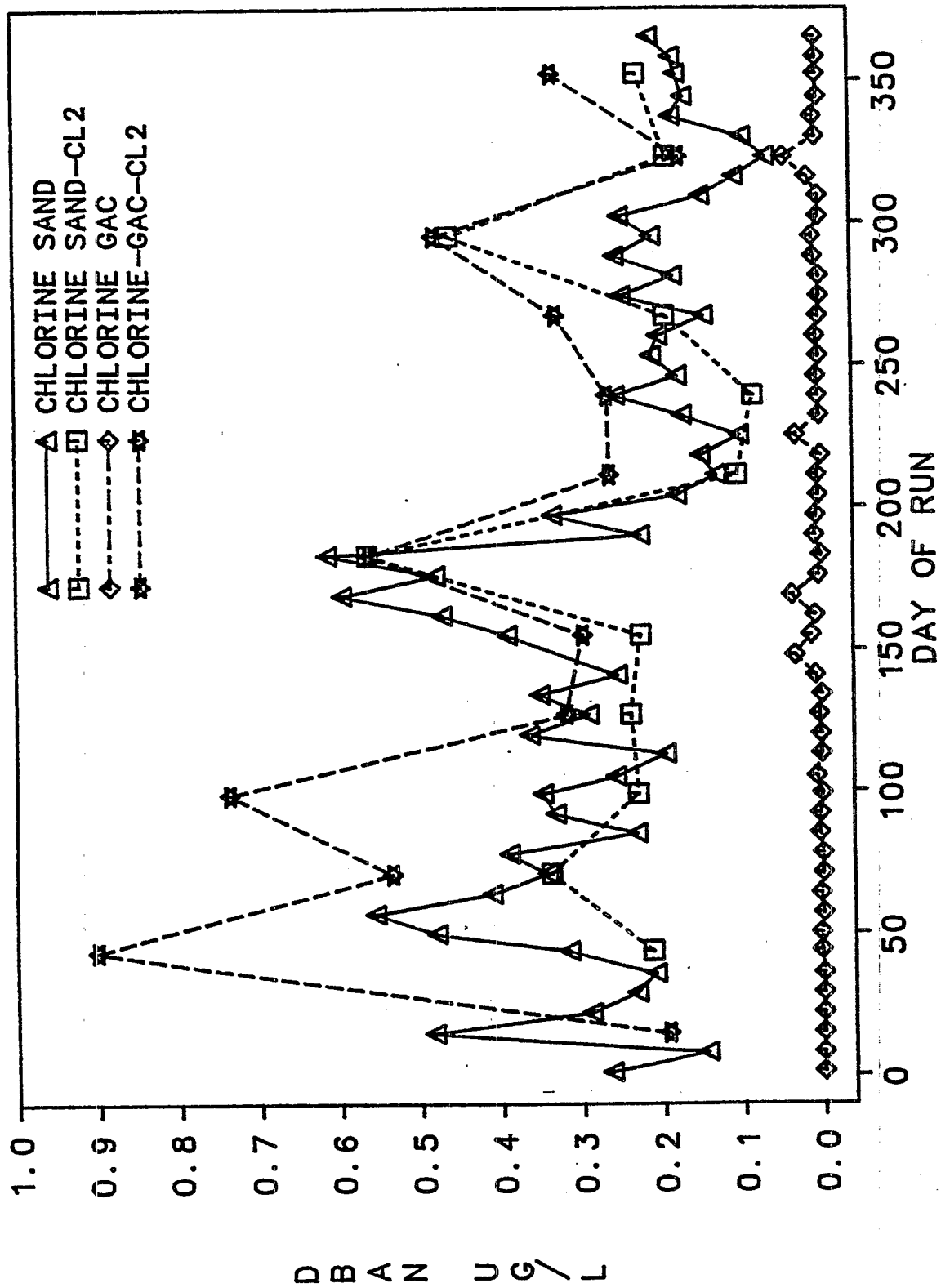


Figure 87. Comparison of DBAN and DBAN-Cl<sub>2</sub> Levels in the Chlorine Process Stream.

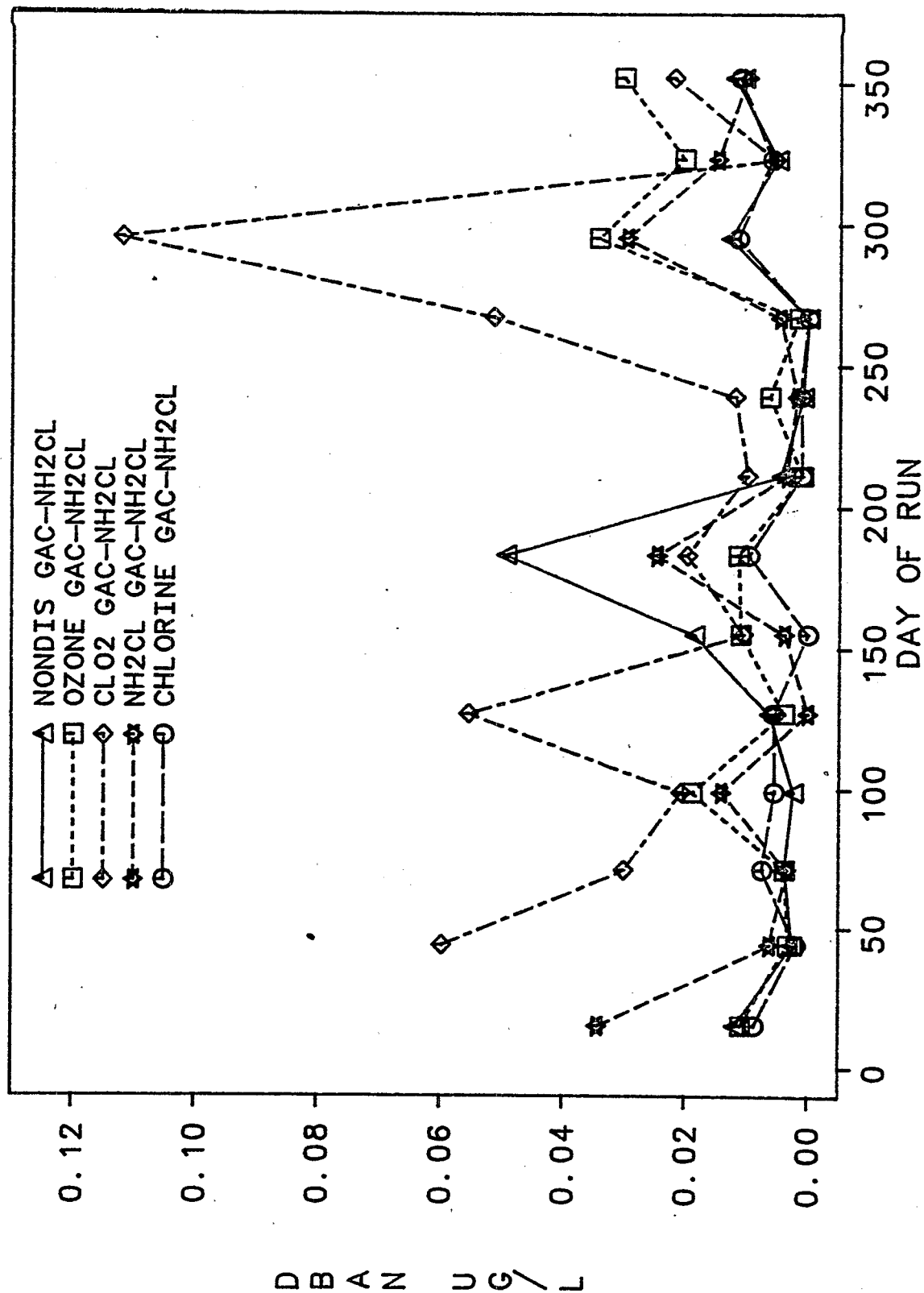


Figure 88. Comparison of DBAN-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

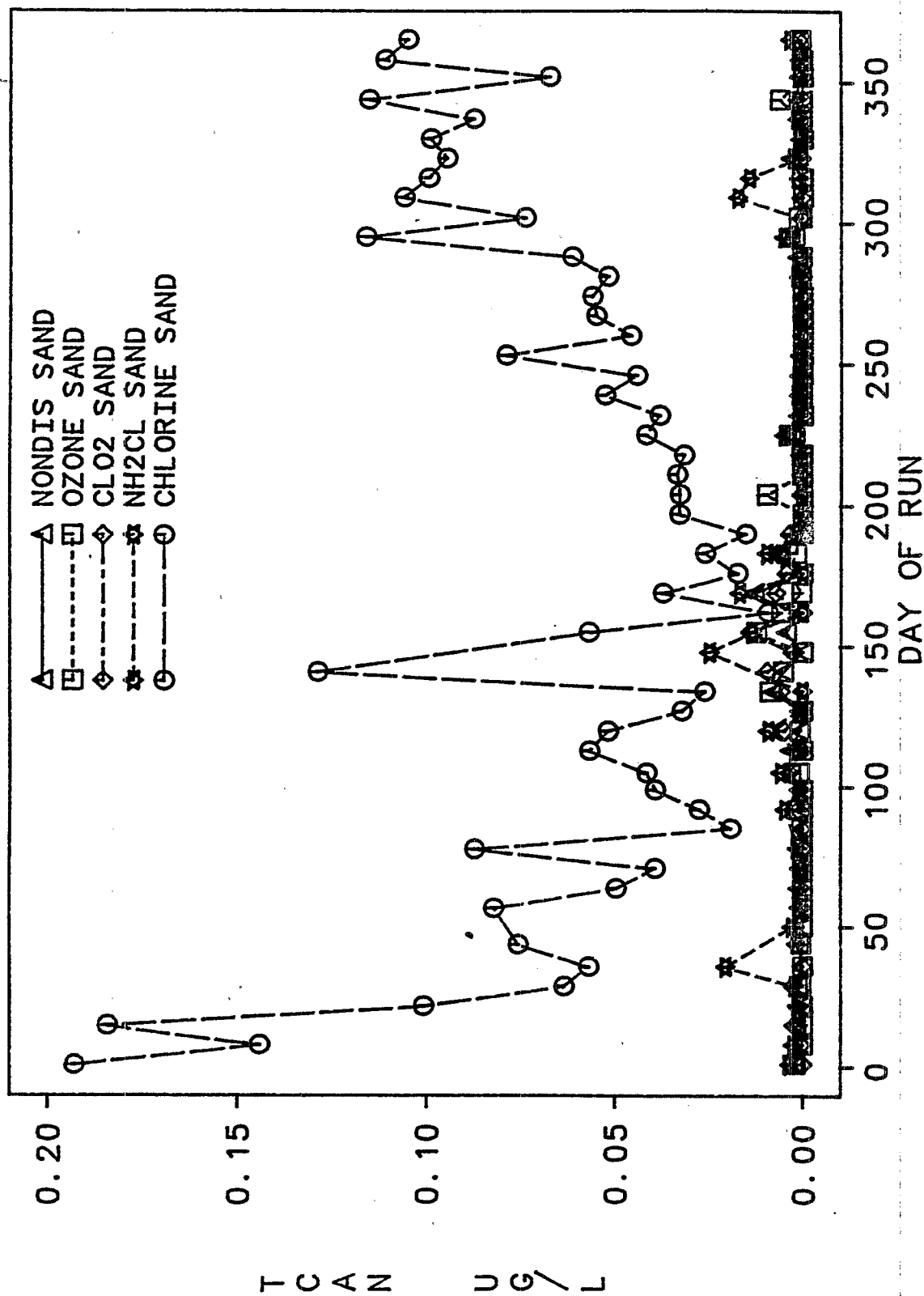


Figure 89. Comparison of TCA Levels in the Sand Column Effluent of each Process Stream.

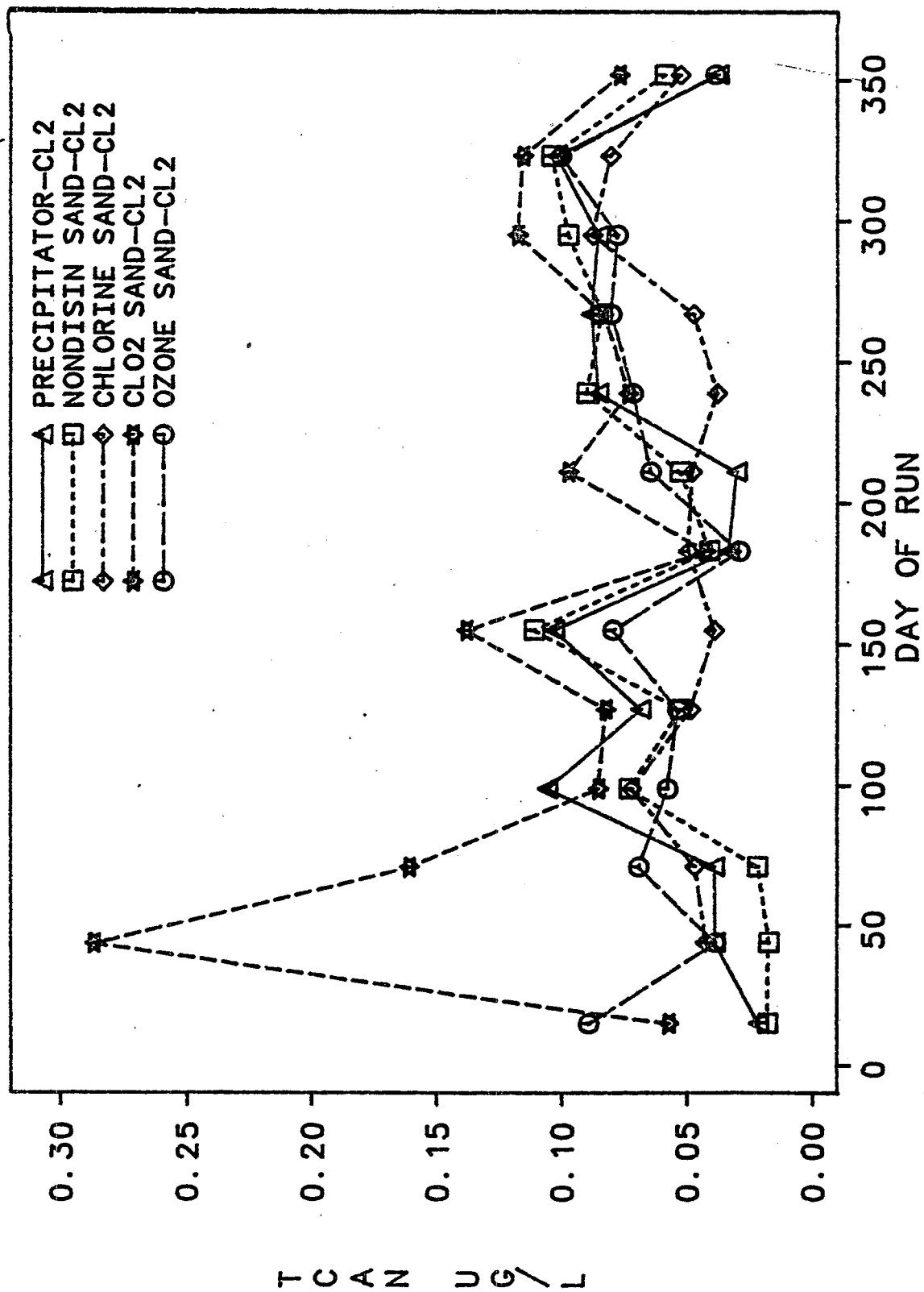


Figure 90. Comparison of TCAN-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

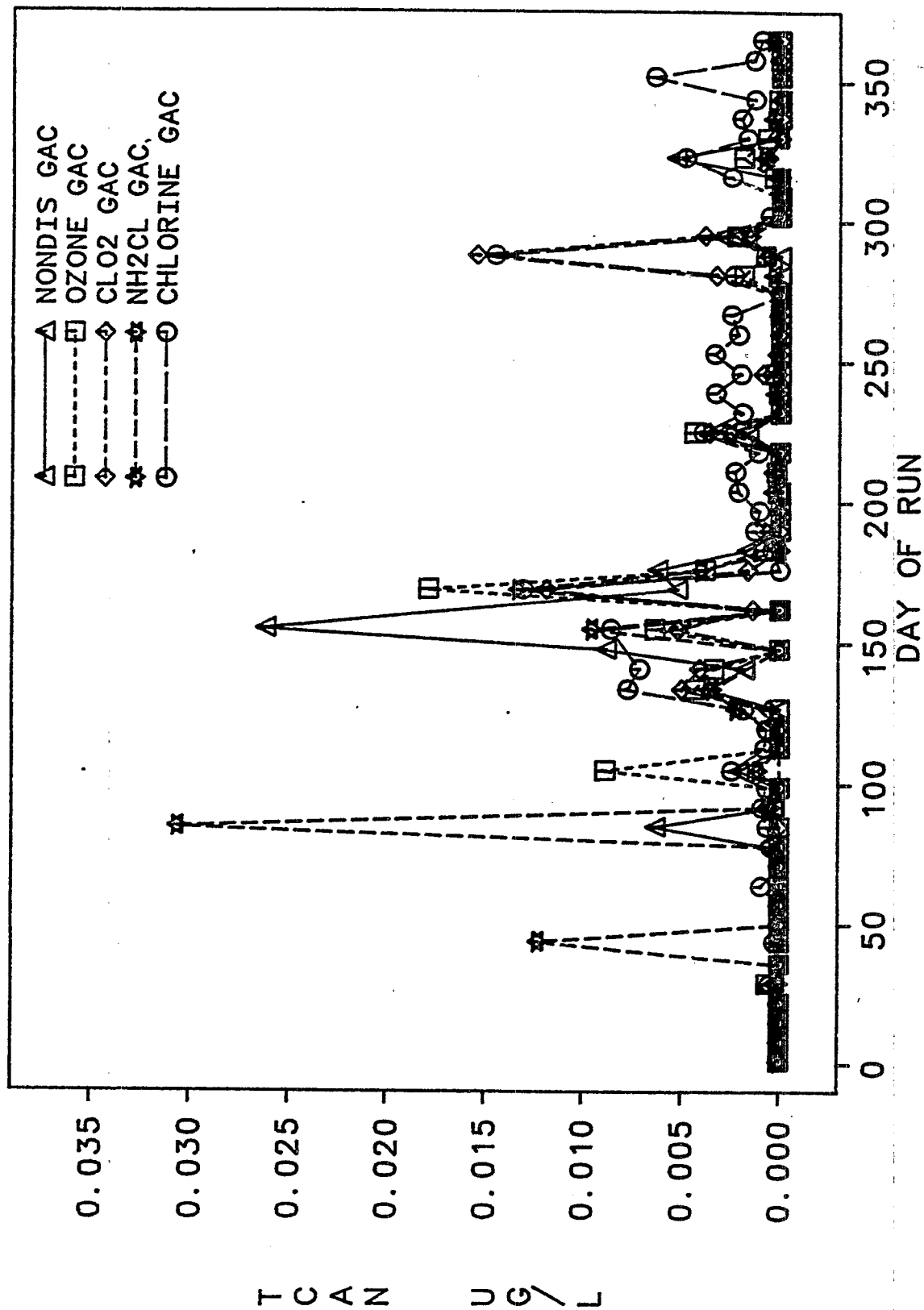


Figure 91. Comparison of TCAN Levels in the GAC Column Effluent of each Process Stream.

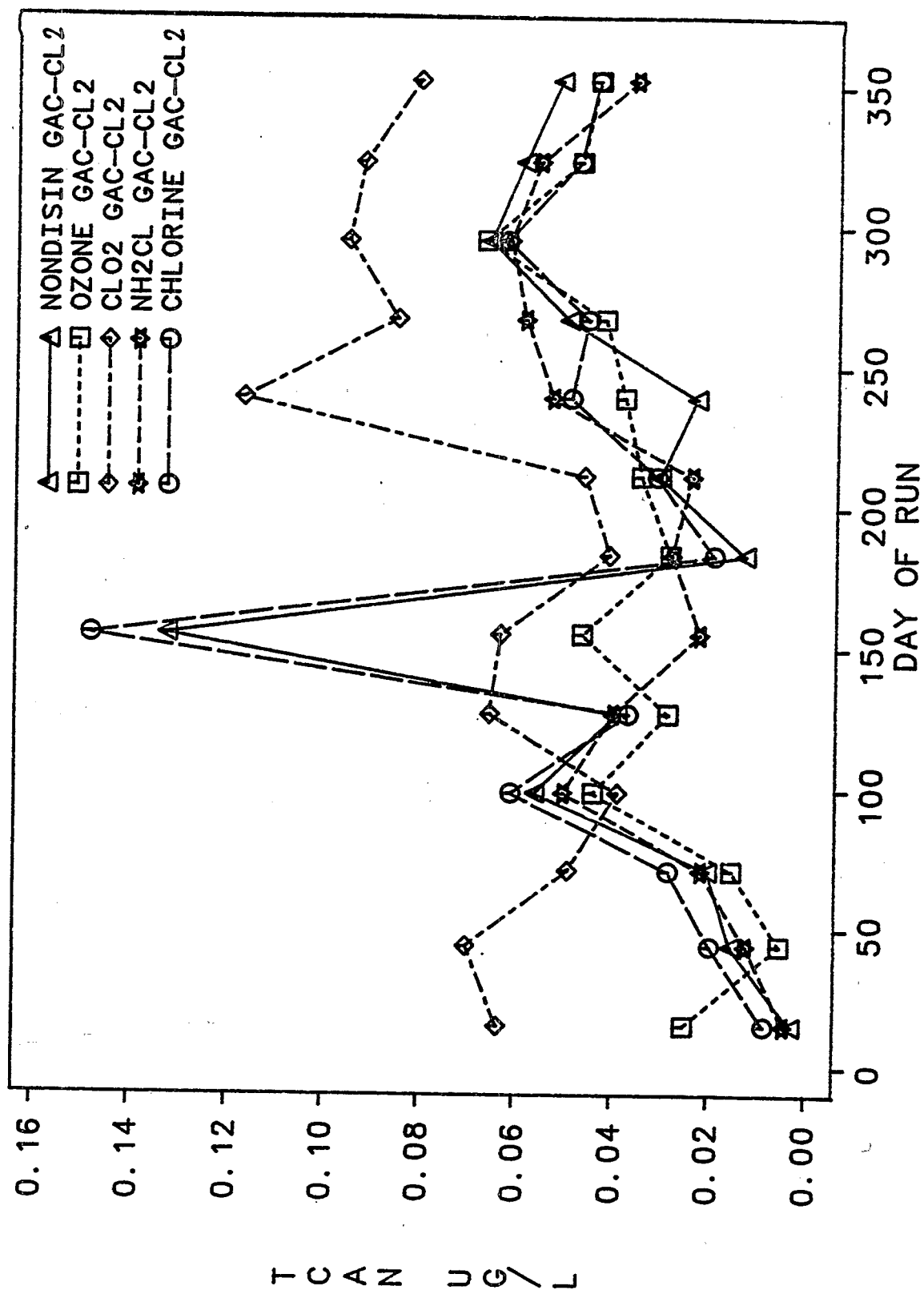


Figure 92. Comparison of TCAN-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

treatment of GAC effluents with chloramine again produced TCAN-NH<sub>2</sub>Cl concentrations less than 0.001 ug/L in all process streams.

#### Haloketones--

Only two haloketones, 1,1,1-trichloropropanone (TCP) and 1,1-dichloropropanone (DCP) were detected with the highest levels (1-2 ug/L) being observed in the chlorine process stream. Although consistent breakthroughs of these haloketones were observed across the GAC columns, removals remained above 85% throughout the one year operational period.

The average TCP concentrations in the effluent of the disinfectant contact chambers were essentially identical to those of the sand column effluent in all process streams except for that of ozone which exhibited some evidence of biodegradation. Average sand column effluent concentrations ranged from 0.034 ug/L for the nondisinfected process stream to 1.64 ug/L for the chlorine process stream with 0.036, 0.062, and 0.15 ug/L for the ozone, chlorine dioxide, and chloramine process streams, respectively (Figure 93). With an average influent concentration of 0.75 ug/L, a 52% reduction attributable to biodegradation was observed across the ozone sand column (Figure 94). Chlorination of the sand column effluents followed by 5-day storage produced similar TCP-Cl<sub>2</sub> levels in each process stream with respective average concentrations of 2.14, 2.45, 4.23, and 2.45 ug/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams indicating the presence of 2-4 ug/L of TCP precursors (Figure 95). Treatment of the sand column effluents with chloramine and subsequent 5-day storage produced significantly lower levels with average TCP-NH<sub>2</sub>Cl levels of 0.003-0.007 ug/L (Figure 96). Similar to the reductions observed for TOX in the terminal chloramine samples, these levels were lower than those of the sand column effluent by a factor of 10 or greater as indicated in Figure 97 for the chlorine dioxide and chloramine process streams.

The breakthrough of TCP across the GAC columns was observed on or about day 100 for all process streams (Figure 98). Steady-state was reached shortly thereafter with average concentrations of 0.002, 0.001, 0.003, 0.004, and 0.057 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine GAC columns resulting in respective removals of 93, 98, 95, 97, and 96 percent throughout the remainder of the operational period. Chlorination of the GAC effluents and subsequent storage for 5 days resulted in respective average TCP-Cl<sub>2</sub> levels of 1.6, 2.1, 2.7, 1.3, and 2.3 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine and chlorine process streams (Figure 99). These levels were comparable to



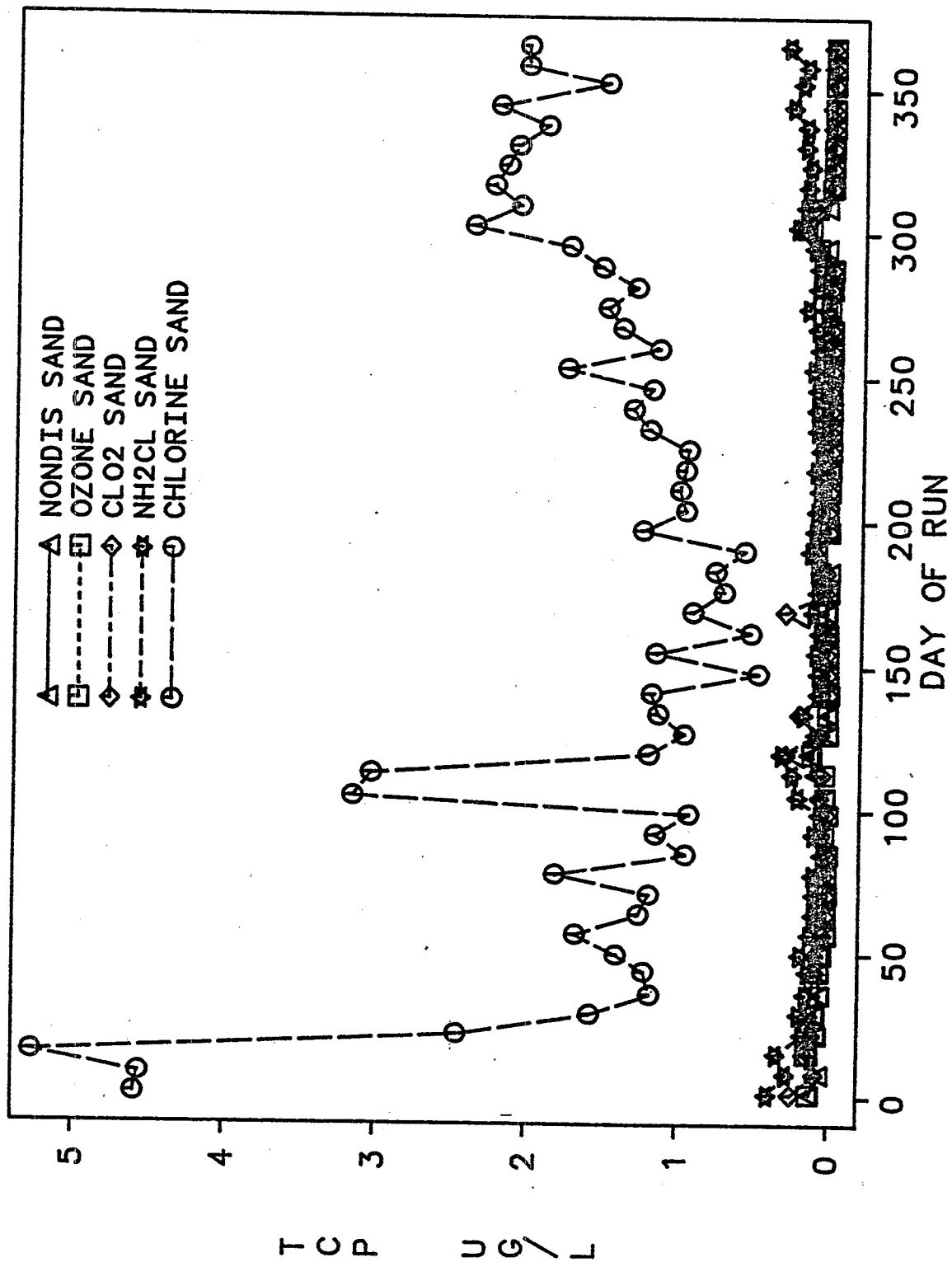


Figure 93. Comparison of TCP Levels in the Sand Column Effluent of each Process Stream.

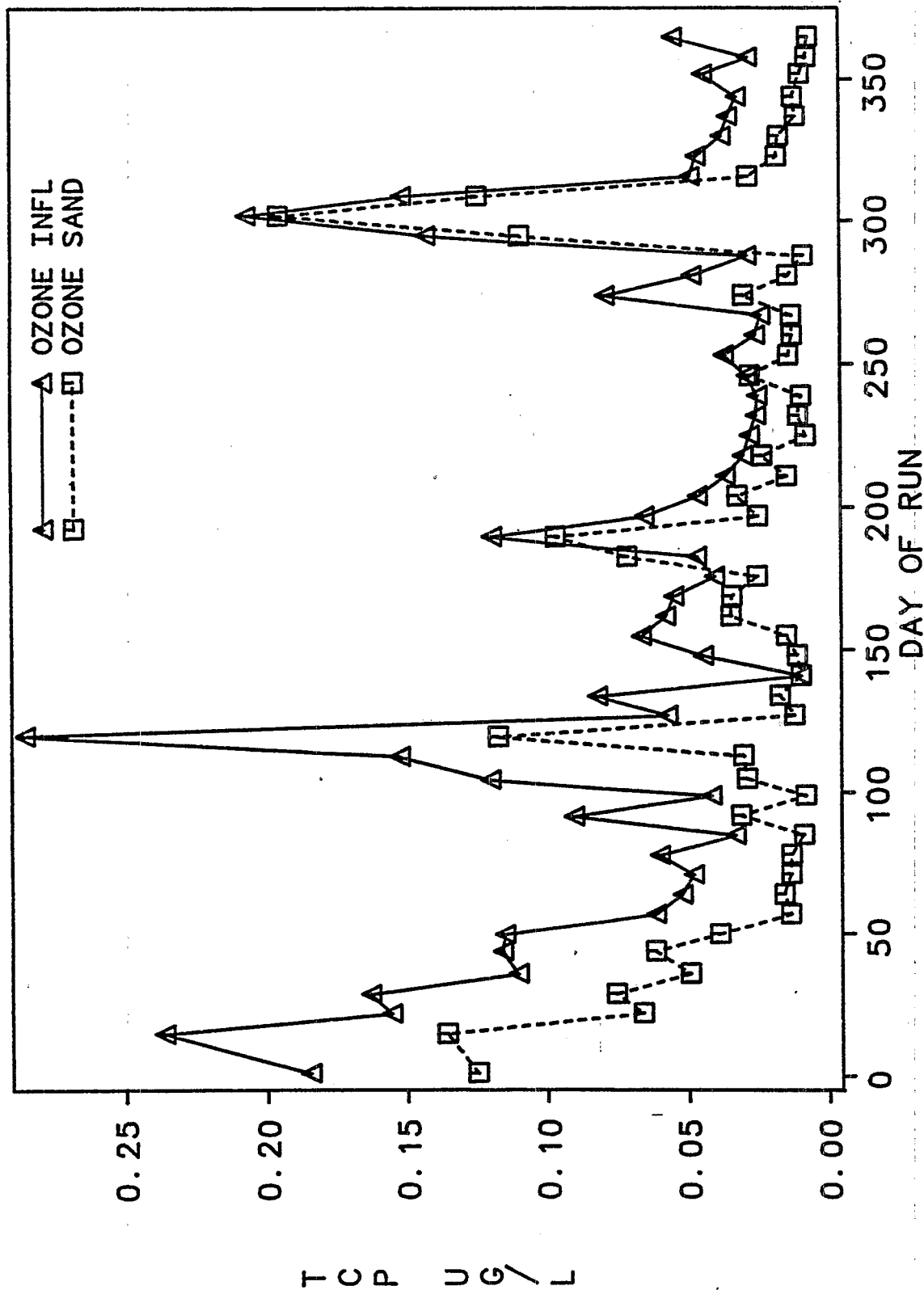


Figure 94. Comparison of TCP Levels in the Ozone Contact Chamber and Sand Column Effluents.

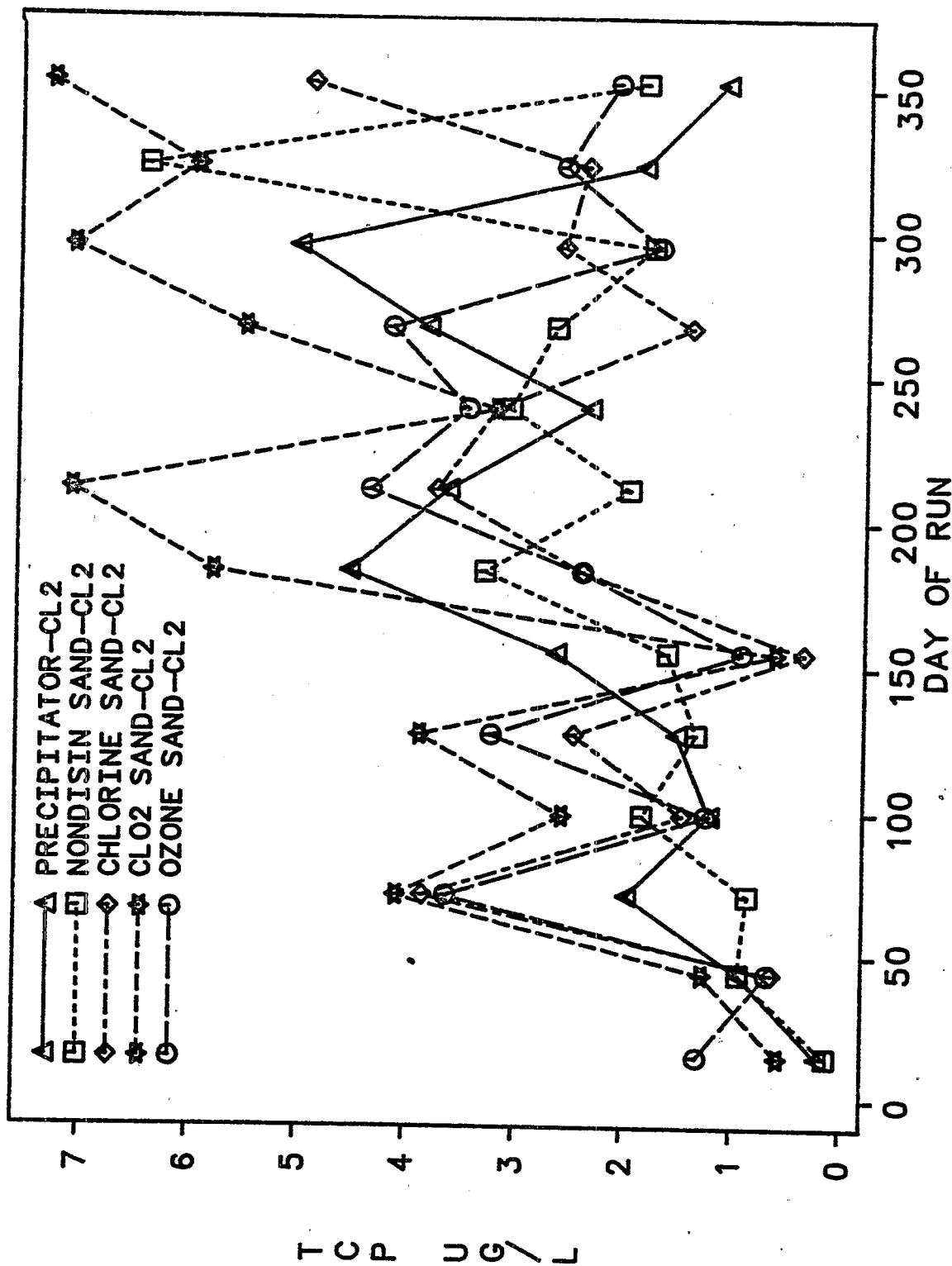


Figure 95. Comparison of TCP-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

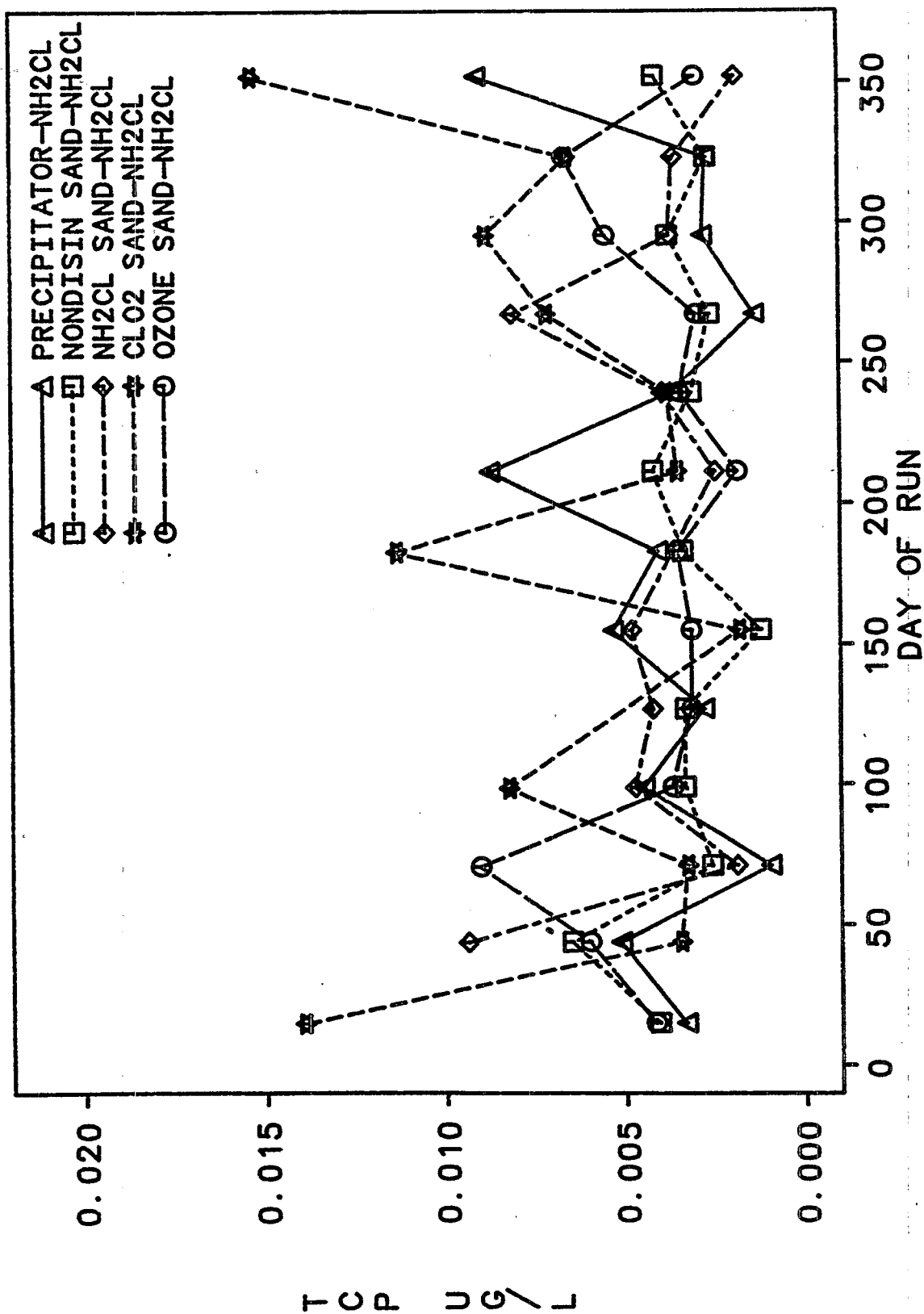


Figure 96. Comparison of TCP-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

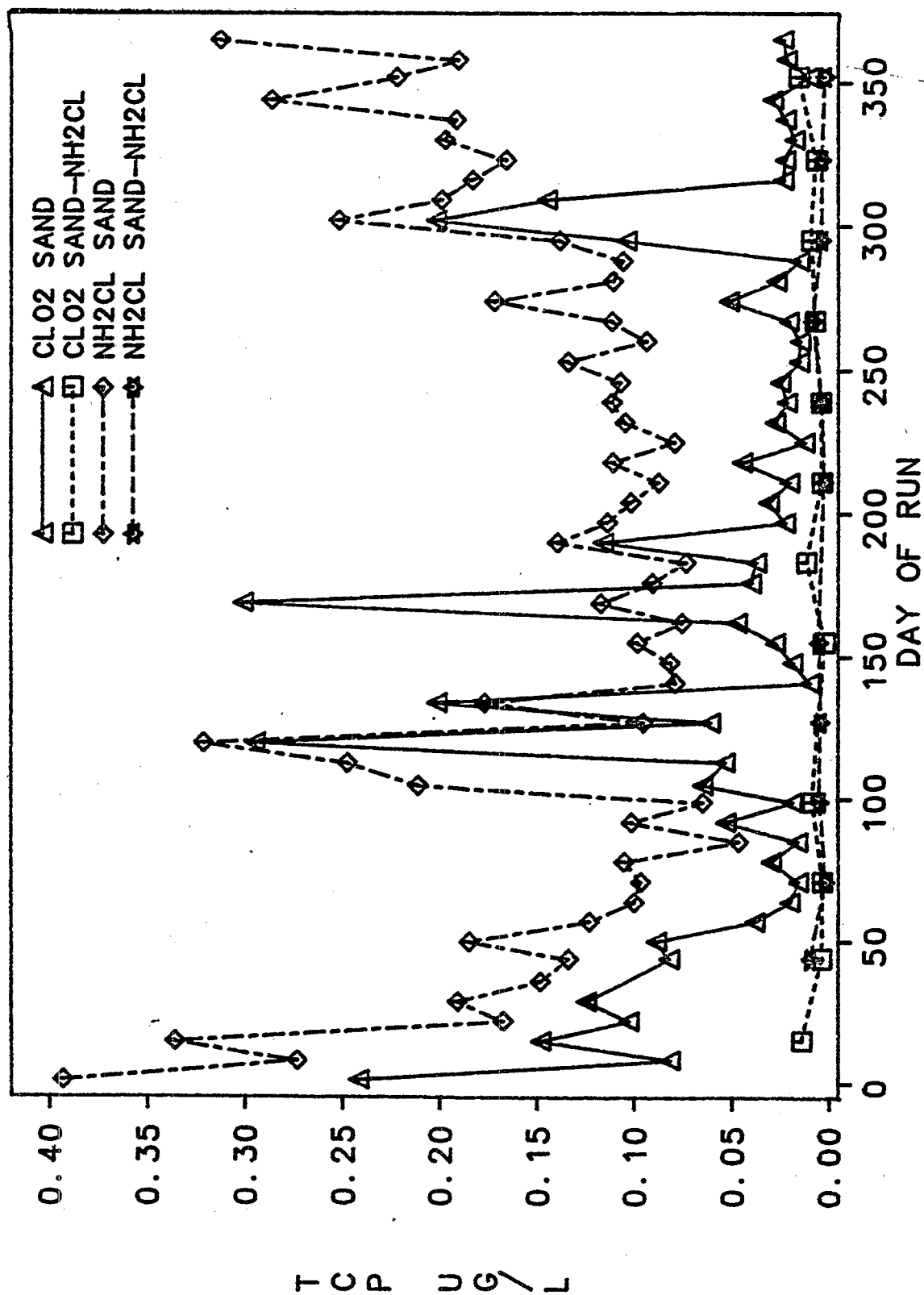


Figure 97. Comparison of TCP and TCP-NH<sub>2</sub>Cl Levels in the Chlorine Dioxide and Chloramine Sand Column Effluents.

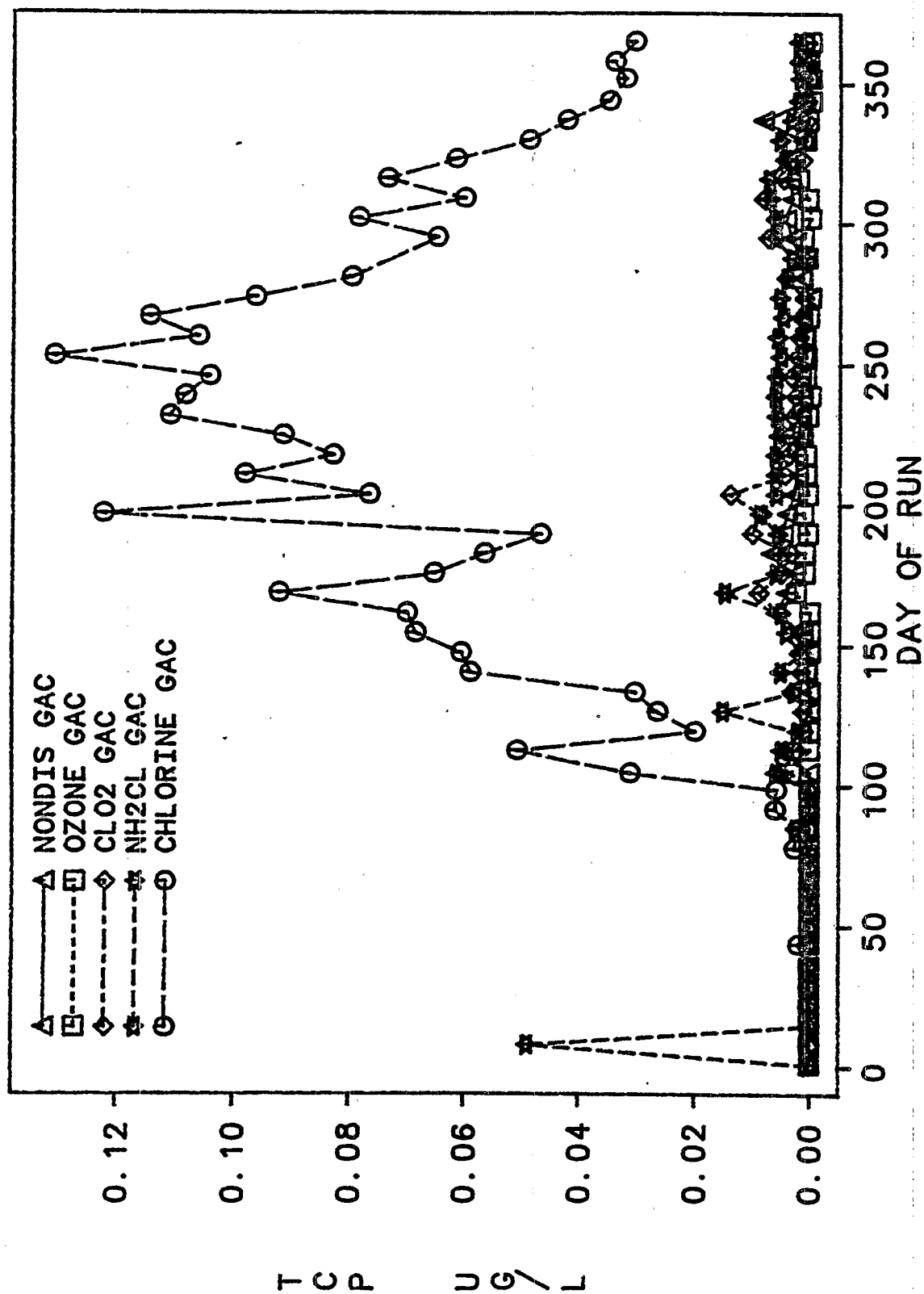


Figure 98. Comparison of TCP Levels in the GAC Column Effluent of each Process Stream.

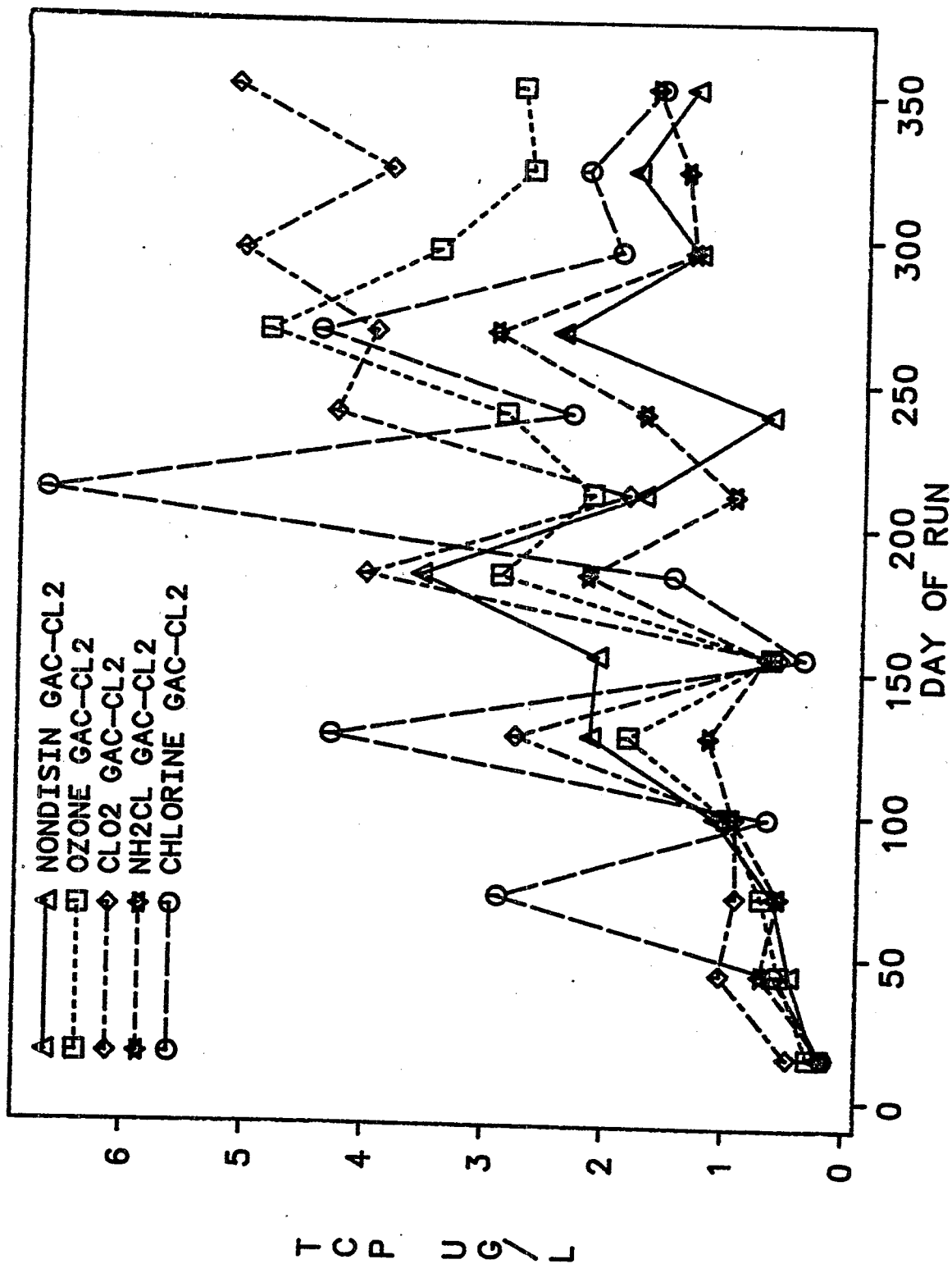


Figure 99. . Comparison of TCP-CL<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

those of the sand column effluents indicating essentially no removal of TCP precursors by GAC filtration. Except for a few outlying data points, the TCP-NH<sub>2</sub>Cl levels in the GAC effluents after similar treatment with chloramine were essentially the same as those of the chloramine treated sand column effluents (Figure 100).

The levels of 1,1-dichloropropanone (DCP) in the effluents of the disinfection contact chambers and the sand columns were essentially equivalent. Average sand column effluent concentrations were very similar in the chloramine and chlorine process streams at 0.43 and 0.47 ug/L, respectively, while those of the nondisinfected, ozone, and chlorine dioxide process streams were somewhat lower at 0.07, 0.04, and 0.10 ug/L (Figure 101). Chlorination of the sand column effluents followed by 5 days of storage produced similar DCP-Cl<sub>2</sub> levels in all process streams with averages ranging from 0.11-0.15 ug/L (Figure 102). Comparison of these data to the average DCP sand column effluent concentrations indicated a 0.36 ug/L reduction (75%) for the chlorine process stream and a 0.11 ug/L increase (400%) for the ozone process stream, while those of the nondisinfected and chlorine dioxide process streams were essentially unchanged. Chloramination of the sand column effluents and subsequent 5-day storage resulted in DCP-NH<sub>2</sub>Cl levels in the nondisinfected, ozone, and chloramine sand column effluents which were essentially identical averaging 0.04-0.05 ug/L (Figure 103). As seen earlier for a number of other parameters, a significant decrease (90%) in the DCP levels in the chloramine sand column effluent was observed after additional chloramination and storage for 5 days (Figure 104). Also, the average DCP-NH<sub>2</sub>Cl level for the chlorine dioxide sand column effluent of 0.30 ug/L was 0.16 ug/L (114%) greater than the DCP level in the sand column effluent.

The breakthrough of DCP across the GAC columns at the 0.002 ug/L level occurred on or about day 60 for the chlorine process stream, while breakthrough was observed about day 100 for the other process streams (Figure 105). Steady-state was reached in all process streams on day 130 with respective average steady-state concentrations of 0.003, 0.003, 0.006, 0.008, and 0.047 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine GAC columns corresponding to removals of 95, 93, 94, 98, and 90 percent. Chlorination of the GAC column effluents and subsequent storage for 5 days resulted in average DCP-Cl<sub>2</sub> levels of 0.06-0.09 ug/L for all process streams (Figure 106) which were comparable to the similarly treated sand column effluents. The same was true for the chloramine treated GAC effluents with respective average DCP-NH<sub>2</sub>Cl levels of 0.03, 0.06, 0.20, 0.04, and 0.02 ug/L for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams (Figure 107).



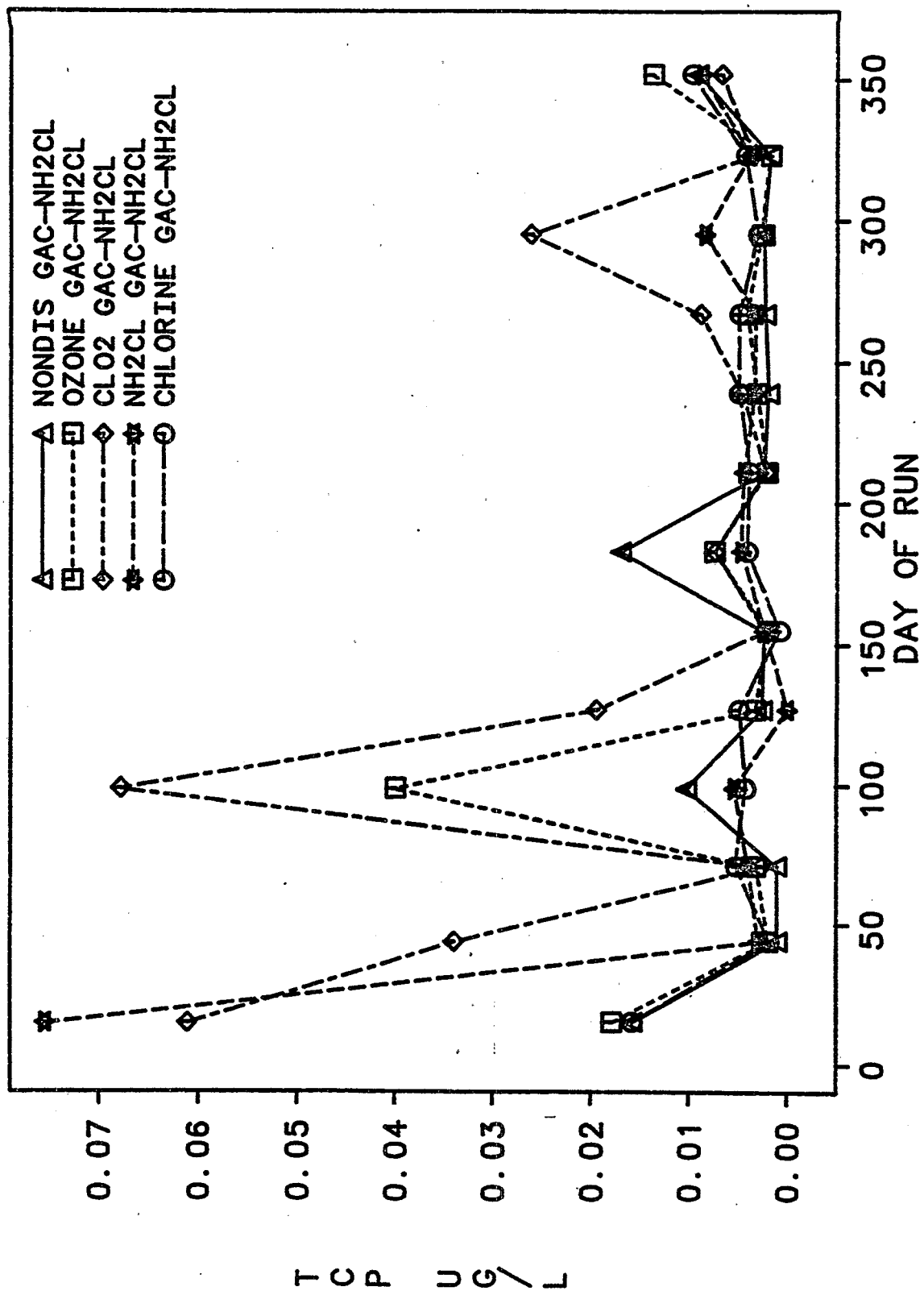


Figure 100. Comparison of TCP-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

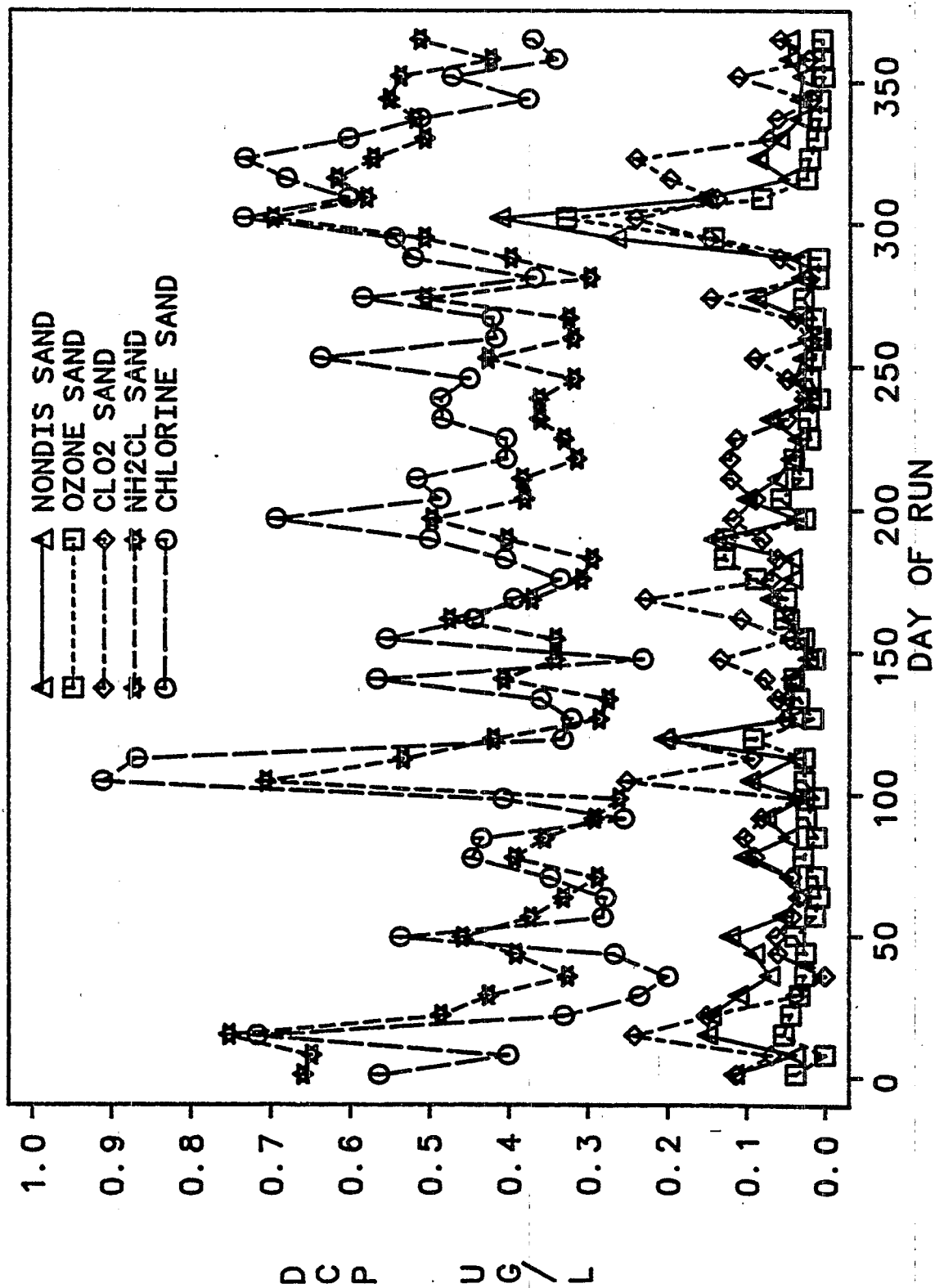


Figure 101. Comparison of DCP Levels in the Sand Column Effluent of each Process Stream.

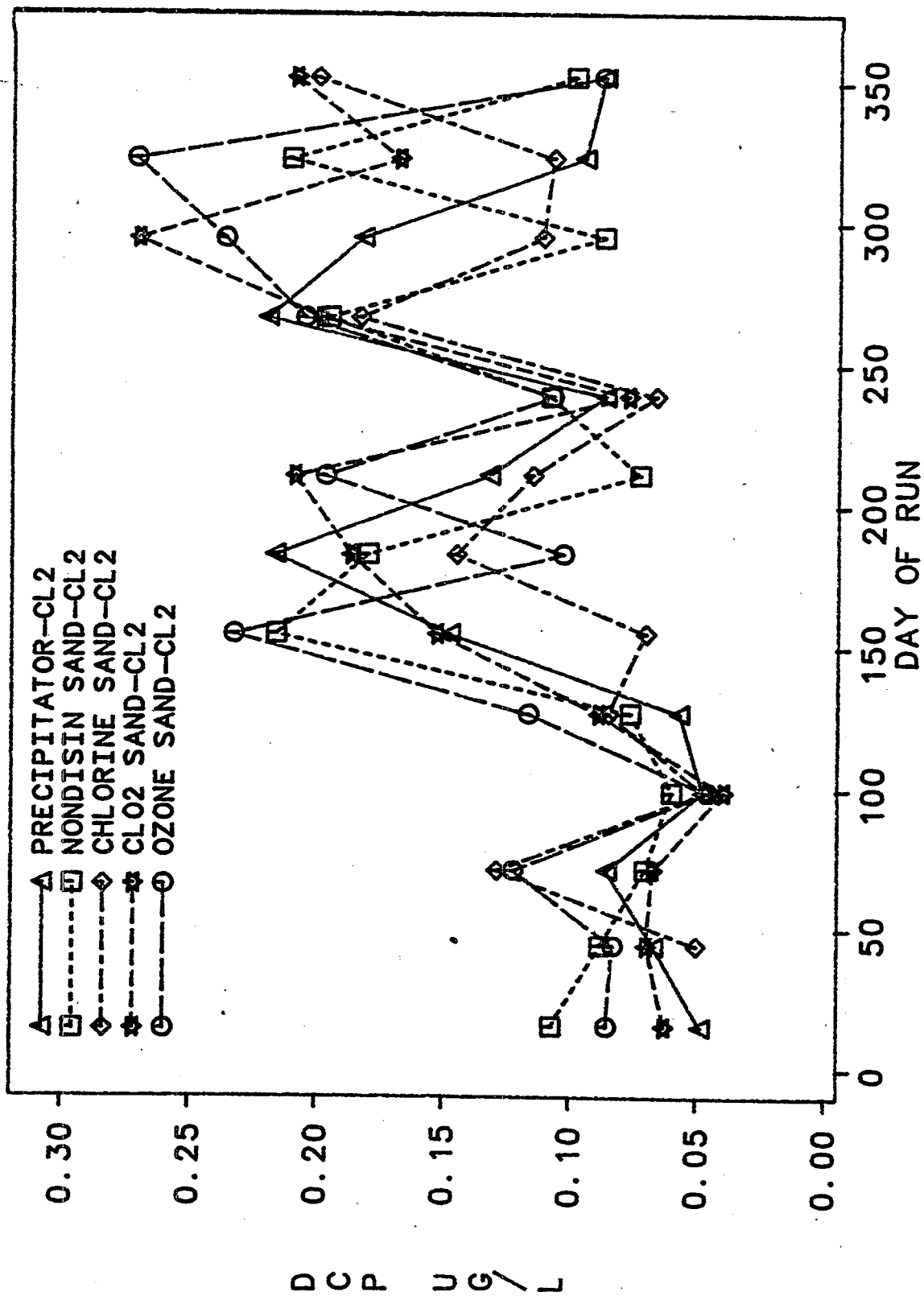


Figure 102. Comparison of DCP-Cl<sub>2</sub> Levels in the Sand Column Effluent of each Process Stream.

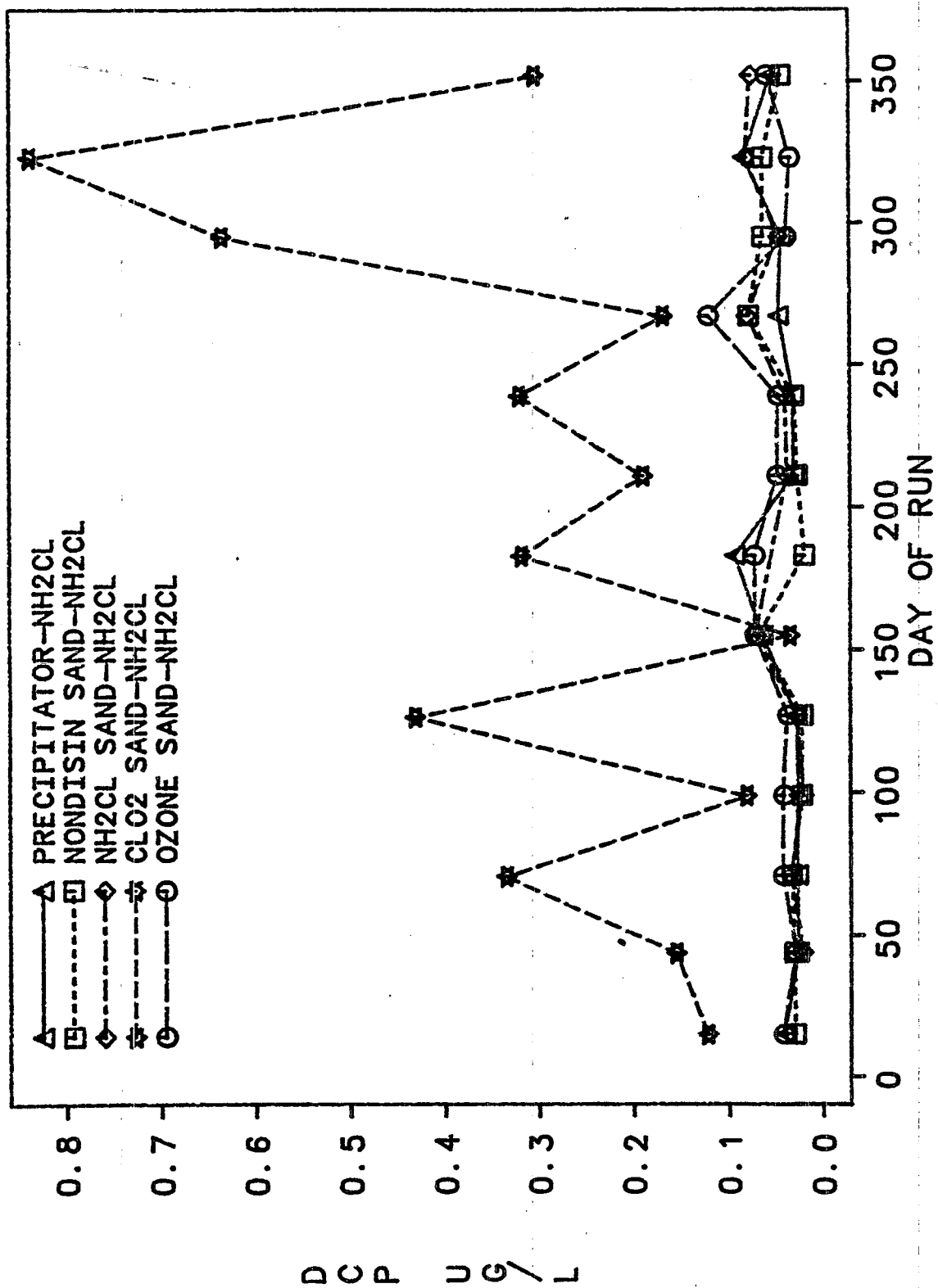


Figure 103. Comparison of DCP-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

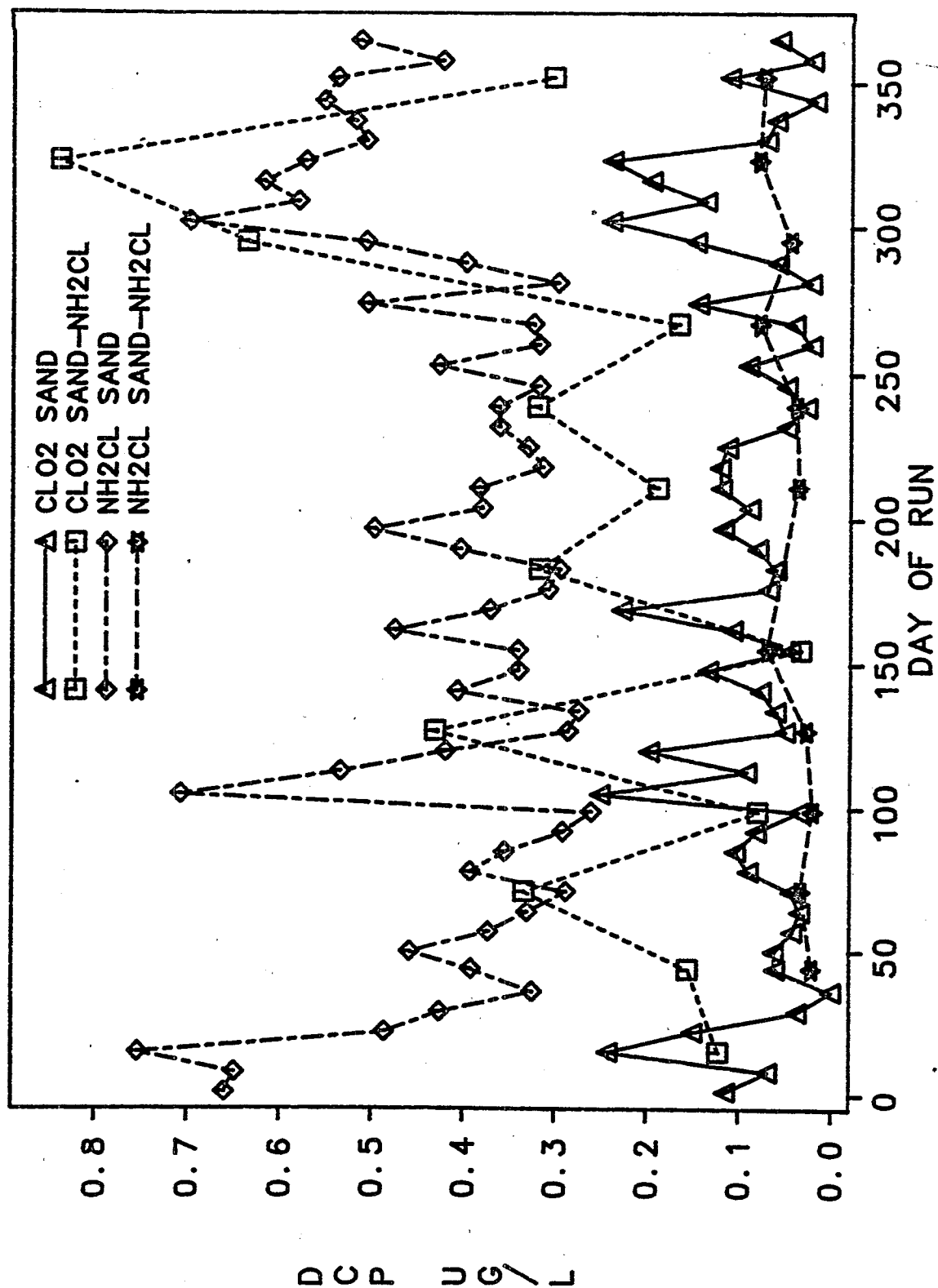


Figure 104. Comparison of the DCP and DCP-NH<sub>2</sub>Cl Levels in the Chlorine Dioxide and Chloramine Sand Column Effluents.

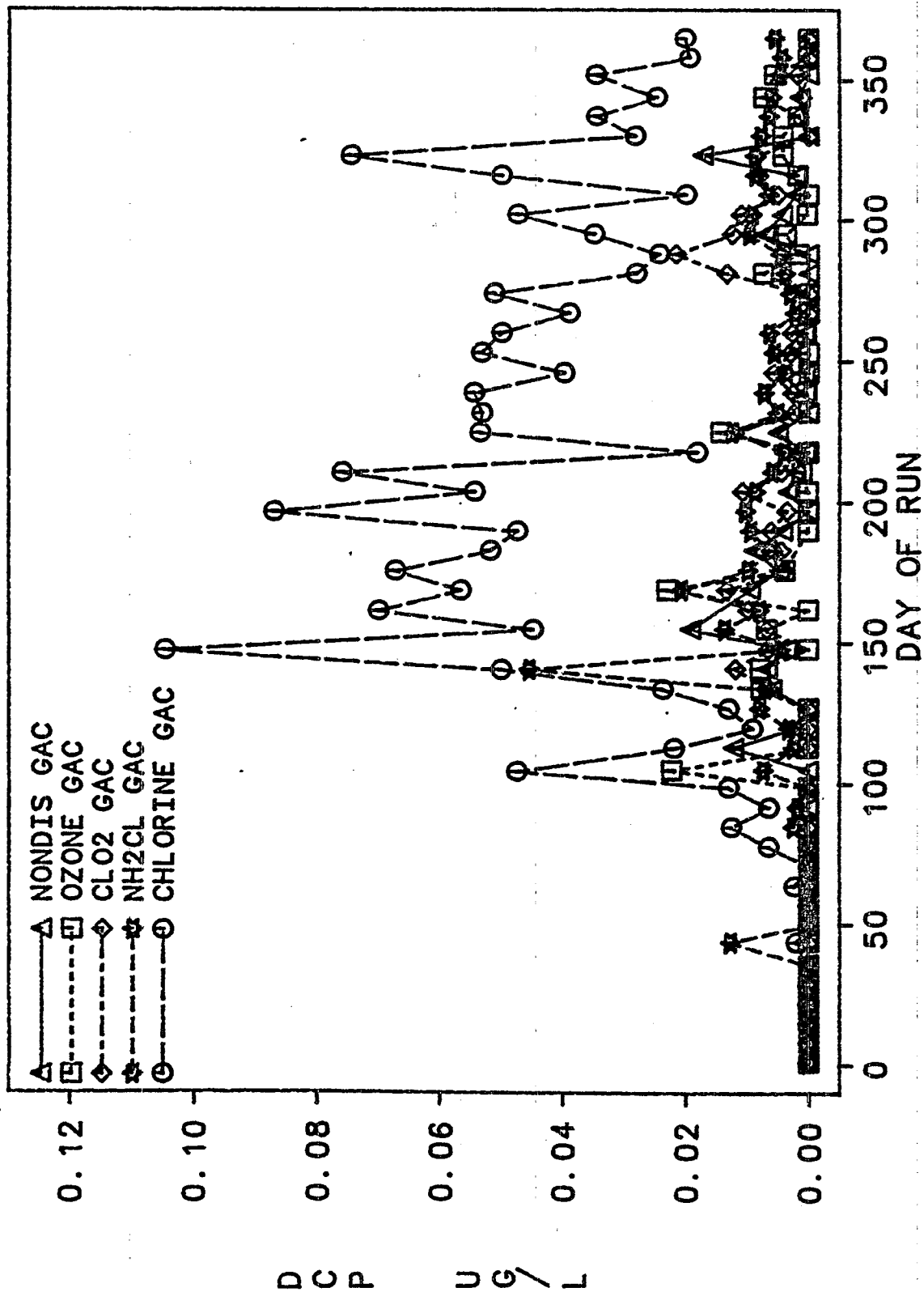


Figure 105. Comparison of the DCP Levels in the GAC Column Effluent of each Process Stream.

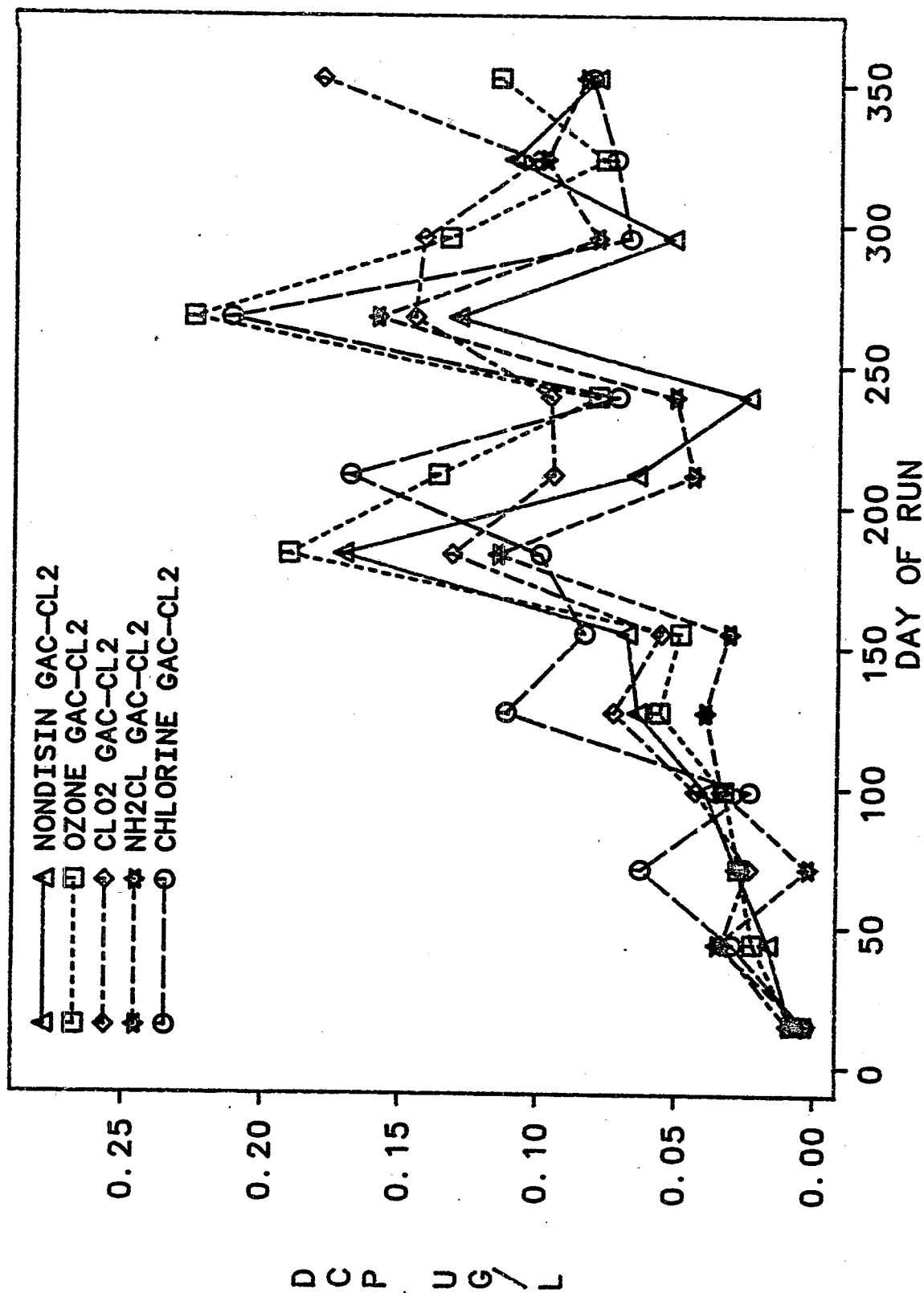


Figure 106. Comparison of the DCP-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

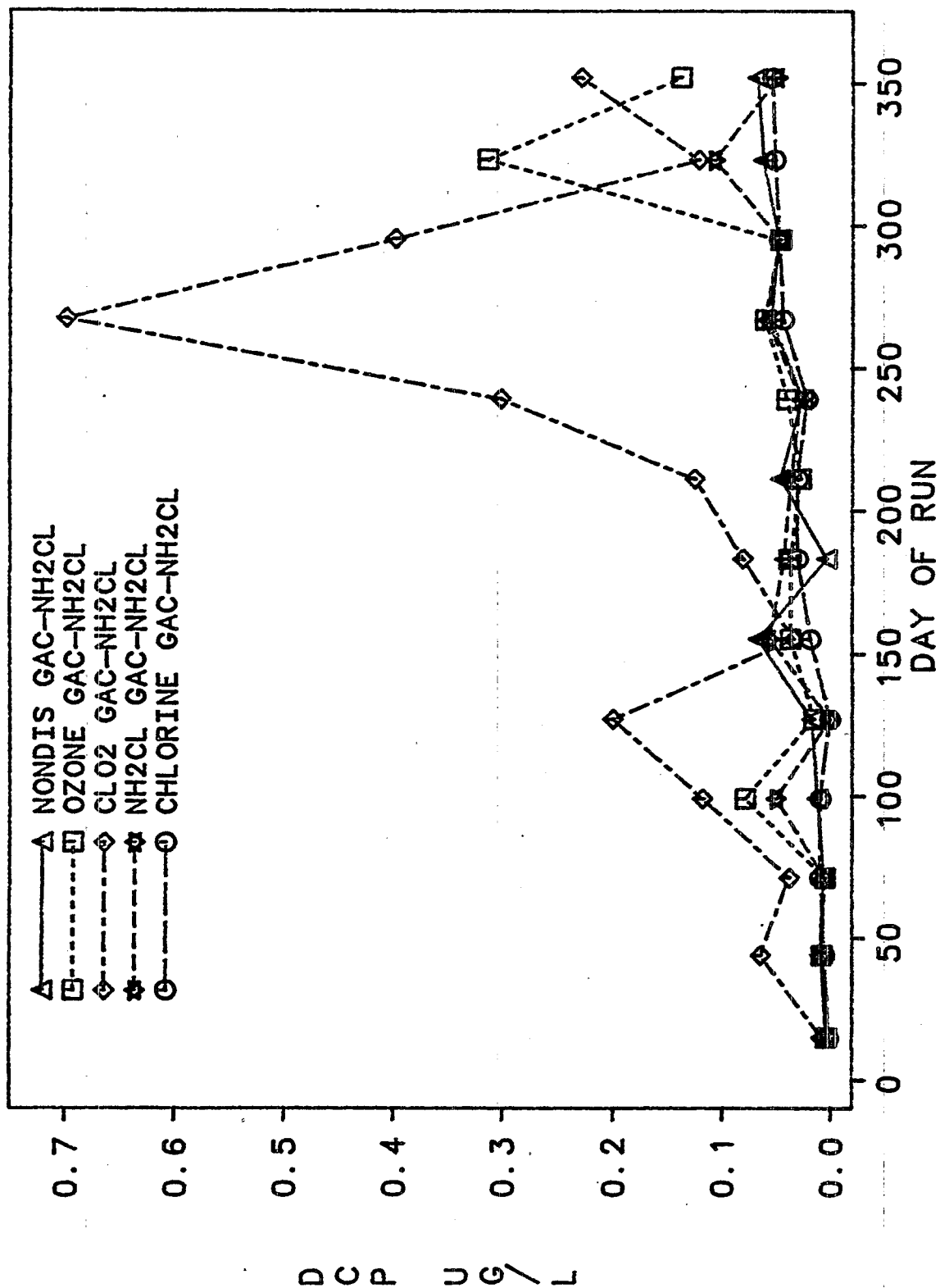


Figure 107. Comparison of DCP-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.



## Chloropicrin (CP)--

The concentrations of chloropicrin (CP) in the effluents of the nondisinfected, ozone, chlorine dioxide, and chloramine contact chambers were essentially equivalent averaging 0.004, 0.004, 0.015, and 0.038 ug/L (Figure 108), respectively, while that for the chlorine process stream was somewhat higher averaging 0.43 ug/L. Chlorination and subsequent storage of the sand column effluents produced elevated CP-Cl<sub>2</sub> levels averaging 1.3, 7.7, 1.4, and 1.3 ug/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams indicating that ozonation resulted in a significant (6.4 ug/L) increase in CP precursor levels (Figure 109). Only slight elevations in CP concentrations were observed after similar chloramine treatment and storage of the sand column effluents with respective average CP-NH<sub>2</sub>Cl levels of 0.03, 0.04, 0.11, and 0.09 ug/L for the nondisinfected, ozone, chlorine dioxide, and chloramine sand columns (Figure 110).

No consistent breakthrough of CP above the 0.003 ug/L level was observed across the GAC column of any process throughout the operational period (Figure 111). This resulted in average removals of 61, 54, 84, 95, and 99 percent for the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams, respectively, with the indicated higher removals being associated with higher sand column effluent concentrations. Chlorination of the GAC column effluents followed by 5-day storage resulted in respective average CP-Cl<sub>2</sub> levels of 0.51, 0.28, 0.48, and 0.37 ug/L for the nondisinfected, ozone, chlorine dioxide, and chlorine process streams indicating relative removals of 67, 96, 69, and 74 percent (Figure 112). No steady-state condition was evident for any process stream. The average CP-Cl<sub>2</sub> concentration in the chloramine GAC column effluent was similar at 0.49 ug/L. While ozonation produced the highest level of CP precursors, ozonation followed by GAC filtration resulted in the lowest levels of CP precursors. Similar treatment of the GAC effluents with chloramine produced respective average CP-NH<sub>2</sub>Cl levels of 0.012, 0.011, 0.050, 0.022 and 0.006 ug/L in the nondisinfected, ozone, chlorine dioxide, chloramine, and chlorine process streams (Figure 113) which were slightly lower than those of the similarly treated sand column effluents.

## Summary of Disinfection By-Products--

The annual average sand filter effluent concentration of total organic carbon (TOC), total organic halide (TOX), trihalomethane (THM), haloacetic acid (HAA), chloral hydrate (CH), haloacetonitrile (HAN), chloropicrin (CP), and halo ketone (HK) for each process stream are compared in Table 19. The total

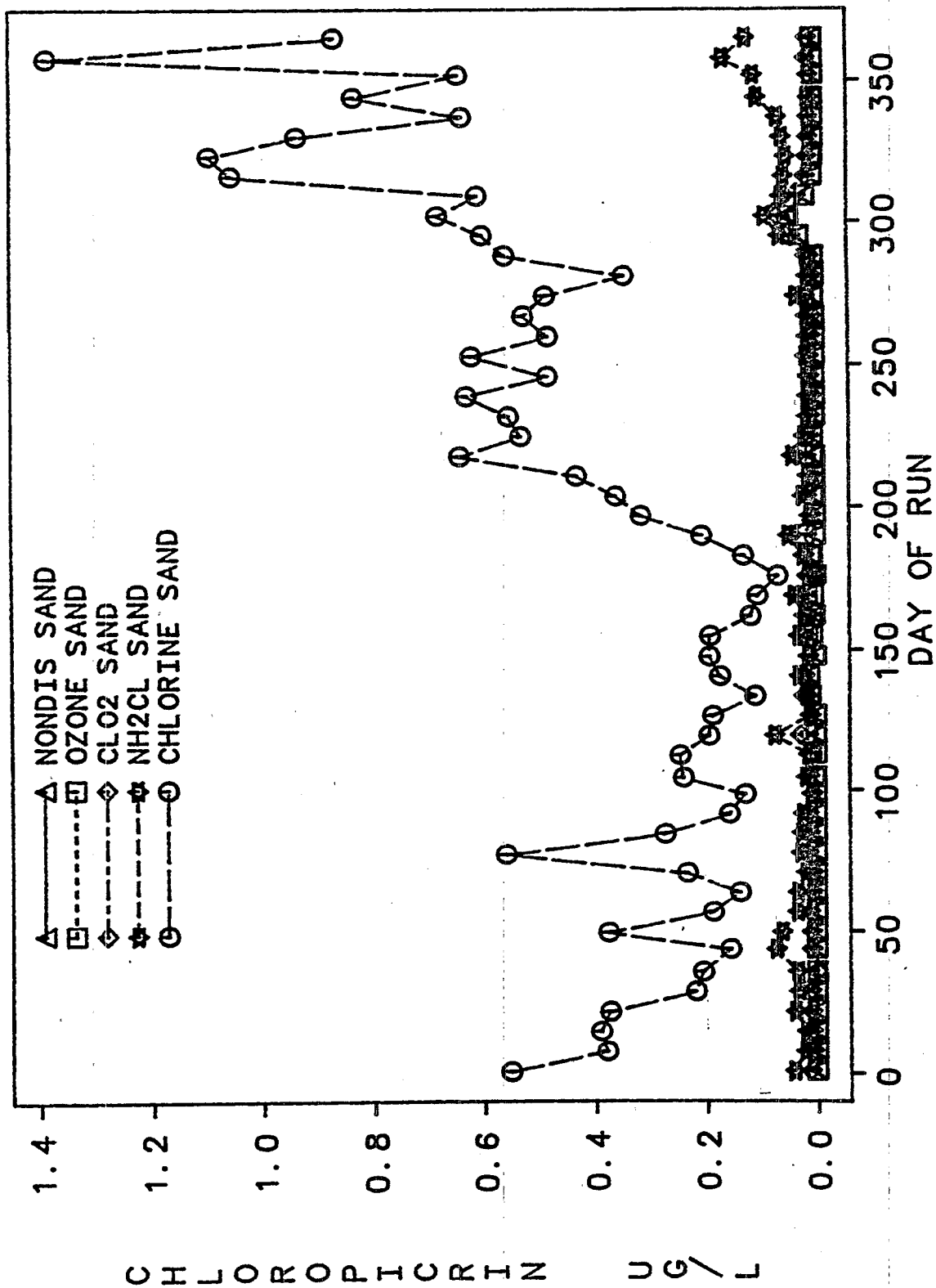


Figure 108. Comparison of the CP Levels in the Sand Column Effluent of each Process Stream.

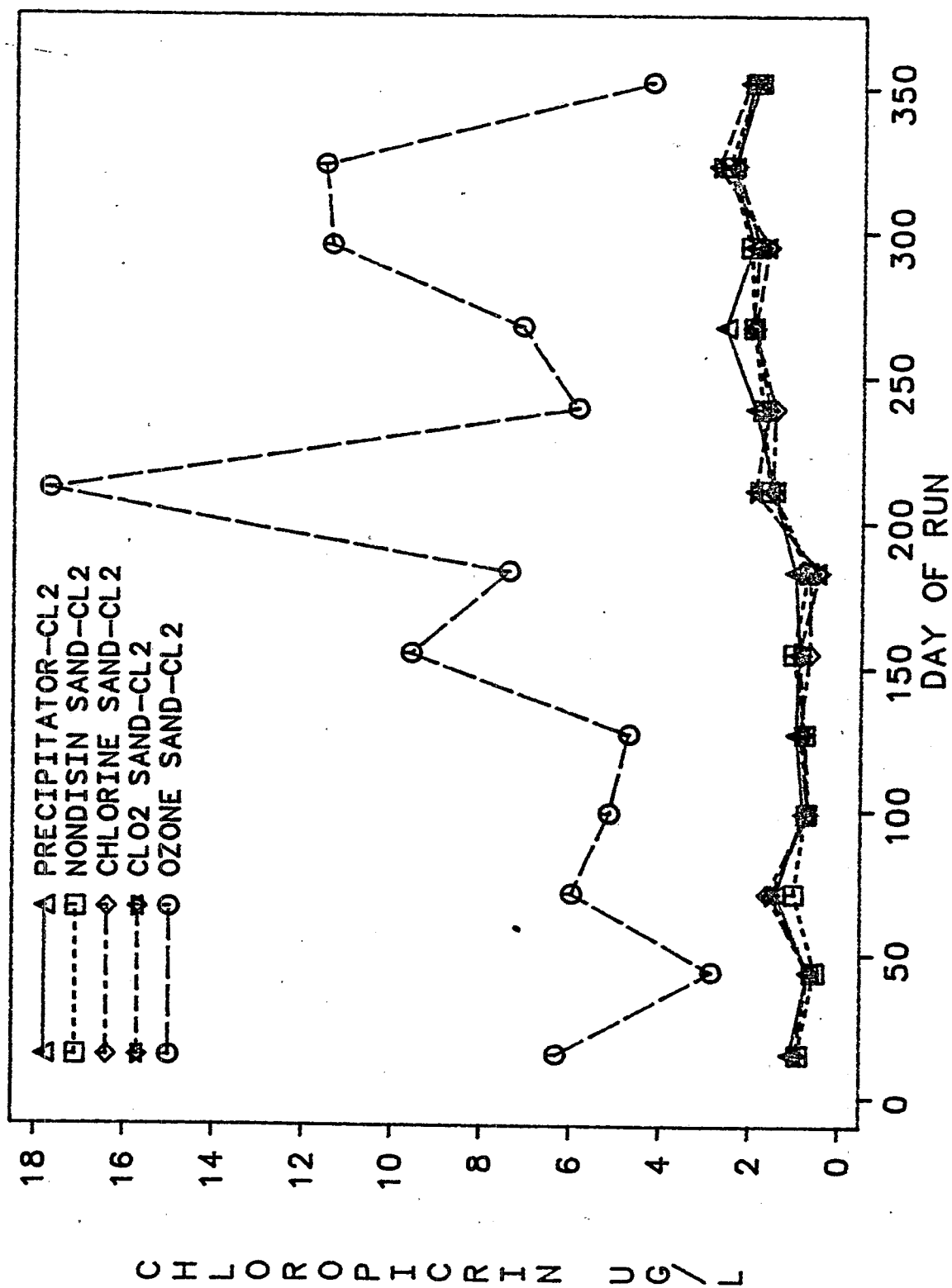


Figure 109. Comparison of the CP- $\text{Cl}_2$  Levels in the Sand Column Effluent of each Process Stream.

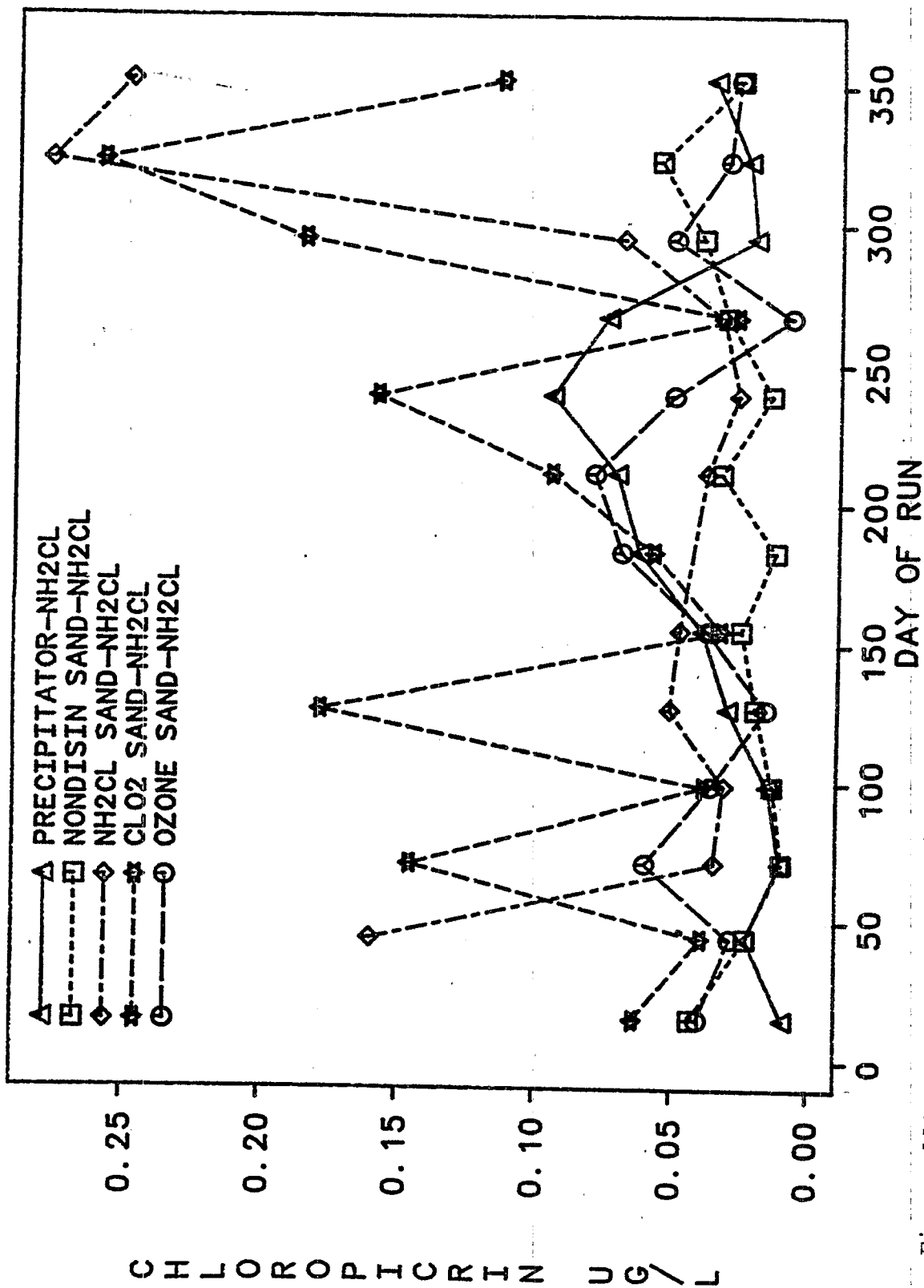


Figure 110. Comparison of the CP-NH<sub>2</sub>Cl Levels in the Sand Column Effluent of each Process Stream.

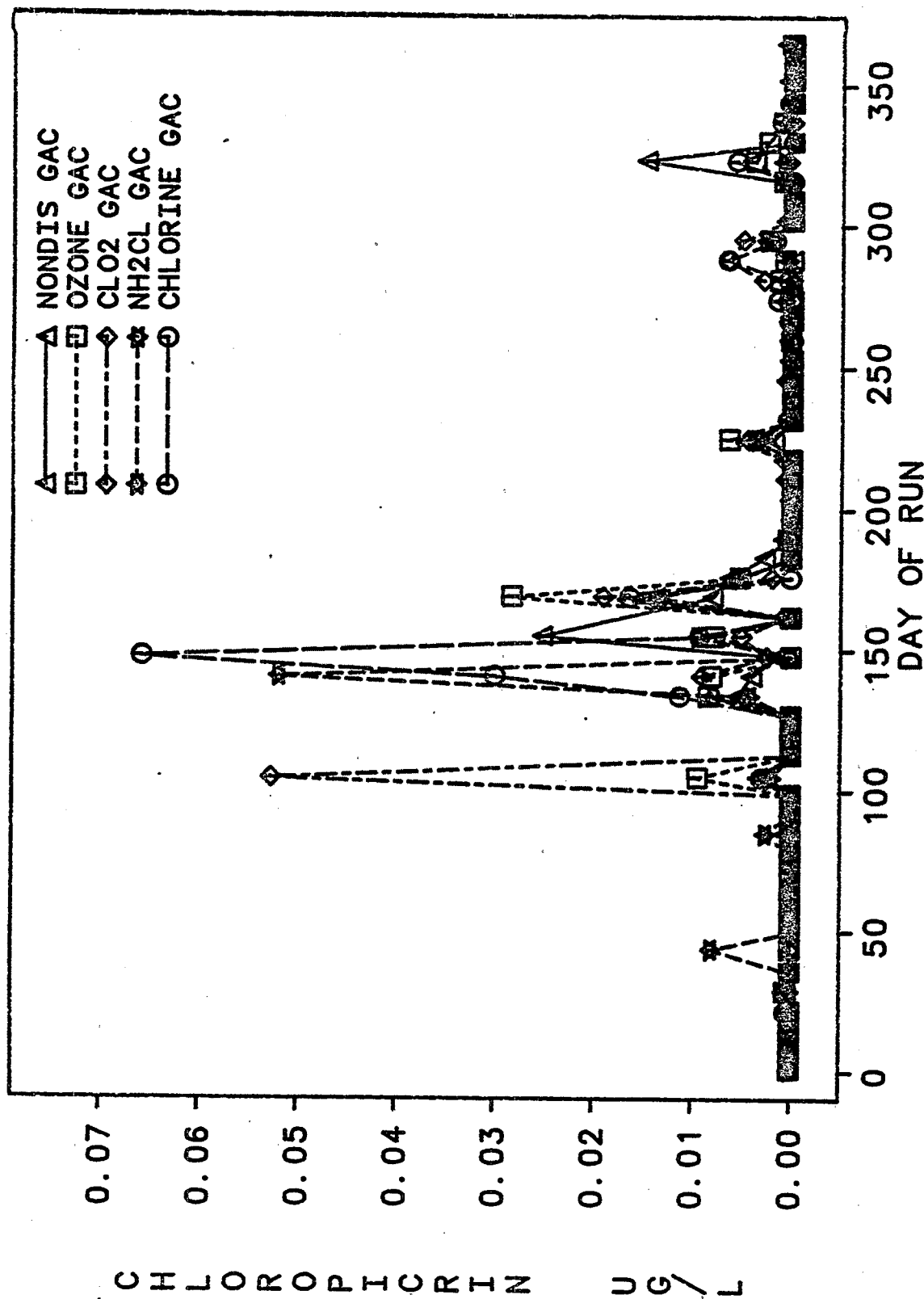


Figure 111. Comparison of the CP Levels in the GAC Column Effluent of each Process Stream.

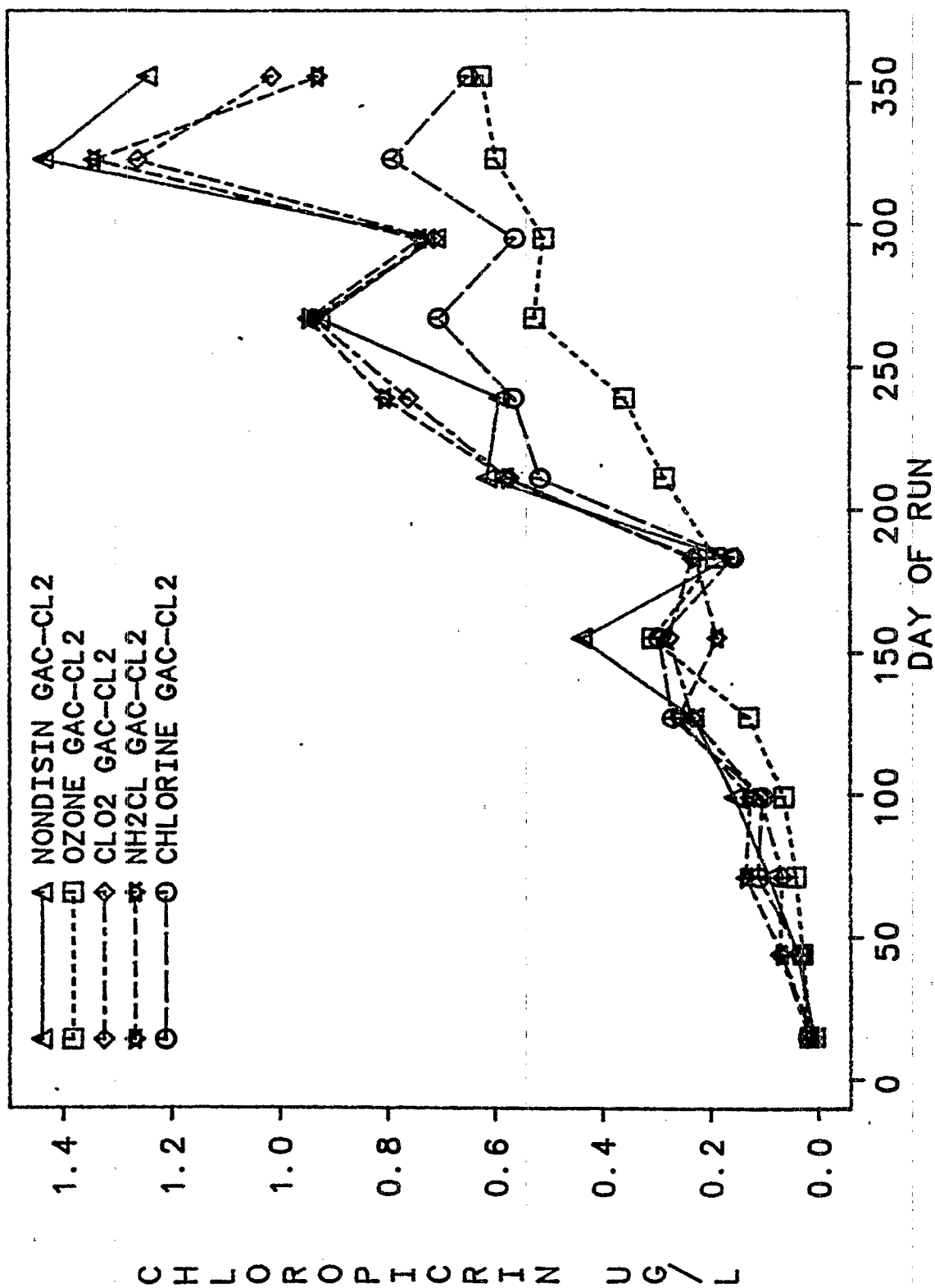


Figure 112. Comparison of the CP-Cl<sub>2</sub> Levels in the GAC Column Effluent of each Process Stream.

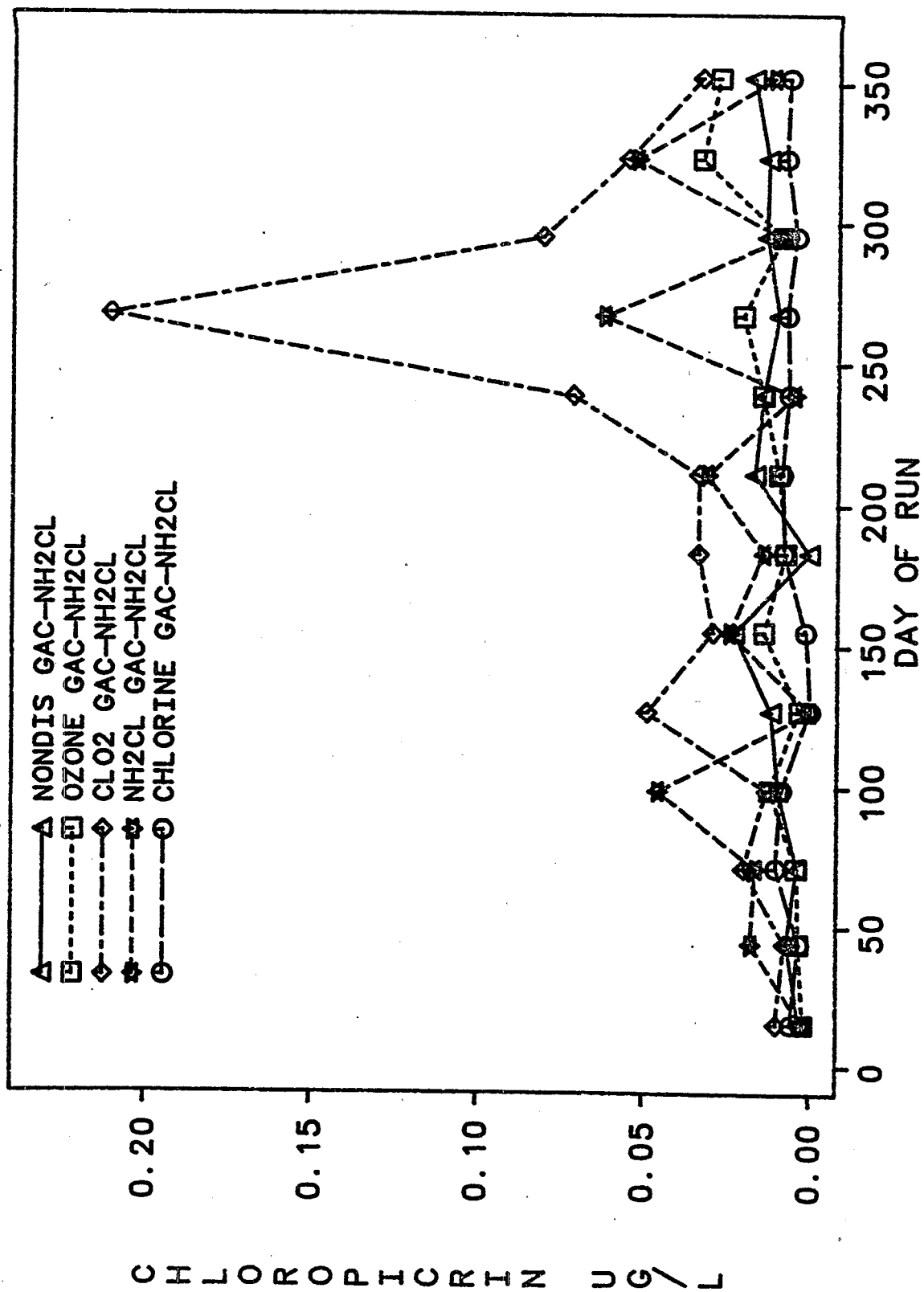


Figure 113. Comparison of the CP-NH<sub>2</sub>Cl Levels in the GAC Column Effluent of each Process Stream.

Table 19. Annual Average Sand Filter Effluent Concentration.

	<u>Nondisinfected</u>	<u>Ozone</u>	<u>Chlorine Dioxide</u>	<u>Chlorine</u>	<u>Chloramine</u>
TOC, mg/L	3.1	2.3	3.1	3.2	3.1
TOX, ug Cl/L	23	11	87	233	89
THM, ug/L	1.1	0.9	1.2	49	3.3
HAA, ug/L	1.2	1.3	3.7	30	5.6
CH, ug/L	0.03	0.01	0.04	4.5	0.3
HAN, ug/L	0.06	0.05	0.1	3.1	0.3
CP, ug/L	0.004	0.004	0.02	0.4	0.04
HK, ug/L	0.1	0.07	0.2	2.1	0.7
Total DBPs, ug/L	2.5	2.3	5.3	89	10

level of DBPs produced was estimated as the sum of the individual DBPs indicated (THM, HAA, CH, HAN, CP, and HK). The highest level of DBPs in the sand filter effluent were produced by free chlorine at 89 ug/L followed by chloramine at 10 ug/L. Treatment with chlorine dioxide produced a total of 5.3 ug/L DBPs while ozonation resulted in the lowest level of DBPs at 2.3 ug/L which was just slightly below that of the nondisinfected control at 2.5 ug/L. These levels of DBPs formed during disinfection were evaluated relative to the  $CT_{10}$  requirements of the Surface Water Treatment Rule<sup>4</sup> using the average disinfectant residuals, water temperature, and pH, as well as the  $T_{10}$  contact times determined for the ozone contact chamber at 10 min and that for the contact chamber in series with the sand column of the other disinfectants at 17 min. With an average water temperature of 16°C, a pH of 7.7, and a sand column effluent chlorine residual of 0.9 mg/L, the chlorine contact chamber in series with the sand column produced a DBP level of 89 ug/L achieving a  $CT_{10}$  of 15.3 mg/L-min which corresponds to a Giardia lamblia removal of approximately 0.5 log and a virus removal of greater than 4 logs. The chlorine dioxide contact chamber and sand column achieved a  $CT_{10}$  of 5.1 mg/L-min at 16°C for a Giardia removal of 0.8 log and a virus removal of 2.4 logs while producing only 5.3 ug/L of DBPs. The ozone process stream which contained the lowest level of DBPs in



the sand column effluent at 2.3 ug/L, achieved a  $CT_{10}$  of 5 mg/L-min in the ozone contact chamber which exceeded a  $10 \log$  removal for Giardia and viruses. Chloramine, while producing only 10 ug/L of DBPs, achieved a  $CT_{10}$  of 34 mg/L-min resulting in only a 0.07 log removal of Giardia and a 0.17 log removal of viruses.

The maximum average level of DBPs in a chlorinated distribution system after 5 days at 30°C following initial predisinfection and sand filtration have been estimated by the terminal- $Cl_2$  data obtained for each process stream. Relatively high levels of DBPs were formed in the chlorinated distribution simulation (terminal- $Cl_2$ ) samples, regardless of the type of predisinfectant employed, as indicated in Table 20. Pretreatment with ozone and chlorine dioxide followed by sand filtration resulted in the lowest maximum levels of DBPs averaging 309 and 308 ug/L, respectively, while maximum average DBP levels of 474 and 446 ug/L were observed for the nondisinfected and chlorine process streams. From these data, it is evident that extended chlorine contact has almost completely negated any beneficial effects derived from ozonation which were apparent in the sand column effluent, and, that the use of chlorine in the distribution system is prohibitive for those waters containing high levels of DBP precursors in systems using only sand

Table 20. Maximum Annual Average Chlorinated Distribution System Concentrations for Sand Filtration.

	<u>Nondisinfected</u>	<u>Ozone</u>	<u>Chlorine Dioxide</u>	<u>Chlorine</u>
TOX, ug $Cl/L$	557	339	379	540
THM, ug/L	236	154	138	225
HAA, ug/L	153	87	113	139
CH, ug/L	79	55	45	75
HAN, ug/L	2.0	2.7	6.0	2.9
CP, ug/L	1.3	7.7	1.4	1.3
HK, ug/L	2.2	2.6	4.3	2.5
Total DBPs, ug/L	474	309	308	446

filtration.

Similar maximum average DBP levels for a chlorinated distribution system following initial predisinfection, sand filtration, and GAC filtration with a 20 min empty bed contact time are presented in Table 21. The respective maximum average annual DBP levels after GAC filtration and 5 days in a chlorinated distribution system were 138, 183, 232, and 223 ug/L for pretreatment with ozone, chlorine dioxide, chlorine, and chloramine with the nondisinfected process stream averaging 213 ug/L. While these levels are also relatively high, it is possible to produce water with lower levels of DBPs by reactivating the GAC within the filters at a frequency of less than 12 months. For example, by assuming that the DBP levels in the effluents of all the treatment plant filters are evenly distributed across the DBP breakthrough profiles in Figure 114, these profiles can be used to estimate the GAC reactivation frequency for maintaining the running average of DBPs below a desired level, such as 100 ug/L. Using these criteria, the reactivation frequencies required to maintain a running average of total DBPs of less than 100 ug/L after 5 days in a chlorinated distribution system were estimated at 240, 170, 115, 100, and 90 days for pretreatment with ozone, chlorine dioxide, chloramine, chlorine, and no pretreatment, respectively. If the criteria for

Table 21. Maximum Average Chlorinated Distribution System Concentrations for GAC Filtration.

	<u>Nondisinfected</u>	<u>Ozone</u>	<u>Chlorine Dioxide</u>	<u>Chlorine</u>	<u>Chloramine</u>
TOX, ug Cl/L	231	127	216	246	235
THM, ug/L	107	74	84	125	112
HAA, ug/L	72	39	65	70	75
CH, ug/L	28	20	26	31	30
HAN, ug/L	4.1	2.5	4.7	3.3	3.9
CP, ug/L	0.5	0.3	0.5	0.4	-0.5
HK, ug/L	1.6	2.2	2.8	2.3	1.3
Total DBPs, ug/L	213	138	183	232	223

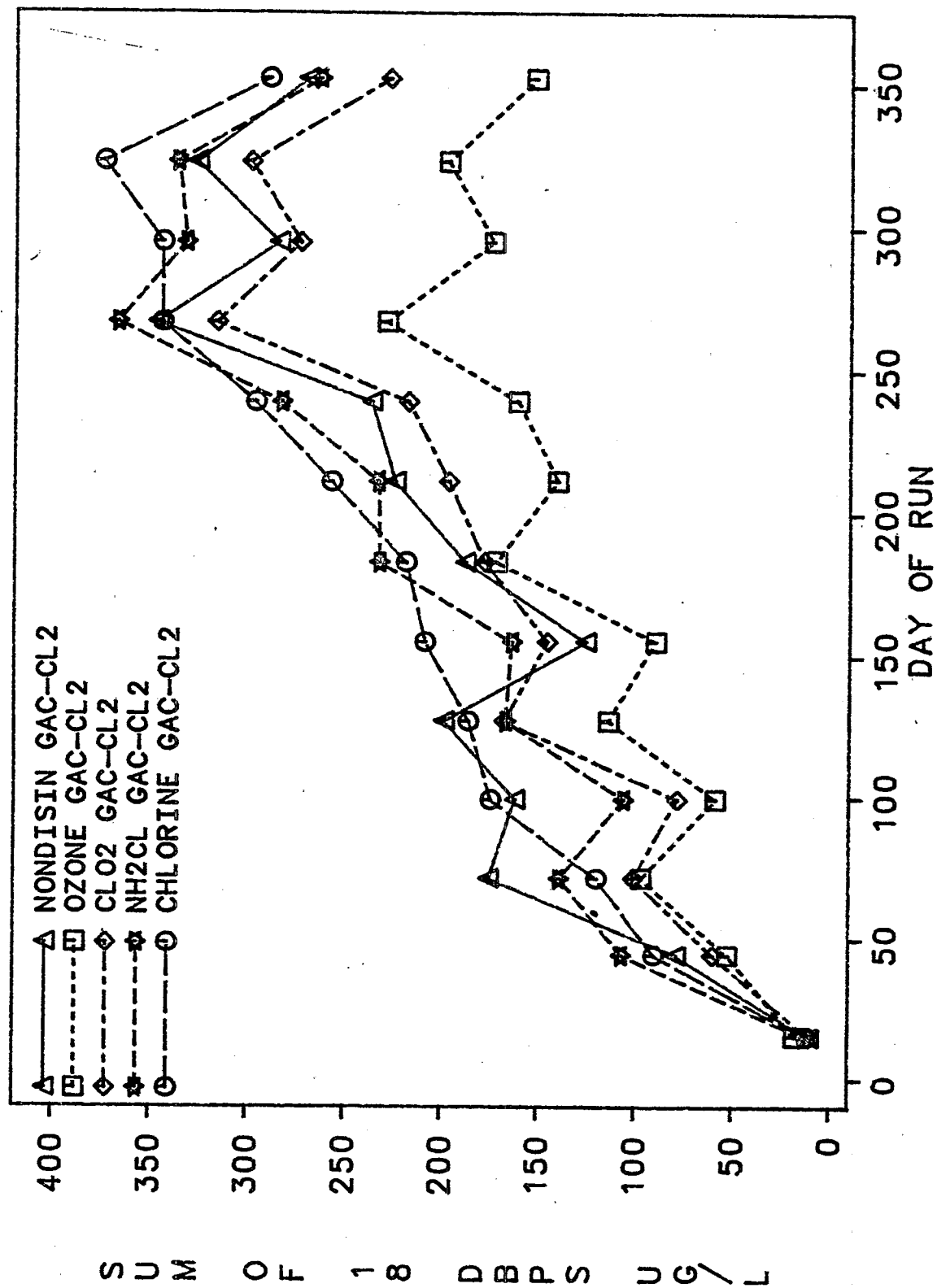


Figure 114. Comparison of Total DBP Levels in the Effluent of each GAC Column.

reactivation was a THM level of less than 50 ug/L, the reactivation frequency would be reduced to approximately 100 days for the ozone and chlorine dioxide process streams and approximately 50 days for the remaining process streams (Figure 19).

The maximum average DBP levels present in a chloraminated distribution system after 5 days at 30°C were estimated from the terminal-NH<sub>2</sub>Cl samples from each process stream in which ammonia was added prior to chlorine. The average DBP levels in a chloraminated distribution system for predisinfection followed by sand filtration, presented in Table 22, indicate that the use of chloramine in the distribution system is particularly effective in minimizing DBPs with respective maximum annual averages of 12, 19, 24, and 21 ug/L for predisinfection with ozone, chlorine dioxide, chloramine and no predisinfection. While ozone and chlorine dioxide can produce effective removals of Giardia and viruses as previously indicated, chlorine dioxide pretreatment also produces a significantly higher level of unknown DBPs than does ozone, as measured by TOX, with respective averages of 89 and 27 ug Cl/L. Chlorine dioxide also produces the inorganic by-products of chlorite (est. at 0.5 mg/L) and chlorate (not measured) which will soon be regulated. Ozone, on the other hand

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Table 22. Maximum Average Chloraminated Distribution System Concentrations for Sand Filtration.

	<u>Nondisinfected</u>	<u>Ozone</u>	<u>Chlorine Dioxide</u>	<u>Chloramine</u>
TOX, ug Cl/L	44	27	89	59
THM, ug/L	8.5	3.2	4.2	9.4
HAA, ug/L	12	8.8	14	14
CH, ug/L	0.03	0.03	0.3	0.08
HAN, ug/L	0.04	0.04	0.3	0.05
CP, ug/L	0.03	0.04	0.1	0.09
HK, ug/L	0.04	0.06	0.3	0.05
Total DBPs, ug/L	21	12	19	24

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produces aldehyde and ketone by-products and results in extremely high heterotrophic plate counts (HPCs) in the sand column effluent as described in a subsequent section. In order to reduce the HPC to an acceptable level, a short chlorine contact period on the order of several minutes would be required prior to the addition of ammonia for the formation of chloramines. This would, of course, slightly increase the level of DBPs in the distribution system.

Slightly lower DBP levels can be achieved in a chloraminated distribution system by using GAC as a filtration media as indicated in Table 23. Maximum annual DBP levels averaging 7, 10, 13, and 45 ug/L were observed for ozone, chlorine dioxide, chloramine, and chlorine predisinfection with the nondisinfected process stream averaging 12 ug/L. The relatively high level of DBPs in the chlorine process stream was due primarily to the breakthrough of instantaneous THMs with some contribution from the haloacetic acids. The use of GAC filtration in conjunction with ozone or chlorine dioxide predisinfection to minimize DBP levels in a chloraminated distribution system would appear to be of little benefit and would be cost prohibitive.

Table 23. Maximum Average Chloraminated Distribution System Concentrations for GAC Filtration.

	<u>Nondis- infected</u>	<u>Ozone</u>	<u>Chlorine Dioxide</u>	<u>Chlorine</u>	<u>Chloramine</u>
TOX, ug Cl/L	29	13	26	69	32
THM, ug/L	5.2	2.2	2.2	37	5.5
HAA, ug/L	6.4	4.5	6.6	7.5	6.7
CH, ug/L	0.04	0.08	0.3	0.06	0.2
HAN, ug/L	0.03	0.05	0.3	0.03	0.05
CP, ug/L	0.01	0.01	0.05	0.006	0.02
HK, ug/L	0.04	0.07	0.2	0.03	0.05
Total DBPs, ug/L	12	7	10	45	13

## TOX as a Surrogate for DBPs--

The TOX data obtained on a weekly basis from the sampling locations in each process stream were compared with the corresponding sum of the eighteen disinfection by-products measured during this study which include the THMs (4), haloacetic acids (6), haloacetonitriles (4), haloketones (2), chloral hydrate, and chloropicrin. Because the response of one mole of bromide is equivalent to that of one mole of chloride by TOX analysis, the difference in weight of the brominated species was compensated for by determining the percent halide as chloride for each compound and applying this factor to the concentration found. This resulted in ug chloride/L which was directly comparable to the ug chloride/L determined by TOX measurement. For example, while 10 ug bromoform/L is equivalent to 9.48 ug bromide/L, the concentration as chloride is only 4.21 ug chloride/L. This difference in response was empirically verified by the TOX analysis of bromobenzene and chlorobenzene.

The TOX and DBP data from each sampling point in each process stream are compared in Figure 115 by process stream, and in Figure 116 by the sampling location within each process stream. The center line in each figure represents the regression line with the outside lines representing two standard deviations. While a relative good correlation was observed for these 1094 data points with a correlation coefficient of 0.90 and a standard deviation of 17, it was evident from the figures that those data points in the area of 0-50 ug Cl/L for the DBPs and 150-350 ug Cl/L for TOX appeared to skew the correlation. Examination of both figures revealed that these data originated from the chlorine contact chamber and sand column effluents. This suggests that the reactions occurring at these locations were not yet near equilibrium due to their relatively short contact times, and that the reaction rate of TOX formation was apparently greater than that of the DBPs. A closer examination of the data in the 0-150 ug Cl/L range for TOX in Figures 117 & 118 indicated that the contact chamber and sand column effluent data of the chlorine dioxide and chloramine process streams also appeared to skew the correlation for similar reasons. In addition, examination of the data for the chloramine process stream in Figure 119 suggested that some TOX species may be precursors of some of the DBPs, such as the THMs, haloacetic acids, and chloropicrin. While the average terminal chloramine DBP and TOX levels in the chloramine sand column effluent were 9 and 59 ug Cl/L, respectively, the average of the corresponding instantaneous DBP and TOX levels from the same location were 4 and 94 ug Cl/L. This indicated that a 35 ug Cl/L (37%) reduction in TOX had occurred with a corresponding increase in DBPs of 5 ug Cl/L (125%) following treatment with additional chloramine and storage for 5 days.

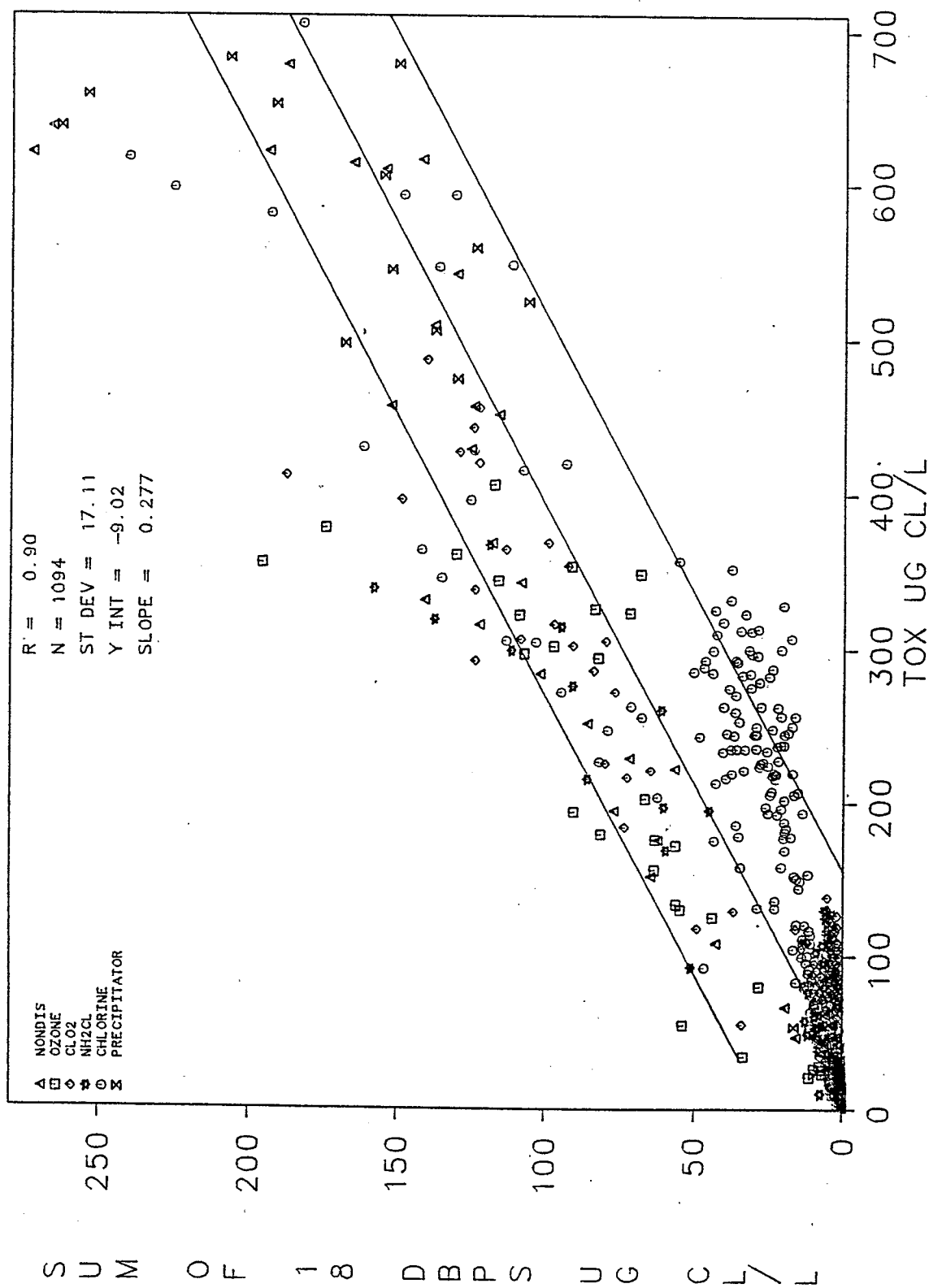


Figure 115. Regression Analysis of TOX and the DBPs at all Locations by Process Stream.

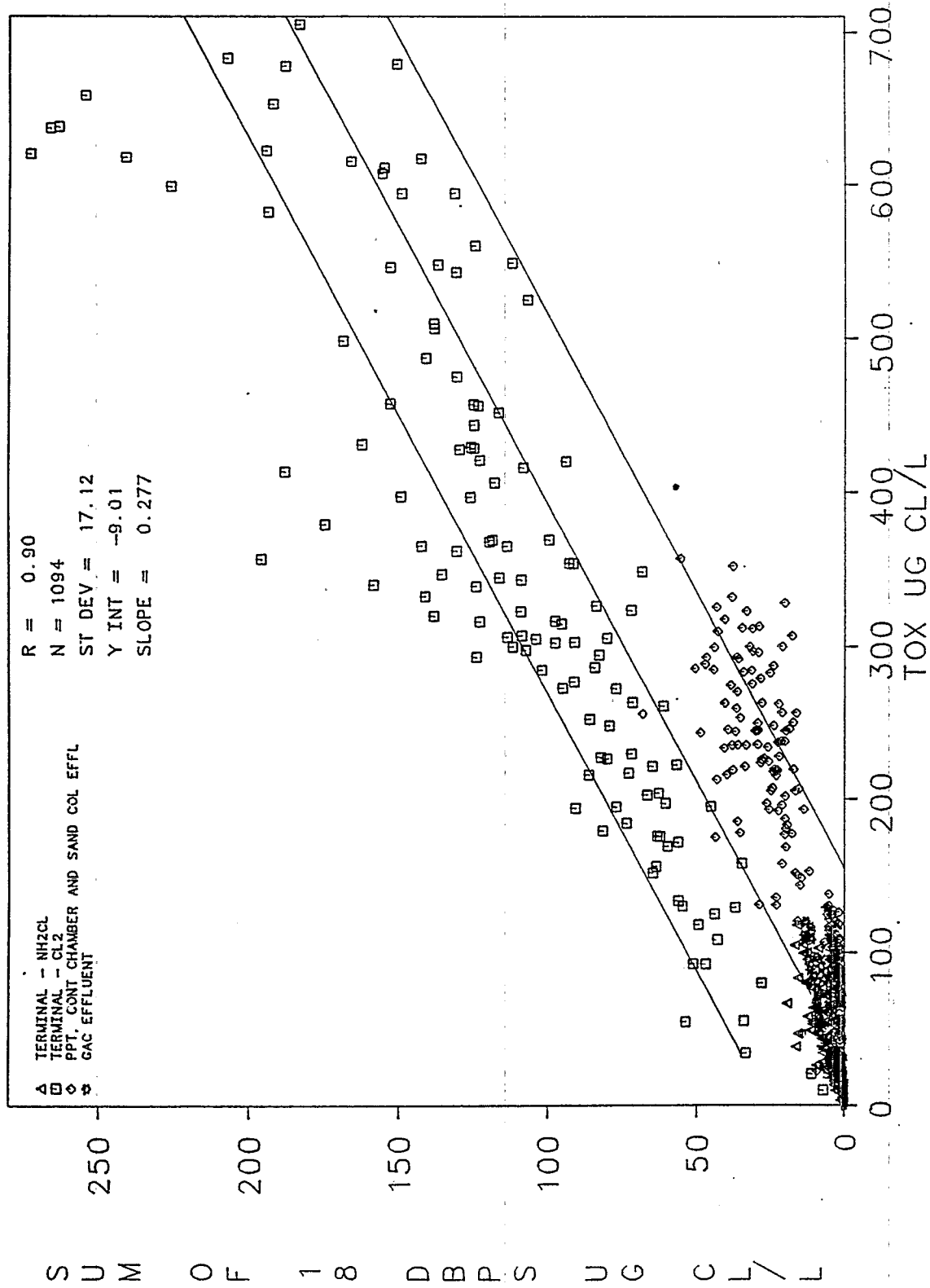


Figure 116. Regression Analysis of TOX and the DBPs at all Locations by Sample Type.



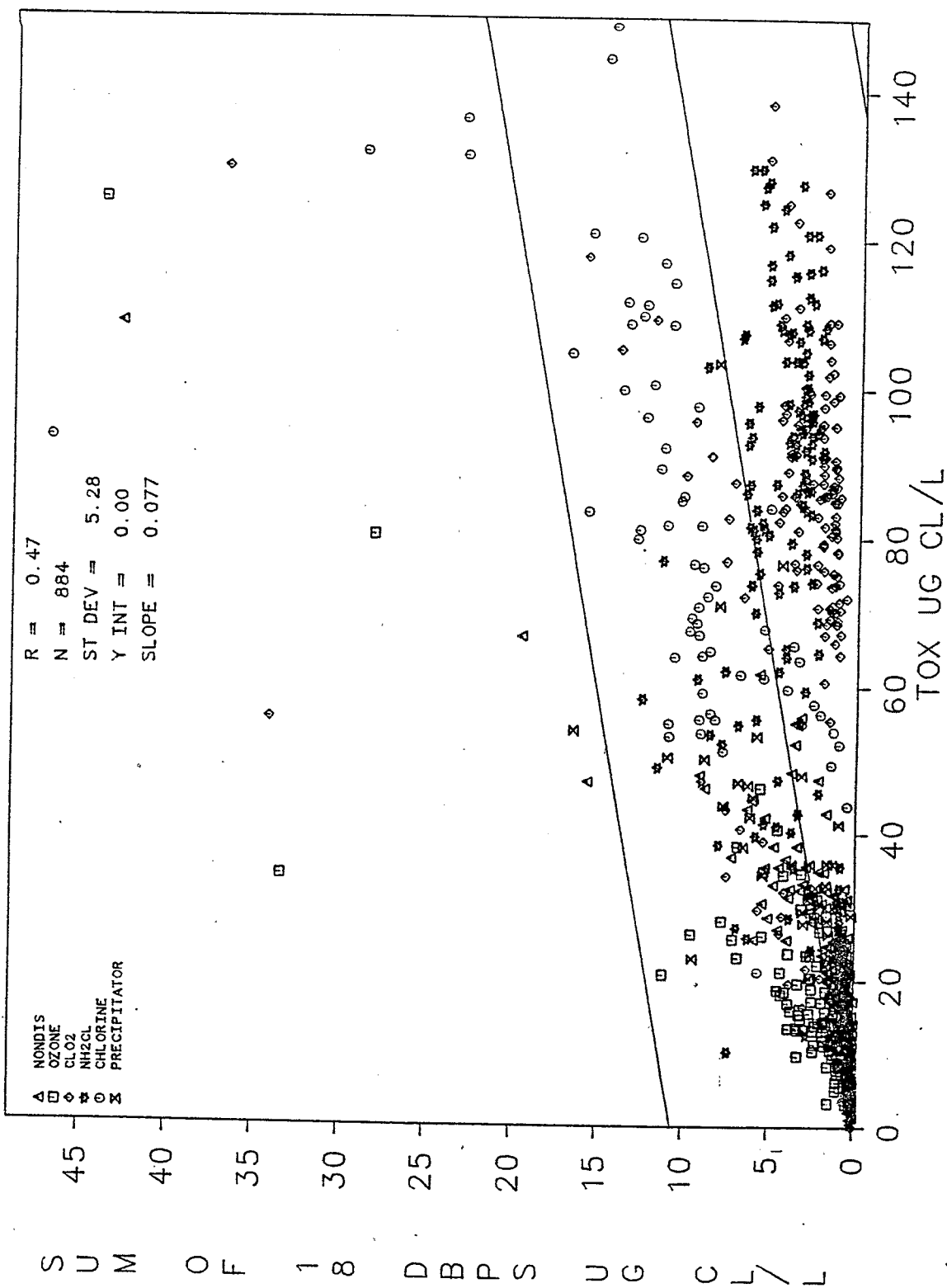


Figure 117. Expansion of Regression Analysis of TOX and the DBPs at all Locations by Process Stream.

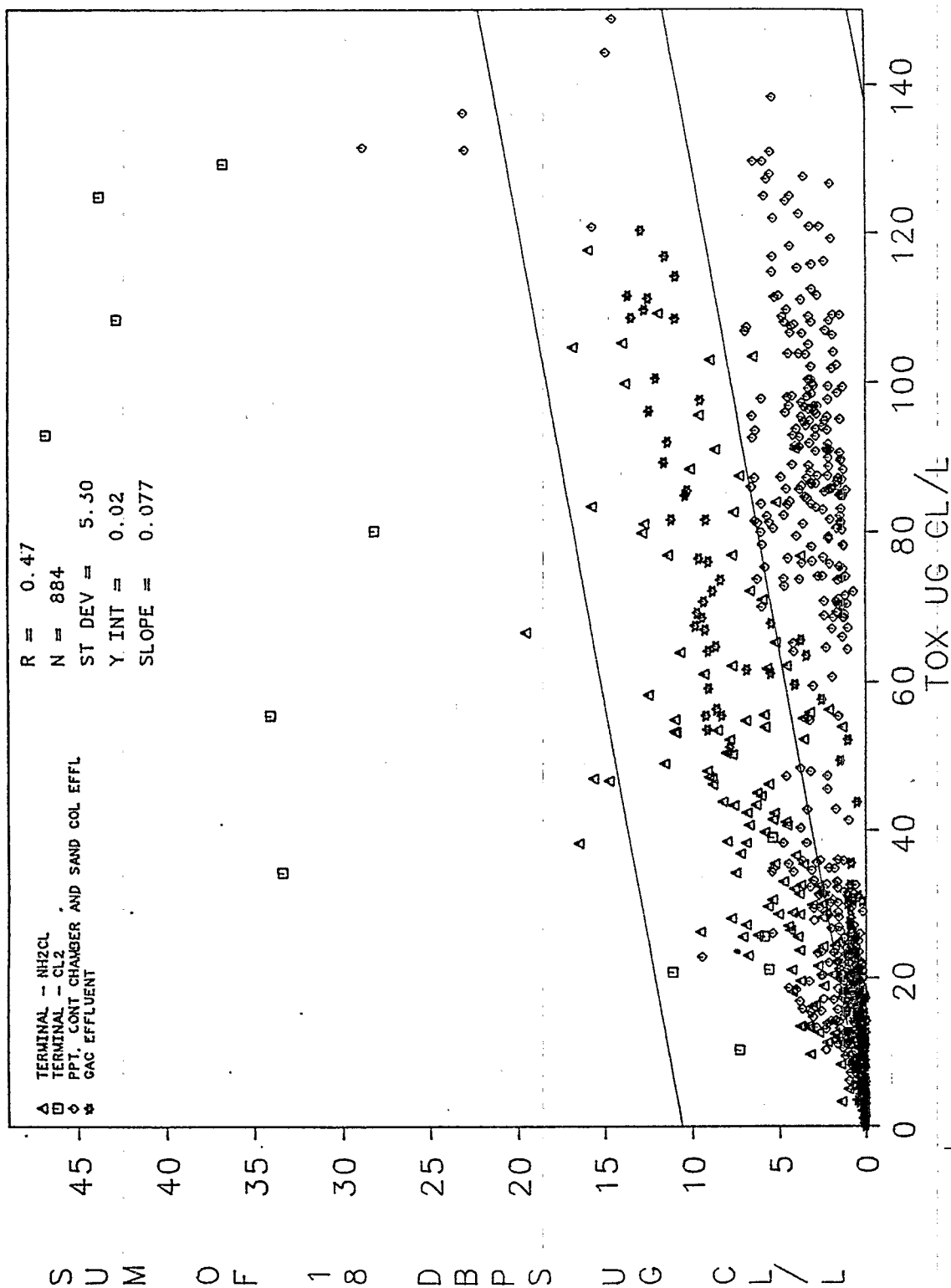


Figure 118. Expansion of Regression Analysis of TOX and the DBPs at all Locations by Sample Type.

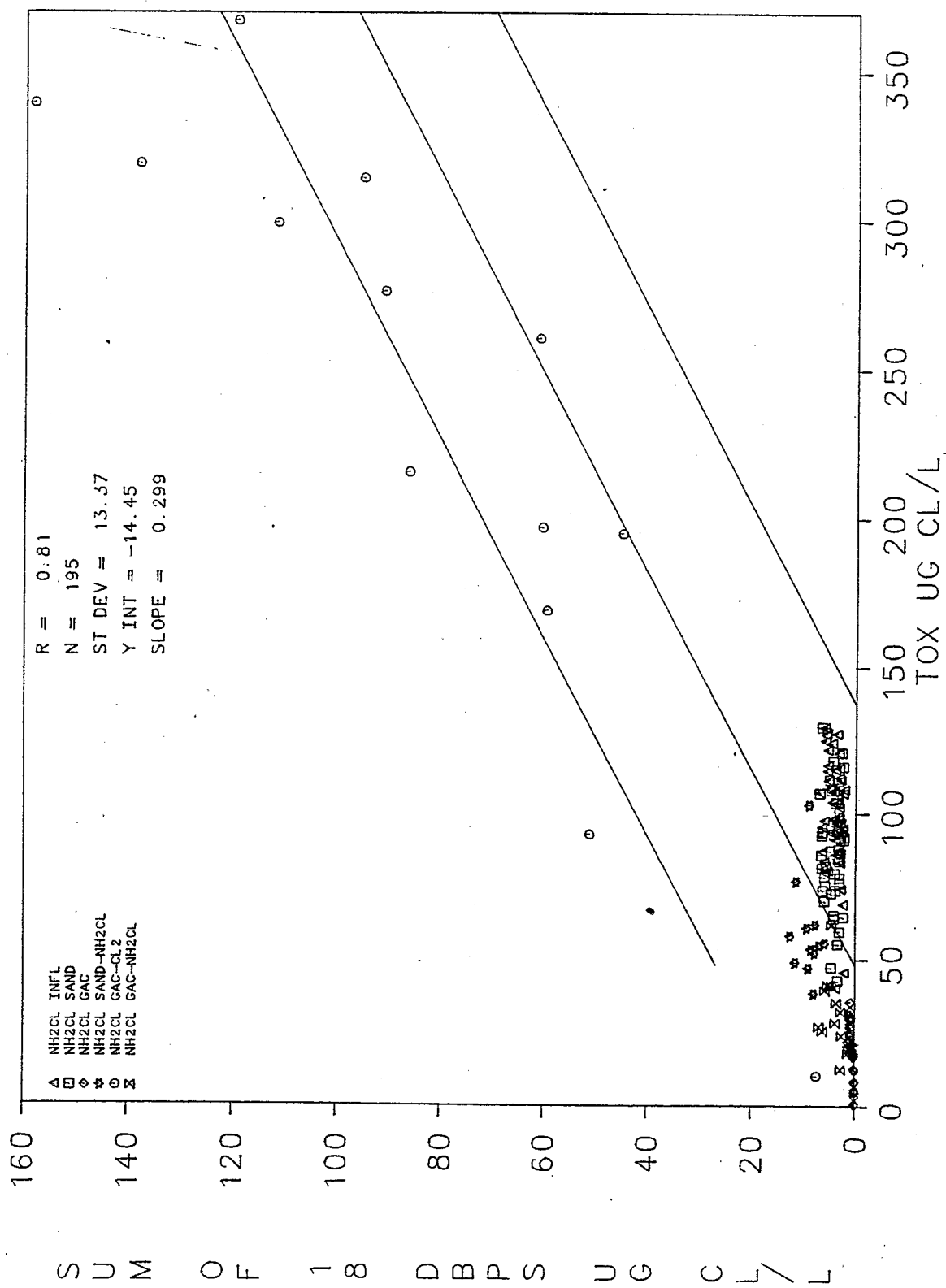


Figure 119. TOX vs DBPs for the Chloramine Process Stream.

Because of the apparent difference in the reaction rates of TOX and DBP formation, and the relatively short disinfectant contact times observed for the instantaneous samples, all instantaneous data was removed from the data pool. This included the removal of the instantaneous GAC effluent data because, while at equilibrium due to the lack of a disinfectant residual, additional disinfection would be required before being distributed to consumers. With only 254 terminal chlorine and chloramine data points remaining, a better correlation was observed with a higher correlation coefficient of 0.95 along with a higher standard deviation of 20.3. From Figure 120, it is apparent that two separate data sets were present, one for chlorine and one for chloramine. While separation of these two data sets in Figures 121 and 122 produced poorer correlations with lower correlation coefficients of 0.88 and 0.71 for terminal-Cl<sub>2</sub> and terminal-NH<sub>2</sub>Cl, respectively, these data sets were the most normally distributed and were considered more representative of the distribution system. A better correlation may be obtained by using actual distribution samples since laboratory distribution system simulation (terminal) samples are generally less precise than instantaneous pilot column or distribution system samples. The correlation of terminal chloramine TOX and DBPs may not have much practical application since these terminal values were generated by adding ammonia prior to chlorine and, thus, are indicative of the minimum levels which may be observed in the distribution system. In most treatment plant applications, the order of addition is reversed with the free chlorine contact time varying with plant design which may soon require modification depending upon the requirements of the Surface Water Treatment and Disinfection By-Product Rules under the Safe Drinking Water Act. With increased free chlorine contact time, the DBPs and TOX produced will fall somewhere in between the terminal chloramine and terminal chlorine regression lines suggesting that TOX may only be of value as a DBP surrogate for those systems which employ free chlorine in the distribution system.

#### MICROBIOLOGICAL OBSERVATIONS

##### Heterotrophic Plate Count (HPC)--

The geometric means of the heterotrophic plate count (HPC) observed across each process stream, presented in Table 24, indicated that ozone exhibited the greatest level of disinfection after 30 minutes of disinfectant contact, followed closely by chlorine and chlorine dioxide. Chloramine was considerably less effective. While a 58% reduction in HPC was observed across the nondisinfected sand column, the HPC in the ozone sand column effluent increased dramatically to 28,000 cfu/mL due to the

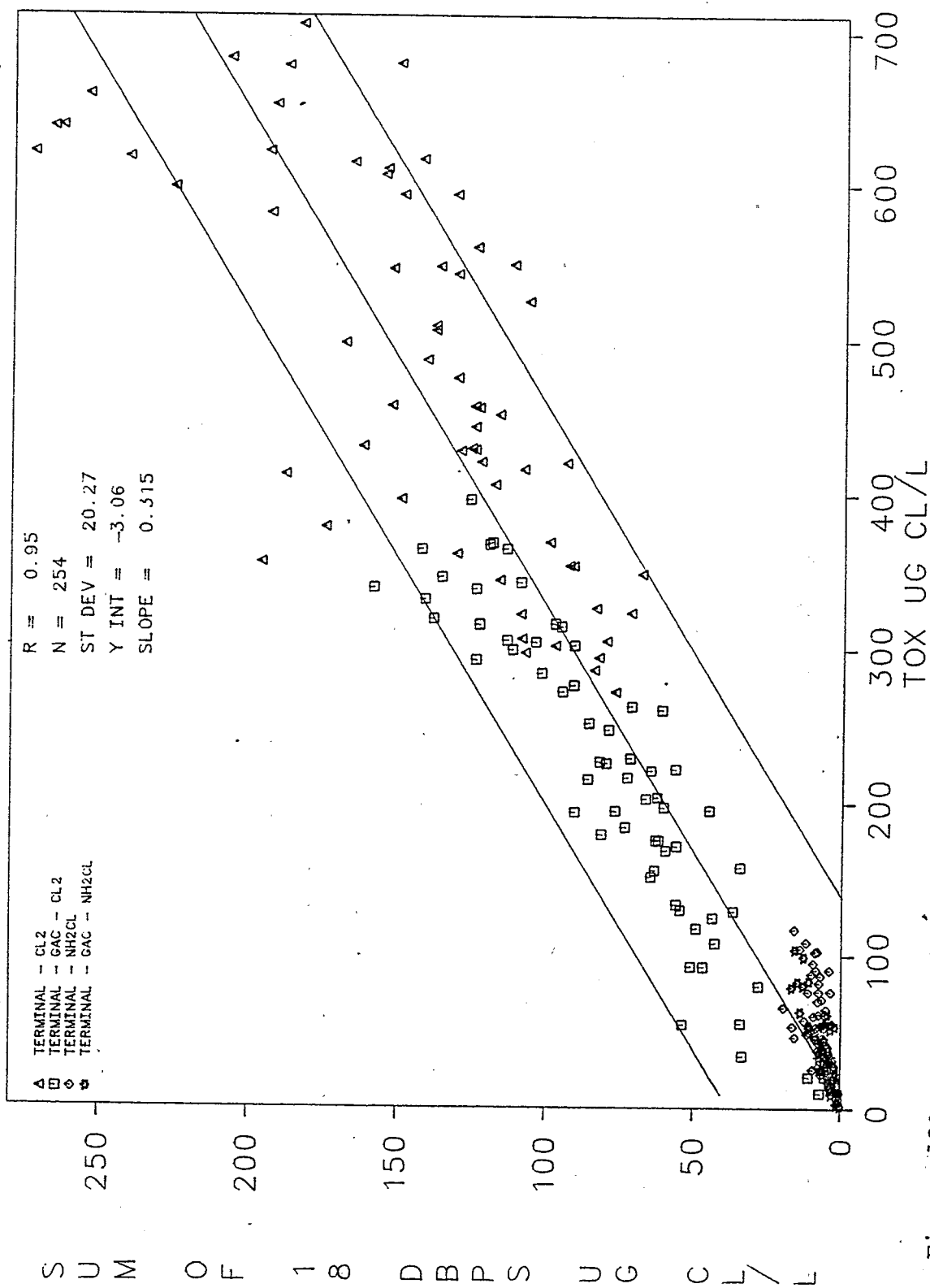


Figure 120. Regression of all Terminal Chlorine and Chloramine TOX and DBPs for all Locations.

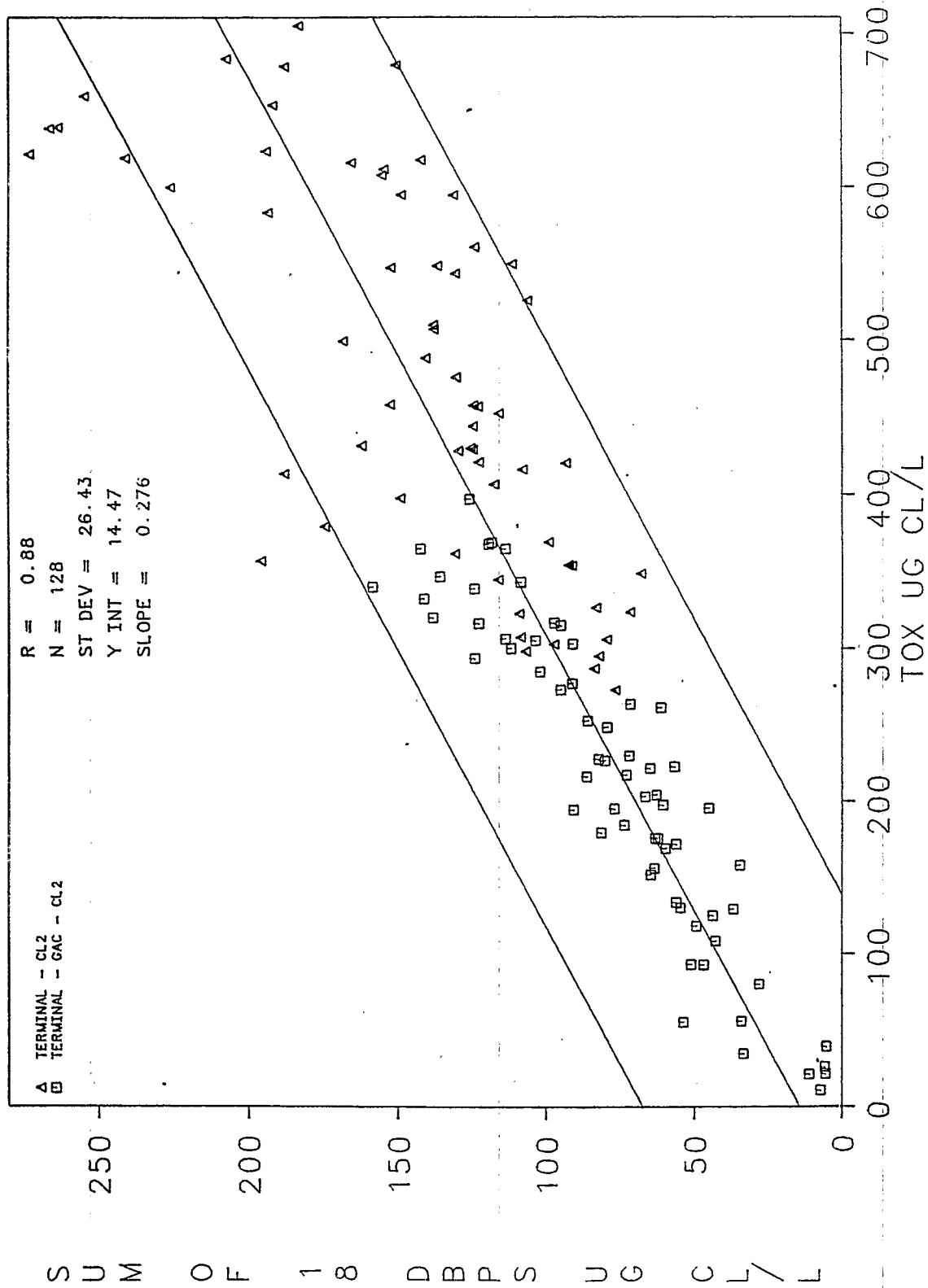


Figure 121. Regression of all Terminal Chlorine TOX and DBPs for all Locations.

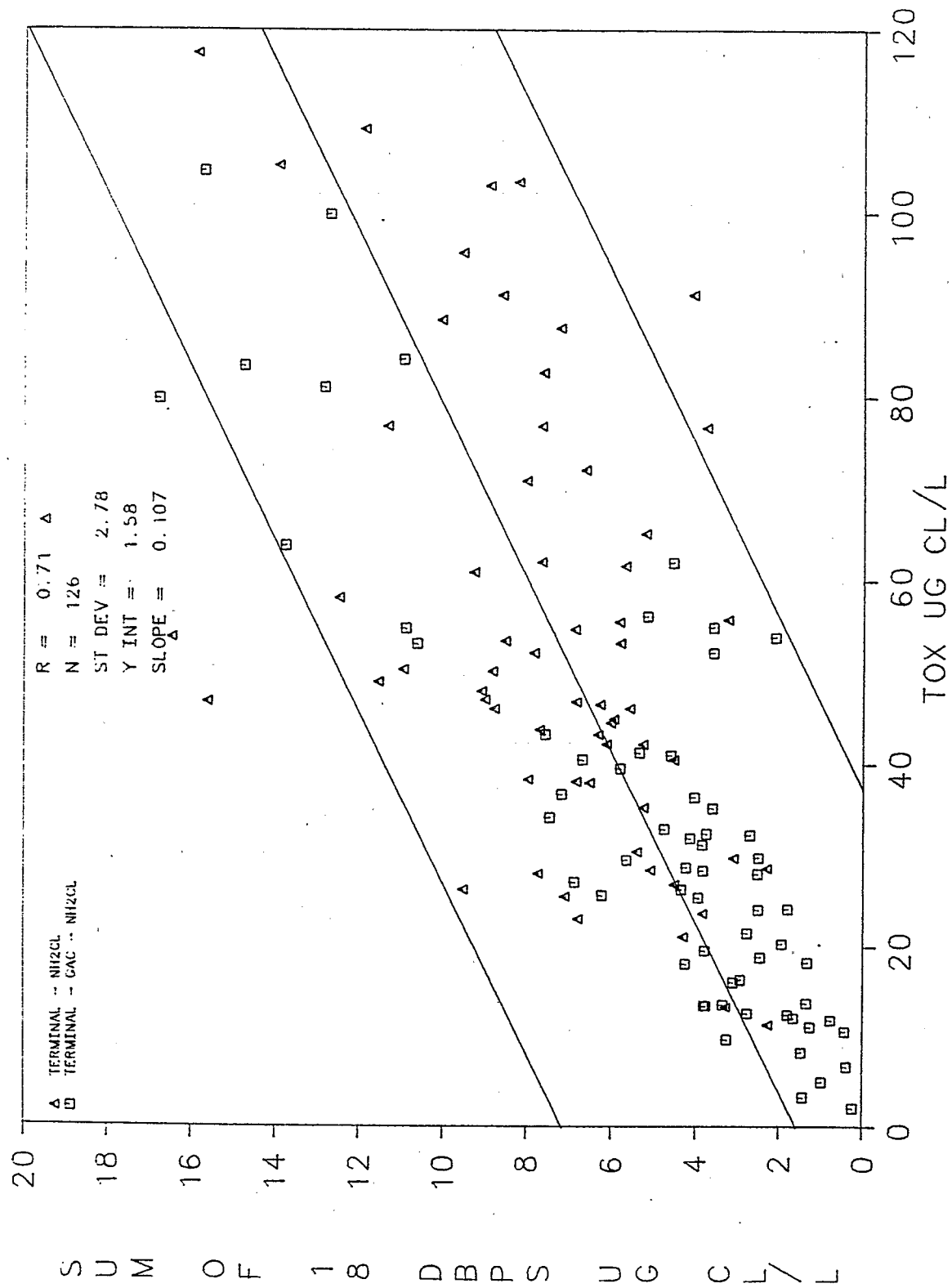


Figure 122. Regression of all Terminal Chloramine TOX and DBPs for all Locations.

Table 24. Comparison of HPC Across each Process Stream.

	Geometric Mean of HPC, cfu/mL		
	Contact Chamber Effluent	Sand Column Effluent	GAC Column Effluent
Nondisinfected	10,900	4,600	1,800
Ozone	10	28,000	2,300
Chlorine Dioxide	21	17	16,300
Chlorine	19	13	12,800
Chloramine	230	195	1,900

dissipation of the ozone residual, the relatively high levels of assimilable organic carbon available from ozone oxidation, and the abundance of dissolved oxygen which averaged 9 mg/L. The HPC levels in the sand column effluents of the chlorine, chlorine dioxide, and chloramine process streams were similar to those of their respective contact chamber effluents. Even though the HPC levels in the ozone sand column effluent were exceedingly high, those of the ozone GAC column were lower by a factor of ten and were similar to those of the nondisinfected and chloramine GAC columns. The HPC levels of the chlorine and chlorine dioxide GAC columns were 6-8 times higher than those of the other process streams and may have resulted from a rapid regrowth response due to the dissipation of the disinfectant residual in the upper position of each GAC column. As indicated in a forthcoming section, elevated levels of assimilable organic carbon were not evident in the chlorine process stream.

#### Total Coliform--

The percentage of positive coliform samples which occurred across each process stream are presented in Table 25 along with the average coliform count of the positive samples observed at each location. As expected, the nondisinfected process stream contained the highest levels of coliforms. A reduction in coliform density of 54% was observed across the nondisinfected sand column with an additional 42% occurring across the nondisinfected GAC column reducing the coliform density to an average of 4 cfu/100 mL. While ozone completely inactivated all coliform bacteria in the disinfectant contact chamber, low level



Table 25. Comparison of Total Coliform Across each Process Stream.

	Total Coliform (% Positive/Average, cfu/100 mL)		
	<u>Contact Chamber Effluent</u>	<u>Sand Column Effluent</u>	<u>GAC Column Effluent</u>
Nondisinfected	100/95	100/44	83/4
Ozone	0/0	14/2	8/4
Chlorine Dioxide	0/0	0/0	28/1
Chlorine	0/0	0/0	28/2
Chloramine	19/1	1/1	7/1

coliforms were frequently observed in the effluent of the biologically active ozone sand column. Similar low levels occurred in the ozone GAC column effluent but at a reduced frequency. While essentially no coliforms were observed in the contact chamber and sand column effluents of the chlorine dioxide and chlorine process streams, low coliform levels occurred with a relatively high frequency in both GAC column effluents. A relatively high frequency of low level coliforms was also observed in the chloramine contact chamber effluent and is believed to have resulted from the use of a pulsating metering pump for the hypochlorite feed. In a previous one year study which had a somewhat higher influent coliform density, a similar ammonia solution feed pump followed by a continuous chlorine gas feeder produced the same chloramine residual in the contact chamber effluent with essentially no coliforms. This suggests that the higher frequency of detection observed in this study may have resulted from the pulsations of the metering pump even though the hypochlorite solution was fed ahead of the ammonia solution. While additional chloramine contact across the sand column removed essentially all of the remaining coliform bacteria, low level coliforms were occasionally observed in the effluent of the chloramine GAC column.

Assimilable Organic Carbon (AOC)--

Due to the work intensive nature of the AOC analysis procedure and limited manpower, AOC measurements were limited to the strongest oxidants, ozone and chlorine, and were conducted on a monthly basis using *Pseudomonas fluorescens* strain P17 to assess seasonal variations (Figure 123). The AOC levels in the nondisinfected influent ranged from 5-25 ug acetate C-eq/L with an average of 10 ug acetate C-eq/L. The highest levels of AOC were observed in the effluent of the ozone contact chamber averaging 166 ug acetate C-eq/L and ranging from 51-268 ug acetate C-eq/L. The seasonal variations of AOC observed in the ozone contact chamber effluent correlated quite well with water temperature (Figure 2) throughout the operational period with lower AOC levels being formed at lower water temperatures. With the exception of one outlying data point on day 300, the biologically active ozone sand column reduced the AOC to an average level of 39 ug acetate C-eq/L for a reduction of 77 percent. The further reduction of AOC down to the 4 ug acetate C-eq/L level occurred across the ozone GAC column. Except for one outlying data point which also occurred on day 300, the AOC levels in the chlorine contact chamber effluent were relatively low averaging 5 ug acetate C-eq/L. Similar AOC levels averaging 3 ug acetate C-eq/L were observed in the effluent of the chlorine GAC column.

#### MS2 Coliphage--

Each month, an MS2 coliphage seed containing approximately  $10^9$  pfu/mL was continuously pumped into the nondisinfected influent following pressure sand filtration<sup>5</sup> to achieve a homogeneous concentration of approximately  $10^5$  pfu/mL in the influent of each disinfected process stream. The log removals observed for MS2 coliphage across the disinfection contact chamber of each process stream are presented in Tables 26 and 27 along with the corresponding water temperature, disinfectant residual, and calculated  $CT_{10}$  value relative to the Surface Water Treatment Rule (SWTR) promulgated under the Safe Drinking Water Act. While the plug-flow contact time calculated for each disinfectant contact chamber was 30 min, the  $T_{10}$  contact time as specified by SWTR guidelines, was measured at 10 min for the ozone contact chamber and 17 min for the other disinfectant contact chambers. The shorter contact time in the countercurrent ozone contact chamber evidently resulted from the additional turbulence created by the rising gas bubbles.

With  $CT_{10}$  values ranging from 2.7-5.1 mg/L-min across the ozone contact chamber, all coliphage was inactivated resulting in removals greater than 4-6 logs. This agrees with the SWTR guidance manual in that the manual requires a  $CT_{10}$  value of 1.2 mg/L-min at 5°C and 0.3 mg/L-min at 25°C for a 4 log virus removal which are approximately 4-10 times lower than those  $CT_{10}$  values observed across the ozone contact chamber. Coliphage

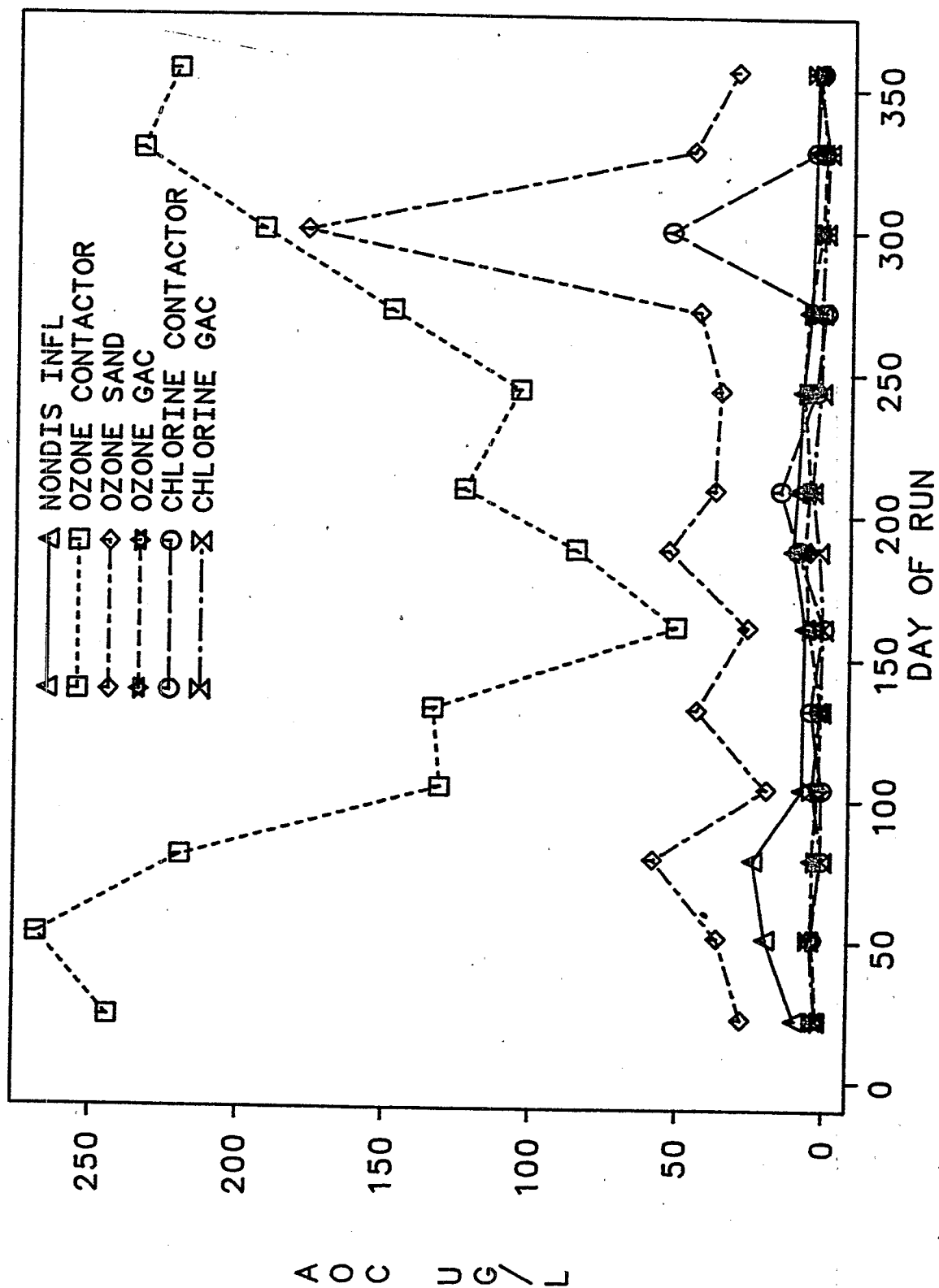


Figure 123. Comparison of AOC Levels Across the Ozone and Chlorine Process Streams.

Table 26. MS2 Coliphage Reductions by Ozone and Chlorine Dioxide.

Temp. °C	Ozone			Chlorine Dioxide		
	Residual, mg/L	CT <sub>10</sub> <sup>1</sup>	Log Removal	Residual mg/L	CT <sub>10</sub> <sup>2</sup>	Log Removal
28.5	0.34	3.4	>4.1	----	----	----
26.1	0.45	4.5	>4.7	0.38	6.5	>4.7
24.7	0.27	2.7	>5.6	0.48	8.2	5.6
18.9	0.51	5.1	>5.9	0.48	8.2	>5.9
15.3	0.41	4.1	>5.7	0.38	6.5	>5.7
8.4	0.37	3.7	>5.9	0.86	14.6	>5.9
3.3	0.44	4.4	>5.6	0.48	8.2	5.5
3.3	0.44	4.4	>5.8	0.55	9.4	5.3
10.4	0.51	5.1	>5.8	0.40	6.8	5.4
11.9	----	----	----	0.51	8.7	>5.4
17.8	0.47	4.7	>5.6	0.49	8.3	>5.6
18.9	0.44	4.4	>5.2	0.57	9.7	>5.2
24.4	0.37	3.7	>5.3	0.48	8.2	>5.3
25.0	0.44	4.4	>4.9	0.53	9.0	>4.9

<sup>1</sup>T<sub>10</sub> for Ozone = 10 min

<sup>2</sup>T<sub>10</sub> for ClO<sub>2</sub> = 17 min

levels ranging from 0-3 pfu/mL were observed in the chlorine dioxide chamber effluent resulting in log removals of 5 or more corresponding to CT<sub>10</sub> values ranging from 7-10 mg/L-min.

Table 27. MS2 Coliphage Reductions by Chlorine and Chloramine.

Temp. °C	Chlorine			Chloramine		
	Residual, mg/L	CT <sub>10</sub> <sup>1</sup>	Log Removal	Residual mg/L	CT <sub>10</sub>	Log Removal
28.5	0.7	11.9	>4.1	1.5	25.5	1.4
26.1	1.	18.7	>4.7	1.4	23.8	1.8
24.7	1.0	17.0	>5.6	1.3	22.1	0.9
18.9	0.8	13.6	>5.9	1.8	30.6	0.8
15.3	1.0	17.0	5.7	1.5	25.5	0.5
8.4	1.2	20.4	5.2	1.5	25.5	0.5
3.3	0.8	13.6	4.8	1.6	27.2	0.4
8.3	0.9	15.3	5.7	1.7	28.9	0.4
10.4	0.8	13.6	>5.8	1.6	27.2	0.6
11.9	0.9	15.3	>5.4	1.6	27.2	0.2
17.0	1.2	20.4	>5.6	1.4	23.8	0.5
18.9	1.8	30.6	>5.2	1.4	23.8	0.6
24.4	1.2	20.4	>5.3	1.6	27.2	1.3
25.0	1.1	18.7	>4.9	1.6	27.2	0.6

<sup>1</sup>T<sub>10</sub> = 17 min

Comparison of these data to the requirements in the SWTR guidance manual indicated that the values in the guidance manual are 5-8 times greater than those observed across the chlorine dioxide contact chamber. For example, the required CT<sub>10</sub> value for a 4 log virus removal at 3°C in the manual is 38 mg/L-min with a 5 log removal in the 60-70 mg/L-min range, while a 5.5 log coliphage removal was observed across the chlorine dioxide

contact chamber at 3°C with a  $CT_{10}$  of 8.2 mg/L-min. Similar to chlorine dioxide, chlorine inactivated essentially all of the coliphage applied with contact chamber effluent levels ranging from 0-7 pfu/mL resulting in log removals of approximately 5 or greater with  $CT_{10}$  values of 14-20 mg/L-min. As was the case for ozone, the  $CT_{10}$  values observed for chlorine were 2-10 times greater than those in the guidance manual of 8 mg/L-min at 5°C and 2 mg/L-min at 25°C for a 4 log virus removal. Coliphage levels in the effluent of the chloramine process stream ranged from  $4.8 \times 10^2$  pfu/mL to  $4.0 \times 10^5$  pfu/mL resulting in log removals of only 0.2-1.8 with  $CT_{10}$  values of 22-31 mg/L-min. Relative to the SWTR guidance manual which requires a  $CT_{10}$  of 857 mg/L-min at 4°C and 214 mg/L-min at 25°C for a 2 log virus removal, the  $CT_{10}$  values observed across the chloramine contact chamber were 2-8 times lower than those required in the manual for equivalent log removals. Because of the dramatic difference between the  $CT_{10}$  requirements of free chlorine and chloramine, e.g. 2 mg/L-min versus 500 mg/L-min for a 4 log virus removal at 25°C, this greater inactivation rate was obviously the result of the amount of free chlorine contact achieved prior to reaction with ammonia to form chloramine. While the in-line free chlorine contact time prior to entering the chloramine contact chamber was estimated at only a few seconds with an average free chlorine residual of 1.5 mg/L, a similar free chlorine residual for a period of only one minute would result in a 3 log virus removal according to the SWTR guidance manual. Thus, a 4 log virus removal could be achieved with a 2 mg/L free chlorine residual and a  $T_{10}$  contact time of only 4 min at 5°C and 1 min at 25°C before quenching with ammonia to form chloramine so as to minimize the level of disinfection by-products formed..

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